Synthesis and Hydroacylation of Tertiary Allyl Amines

Presented to the faculty of Lycoming College in partial fulfillment of the
requirements for Departmental Honors in Chemistry

by

Kyle E. Ruhl

Lycoming College

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Approved by:

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Acknowledgements:

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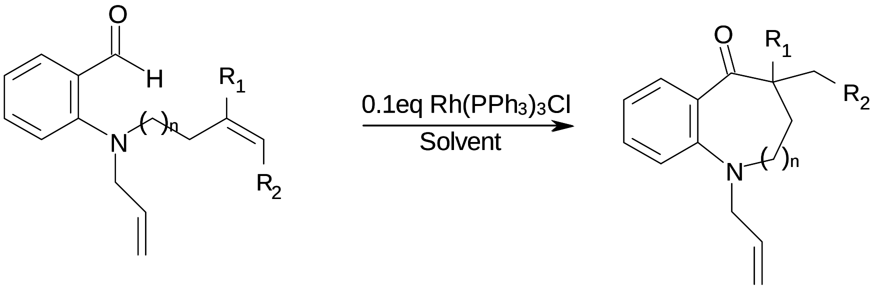
Abstract

Preparation of cyclopentanones from 4-pentenals via hydroacylation has been well established.[1,2] However, only a few syntheses of medium ring compounds via hydroacylation exist. Our work has shown substrates containing a sulfur or nitrogen atom in the chain undergo intramolecular hydroacylation in good yields.[3] Experiments have also shown the presence of an allyl substituent on nitrogen is crucial to promoting cyclization of the amine substrates, presumably by further increasing coordination to rhodium (I).

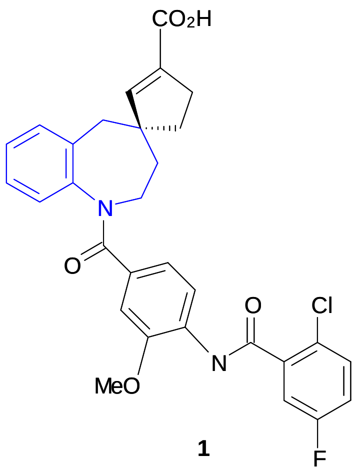


(Eq 1)

This project focuses on determining the scope and limitations of intramolecular hydroacylation. The effect of substitution on the alkene fragment is examined (Eq 1). The formation of dibenzazepines via hydroacylation is also attempted by cyclization of diphenyl allyl amines.

Introduction and Background

A variety of biologically active molecules, such as compounds **1** and **2** which are currently anti-convulsants on the market**,** contain medium ring nitrogen heterocycles.[4,5] These molecules are of interest as pharmaceuticals but their synthesis can be laborious. Research in the Bendorf lab has shown medium ring nitrogen heterocycles can be prepared via chelation-assisted intramolecular hydroacylation.[6] This approach offers rapid access to nitrogen heterocycles in a high yielding reaction.



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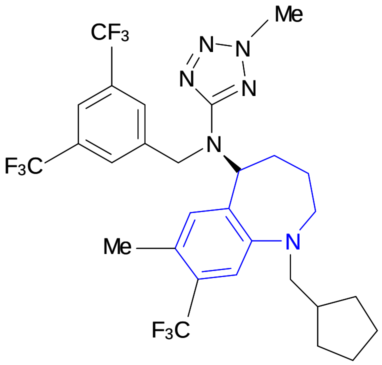
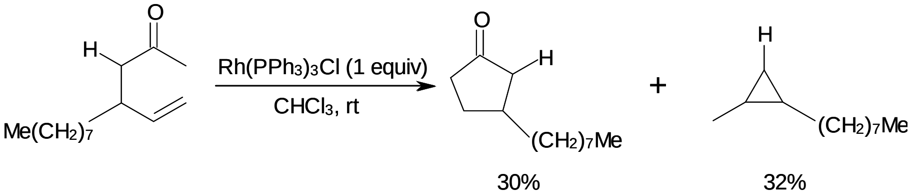


2

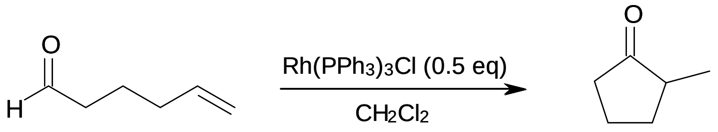
Hydroacylation was first reported by Sakai.[1] He found that treating 4-pentenal with Wilkinson's catalyst yielded substituted cyclopentanone products in 17-34% yields. Other products observed included stereoisomers of substituted cyclopropanes in 20-35% yields (Eq 2).



(Eq 2)

Results showed the formation of substituted cyclopentanones was favored over formation of a cyclohexanone product (Eq 3).[2] Larock went on to improve the reaction conditions by examining solvent choice and transition-metal catalysts as well as effects of acetylenes, water and air. He reported that $Rh(PPh_3)_3Cl$ in methylene chloride at room temperature gave the best results. The use of acetylenes nor other alkenes boost yields to rival ethylene saturation and lastly, water showed no dramatic effect on the reaction but air destroyed the catalyst. Experiments were then conducted using 5-hexenals with the anticipation of a cyclohexanone product.

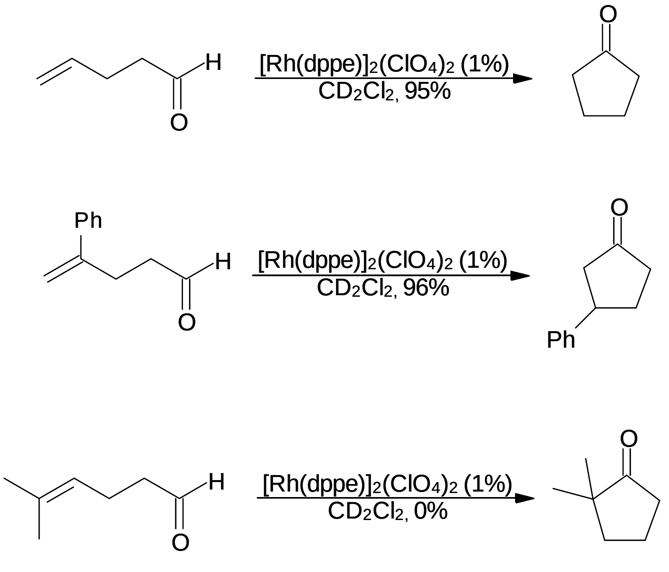
A series of experiments were also completed to determine the reactions tolerance to substitution. In summary, substitution at the two and five position on the carbon backbone inhibited ketone formation and dimethyl substitution at any position caused the reaction to fail.



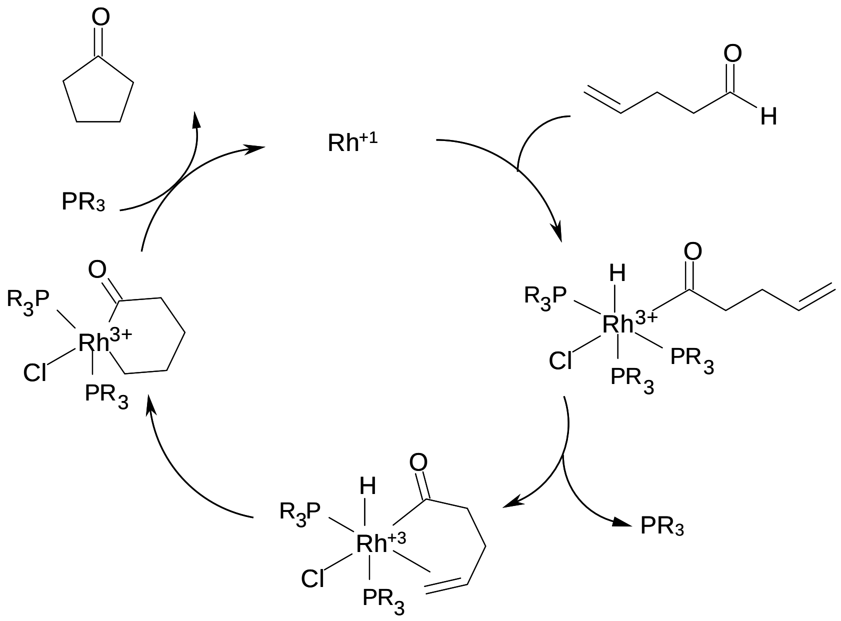
(Eq 3)

Bosnich found that high yields of cyclopentanones, with less decarbonylation products, can be achieved with the use of a cationic rhodium catalyst (Scheme 1).[7] Substitution about the alkene and backbone was examined again to give similar results to those published by Larock. The reaction tolerated moderate substitution at the two, three and five positions but the reaction still failed with dimethyl substitution at carbon five. Bosnich's mechanism is shown in Scheme 2.[8]

Scheme 1



Scheme 2

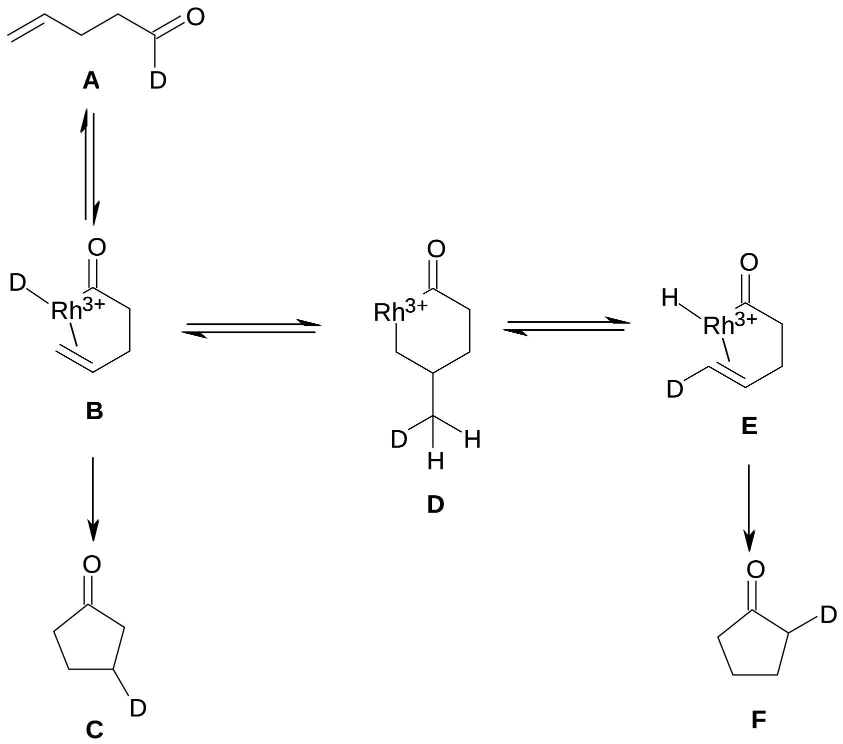


Oxidative addition of the aldehydic C-H bond to rhodium (I) yields a rhodium (III) intermediate. Coordination of the alkene to the metal center is followed by insertion of the alkene into the rhodium-hydride bond. The six-membered metallocycle intermediate undergoes reductive elimination to yield the cyclopentanone product and regenerate the rhodium (I) catalyst.

Labeling studies were performed to help elucidate reversibility and direction of the reaction. C-H activation and alkene insertion are rapid and reversible. Reductive elimination is irreversible and is exothermic. Due to the nature of C-H activation requiring interaction with the metal, oxidative addition is promoted when substrates have the ability to chelate to the metal via the alkene and aldehyde oxygen atom.

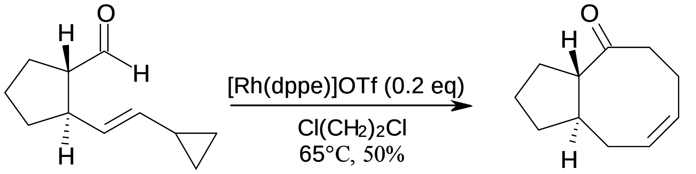
Labeling studies were also conducted to examine the scrambling of the hydride (Scheme 3) A 1,2 insertion can result in the deuteride being delivered to the internal or external carbon of the alkene. If the internal carbon is substituted, reductive elimination will yield a product with the deuteride in the three position (B -> C). If the external carbon is substituted (D), a β-hydride elimination followed by a reinsertion will give the deuteride being in the two position (D -> F). In the case where substituted cyclopentanones are formed in preference to cyclohexanone products, this is due to regioselectivity favoring exo- over endo-substituion.[8]

Scheme 3



In the first thirty years of hydroacylation, reports were limited to small ring synthesis. This made it appear that medium rings are difficult to form. Factors which can inhibit medium ring formation include high substrate concentrations, unfavorable entropy situations and ring strain effects.[9] High substrate concentrations can favor intermolecular reactions and therefore compete with the desired intramolecular reaction to form medium rings. Entropy barriers and ring strain effects arise during the formation of medium rings and this is likely an issue for intermediates necessary for hydroacylation as well. These barriers can be surmounted by employing ring expansion techniques and tether atoms. Ring expansion techniques progress through a more favorable metallacycle intermediate. After formation, these intermediates undergo ring expansions to form the desired medium ring. Tether atoms facilitate the reaction between distant groups by coordinating to the metal, positioning the reacting groups near the metal and each other.

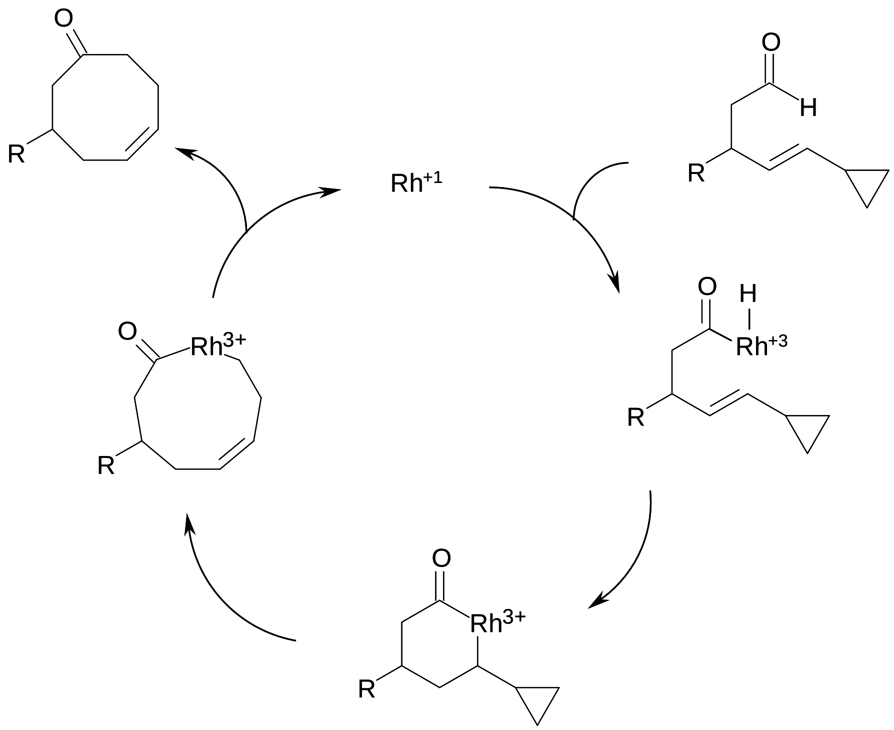
In 2001 Shair reported a synthesis for medium ring carbocycles. This was accomplished using a ring expansion technique in tandem with hydroacylation.[10] Instead of forming substituted cyclopentanones, which were sometimes seen as a minor product, eight-membered carbocycles were observed (Eq 4). Typical yields for the eight-membered carbocycles ranged from 23-65%.



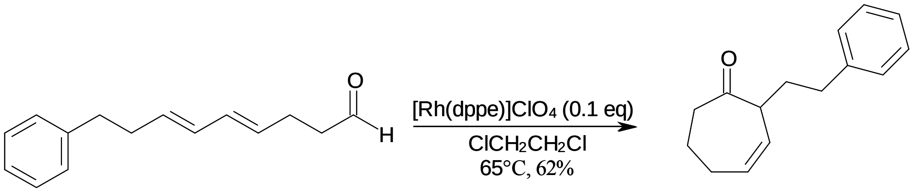
(Eq 4)

The mechanism of this reaction is shown in Scheme 4. Initial oxidative addition and alkene insertion gives a six-membered metallocycle. Fragmentation of the cyclopropane ring results in the formation of a nine-membered metallocycle. Reductive elimination then yields the eight-membered carbocycle and regenerates the Rh^{+1} catalyst.

Scheme 4



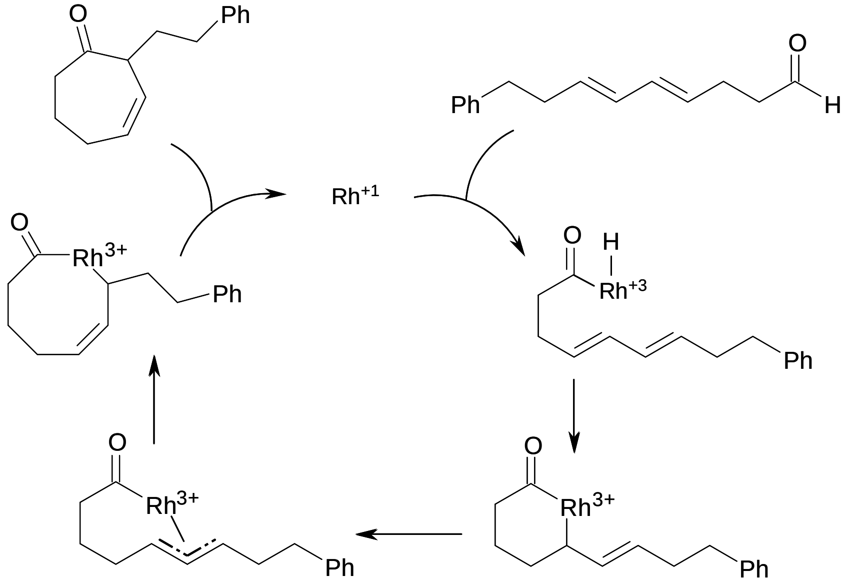
The formation of cycloheptenones was also reported by Mori in 2002.[9] Seven-membered carbocycles were achieved by the treatment of dienes with a cationic catalyst (Eq 5).[11]



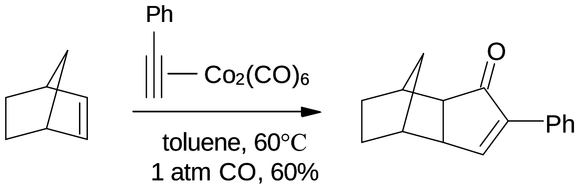
(Eq 5)

This reaction proceeds through an intermediate which undergoes a ligand migration as shown in Scheme 5. Oxidative addition and insertion of the proximal alkene into the rhodium-hydride bond gives the six-membered metallocycle. In this metallocycle an isomerization from an η^1-ligand to η^3-ligand occurs. Isomerization of the η^3-ligand then gives the eight-membered metallocycle and reductive elimination yields the seven-membered carbocycle product shown.

Scheme 5

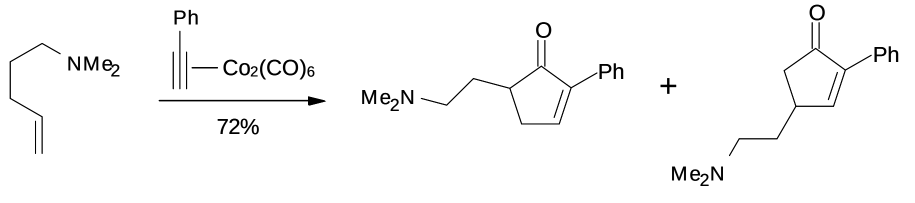


Our approach to the synthesis of medium rings by hydroacylation was inspired by Krafft's work on the Pauson-Khand reaction. The Pauson Khand (Eq 6) involves the reaction of an alkene and an alkyne in a cobalt-mediated cycloaddition to form cyclopentenones.



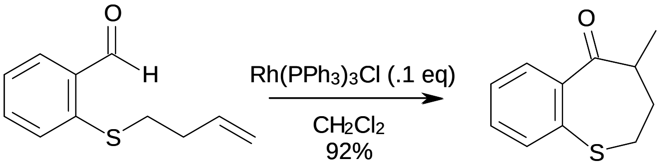
(Eq 6)

When an unsymmetric alkene is used, a mixture of regioisomeric products are obtained. The reaction is also limited to strained or highly substituted alkenes. Krafft found that by placing an amine near the alkene, selectivity and reaction rate was improved (Eq 7).[12] It is important to point out the distance between tether atom and alkene is crucial. Allylic substrates gave low yields and poor regioselectivity. This issue arises due to the formation of a strained complex during substrate coordination to the metal. The best results were observed for substrates containing two or three carbon atoms between amine and alkene.



(Eq 7)

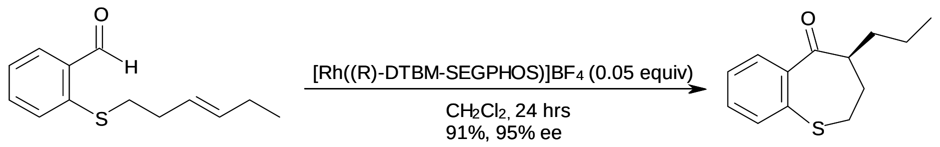
With an inspiration from the Krafft chemistry, chelation-assisted hydroacylation allowed the synthesis of medium rings. This donation of electrons from the tether atom assists in coordination of the hydroacylation substrate collectively, which encourages the reaction to a greater extent than just the coordination of a distal and labile alkene. Increased coordination yields more opportunity to react and increases reaction rate.



(Eq 8)

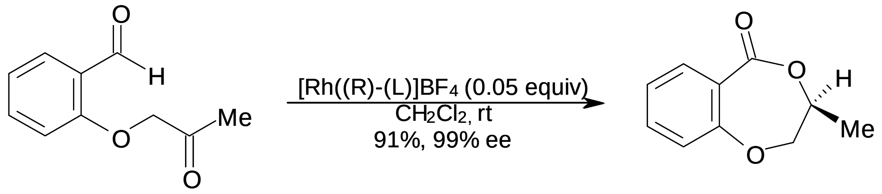
Original work in our group focused on the use of sulfur as a tether atom. Bendorf reported seven and eight-membered sulfur heterocycles in 62-92% yields (Eq 8). The reaction tolerated substitution on the carbon backbone as well as some moderate substitution on the alkene. Substitution of the internal carbon of the alkene failed to give any appreciable yields. This differs from the results from Larock and Bosnich which displayed the ability to cyclize moderately substituted alkenes. It was also reported separating the sulfur tether atom and aldehyde by more than two atoms resulted in reaction failure.

An extension of Bendorf's sulfur work, completed by Dong, introduced the concept of stereoselective hydroacylation.[13] With the use of chiral ligands in conjunction with cationic catalysts, the hydroacylation reaction shows enantioenriched products of sulfur heterocycles (Eq 9).

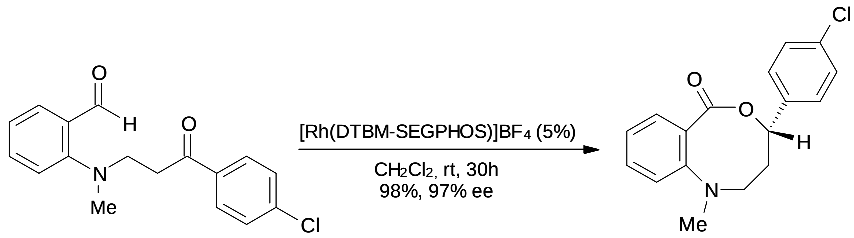


(Eq 9)

Oxygen and nitrogen substrates also underwent enantioselective hydroacylation to form lactones (Eq 10, 11). Seven- and eight-membered lactones were formed in 85-99% yields, most with an enantiomeric excess of 99%.[14] The formation of lactones via hydroacylation also proved that insertion of a ketone into the rhodium-hydride bond is possible.[15]

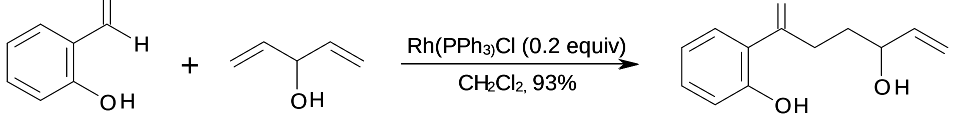


(Eq 10)



(Eq 11)

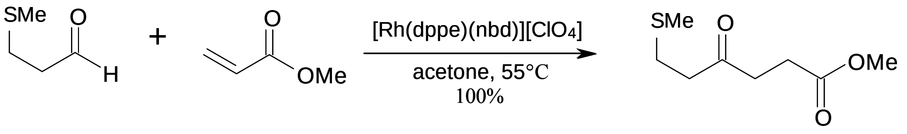
In addition to intramolecular hydroacylation, chelation-assisted intermolecular hydroacylation has also been reported. Without the use of a chelating aldehyde the intermolecular hydroacylation reaction fails. Salicyladldehyde, which is a chelating aldehyde, will undergo intermolecular hydroacylation with dienes to give ketones (Eq 12).[16]



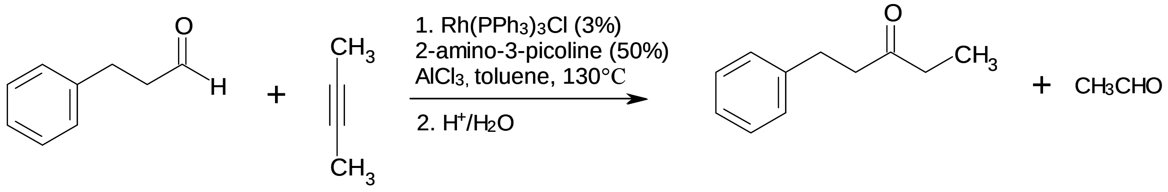
(Eq 12)

A similar approach has also been reported by Willis. He demonstrated intermolecular hydroacylation was possible using 6-thio aldehydes and cationic rhodium catalysts (Eq 13).[17]

Jung was able to effect intermolecular hydroacylation using 2-amino-3-picoline as a removeable chelating atom source (Eq 14).[18] The picoline is initially reacted with the aldehyde to form the imine. Rh^{+1} can insert into the C-H bond yielding a iminoacylrhodium(III) hyride. Alkene coordination and inerstion followed by reductive elimination forms the ketimine and the Rh^{+1} catalyst. Hydrolysis with water then gives the final intermolecular hydroacylation product.

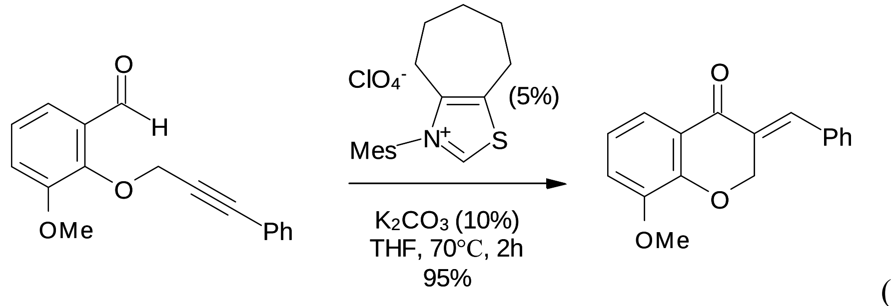


(Eq 13)



(Eq 14)

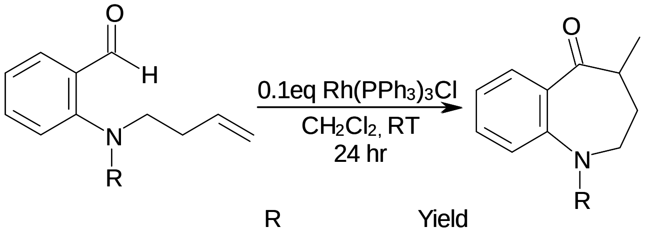
Until recently, intramolecular or intermolecular hydroacylation has required a transition metal catalyst, such as rhodium. However, a paper reports that hydroacylation can be achieved using *N*-heterocyclic carbenes (Eq 15).[19]



(Eq 15)

Results and Discussion

Recent work in the Bendorf lab examined the use of nitrogen as a tether atom and the synthesis of nitrogen heterocycles.[6] Initial experiments showed higher yields with for allyl substituted amines (Eq 16). Given these results, it is believed nitrogen falls short of sulfur as a tether atom. Because nitrogen is a weaker tether atom, it was hypothesized the allyl group assists in coordination of the substrate in a sort of bidentate fashion and promotes the reaction.



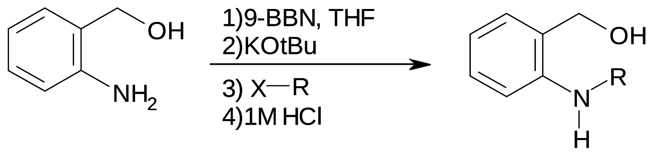
R	Yield
CH_3	11%
CH_2Ph	35%
$CH_2CH{=}CH_2$	75%

(Eq 16)

My project involves the synthesis and cyclization of substrates which contain substituted alkenes and alkynes at varying distances from the nitrogen tether atom. A preliminary task is to determine ideal reactions conditions based on solvent and temperature. The synthesiszed substrates will illustrate the ring sizes available using hydroacylation and the tolerance of the reaction with respect to substitution and steric hindrance. I am also interested in the synthesis of diphenyl allyl amine substrates to see if cyclization is possible to produce dibenzazepines.

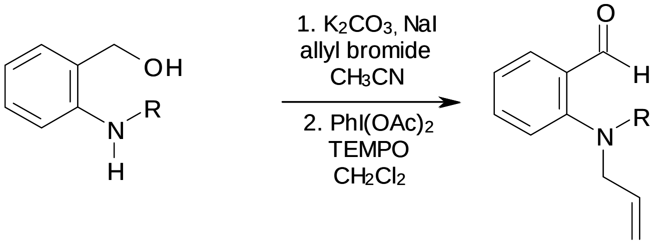
Synthesis of Substrates:

The synthesis of many of our substrates (Eq 17) begin with chelation of 9-BBN to 2-aminobenzyl alcohol. The 9-BBN complex allows mono-deprotonation of the quaternary nitrogen with potassium t-butoxide limiting the reaction to mono-alkylation. Hydrolysis with HCl then gives the mono-alkylated product.[20] Attempting direct mono-alkylation without the use of 9-BBN results is a mixture of mono- and di-alkylated products.



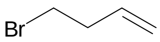
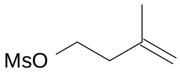
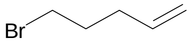
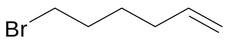
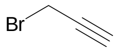
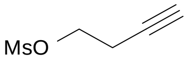
(Eq 17)

The next step is the installation of the allyl group (Eq 18). This is done by treating the secondary amine with allyl bromide and potassium carbonate in acetonitrile. Oxidation of the benzylic alcohol is then effected using iodobenzene diacetate in the presence of catalytic amounts TEMPO in methylene chloride to give the aldehyde.[21] A summary of several substrates (table 1) shows the yields for each reaction step as well as the alkylating agent used.

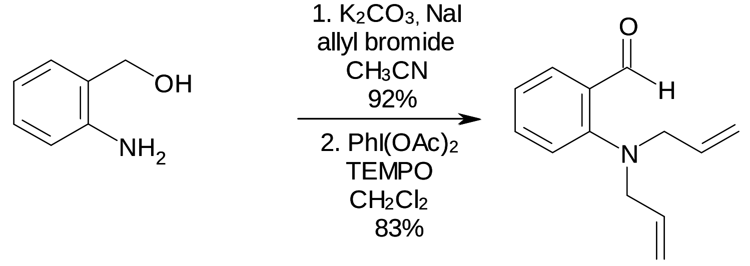


(Eq 18)

Table 1

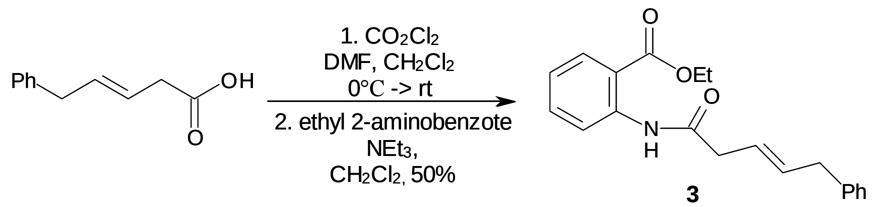
R-X	**Alkylation** **(Eq 15)**	**Allylation** **(Eq 16)**	**Oxidation** **(Eq 16)**
	72%	92%	83%
	31%	92%	85%
	78%	89%	79%
	83%	74%	82%
	31%	70%	81%
	40%	92%	82%

Synthesis of the diallyl substrate did not require the use of 9-BBN and began with the di-alkylation of 2-amino benzyl alcohol using two equivalents of allyl bromide (Eq 19). Oxidation gave the diallyl amine substrate.



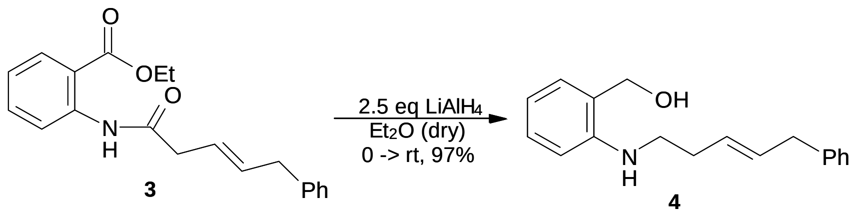
(Eq 19)

The following task was to prepare two substrates to offer more examples of substituted alkenes. The synthesis of a benzyl-substituted alkene substrate begins with the conversion of trans-styrylacetic acid to the corresponding acid chloride using oxalyl chloride (Eq 20).[22] Treatment of the crude acid chloride with the amino ester in the presence of triethylamine gives compound **3.**

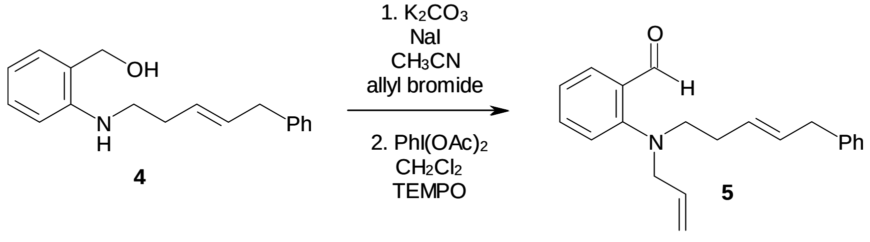


(Eq 20)

Treatment of compound **3** with lithium aluminum hydride yields compound **4** (Eq 21).[23] Subsequent allylation with allyl bromide and oxidation of the alcohol with iodobenzene diacetate and catalytic TEMPO is expected to give the hydroacylation substrate, compound **5** (Eq 22).



(Eq 21)

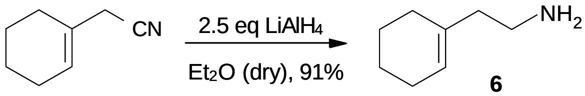


4

5

(Eq 22)

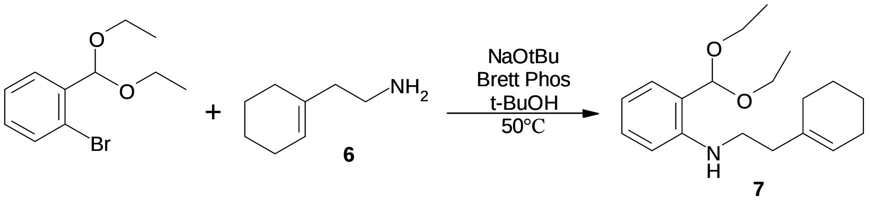
An alkene encompassed in a cyclohexane ring should offer significant steric hindrance and will further determine the tolerance of the reaction. The synthesis of a cyclohexane substituted alkene began with the reduction of 2-cyclohexene acetonitrile to compound **6** as shown in Eq 23.



6

(Eq 23)

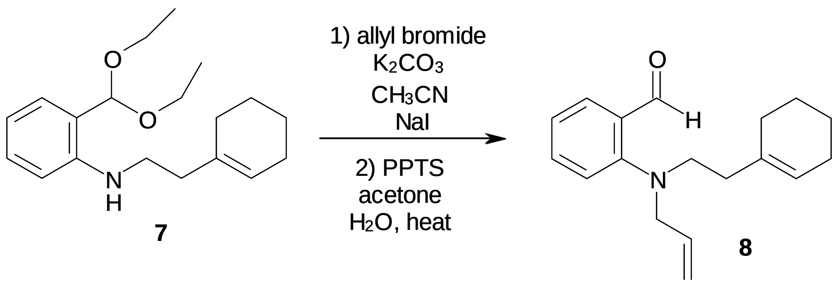
It is then proposed to couple compound **6** with 2-bromobenzaldehyde di-ethyl acetal to give compound **7** the secondary amine show in Eq 24.[24] Allylation of the secondary amine followed by deprotection of the di-ethyl acetal will yield compound **8,** the final hydroacylation substrate (Eq 25).



6

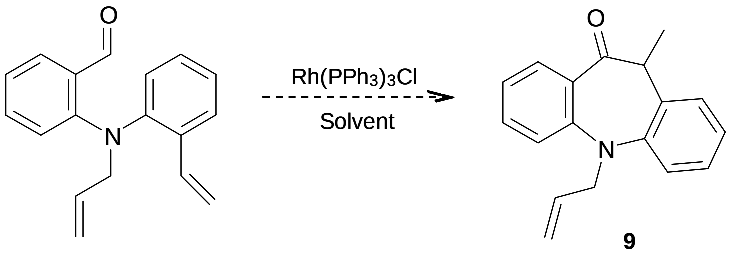
7

(Eq 24)

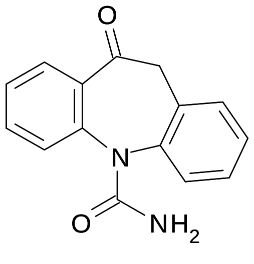


(Eq 25)

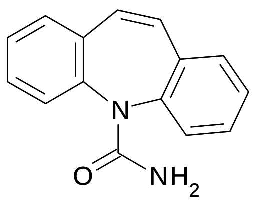
The cyclization of diphenyl allyl amine substrates would produce dibenzazepines (Eq 26) such as **9**. These compounds, such as Trileptal and Tegretol, are well established as treatments for depression and anxiety.[25] Hydroacylation may offer an easy way to synthesize such compounds.



(Eq 26)



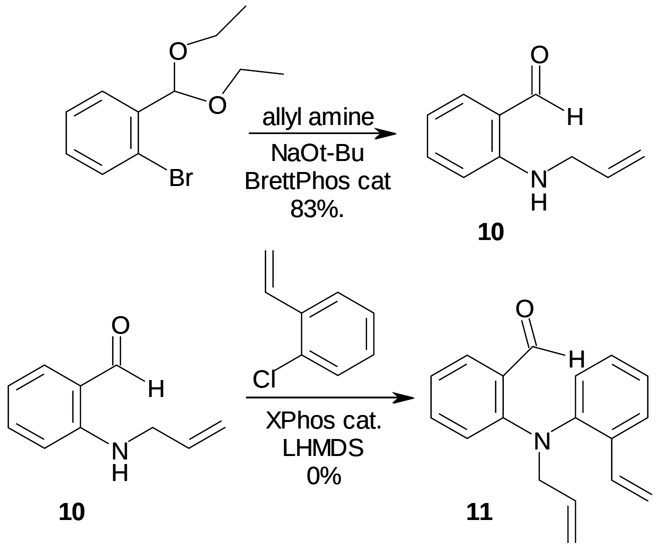
Trileptal



Tegretol

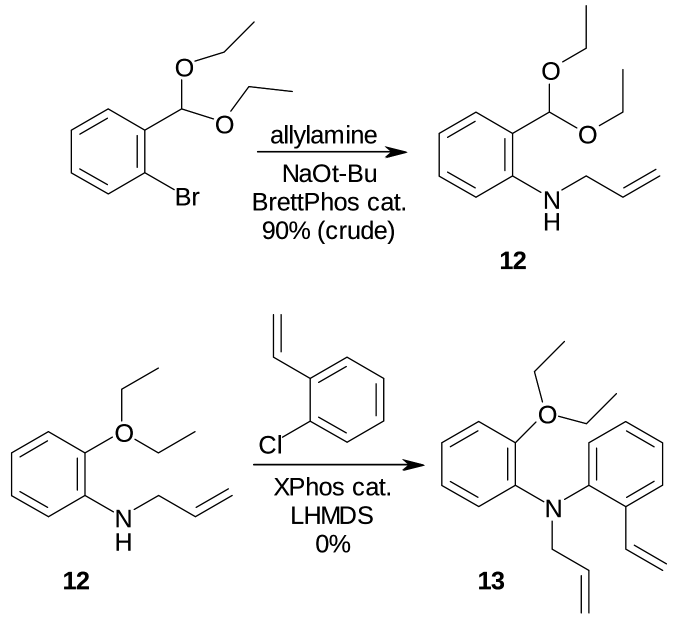
The original synthetic approach to the biaryl amine substrate, Scheme 6, began with the palladium cross-coupling of 2-bromobenzaldehyde diacetal with allylamine.[25] The reaction proved to be quick, clean and high yielding. However, purification of this compound via column chromatography effected deprotection of the acetal. Compound **10** was taken forward to a secondary amine palladium cross-coupling reaction, and despite several trials, compound **11** was not observed.[26]

Scheme 6



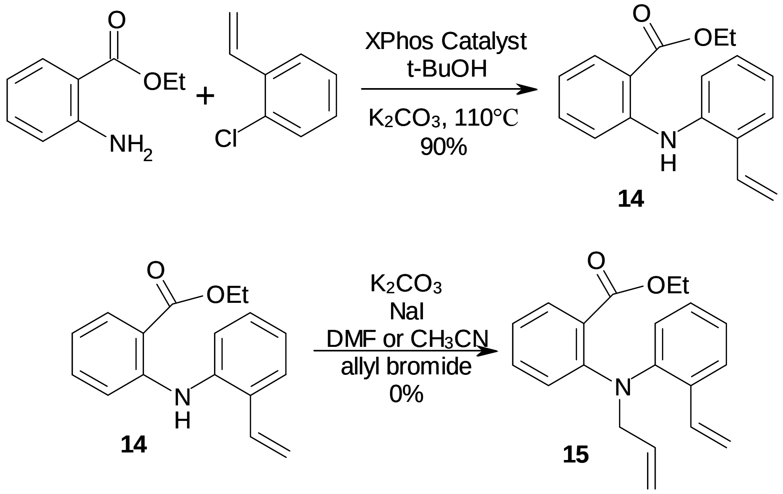
It was hypothesized the electron withdrawing aldehyde was reducing the nucleophilicity of the nitrogen to a degree which prevented the coupling. The following attempt, shown in Scheme 7, eliminates the electron withdrawing group by carrying the crude compound **12** to the coupling.[26] However , the secondary amine coupling failed yet again to give any product.

Scheme 7



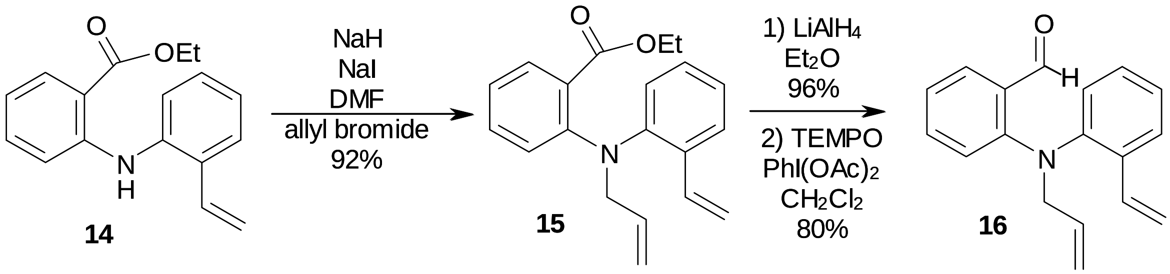
The second synthetic approach, shown in Scheme 8, uses the palladium cross-coupling of ethyl-2-aminobenzoate and chlorostryene to give compound **14**. This reaction was a clean high-yielding step.[26] Allylation of compound **8** was attempted first in refluxing acetonitrile and second in refluxing DMF, neither gave an appreciable amount of product. The similar issue of reduced nucleophilicity of the nitrogen, this time caused by the ester functional group, lead to the S_N2 failing.

Scheme 8



To increase the nucleophilicity of the nitrogen, sodium hydride was used to completely deprotonate the amine as shown in Scheme 9. The allylation of compound **14** occurred in excellent yield. Subsequent reduction of compound **15** with lithium aluminum hydride and oxidation of the alcohol gave compound **16**, the final hydroacylation substrate.

Scheme 9



Optimization of Reaction Conditions:

Initial studies involved optimizing reaction conditions. Methylene chloride, dichloroethane and acetonitrile were both examined at room temperature as well as reflux. The choice of these two solvents allowed the comparison of coordinating and non-coordinating solvents. Table 2 highlights the effects of the solvent results. The data shows coordinating solvents boost reaction rates but they cannot compete with the purity and overall yield produced by non-coordinating solvents. A competing reaction, caused by a more electron rich metal center, decarbonylates the substrate and produces a catalytically inactive complex $Rh(PPh_3)_2(CO)Cl$. In conjunction with rendering the catalyst inactive, decarbonylation of the substrate gives compound **17.** Compound **18,** a result of deallylation of the nitrogen, was also seen and is likely caused by the presence of water in the reaction.

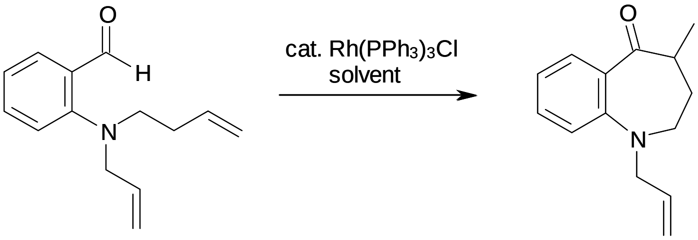
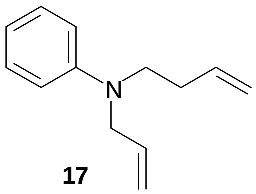


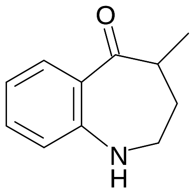
Table 2: Solvent Effects

Solvent	1 Hour	Yield
CH_2Cl_2, RT	27%	71%
CH_2Cl_2, reflux	46%	81%
$C_2H_4Cl_2$, reflux	53%	86%
acetone, reflux	55%	71%
CH_3CN, reflux	76%	58%

Yields (Table 2) reported are isolated yields.



17



18

Rings Size:

After determining ideal reaction conditions, the next set of experiments was designed to determine the size of rings accessible. Table 3 displays the results obtained for substrates when the distance between tether atom and alkene functional group was varied. The data shows upon increasing the distance by more than three atoms the reaction fails to give any appreciable yields. Longer chains have more conformational freedom and coordination of the nitrogen atom is less likely to promote the coordination of the alkene which is necessary for the reaction.

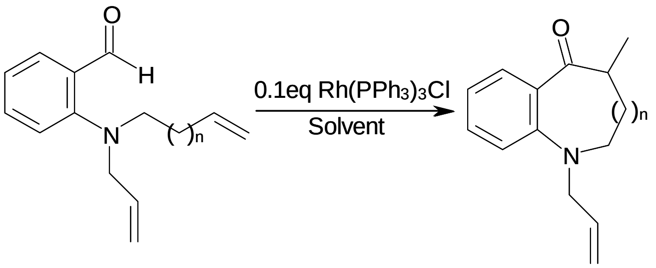
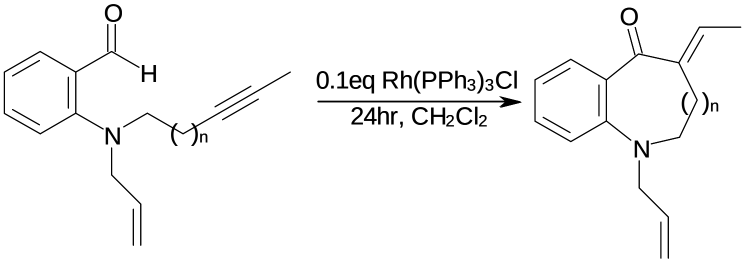


Table 3: Chain Length (Alkenes)

n	Solvent	24 hr
0	CH_3CN, reflux	0%
1	CH_2Cl_2,reflux	80%
2	CH_3CN, rt to reflux	trace
	$C_2H_4Cl_2$, rt to reflux	trace
3	CH_3CN, reflux	no rxn
	CH_2Cl_2, rt to reflux	no rxn

Note: yields reported in table 3 are isolated yields.

Several reactions were also carried out on analogous alkynes to probe possible ring sizes (Eq 26). The reactions were performed in methylene chloride or acetonitrile under various temperatures and the results are summarized in Table 4.



(Eq 26)

Table 4: Chain Length (Alkynes)

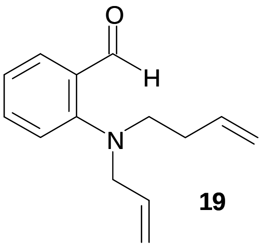
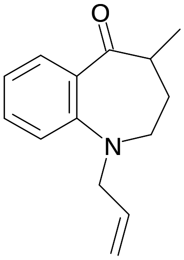
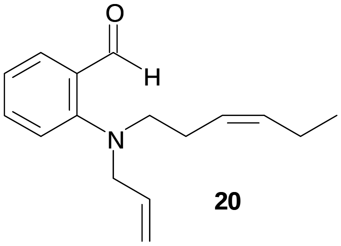
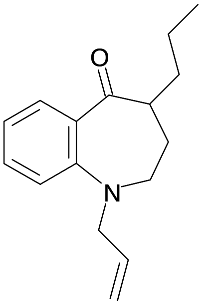
n	Solvent	24 hr
1	CH_2Cl_2,rt	65%
	CH_3CN, reflux	76%
	CH_3CN, reflux	84%
2	CH_2Cl_2, rt	77%
	CH_2Cl_2, rt	75%
	CH_3CN, reflux	72%

Note: yields reported (table 4) are isolated yields.

Data shows (table 4) cyclization of alkynes gave access to seven- and eight-membered nitrogen heterocycles. Formation of these rings were accomplished in both room temperature methylene chloride as well as refluxing acetonitrile. Reactions run in methylene chloride offered similar yields to those run in acetonitrile but also produced fewer byproducts such as decarbonylation. The formation of eight-membered rings from alkyne substrates demonstrates a higher reactivity than that of the alkenes.

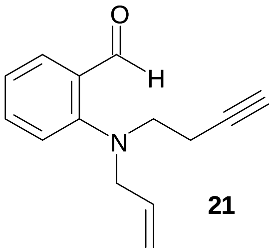
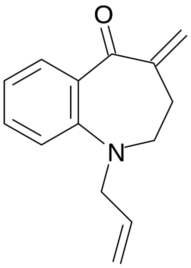
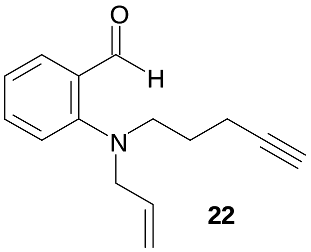
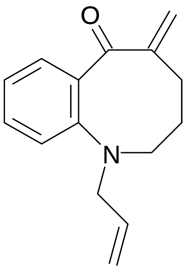
These results have already shown via the use of a tether atom, seven- and eight-membered rings can be formed. The formation of seven- and eight-membered nitrogen containing lactones was reported by Dong which agrees with the results found in our lab. The formation of nine-membered rings by hydroacylation has not yet been reported.

Table 5: Cyclization of Alkenes

Substrate	Product	Yield
 **19**		79%
 **20**		84%

Two separate examples of alkenes are shown in Table 5. Treatment of the butenyl substrate yielded a seven-membered nitrogen heterocyle in 79% yield (table 5). The reaction showed consumption of starting material after 3.25 hours with only small amounts of decarbonylation and deallylated product. A similar reaction was conducted with the cis-disubtituted alkene (table 5). After 3.5 hours at reflux the reaction showed complete consumption of the starting material and the propyl-substituted seven-membered nitrogen heterocycle was obtained in 84% yield.

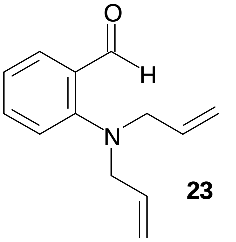
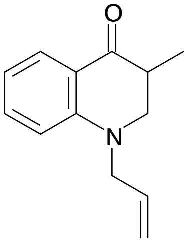
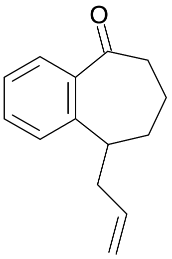
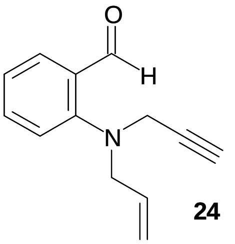
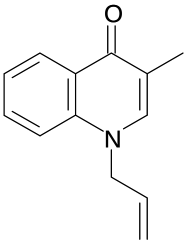
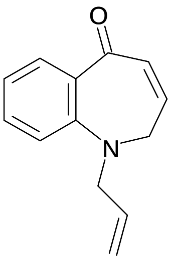
Table 6: Un-substituted Alkynes

Substrate	Product	Yield
 **21**		34%
 **22**		Pending

Substrates containing terminal alkynes were attempted in room temperature methylene chloride. The first was the treatment of a 3-butynyl substrate 21, to give a seven-membered nitrogen heterocycles (table 6). After 24 hours, small amounts of starting material remained and the product was isolated in a 34% yield. This reaction resulted in the formation of a reactive enone functional group in the final hydroacylation product. It is believed this enone functional group allows for a product consuming side reaction which lowers yields.

The pentynl substrate after 24 hours showed no appreciable progress by TLC, mostly starting material remained with several other smaller spots. The formation of the enone functional group as well as the eight-membered ring may prevent the reaction from occurring. Earlier, unpublished work from the Bendorf lab showed the ability to trap such enone functional groups when working with similar sulfur analogues. This was accomplished by the addition of nucleophilic amines to the enone functional group via conjugate addition. This method may be able to be used to trap these nitrogen heterocycles and allow us to isolate the hydroacylation products.

Table 7: Allyl and Propargyl Substrates

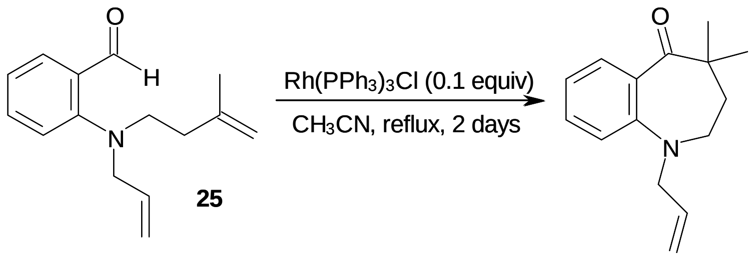
Substrate	Product	Yield
 **23**	 or 	trace
 **24**	 or 	trace

Experiments were also performed on allyl and propargyl substrates. Treatment of the allyl substrate after 24 hours at reflux only gave trace amounts of cyclized product and starting material by GC (table 7).[6] This does not come as a surprise due to the lack of precedence in the literature form the formation of six-membered rings. Only substituted cyclopentanones are reported in literature from Larock and Bosnich when attempts for cyclohexanones were made.

The cyclization attempt of the propargyl substrate yielded similar results to that of the allyl substrate (table). After 24 hours at reflux the reaction only showed trace amounts of product by GC and starting material was recovered.

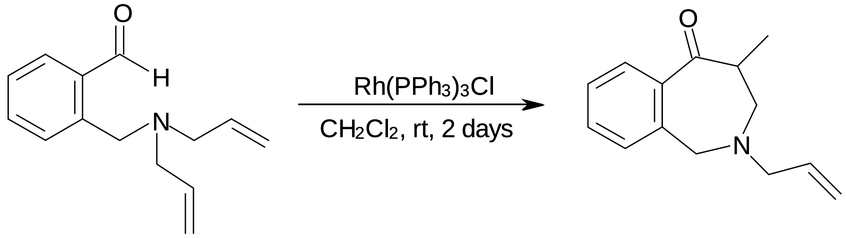
Substitution:

To further probe steric hindrance, the cyclization of a methyl substituted alkene was attempted (Eq 27). Reactions in the literature published by Larock and Bosnich showed that similar compounds underwent hydroacylation. However, it appears our reaction using the non-ionic Wilkinson's catalyst is much more sensitive to steric hindrance on the alkene.[6]



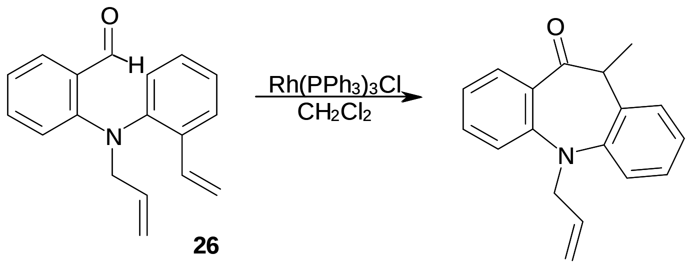
(Eq 27)

Experiments were also conducted to probe the sensitivity of the distance between aldehyde and tether atom (Eq 28).[6] This reaction, which placed tether atom three atoms from aldehyde, gave no product. Only starting material and small amounts of decarbonylation were observed.



(Eq 28)

Initial hydroacylation experiments (Eq 29) on the biaryl amine substrate were carried out using Wilkinson's catalyst in methylene chloride. The first attempt, initially at room temperature, showed no progress after two hours, at which point it was heated to reflux. After 24 hours at reflux, the reaction showed small amounts of the decarbonylation product and 70% of starting material was recovered.



26

(Eq 29)

A second experiment was performed in methylene chloride at 90 ˚C in a sealed Schlenk tube. After 8 hours, the reaction proceeded in a similar manner as the previous and starting material was recovered.

Conclusions

Work in the Bendorf lab has successfully developed a route to medium ring nitrogen heterocycles via intramolecular hydroacylation. With the use of $Rh(PPh_3)_3Cl$, optimized reaction conditions have allowed the formation of seven- and eight-membered nitrogen heterocycles in moderate to high yields. The reaction does however show sensitivity to the distance between chelating atom and alkene which limits the reaction to the formation of seven- and eight-membered rings. Experiments have also shown hydroacylation will shutdown in the case where an alkene is too sterically hindered.

Hydroacylation experiments will also be conducted on the benzyl substituted alkene substrate as well as synthesis of the cyclohexene substrate will be completed. This will give further knowledge into the reactions tolerance to alkene substitution.

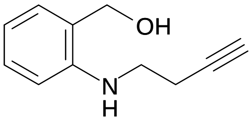
A four step, high yielding synthetic scheme was developed using commercially available compounds for the synthesis of the biaryl amine hydroacylation substrate. Initial experiments on hydroacylation demonstrate the formation of dibenzazpeines via $Rh(PPh_3)_3Cl$-catalyzed hydroacylation is not possible. However, cationic catalyst may offer a way to form dibenzazepines.

Experimental

General Methods:

All reactions were carried out under an inert atmosphere of argon unless otherwise noted. Glassware, including syringes, was oven-dried and cooled under argon. Anhydrous solvents and reagents were used as received from Aldrich. Methylene chloride and acetonitrile were distilled from calcium hydride. Palladium catalysts were purchased from Strem Chemicals Inc.. Compounds were purified by column chromatography, with 70-230 mesh silica gel using specified ratios of hexane:ethyl acetate. Reactions were monitored using a GC-2014 Shimadzu Gas Chromatograph. Spectra were obtained using a 300 MHz Bruker Avance NMR Spectrometer, Thermo Electron IR100 and a Thermo Polaris Q GC/MS.

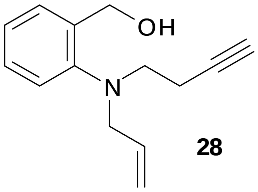
2-(1-butyn-4-ylamino)benzyl alcohol



27

An oven dried schlenk tube was charged with 2-aminobenzyl alcohol (750 mg, 6.09 mmol). The flask was placed under an argon atmosphere by three consecutive evacuations and backfills. THF (30 mL, 0.2 M in aminobenzyl alcohol) was added as solvent. 9-BBN was then added via syringe (16.0 mL, 6.39 mmol, 0.40 M in hexane) and stirred for three hours. At 3 hr, KOtBu (6.7 mL, 6.7 mmol, 1.0 M in THF) was added via syringe. After stirring for two hours at room temperature, 3-butynl-1-methanesulfonate was added via syringe (1.00 g, 6.70 mmol). The reaction was stirred overnight, filtered and concentration *in vacuo*. The 9-BBN complex was hydrolyzed using 1 M HCl (120 mL). After stirring for 48 hours, an organic wash was performed with ether (3 x 40 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction (3 x 40 mL) and concentration *in vacuo* gave the crude mono-alkylated product. Chromatography using a solvent gradient of 95:5 Hex/EtOAc → 90:10 Hex/EtOAc yielded an off white solid (430 mg, 2.44 mmol, 40%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.25 (t, *J*=7.6, 1H), 7.10 (d, *J*=7.0, 1H), 6.72 (m, 2H), 5.05 (bs, 1H) 4.69 (s, 2H), 3.39 (t, *J*=6.7, 2H), 2.56 (td, *J*=6.7, 2.5, 2H), 2.06 (t, *J*=2.5, 1H), 1.65 (bs, 1H) ppm. IR (neat, cm^{-1}): 3378, 3286, 2916, 2100, 1602, 1584, 1512.

2-(allyl-1-butyn-4-yl)benzyl alcohol

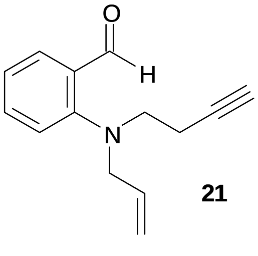


28

Compound **27** (400 mg, 2.34 mmol) was dissolved in acetonitrile (15 mL, 0.15 M in amine) as solvent. Potassium carbonate (648 mg, 4.69 mmol) and sodium iodide (527 mg, 3.51 mmol) were added. Allyl bromide (340 mg, 2.81 mmol) was added via syringe and the reaction was brought to reflux for 24 hours. The reaction was added to water and extracted with ether (4 x 30 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 30 mL) and brine (2 x 50 mL). The crude product was concentrated *in vacuo* and purified via chromatography running at 95:5 Hex/EtOAc -> 90:10 Hex/EtOAc gradient to afford a colorless oil (450 mg, 2.09 mmol, 92%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.18 (m, 4H), 5.87 (m, 1H), 5.18

(m, 2H), 4.83 (bs, 1H), 4.78 (s, 2H), 3.59 (d, *J*=6.4, 2H), 3.20 (t, *J*=7.0, 2H), 2.34 (td, *J*=7.0, 2.5, 2H), 2.02 (t, *J*=2.5, 1H) ppm.

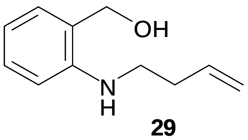
2-(allyl-1-butyn-4-ylamino)benzaldehyde



21

A 25 mL round bottom flask was charged with compound **28** (434 mg, 2.02 mmol) and freshly distilled methylene chloride (10 ml, .20 M in alcohol). Iodobenzene diacetate (910 mg, 2.83 mmol) and TEMPO (88 mg, 0.57 mmol) were added to the flask. The reaction was stirred at room temperature for 24 hours and the reaction showed complete consumption of starting material as indicated by TLC. The reaction was diluted in ether (75 ml), washed with sodium bicarbonate solution (2x40ml), sodium thiosulfate solution (2x40ml), and brine (1x 50ml). The resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (353 mg, 1.66 mmol, 82%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.42 (s, 1H), 7.84 (d, *J*=7.6, 1H), 7.52 (t, *J*=7.7, 1H), 7.18 (m, 2H), 5.85 (m, 1H), 5.21 (m, 2H), 3.78 (d, *J*=6.1, 2H), 3.38 (t, *J*=7.3, 2H), 2.37 (td, *J*=7.3,2.5, 2H), 1.97 (t, *J*=2.5, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.8, 153.6, 134.5, 133.8, 130.7, 129.4, 123.3, 121.9, 118.4, 81.8, 69.8, 59.4, 51.9, 17.2 ppm. IR (neat, cm^{-1}): 3329, 2843, 2090, 1682, 1594, 1480, 1453, 1282.

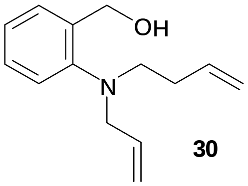
2-(1-buten-4-ylamino)benzyl alcohol



29

A schlenk flask was charged with 2-aminobenzyl alcohol (2.89 g, 23.5 mmol) and placed under an argon atmosphere. THF (80 mL, 0.20 M in aminobenzyl alcohol) was added as solvent. 9-BBN was added via syringe (61.6 mL, 24.6 mmol, 0.40 M in hexane) and stirred for three hours. KOtBu (25.8 mL, 25.8 mmol, 1.0 M in THF) was added via syringe. After stirring for two hours at room temperature, butenyl bromide was added via syringe (2.86ml, 28.1 mmol). The reaction stirred overnight followed by filtration and concentration *in vacuo*. The 9-BBN complex was hydrolyzed using 1M HCl (120 mL). After stirring for 48 hours, an organic wash was performed with ether (3 x 60 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction and concentration *in vacuo* gave the crude product. Chromatography using a solvent gradient of 98:2 Hex/EtOAc -> 90:10 Hex/EtOAc yielded a colorless oil (3.04g, 17.13 mmol, 73%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.24 (t, *J*=7.9, 1H), 7.09 (d, *J*=7.2, 1H), 6.69 (m, 2H), 5.87 (m, 1H), 5.15 (m, 2H), 4.70 (bs, 1H), 4.64 (s, 2H), 3.24 (t, *J*=6.8, 2H), 2.45 (q, *J*=6.8, 2H), 1.68 (bs, 1H) ppm. NMR (75 MHz, $CDCl_3$) δ: 146.2, 135.8, 130.4, 129.3, 127.6, 125.5, 124.8, 111.0, 64.7, 42.8, 37.2 ppm. IR (neat, cm^{-1}): 3392, 2920, 2857, 1607, 1587, 1466, 1390, 1243.

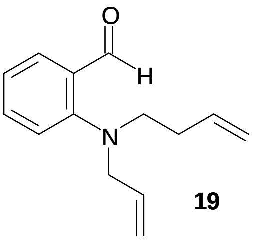
2-(allyl-1-buten-4-yl)benzyl alcohol



30

Compound 29 (1.0 g, 5.64 mmol) was dissolved in acetonitrile (50 mL, 0.15 M in amine) in an oven-dried flask. Potassium carbonate (1.56g, 11.3 mmol) and sodium iodide (1.27g, 8.46 mmol) were added to the reaction flask. Allyl bromide (.590 mL, 6.77 mmol) was added via syringe and the reaction was brought to reflux for 24 hours. The reaction was added to water and extracted with ether (3 x 35 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 40 mL) and brine (2 x 50 mL). The crude product was concentrated *in vacuo* and purified via chromatography running at 95:5 Hex/EtOAc -> 90:10 Hex/EtOAc gradient to afford a colorless oil (1.11g, 5.11 mmol, 91%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.12 (m, 4H), 5.83 (m, 2H), 5.37 (bs, 1H), 5.20 (m, 2H), 5.05 (m, 2H), 4.81 (s, 2H), 3.56 (dt, J=6.6, 1.2, 2H), 3.08 (t, *J*=7.5, 2H), 2.22 (q, *J*= 7.5, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.8, 137.1, 135.9, 134.1, 128.6, 127.8, 125.1, 122.8, 118.5, 116.3, 64.5, 58.5, 52.3, 31.5 ppm. IR (neat, cm^{-1}): 3073, 2921, 2857, 1450, 1390, 1162.

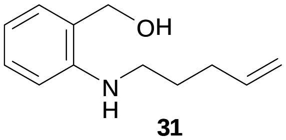
2-(allyl-1-buten-4-ylamino)benzaldehyde



19

A 25 mL round bottom flask was charged with compound **30** (161 mg, 0.74 mmol) and freshly distilled methylene chloride (5.0 ml, 0.2 M in compound **30**). Iodobenzene diacetate (287 mg, 0.89 mmol) and TEMPO (23.0 mg, 0.15 mmol) were added to the flask. The reaction was stirred at room temperature for 24 hours and TLC showed the reaction was complete. The reaction was diluted in ether (35 ml), washed with sodium bicarbonate solution (2x30ml), sodium thiosulfate solution (2x30ml), and brine (2x 35ml). Resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% Hex → 99% hexane:1% ethyl acetate to afford a bright yellow oil (119 mg, 0.5 mmol, 75%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.37 (s, 1H), 7.83 (dd, *J*=6.0, 1.7, 1H), 7.51 (td, *J*=7.2, 1.7, 1H), 7.15 (m, 2H), 5.77 (m, 2H), 5.20 (m, 2H), 4.98 (m, 2H), 3.77 (d, *J*=6.0, 2H), 3.25 (t, *J*=7.4, 2H), 2.27 (q, *J*=7.7, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 182.0, 153.0, 138.0, 136.0, 135.8, 132.0, 128.0, 124.0, 122.0, 117.0, 115.0, 60.0, 52.0, 32.0 ppm.

2-(1-penten-5-ylamino)benzyl alcohol

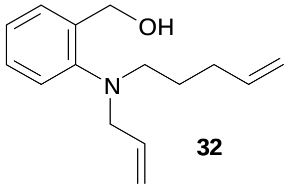


31

A 25 mL schlenk flask was charged with amino benzyl alcohol (562 mg, 4.56 mmol) and placed under an argon atmosphere. THF (20 mL, 0.2 M in aminobenzyl alcohol) was added as solvent. 9-BBN was added via syringe (12.6 mL, 5.02 mmol, 0.4 M in hexane) and stirred for three hours. KOtBu (5.00 mL, 5.02 mmol, 1.0 M in THF) was added via syringe. After stirring for two hours at room temperature, pentenyl bromide was added via syringe (.650 mL, 5.48 mmol). The reaction was stirred overnight followed by filtration and concentration *in vacuo.*

The 9-BBN complex was then hydrolyzed using 1M HCl (120 mL) and after 48 hours, an organic wash was performed with ether (4 x 30 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction and concentration *in vacuo* gave the crude product as a thick yellow oil (678 mg, 3.55 mmol, 78%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.24 (t, *J*=7.7, 1.5, 1H), 7.07 (d, *J*=7.2, 1.5, 1H), 6.68 (m, 2H), 5.86 (m, 1H), 5.06 (m, 2H), 4.70 (bs, 1H), 4.67 (s, 2H), 3.19 (t, *J*=7.1, 2H), 2.21 (q, *J*=7.1, 2H), 1.80 (p, *J*=7.2, 2H), 1.65 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.4, 138.1, 130.6, 129.2, 127.7, 125.6, 115.2, 111.0, 64.6, 37.6, 31.5, 28.6 ppm. IR (neat, cm^{-1}): 3392, 3073, 2922, 2851, 1630, 1603, 1513.

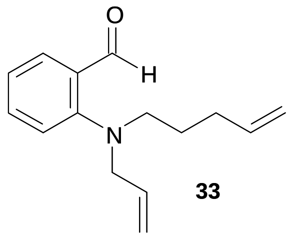
2-(allyl-1-penten-5-yl)benzyl alcohol



32

Compound **31** (362 mg, 1.89 mmol) was dissolved in acetonitrile (20 mL, 0.15 M in compound **31**). Potassium carbonate (523 mg, 3.79 mmol) and sodium iodide (426 mg, 2.84 mmol) were added to the reaction flask. Allyl bromide (0.20 mL, 2.27 mmol) was added via syringe and the reaction was brought to reflux for 24 hours. The reaction was added to water and extracted with ether (4 x 20 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 20 mL) and brine (2 x 40 mL). The crude product was concentrated *in vacuo* and purified via chromatography running 100% Hex → 95:5 Hex/EtOAc gradient to afford a colorless oil (388 mg, 1.68 mmol, 89%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.21 (m, 4H), 5.84, (m, 2H), 5.67 (s, 1H), 5.18 (m, 2H), 4.97 (m, 2H), 4.83 (s, 2H), 3.56 (d, *J*=6.5, 2H), 3.00 (t, *J*=7.4, 2H), 2.04 (q, *J*=7.4, 2H), 1.57 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.1, 138.0, 137.0, 134.3, 128.4, 127.8, 125.0, 122.9, 188.4, 115.0, 65.0, 58.6, 52.8, 31.4, 26.3 ppm. IR (neat, cm^{-1}): 3393, 3073, 2931, 2835, 1630, 1488, 1450, 911.

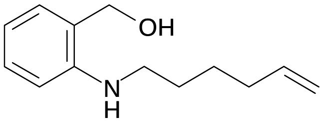
2-(allyl-3-pentenylamino)benzaldehyde



33

A 25 mL round bottom flask was charged with the compound **32** (297 mg, 1.29 mmol) and freshly distilled methylene chloride (6.0 ml, .20 M in compound **32**). Iodobenzene diacetate (580 mg, 1.80 mmol) and TEMPO (40 mg, 0.26 mmol) were added to the flask. The reaction was stirred at room temperature overnight and the reaction showed complete consumption of starting material as indicated by TLC. The reaction was diluted in ether (30 ml), washed with sodium bicarbonate solution (2x30ml), sodium thiosulfate solution (2x30ml), and brine (2x 40ml). Resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (233 mg, 1.02 mmol, 79%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.37 (s,1H), 7.82 (dd, *J*=7.7, 1.7, 1H), 7.50 (td, *J*=7.7, 1.8, 1H), 7.12 (m, 2H), 5.81 (m, 2H), 5.21 (m, 2H), 4.97 (m, 2H), 3.75 (d, *J*=6.2, 2H), 3.17 (t, *J*=7.3, 2H), 2.04 (q, *J*=7.3, 2H), 1.61 (h, *J*=7.3, 2H) ppm. NMR (75 MHz, $CDCl_3$) δ: 191.7, 154.6, 137.9, 134.3, 134.2, 130.1, 129.3, 122.4, 121.5, 117.9, 115.0, 59.6, 52.6, 31.2, 26.3 ppm. IR (neat, cm^{-1}): 3074, 2932, 2839, 1684, 1658, 1594, 1480, 1452.

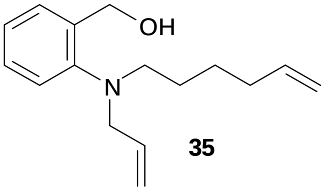
2-(1-hexen-6-ylamino)benzyl alcohol



34

A schlenk tube was charged with amino benzyl alcohol (1.22 g, 9.92 mmol). The flask was placed under an argon atmosphere and THF (35 mL, 0.20 M in aminobenzyl alcohol) was added. 9-BBN was added via syringe (27.3 mL, 10.9 mmol, 0.40 M in hexane) and stirred for three hours. KOtBu (10.9 mL, 10.9 mmol) was added via syringe (1.0 M in THF). After stirring for two hours at room temperature, hexenyl bromide was added via syringe (1.67 mL, 11.9 mmol). The reaction was allowed to stir overnight followed by filtration and concentration *in vacuo*. The 9-BBN complex was hydrolyzed using 1M HCl (120 mL) and after 48 hours an organic wash was performed with ether (3 x 40 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction and concentration *in vacuo* gave the crude product as a colorless oil (1.69 g, 8.24 mmol, 83%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.25 (td, *J*=7.7, 1.4, 1H), 7.07 (dd, *J*=7.2, 1.4, 1H), 6.69 (m, 2H), 5.85 (m, 1H), 5.02 (m, 2H), 4.75 (bs, 1H), 4.66 (s, 2H), 3.17 (t, *J*=7.0, 2H), 2.15 (qt, *J*=7.0, 1.3, 2H), 1.71 (m, 2H), 1.60 (bs, 1H), 1.55 (m, 2H) ppm. NMR (75 MHz, $CDCl_3$) δ: 147.7, 138.7, 129.6, 129.1, 124.4, 116.3, 114.8, 110.7, 64.6, 43.5, 33.6, 28.9, 26.5 ppm. IR (neat, cm^{-1}): 3380, 3074, 2927, 2856, 1640, 1606, 1586, 1514, 1460, 992.

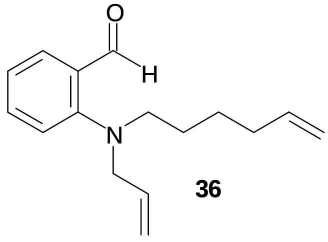
2-(allyl-1-hexen-4-yl)benzyl alcohol



35

Compound **34** (1.56 g, 7.62 mmol) was dissolved in acetonitrile (50 mL, 0.15 M in amine) as solvent. Potassium carbonate (2.10 g, 15.3 mmol) and sodium iodide (1.71 g, 11.4 mmol) were added to the reaction flask and rinsed with a small amount of solvent. Allyl bromide (0.80 mL, 9.2 mmol) was added via syringe and the reaction was brought to reflux for 24 hours. The reaction was added to water and extracted with ether (4 x 35 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 40 mL) and brine (2 x 50 mL). The crude product was concentrated *in vacuo* and purified via chromatography running at 98:2 Hex/EtOAc -> 95:5 Hex/EtOAc gradient to afford a colorless oil (1.38 g, 5.63 mmol, 74%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.22 (m, 4H), 5.82 (m, 2H), 5.75 (bs, 1H), 5.17 (m, 2H), 4.96 (m, 2H), 4.83 (s, 2H), 3.56 (d, *J*=6.5, 2H), 2.99 (t, *J*=7.6, 2H), 2.02 (q, *J*=7.1, 2H), 1.38 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ:149.2, 138.5, 136.9, 134.1, 128.3, 127.8, 124.9, 122.9, 118.5, 114.6, 64.8, 58.5, 56.6, 53.1, 33.5, 26.6. IR (neat, cm^{-1}): 3400, 3073, 2929, 2855, 1630, 1488, 1451, 1417, 913.

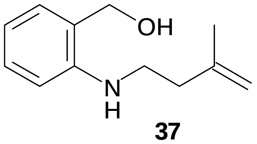
2-(allyl-3-hexenylamino)benzaldehyde



36

A 100 mL round bottom flask was charged with the compound **35** (1.21 g, 4.95 mmol) and freshly distilled methylene chloride (20 ml, .2 M in compound **35**). Iodobenzene diacetate (2.23 g, 6.92 mmol) and TEMPO (154 mg, 0.99 mmol) were added to the flask. The reaction was stirred at room temperature for 24 hours and the reaction showed complete by TLC. The reaction was diluted in ether (60 ml), washed with sodium bicarbonate solution (2x40ml), sodium thiosulfate solution (2x40ml), and brine (2x 50ml). Resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (982 mg, 4.04 mmol, 82%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.37 (s, 1H), 7.82 (dd, *J*=7.7,1.7, 1H), 7.50 (td, *J*=7.7, 1.7, 1H), 7.12 (m, 2H), 5.81 (m, 2H), 5.19 (m, 2H), 4.95 (m, 2H), 3.75 (d, *J*=6.1, 2H), 3.16 (t, *J*=7.3, 2H), 2.02 (q, *J*=7.1, 2H), 1.51 (m, 2H), 1.38 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.8, 154.6, 138.5, 134.3, 134.2, 130.0, 129.3, 122.3, 121.4, 117.9, 114.7, 59.5, 53.1, 33.4, 26.4, 26.3 ppm. IR (neat, cm^{-1}): 3074, 2931, 2854, 1684, 1650, 1594, 1480, 1452, 1280.

2-(2-methyl-1-buten-4-ylamino)benzyl alcohol

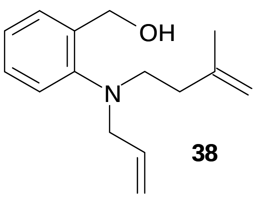


37

A 50 mL schlenk flask was charged with amino benzyl alcohol (558 mg, 4.53 mmol). The flask was placed under an argon atmosphere and THF (20 mL, 0.20 M in aminobenzyl alcohol) was added. 9-BBN was added via syringe (12.5 mL, 4.98 mmol, 0.40 M in hexane) and stirred for three hours. KOtBu (4.98 mL, 4.98 mmol, 1.0 M in THF) was added via syringe. After stirring for two hours at room temperature, 3-methyl-3-butene methanesulfonate was added via syringe (893 mg, 5.44 mmol). The reaction was stirred overnight followed by filtration and concentration *in vacuo*. The 9-BBN complex was hydrolyzed using 1M HCl (60 mL). After stirring for 48 hours, an organic wash was performed with ether (4 x 30 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction and concentration *in vacuo* gave the crude product. Chromatography using a solvent gradient of 95:5 Hex/EtOAc -> 90:10

Hex/EtOAc yielded a colorless oil (266 mg, 1.39 mmol, 31%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.26 (t, *J*=7.3, 1H), 7.15 (td, *J*=7.7, 1.6, 1H), 7.07 (dd, *J*=7.3, 1H), 6.71 (m, 2H), 4.86 (d, *J*=13.5, 1H), 4.63 (d, *J*=5.6, 2H), 4.16 (bs, 1H), 3.27 (t, *J*=6.8, 2H), 2.41 (t, *J*=6.8, 2H), 2.05 (bs, 1H), 1.29 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.5, 143.1, 129.7, 129.1, 124.4, 116.4, 112.2, 110.7, 64.7, 41.2, 37.4, 22.1 ppm. IR (neat, cm^{-1}): 3378, 3073, 2932, 1630, 1607, 1586, 1513, 1460, 1314.

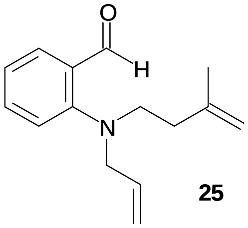
2-(3-allyl-2-methyl-1-buten-4-ylamino)benzyl alcohol



38

Compound **37** (200 mg, 1.05 mmol) was dissolved in acetonitrile (7.0 mL, 0.15 M in compound **37**). Potassium carbonate (290 mg, 2.09 mmol) and sodium iodide (235 mg, 1.57 mmol) were added to the 50 mL reaction flask with condenser. Allyl bromide (0.109 mL, 1.26 mmol) was added via syringe and the reaction was brought to reflux for 24 hours. The reaction was added to water and extracted with ether (3 x 30 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 30 mL) and brine (2 x 50 mL). The crude product was concentrated *in vacuo* and purified via chromatography running at 98:2 Hex/EtOAc -> 95:5 Hex/EtOAc gradient to afford a colorless oil (221 mg, 0.96 mmol, 92%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.20 (m, 4H), 5.87 (m, 1H), 5.40 (bs, 1H), 5.20 (m, 2H), 4.78 (m, 3H), 4.67 (bs, 1H), 3.58 (d, *J*=6.6, 2H), 3.15 (t, *J*=7.7, 2H), 2.17 (t, *J*=7.7, 2H), 1.71 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.1, 143.4, 137.0, 134.1, 128.6, 127.9, 125.0, 122.9, 118.6, 111.3, 65.0, 58.6, 50.9, 35.2, 22.6 ppm. IR (neat, cm^{-1}): 3396, 3072, 2934, 2840, 1650, 1600, 1488, 1451, 1026.

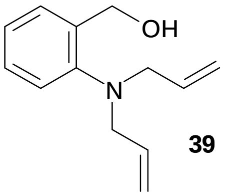
2-(3-allyl-2-methyl-1-buten-4-ylamino)benzaldehyde



25

A 25 mL round bottom flask was charged with the compound **38** (189 mg, 0.89 mmol) and freshly distilled methylene chloride (9.0 mL, .20 M in alcohol). Iodobenzene diacetate (399 mg, 1.24 mmol) and TEMPO (26 mg, 0.16 mmol) were added to the flask. The reaction was stirred at room temperature for 24 hours. The reaction was diluted in ether (40 ml), washed with sodium bicarbonate solution (2x25ml), sodium thiosulfate solution (2x25ml), and brine (2x 40ml). The organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (187 mg, 0.89 mmol, 85%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.82 (dd, *J*=7.7, 1.7, 1H), 7.51 (td, *J*=7.7, 1.8, 1H), 7.14 (m, 2H), 5.85 (m, 1H), 5.20 (m, 2H), 4.73 (s, 1H), 4.61 (s, 1H), 3.76 (d, *J*=6.0, 2H), 3.29 (t, *J*=7.6, 2H), 2.22 (t, *J*=7.6, 2H), 1.70 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.9, 154.4, 143.2, 134.3. 134.1, 130.4, 129.2, 122.6, 121.7, 118.0, 111.6, 59.7, 51.4, 35.1, 22.4 ppm. IR (neat, cm^{-1}): 3073, 2934, 2840, 1684, 1653, 1594, 1480, 1452.

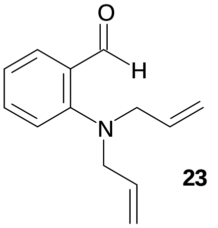
2-(diallyamino)benzyl alcohol



39

2-Aminobenzyl alcohol (1.13 g, 9.16 mmol) was dissolved in an oven-dried flask in acetonitrile (70 mL, 0.15 M in aminobenzyl alcohol). Potassium carbonate (5.06 g, 36.6 mmol) and sodium iodide (4.12 g, 27.5 mmol) were added to the reaction flask. Allyl bromide (1.84 mL, 20.1 mmol) was added via syringe and the reaction was brought to reflux. After 24 hours, the reaction was added to water and extracted with ether (4 x 35 mL). Organic layers were combined and washed with sodium thiosulfate (3 x 35 mL) and brine (2 x 40 mL). The crude product was concentrated *in vacuo* and isolated as a colorless oil (1.71 g, 8.42 mmol, 92%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.19 (m, 4H), 5.83 (m, 2H), 5.30 (bs, 1H), 5.17 (m, 4H), 4.82 (s, 2H), 3.61 (d, *J*=6.5, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.9, 136.7, 134.0, 128.5, 137.7, 124.9, 123.3, 118.6, 64.8, 56.7 ppm. IR (neat, cm^{-1}): 3367, 3073, 2978, 2821, 1620, 1488, 1451, 1417, 1209.

2-(diallylamino)benzaldehyde

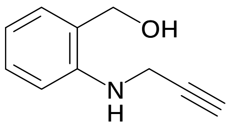


23

A 100 mL round bottom flask was charged with compound **39** (1.62 g, 7.97 mmol) and freshly distilled methylene chloride (40 ml, .2 M in compound **39**). Iodobenzene diacetate (3.60

g, 11.2 mmol) and TEMPO (250 mg, 1.59 mmol) were added to the flask. The reaction was stirred at room temperature for 24 hours. The reaction was diluted in ether (50 ml), washed with sodium bicarbonate solution (2x40ml), sodium thiosulfate solution (2x40ml), and brine (2x 50ml). The resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (1.33 g, 6.62 mmol, 83%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.4 (s, 1H), 7.82 (dd, *J*=7.7, 1.7, 1H), 7.48 (td, *J*=7.7, 1.7, 1H), 7.10 (m, 2H), 5.84 (m, 2H), 5.20 (m, 4H), 3.80 (d, *J*=5.9, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.6, 154.2, 134.3, 133.9, 129.4, 129.3, 122.1, 121.3, 118.1, 57.3 ppm. IR (neat, cm^{-1}): 3075, 2980, 2837, 1683, 1659, 1594, 1480, 1280.

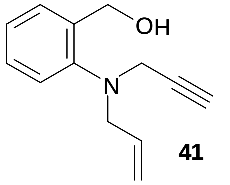
2-(propargylamino)benzyl alcohol



40

An schlenk flask was charged with amino benzyl alcohol (561 mg, 4.55 mmol). The flask was placed under an argon atmosphere and THF (60 mL, 0.2 M in aminobenzyl alcohol) was added. 9-BBN was added via syringe (12.5 mL, 5.01 mmol, 0.4 M in hexane) and stirred for three hours. KOtBu (5.0 mL, 5.0 mmol, 1.0 M in THF) was added via syringe. After stirring for two hours at room temperature, propargyl bromide (2M solution toluene) was added via syringe (.609 mL, 5.47 mmol). The reaction was let to stir overnight followed by filtration and concentration *in vacuo*. The 9-BBN complex was hydrolyzed using 1M HCl (60 mL) and after stirring for 48 hours, an organic wash was performed with ether (3 x 40 mL). Neutralization with 20% sodium hydroxide followed by an ether extraction and concentration *in vacuo* gave the crude product as an off-white solid (480 mg, 2.98 mmol, 65%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.10 (m, 4H), 5.06 (bs, 1H), 3.73 (m, 2H), 3.53 (m, 2H), 1.89 (s, 1H), 0.66 (bs, 1H) ppm. IR (neat, cm^{-1}): 3378, 3277, 2918, 1607, 1584, 1508, 1306, 1255.

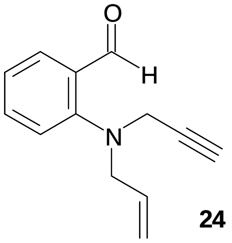
2-(2-allyl-2-propargylamino)benzylalcohol



41

Compound **40** (486 mg, 2.97 mmol) was dissolved in acetonitrile (20 mL, 0.15 M in compound **40**) in an oven-dried flask. Potassium carbonate (822 mg, 5.95 mmol) and sodium iodide (669 mg, 4.46 mmol) were added to the reaction flask. Allyl bromide (0.40 mL, 3.57 mmol) was added via syringe and the reaction was brought to reflux. After 24 hours the reaction was added to water and extracted with ether (4 x 35 mL). Organic layers were combined and washed with sodium thiosulfate (2 x 35 mL) and brine (2 x 40 mL). The crude product was concentrated *in vacuo* to give an off-white solid (421 mg, 2.08 mmol, 70%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.29 (m, 4H), 5.86 (m, 1H), 5.32 (d, *J*=17.1, 1H), 5.22 (d, *J*=10.1, 1H), 4.80 (s, 2H), 4.41 (bs, 1H), 3.81 (d, *J*=2.4, 2H), 3.73 (d, *J*=6.5, 2H), 2.27 (t, *J*=2.4, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.6, 136.5, 133.9, 128.7, 127.9, 125.3 123.3, 119.1, 78.8, 73.8, 63.8, 55.8, 42.6 ppm. IR (neat, cm^{-1}): 3380, 3289, 3070, 2837, 1610, 1489, 1451, 1209.

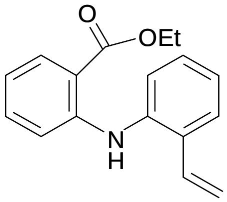
2-(2-allyl-2-propargylamino)benzaldehyde



24

A 50 mL round bottom flask was charged with compound **41** (317 mg, 1.56 mmol) and freshly distilled methylene chloride (15 ml, .20 M in alcohol). Iodobenzene diacetate (706 mg, 2.19 mmol) and TEMPO (49 mg, 0.31 mmol) were added to the flask. The reaction was allowed to stir at room temperature overnight and was complete by TLC. The reaction was diluted in ether (50 ml), washed with sodium bicarbonate solution (2x30ml), sodium thiosulfate solution (2x30ml), and brine (2x 50ml). The resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford an off-white solid (255 mg, 1.28 mmol, 81%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.38 (s, 1H), 7.84 (dd, *J*=7.7,1.7, 1H), 7.55 (td, *J*=7.7, 1.8, 1H), 7.35 (dd, *J*=7.7, 0.7, 1H), 7.18 (tt, *J*=7.5,0.7, 1H), 5.92 (m, 1H), 5.38 (m, 1H), 5.28 (m, 1H), 3.94 (d, *J*=2.4, 2H), 3.86 (d, *J*=6.1, 2H), 2.31 (t, *J*=2.4, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.5, 153.7, 134.5, 133.7, 129.64, 129.61, 123.3, 121.6, 118.9, 78.5, 74.1, 57.3, 43.4 ppm. IR (neat, cm^{-1}): 3255, 2849, 2120, 1672, 1653, 1593, 1480.

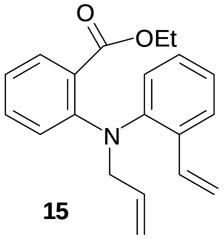
Ethyl 2-[N-(2-styrenyl)amino]benzoate



14

A 10 mL oven-dried flask was charged with anhydrous potassium carbonate (49 mg, 0.35 mmol), XPhos catalyst[26] (1.9 mg, 2.5 x10^{-3} mmol) and placed under argon. t-Butanol (1.5 mL, 0.15 M in compound Ethyl-2-aminobenzoate) was then added to the flask via syringe and the solution was freeze/thaw degassed three times. Ethyl-2-aminobenzoate (56 µL, 0.30 mmol) and chlorostyrene (38 µL, 0.25 mmol) were added via syringe. The reaction was sealed and stirred in a 110 ˚C oil bath. After six hours the reaction showed complete consumption of starting material as indicated by TLC. The reaction was allowed to cool to room temperature, diluted with ether (50 mL), washed with water (3x30 mL) and brine (2x30 mL), dried over sodium sulfate and concentrated *in vacuo*. The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a pale yellow oil (56 mg, 0.20 mmol, 83%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 9.37 (s, 1H), 8.00 (d, *J*= 7.9, 1H), 7.62 (d, *J*= 7.6, 1H), 7.31 (m, 3H), 7.19 (d, *J*= 7.4, 1H), 6.94 (m, 2H), 6.73 (t, *J*= 7.5, 1H), 5.75 (d, *J*= 17.5, 1H), 5.31 (d, *J*= 11.0, 1H), 4.39 (q, *J*= 7.1, 2H), 1.43 (t, *J*= 7.1, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.6, 148.8, 138.0, 134.0, 133.4, 132.6, 131.5, 128.5, 126.6, 125.0, 124.9, 116.7, 115.9, 114.1, 111.7, 60.63, 14.38 ppm. IR (neat, cm^{-1}): 3309, 2979, 1678, 1624, 1580, 1506, 1449, 1230.

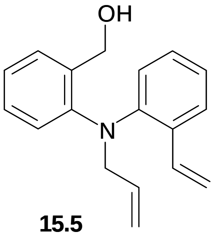
Ethyl 2-[N-allyl-N-(2-styrenyl)amino]benzoate



15

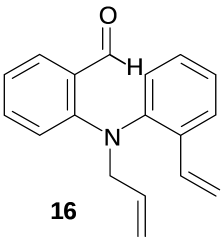
An oven-dried flask was charged with sodium hydride (60% slurry in mineral oil 72 mg, 1.8 mmol) and placed under nitrogen. The sodium hydride was washed with dry hexane (2x1ml). Freshly distilled DMF solvent (15 mL) was then added to the flask via syringe. Compound **14** was dissolved in DMF and added slowly via syringe to the sodium hydride. After five minutes allyl bromide (0.26 ml, 3.0 mmol) was added via syringe and the reaction was stirred at room temperature. After one hour the reaction showed complete consumption of starting material as indicated by TLC. The reaction was quenched with saturated ammonium chloride solution (10 mL), diluted with ether (50 mL), washed with sodium bicarbonate solution (2x40 mL), sodium thiosulfate solution (2x30ml), and brine (2x50 mL), dried over sodium sulfate and concentrated *in vacuo*. The crude product was purified via column chromatography using a gradient of 100% hexane to 98% hexane:2% ethyl acetate to afford a pale yellow oil (425 mg, 1.38 mmol, 92%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.55 (d, *J*=7.5, 1H), 7.46 (d, *J=7.6*, 1H), 7.36 (t, *J*=7.5,1H), 7.10 (m, 4H), 6.92 (m, 2H), 5.94 (m, 1H), 5.65 (d, *J*=17.7, 1H), 5.24 (d, 3H), 4.24 (d, *J*= 5.16, 2H*)* 3.85 (q, *J*=7.1, 2H), 1.10 (t, *J*=7.1, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.4, 147.4, 147.3, 134.6, 134.4, 134.3, 131.4, 130.5, 128.2, 126.9, 125.5, 125.2, 124.6, 120.3, 120.1, 117.3, 114.4, 60.6, 56.0, 14.0 ppm. IR (neat, cm^{-1}): 3065, 2978, 1716, 1595, 1570, 1480, 1450, 1217.

2-[N-allyl-N-(2-styrenyl)amino]benzyl alcohol


15.5

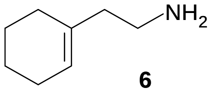
An oven-dried flask was charged with lithium aluminum hydride (71 mg, 1.9 mmol) and placed under nitrogen. The lithium aluminum hydride was diluted with dry ether (4.0 mL). Compound **15** was dissolved in dry ether (2 mL) and added slowly via syringe to the lithium aluminum hydride mixture. After one hour the reaction showed complete consumption of starting material as indicated by TLC. The reaction was chilled to 0 ˚C and quenched with water (1ml), 10% sodium hydroxide solution (.5 ml), and water (1ml) respectively. The reaction was warmed to room temperature, filtered through celite and concentrated *in vacuo.* The crude product was taken forward as a pale yellow oil (358 mg, 1.28 mmol, 96%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.56 (dd, *J*=6.81, 2.16, 1H), 7.43 (d, *J=7.56,* 1H), 7.28 (m, 2H), 7.10 (m, 4H), 6.73 (d, *J=7.05,* 1H), 5.92 (m, 1H), 5.75 (d, *J*= 17.5, 1H), 5.24 (m, 3H), 4.31 (s, 2H), 4.17 (d, J=5.49, 2H), 1.42 (bs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.5, 145.9, 135.3, 134.7, 133.5, 133.0, 128.9, 128.5, 127.8, 127.2, 124.5, 124.1, 123.5, 122.2, 117.4, 115.0, 62.2, 56.5 ppm. IR (neat, cm^{-1}): 3374, 3064, 2859, 1596, 1624, 1577, 1480, 1451, 1214.

2-[N-allyl-N-(2-styrenyl)amino]benzaldehyde


16

A 25 mL round bottom flask was charged with compound **15.5** (340 mg, 1.2 mmol) and freshly distilled methylene chloride (6 ml, .20 M in compound **15.5**). Iodobenzene diacetate (550 mg, 1.7 mmol) and TEMPO (38 mg, .24 mmol) were then added to the flask. The reaction was stirred at room temperature for 24 hours and the reaction showed complete consumption of starting material as indicated by TLC. The reaction was diluted in ether (75 ml), washed with sodium bicarbonate solution (2x40ml), sodium thiosulfate solution (2x40ml), and brine (1x 50ml). Resulting organic layer was dried over sodium sulfate and concentrated *in vacuo.* The crude product was purified via column chromatography using a gradient of 100% hexane to 99% hexane:1% ethyl acetate to afford a bright yellow oil (270 mg, 0.973 mmol, 80%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 10.0 (s, 1H), 7.77 (d, *J*=7.68, 1H), 7.56 (d, *J*=7.35,1H), 7.49 (t, *J*=7.62,1H), 7.10 (m, 5H), 6.86 (d, *J*=7.56, 1H), 5.95 (m, 1H), 5.75 (d, *J*=17.6 , 1H), 5.26 (m, 3H), 4.28 (d, *J=5.22,* 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.6 151.1, 149.6, 134.3, 133.9, 133.3, 133.1, 129.8, 128.9, 128.4, 127.5, 125.9, 125.1, 122.1, 121.3, 117.9, 115.7, 57.0 ppm. IR (neat, cm^{-1}): 3066, 2890, 2849, 1682, 1625, 1593, 1568, 1476, 1453, 1187.

1-cyclohexene-1-ethanamine

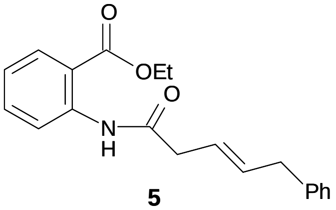


6

2-Cyclohexenyl acetonitrile was first distilled under aspirator vacuum. The nitrile (500 mg, 4.13 mmol) was then added to a slurry of lithium aluminum hydride (392 mg, 10.3 mmol) in anyhydrous ether (25 mL, 0.15 M in nitrile) at 0˚C. After addition of nitrile, reaction was allowed to warm to room temperature and stirred over night. The reaction was cooled back to 0˚C and quenched with H_2O (0.4 mL) followed by 10% sodium hydroxide (0.4 mL) then H_2O

(0.4 mL). The reaction was then warmed to room temperature and magnesium sulfate was added (0.5 g). The resulting mixture was then filtered through a thing pad of cielite to remove metal salts and concentrated *in vacuo*. Product was taken forward crude as a light yellow liquid (462 mg, 3.75 mmol, 91%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 5.46 (s, 1H), 2.65 (t, *J*=6.7, 2H), 2.08 (t, *J*=6.7, 2H), 2.00 (m, 2H), 1.92 (m, 2H), 1.58 (m, 6H) ppm. NMR (75 MHz, $CDCl_3$) δ: 134.8, 122.9, 42.9, 39.6, 27.9, 25.1, 22.8, 22.4 ppm. IR (neat, cm^{-1}): 3285, 2922, 2854, 1620, 1437, 798.

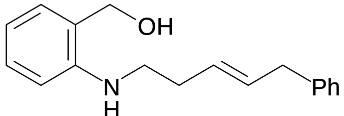
Ethyl (E)-2-(1-oxo-5-phenyl-3-pentenylamino)benzoate



5

An oven-dried flask was charged with trans-styrylic acid (500mg, 3.09 mmol) and freshly-distilled methylene chloride (15 mL, 0.2 M in acid). The solution was cooled to 0˚C and oxalyl chloride (588 mg, 4.63 mmol) was added slowly via syringe. The reaction was allowed to warm to room temperature and stirred for two hours to give a bright yellow solution. Reaction was then cooled to room temperature and a solution of triethylamine (625 mg, 6.18 mmol) and 2-ethyl 2-aminobenzoate (561 mg, 340 mmol) in minimal methylene chloride (1-2 mL) was added slowly via syringe to give a bright orange solution. Reaction was stirred over night and then quenched with water. The product was extracted with ether (3 x 40 mL) and washed with 5% HCl (2 x 35 mL) followed by sodium bicarbonate (2 x 35 mL). Resulting organic layer was dried over sodium sulfate and concentrated *in vacuo* to give a pale yellow oil. ^{1}HNMR (300 MHz, $CDCl_3$) δ: 8.74 (dd, *J*=8.5, 1.0, 1H), 8.05 (dd, *J*=8.0, 1.6, 1H), 7.55 (dt, *J*=7.9, 1.6, 1H), 7.46 (m, 2H), 7.34 (m, 2H), 7.26 (m, 1H), 7.10 (dt, *J*=7.7, 1.1, 1H), 6.67 (d, *J*=15.8, 1H), 6.44 (dt, *J*=15.8, 7.3, 1H), 4.35 (q, *J*=7.1, 2H), 3.41 (d, *J*=7.3, 2H), 1.45 (bs, 1H), 1.40 (t, *J*=7.1, 3H) ppm. NMR (75 MHz, $CDCl_3$) δ: 169.9, 168.1, 141.5, 136.9, 134.8, 134.5, 130.8, 128.5, 127.6, 126.5, 122.5, 122.0, 120.4, 115.4, 61.4, 42.8, 14.2 ppm. IR (neat, cm^{-1}): 3251, 2978, 1702, 1687, 1589, 1522, 1252.

Ethyl (E)-2-(5-phenyl-3-pentenylamino)benzyl alcohol



4

Lithium aluminum hydride (32 mg, .850 mmol) was suspended in anhydrous ether (3 ml, 0.3 M in compound **5**) in a 25 mL round bottom flask. This slurry was cooled to 0˚C and the compound **5** (105 mg, .340 mmol) was dissolved in a small amount of ether and added slowly via pipette. The reaction was allowed to warm to room temperature and stirred for six hours. The reaction was then cooled to 0˚C and quenched with H_2O (0.1 mL) followed by 10% sodium hydroxide (0.1 mL) and H_2O (0.1 mL). Mixture was then warmed to room temperature and magnesium sulfate was added (0.2 g). Metal salts were then filtered through a thin pad of ceilite and solvent was removed using rotary evaporation. The crude product was obtained as a colorless liquid (84 mg, 3.32 mmol, 98%). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 7.33 (m, 6H), 7.08 (d, *J*=7.2, 1H), 6.70 (m, 2H), 6.53 (d, *J*=15.9, 1H), 6.24 (dt, 15.8,7.0, 1H), 4.66 (s, 1H), 3.33 (t, *J*=6.8, 2H), 2.61 (q, *J*=6.8, 2H), 1.75 (bs, 1H). NMR (75 MHz, $CDCl_3$) δ: 147.5, 137.4, 132.2, 129.7, 128.6, 128.5, 128.4, 127.6, 127.3, 126.1, 124.5, 116.6, 110.8, 64.7, 43.1, 32.9 ppm. IR (neat, cm^{-1}): 3372, 3024, 2920, 1606, 1580, 1513, 1460, 964.

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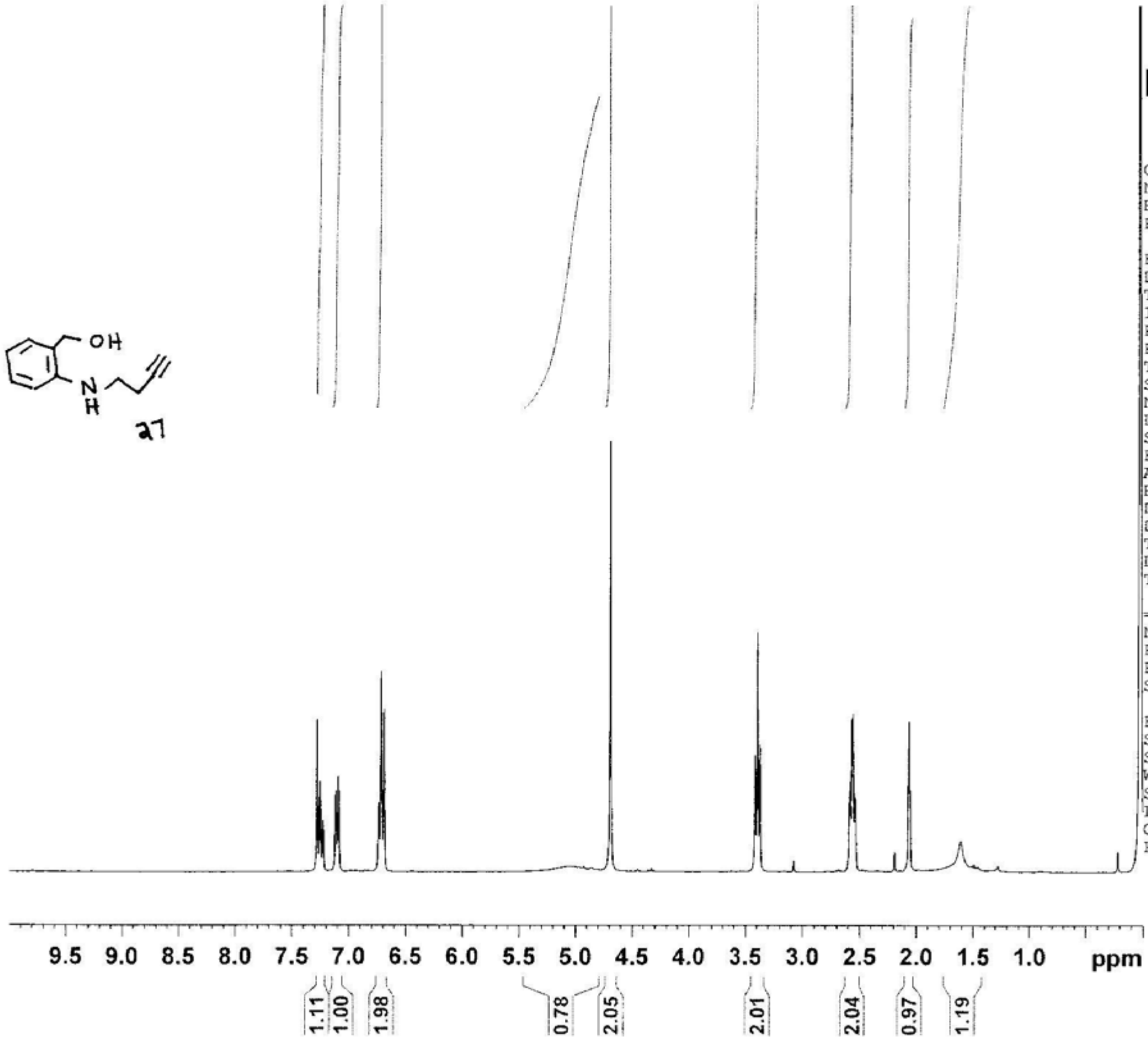

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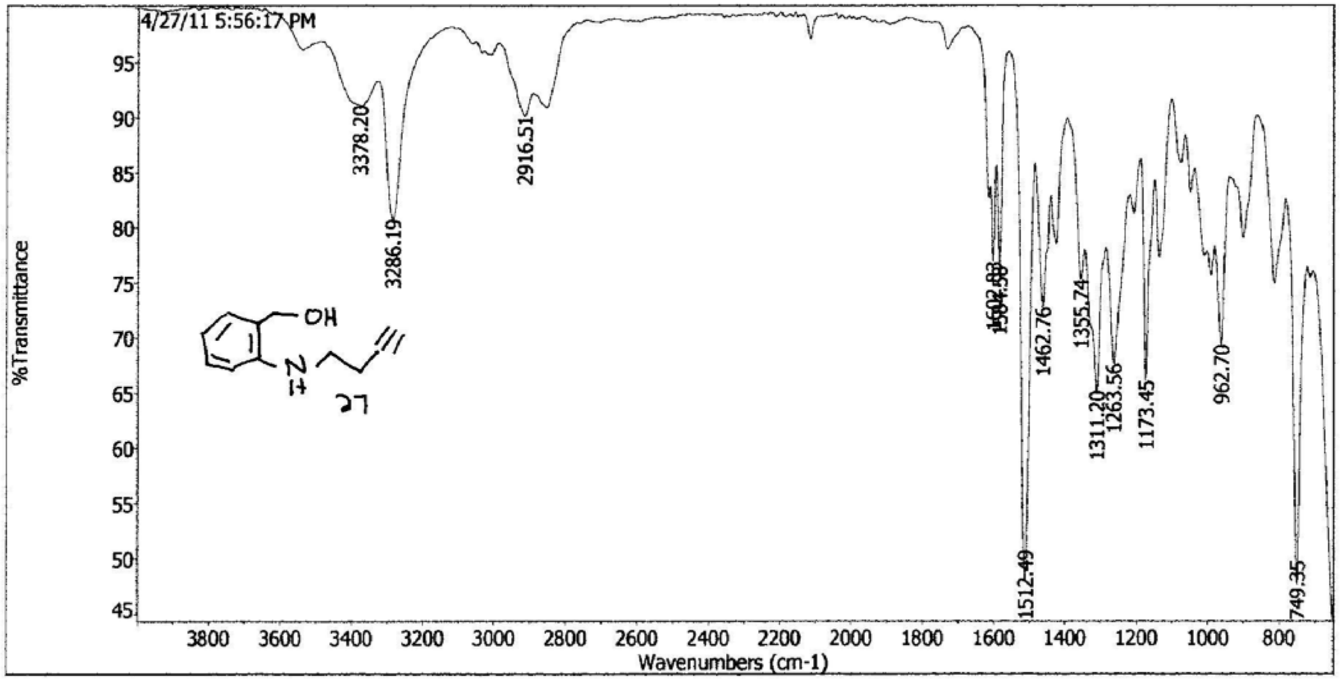
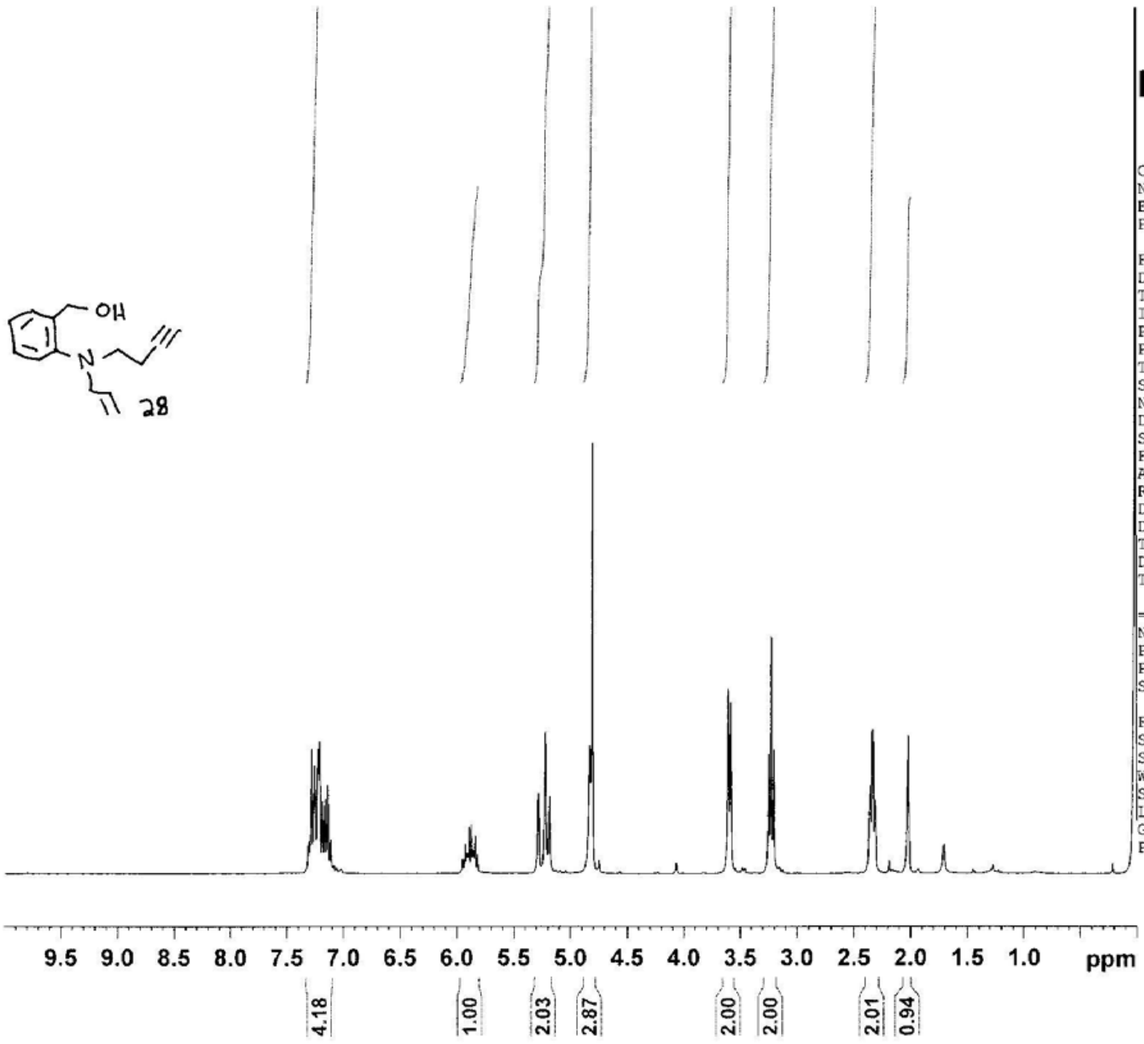


27

28



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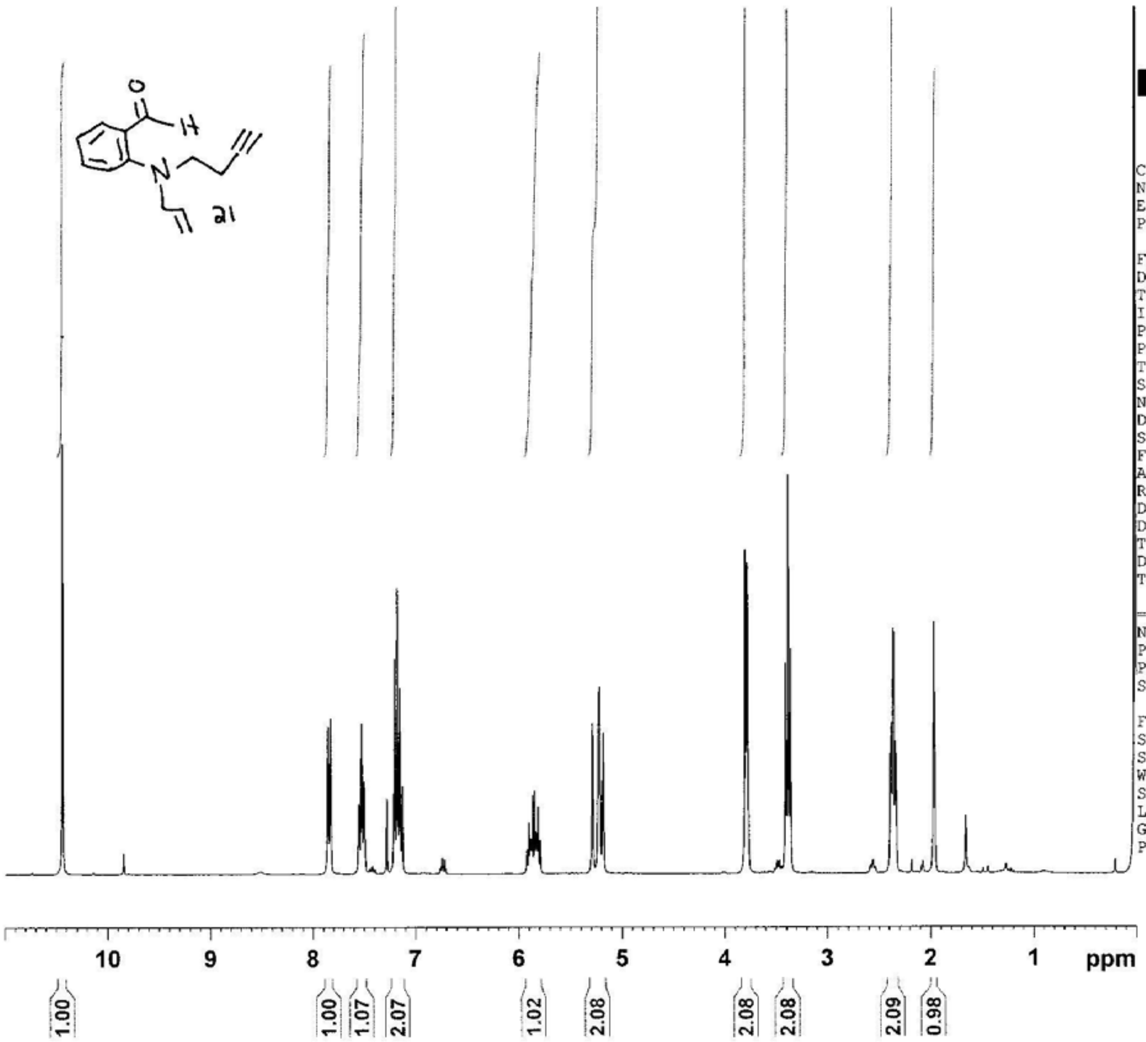

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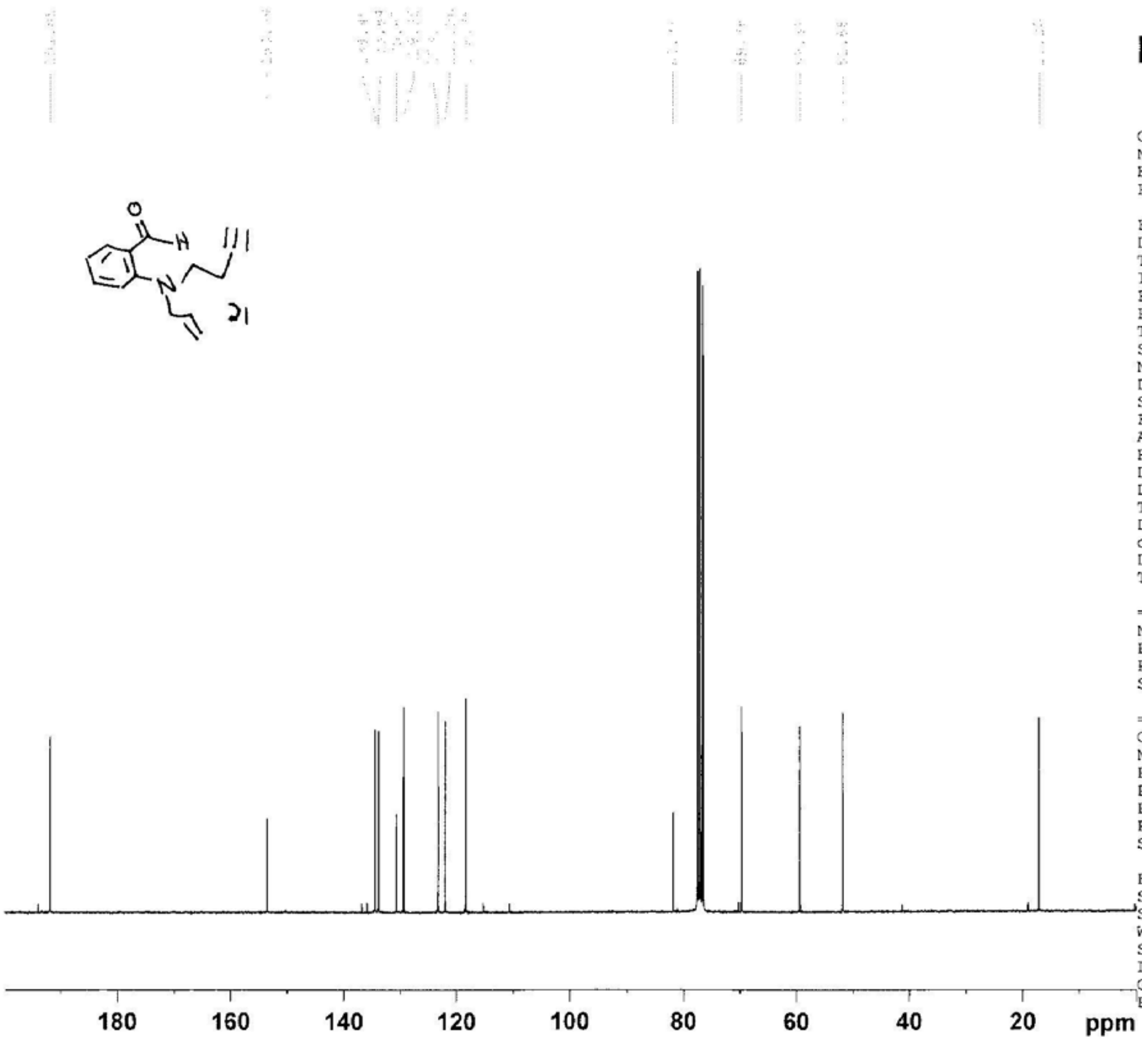
SOLVENT              CDC13
NS                      16
DS                       2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084660 sec
RG                     114
DW              81.000 usec
DE                6.00 usec
TE               304.2 K
D1          1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1               11.00 usec
PL1               0.00 dB
SFO1       300.1318534 MHz

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


21

```
Current Data Parameters
NAME      KER-II-011carbon
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110318
Time                  2.45
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    9216
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                  5792.6
DW                  27.800 usec
DE                    6.00 usec
TE                   305.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2           300.1312005 MHz

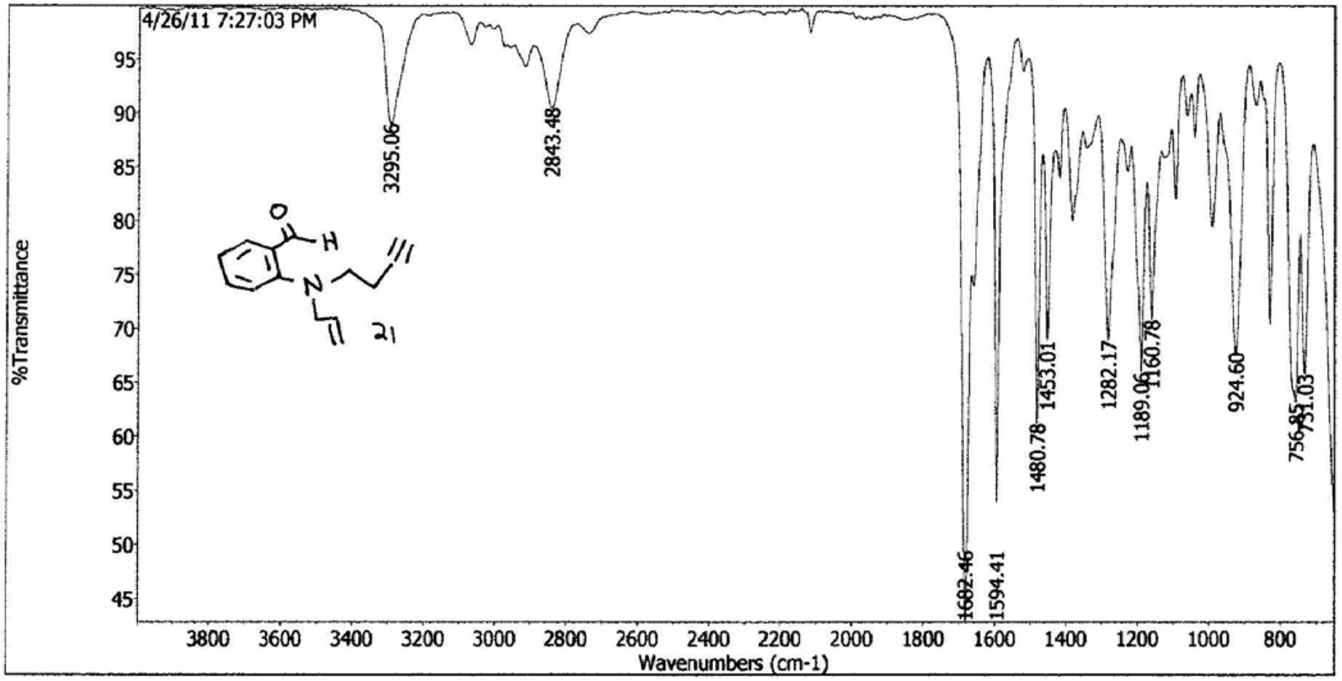
F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

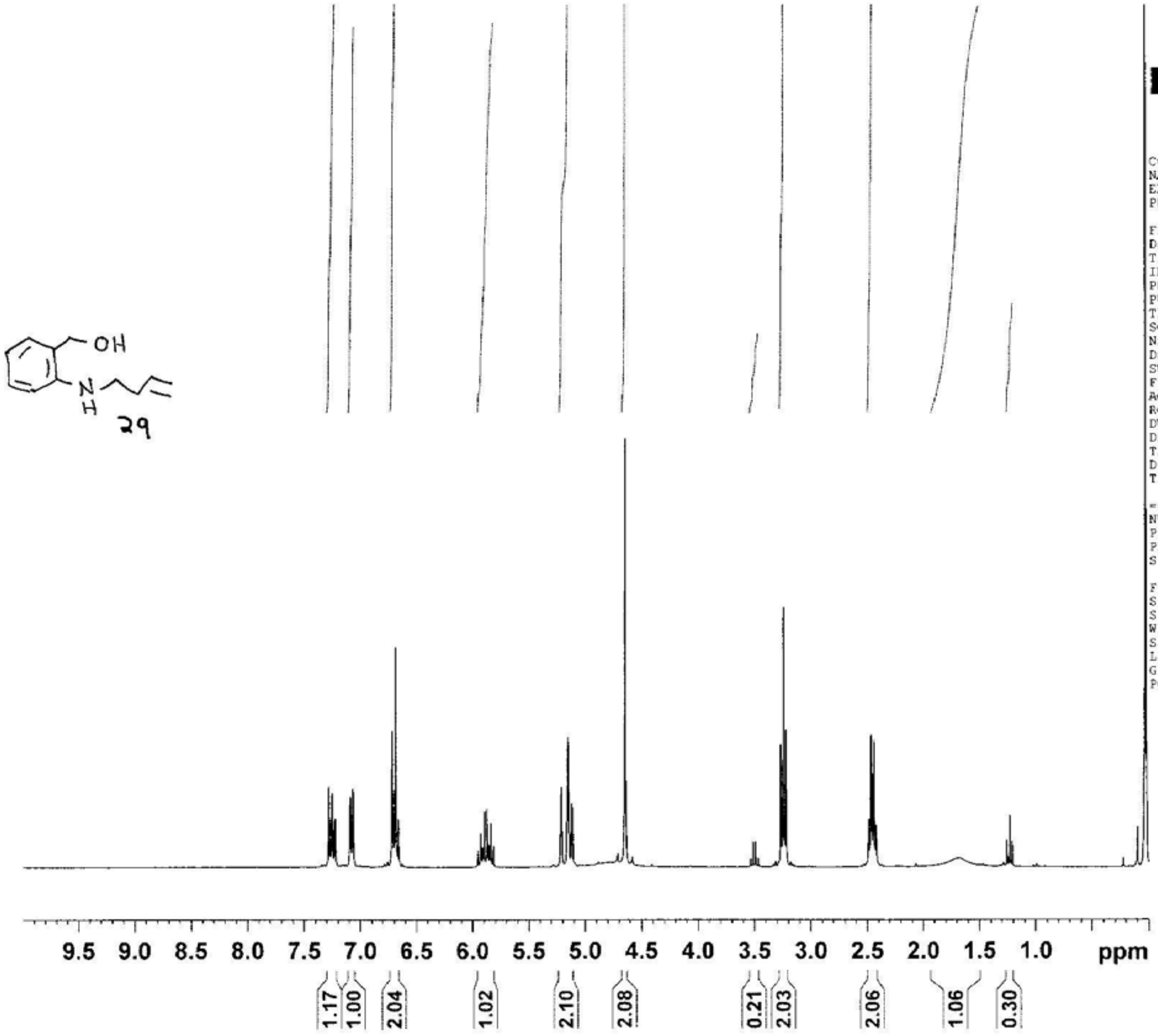
KER-II-011

Peak finding results for: **4/26/11 7:27:03 PM**
Frequency: 687.71 - 3365.20, threshold: 67.681-98.056, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3295.06	2843.48	1682.46	1594.41	1480.78	1453.01	1282.17	1189.06	1160.78
Height	88.844	90.370	42.666	53.826	61.094	68.692	68.762	65.797	70.690

Peak#	10	11	12						
Position	924.60	756.85	731.03						
Height	67.636	62.941	65.654						





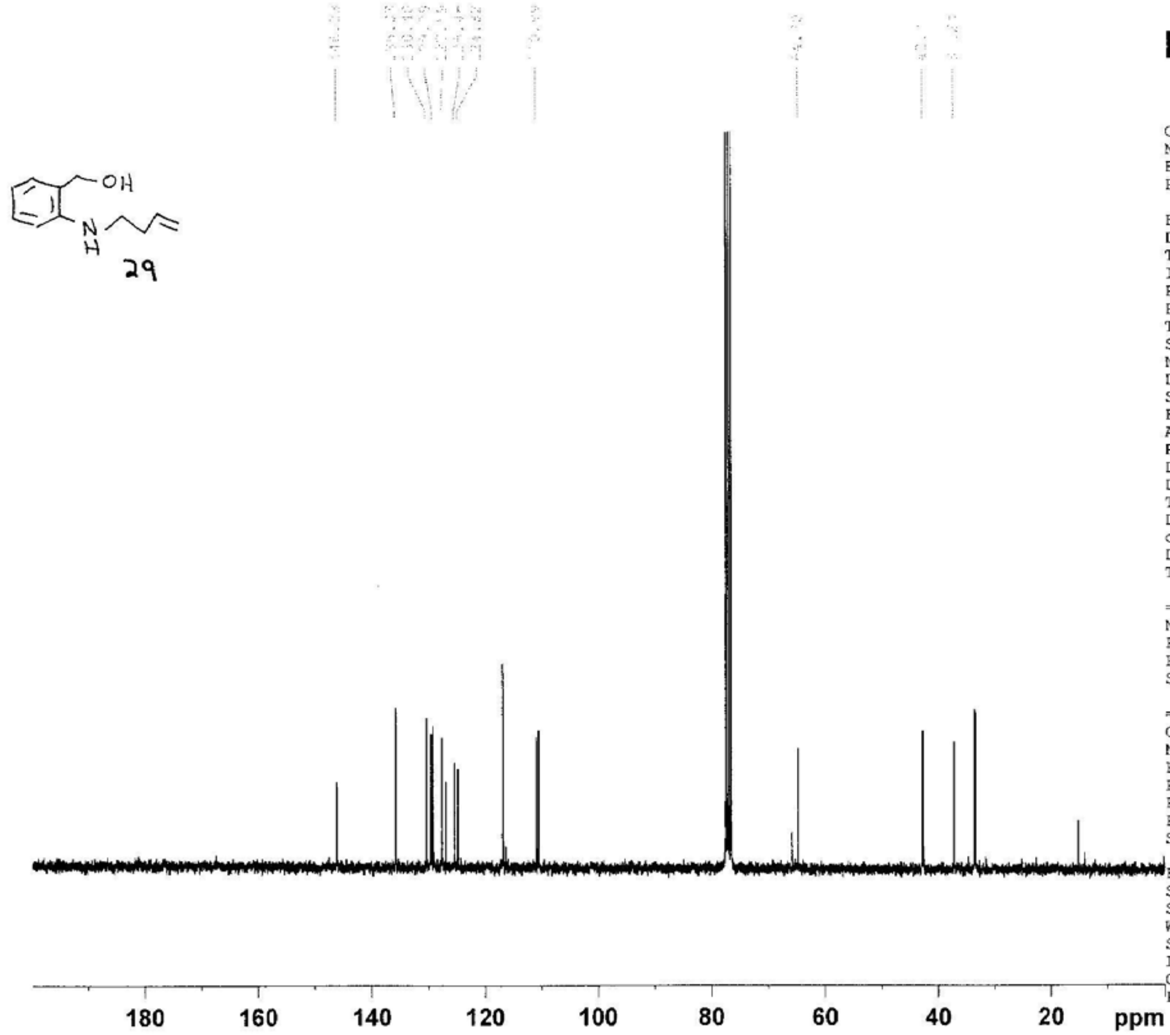
29

```
Current Data Parameters
NAME     KER-J-040(pst col. Product)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090821
Time                 10.46
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                   101.6
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

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



29

```
Current Data Parameters
NAME     KER-I-040(cl3, odd)
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20090821
Time                   12.19
INSTRUM                spect
PROBHD   5 mm Multinucl
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                     4096
DW                   27.800 usec
DE                     6.00 usec
TE                    294.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     7.10 usec
PL1                   -1.50 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  17.23 dB
PL13                  19.00 dB
SFO2           300.1312005 MHz

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

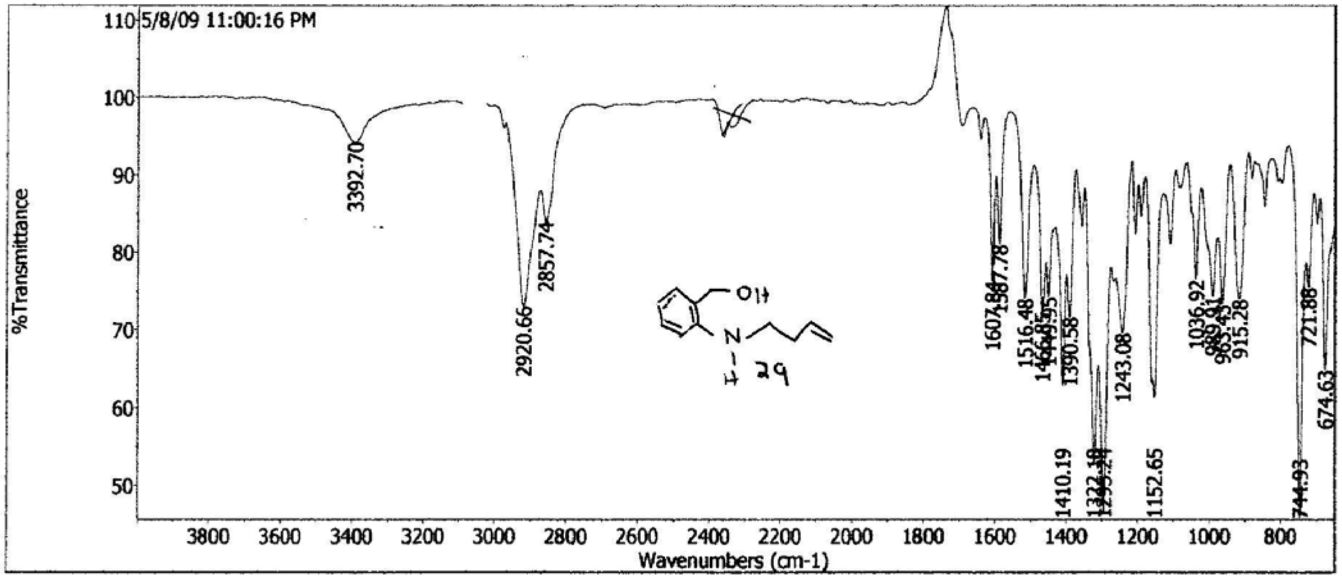
KER-I-004

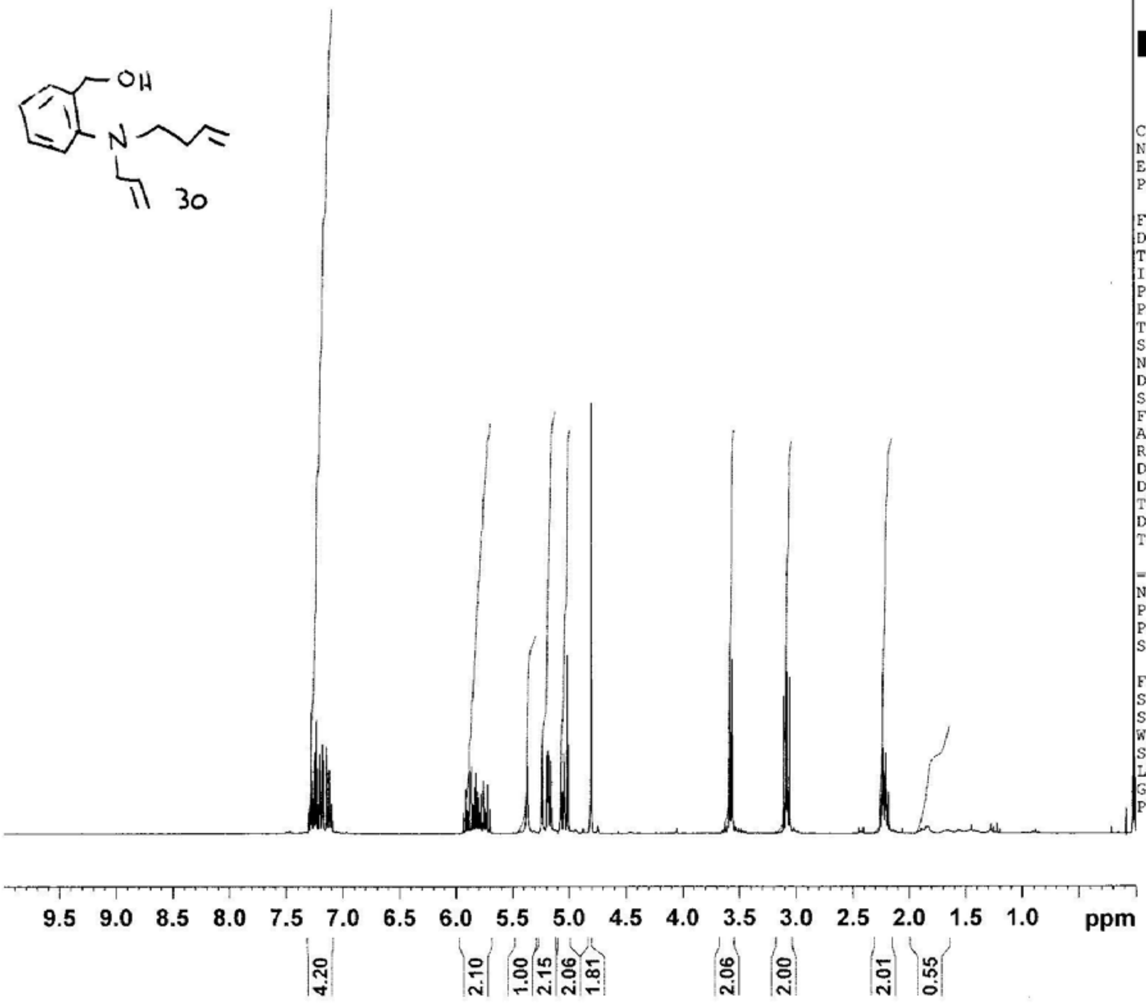
Peak finding results for: 5/8/09 11:00:16 PM
Frequency: 662.57 - 4000.00, threshold: 75.978-98.547, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3392.70	2920.66	2857.74	1607.84	1587.78	1516.48	1466.85	1449.95	1410.19
Height	94.001	72.818	83.682	76.038	80.832	73.877	72.048	74.043	62.554

Peak#	10	11	12	13	14	15	16	17	18
Position	1390.58	1322.18	1295.24	1243.08	1152.65	1036.92	989.91	963.43	915.28
Height	71.450	52.664	46.295	69.395	61.129	76.255	74.106	73.021	73.742

Peak#	19	20	21						
Position	744.93	721.88	674.63						
Height	45.449	75.227	64.670						





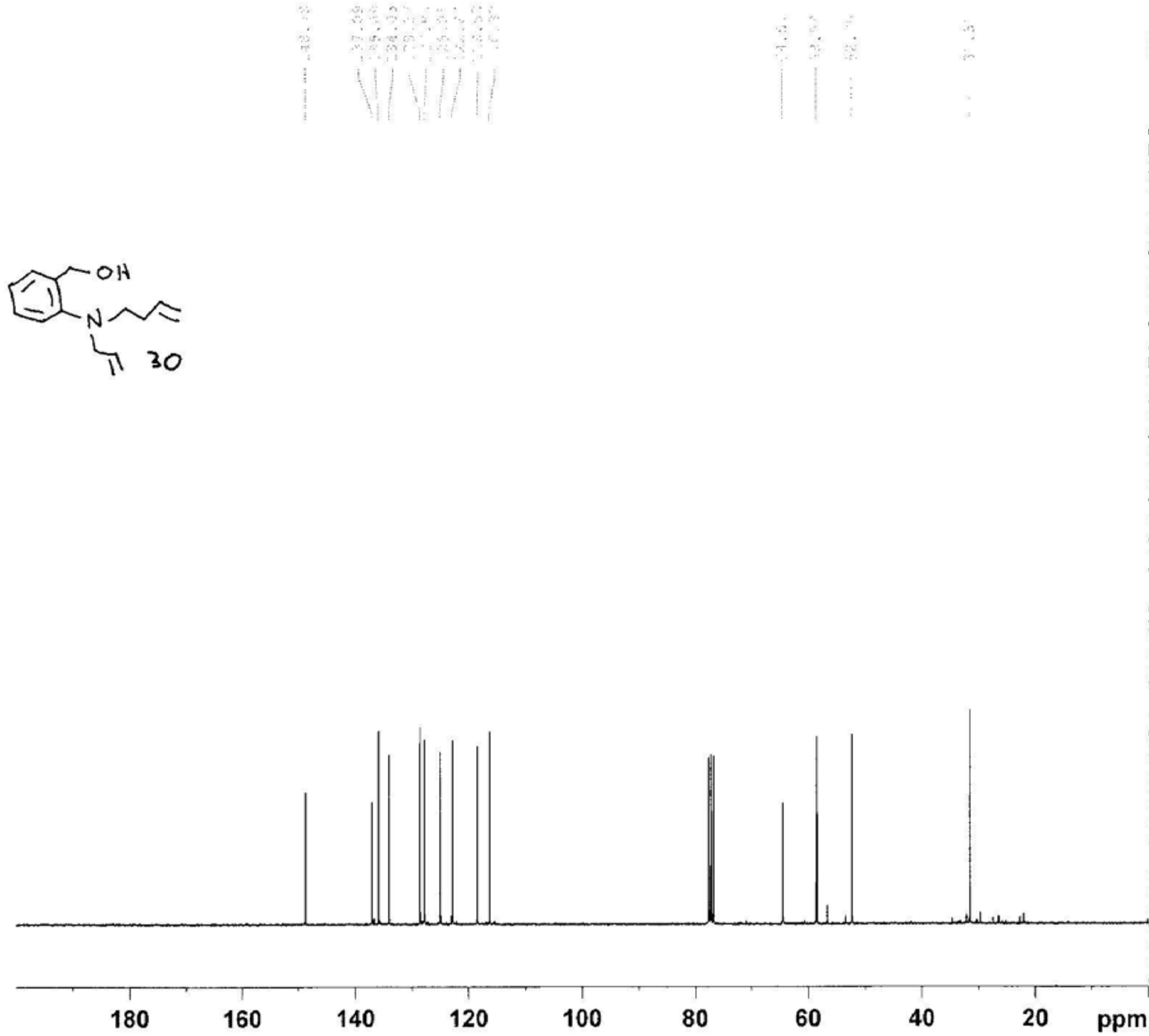
30

```
Current Data Parameters
NAME      KER-I-014(Pst. col)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090527
Time               16.59
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                  71.8
DW                81.000 usec
DE                  6.00 usec
TE                 294.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```


30

```
Current Data Parameters
NAME      KER-I-014carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110426
Time_               22.06
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                2298.8
DW                27.800 usec
DE                  6.00 usec
TE                 296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2        300.1312005 MHz

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

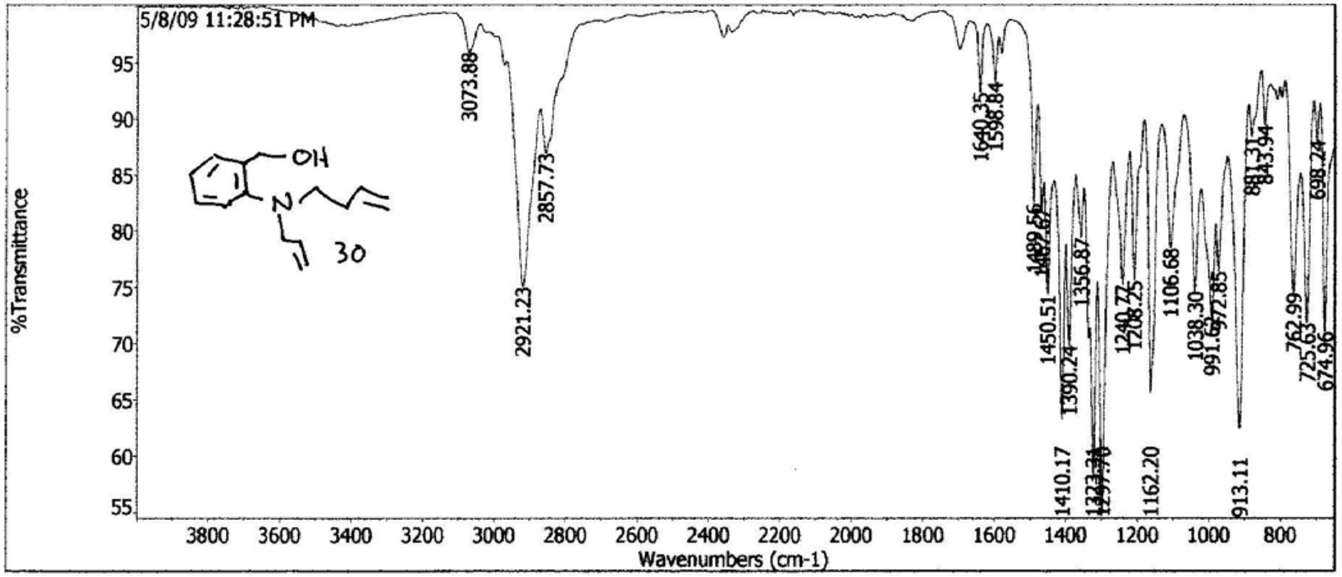
Peak finding results for: 5/8/09 11:28:51 PM
Frequency: 662.57 - 4000.00, threshold: 94.264-98.359, sensitivity: 50.00
Peak finding result table:

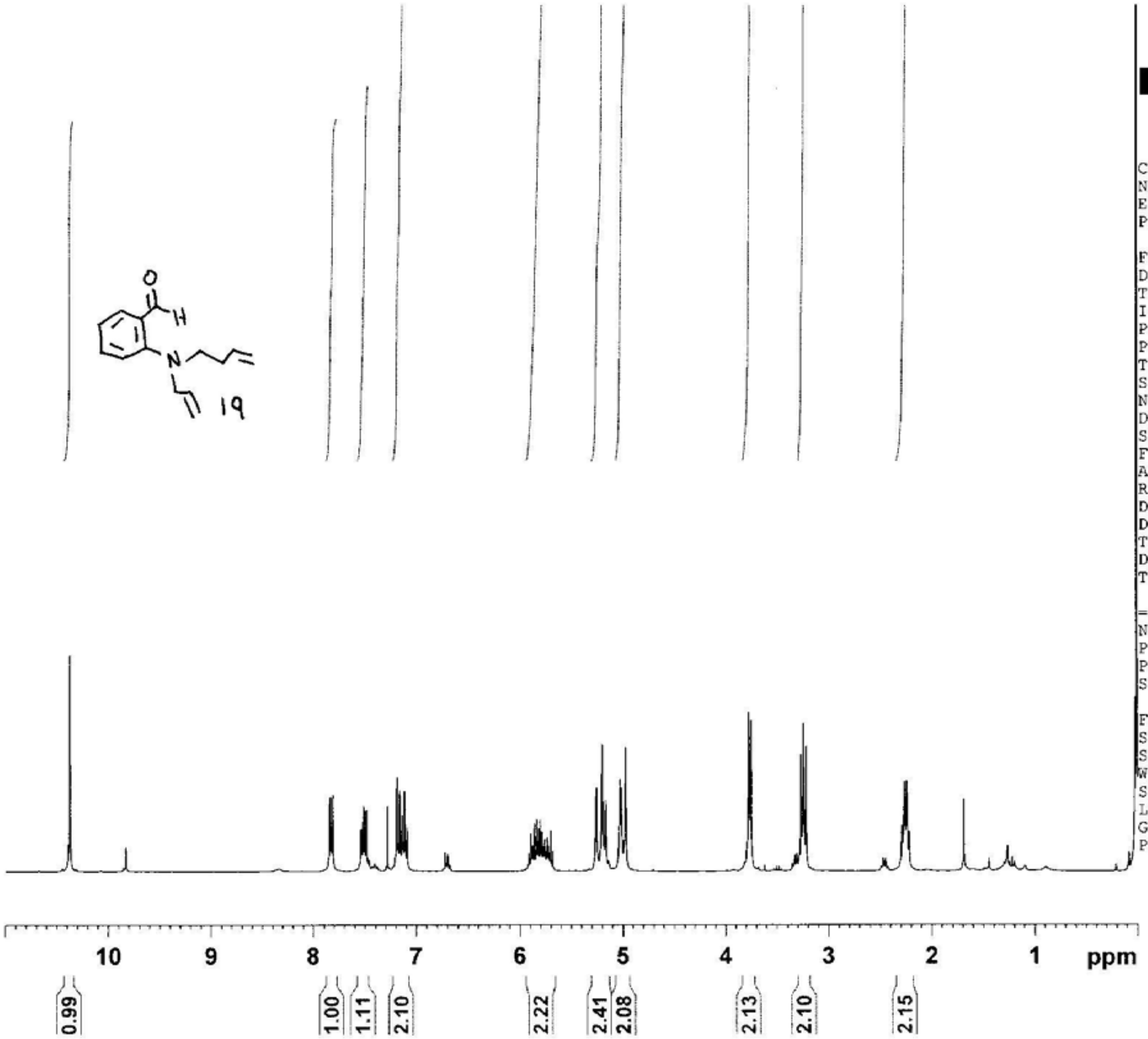
KER-I-010

Peak#	1	2	3	4	5	6	7	8	9
Position	3073.88	2921.23	2857.73	1640.35	1598.84	1489.56	1467.67	1450.51	1410.17
Height	95.813	74.917	86.791	92.193	93.125	82.259	81.890	74.129	63.114

Peak#	10	11	12	13	14	15	16	17	18
Position	1390.24	1356.87	1323.31	1297.70	1240.77	1208.25	1162.20	1106.68	1038.30
Height	69.641	79.254	57.898	54.492	75.027	75.418	65.417	78.315	74.457

Peak#	19	20	21	22	23	24	25	26	27
Position	991.62	972.85	913.11	881.31	843.94	762.99	725.63	698.24	674.96
Height	72.262	76.242	62.308	88.257	89.252	74.369	71.679	87.870	70.890





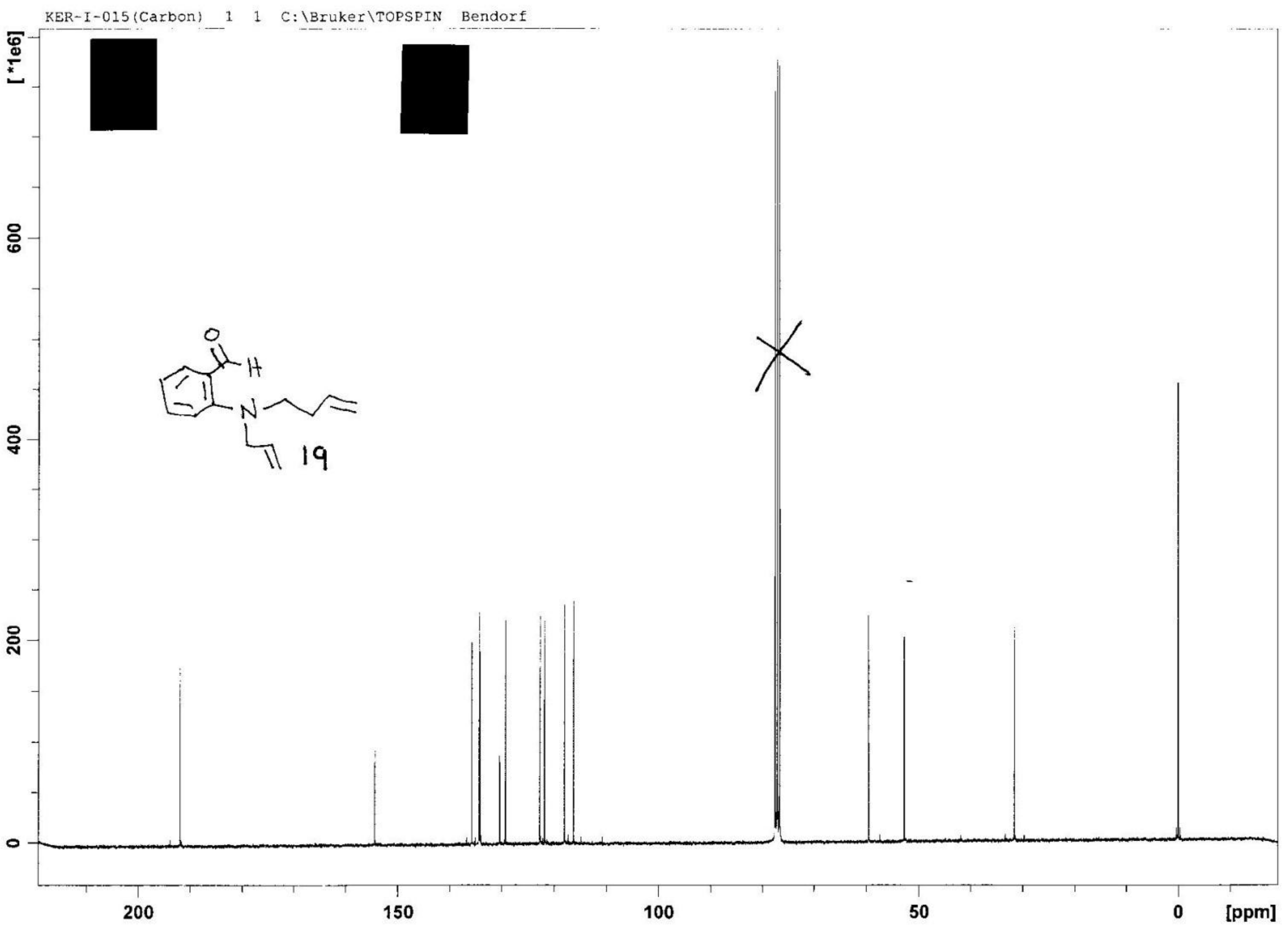
```
Current Data Parameters
NAME      KER-I-026(Post col)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090622
Time                15.50
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                   90.5
DW                 81.000 usec
DE                   6.00 usec
TE                  292.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

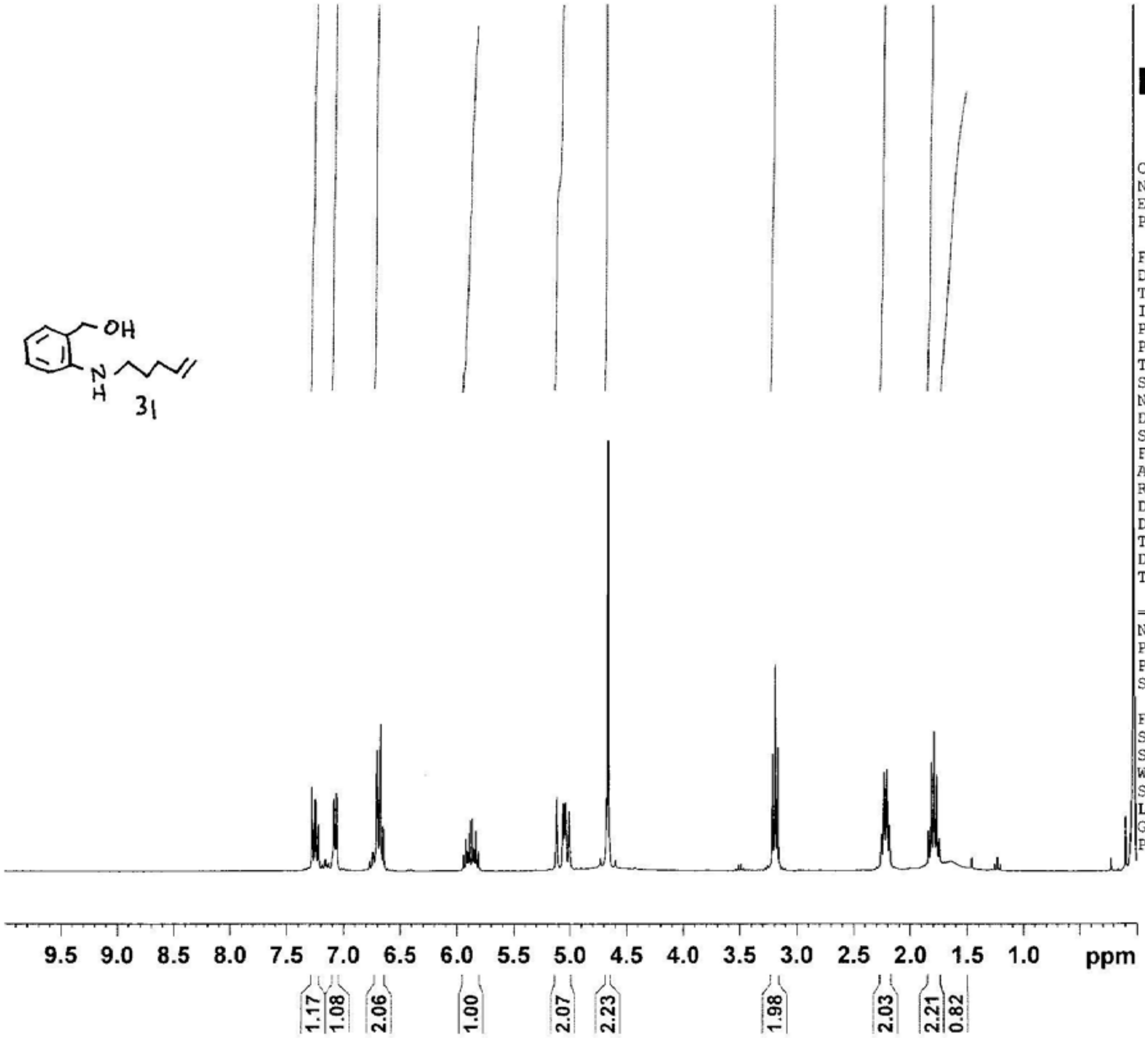
F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

CDCl$_3$



[redacted]

[redacted]



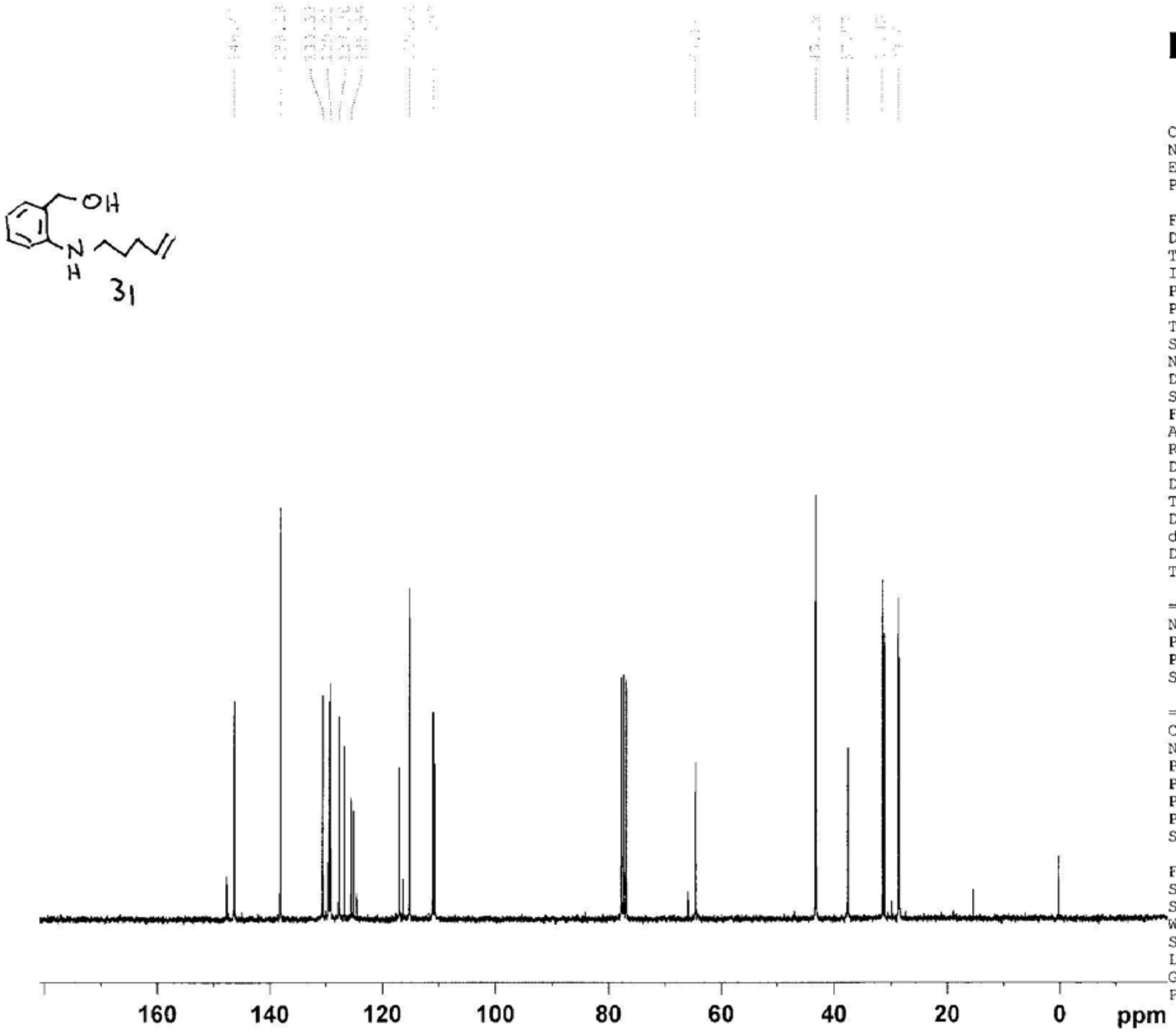
31

```
Current Data Parameters
NAME        KER-I-027 Kug
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091022
Time                11.19
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                  101.6
DW                 81.000 usec
DE                   6.00 usec
TE                  294.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



BRUKER

```
Current Data Parameters
NAME       KER-I-047carbon
EXPNO                    1
PROCNO                   1

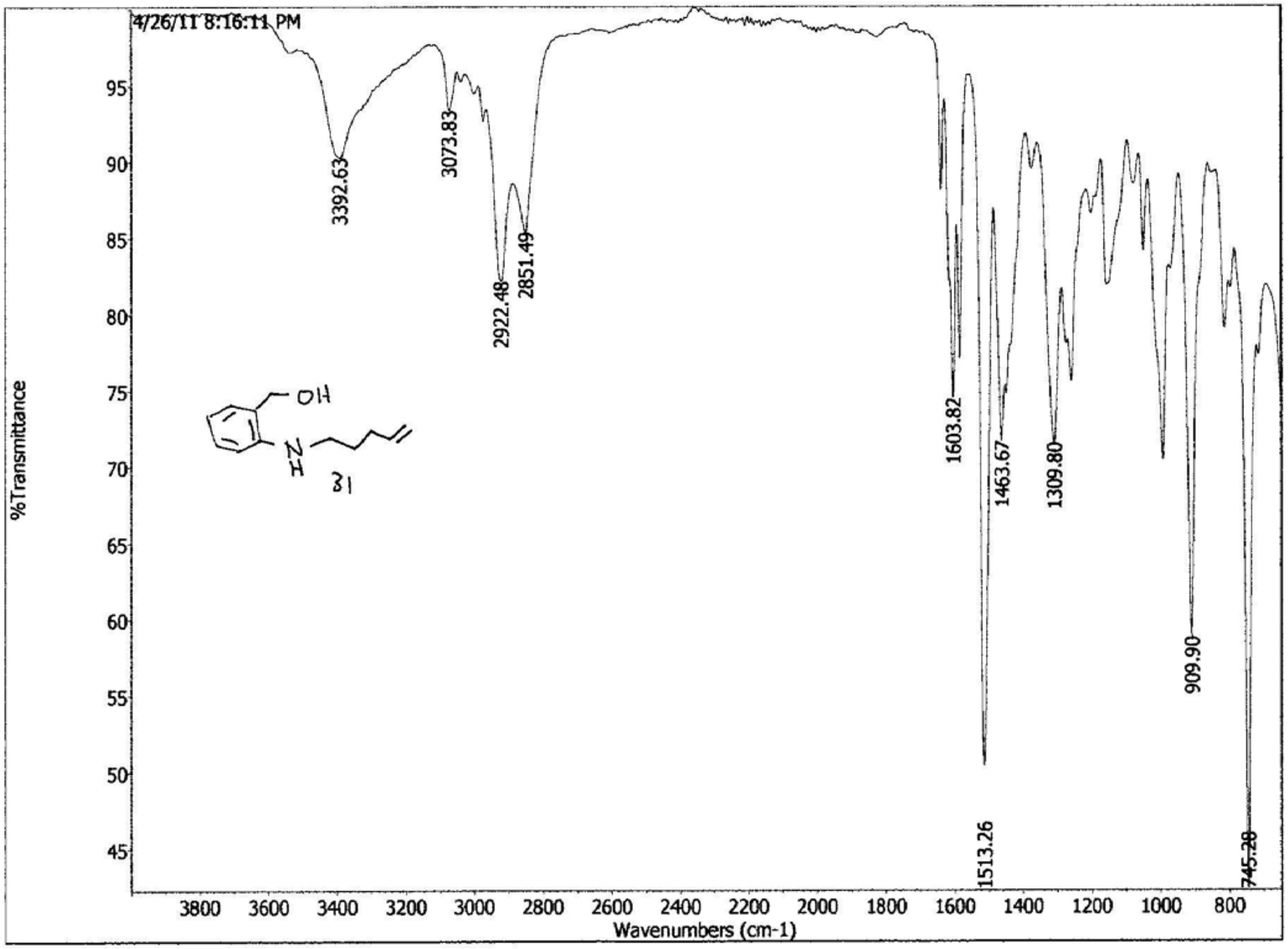
F2 - Acquisition Parameters
Date_             20110427
Time_                16.12
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     500
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                    6502
DW                  27.800 usec
DE                    6.00 usec
TE                   301.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

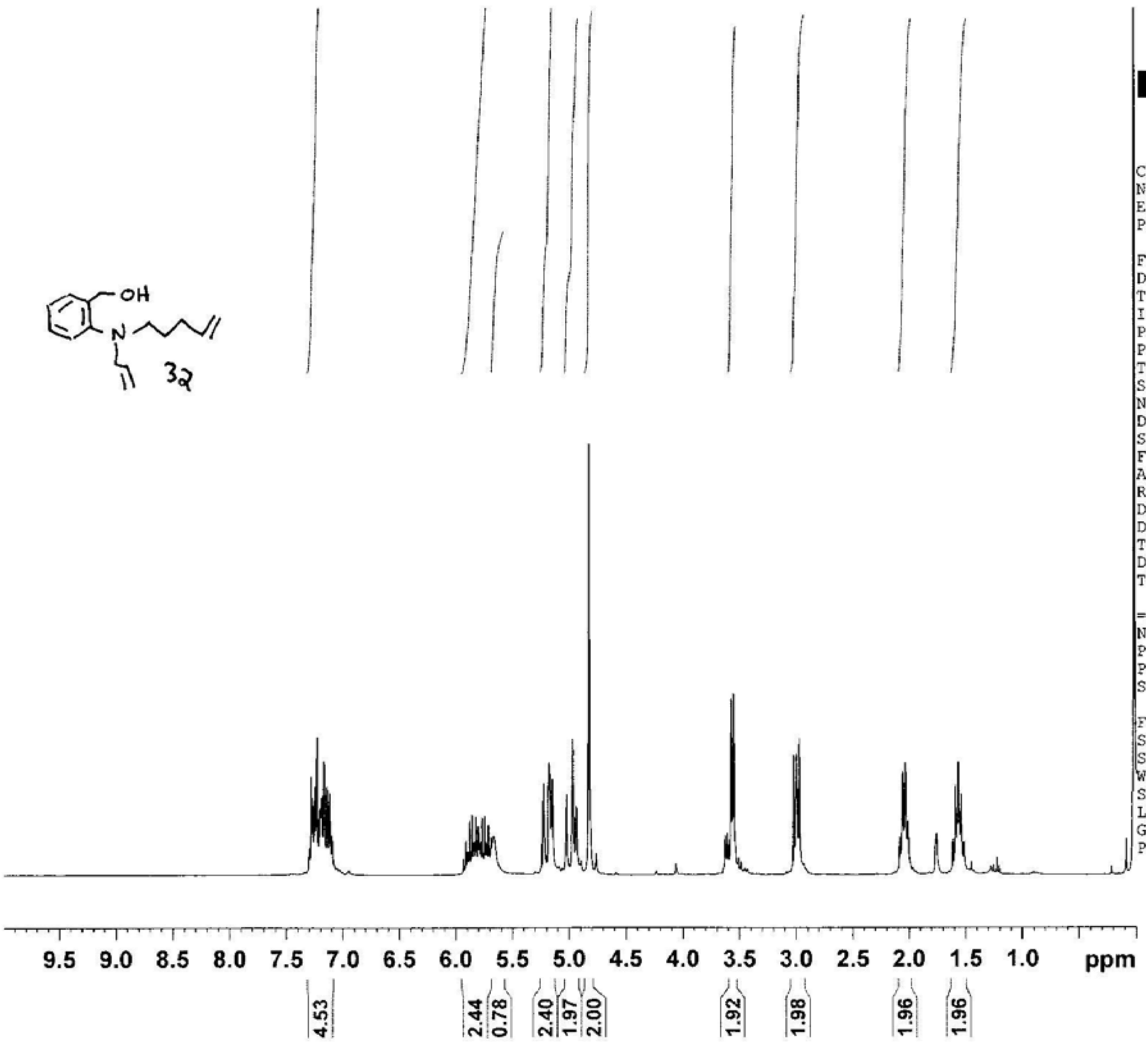
======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2           300.1312005 MHz

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

KER-I-047


4/26/11 8:16:11 PM
OH
N
H
31
%Transmittance
95
90
85
80
75
70
65
60
55
50
45
3392.63
3073.83
2922.48
2851.49
1603.82
1513.26
1463.67
1309.80
909.90
745.28
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumbers (cm-1)

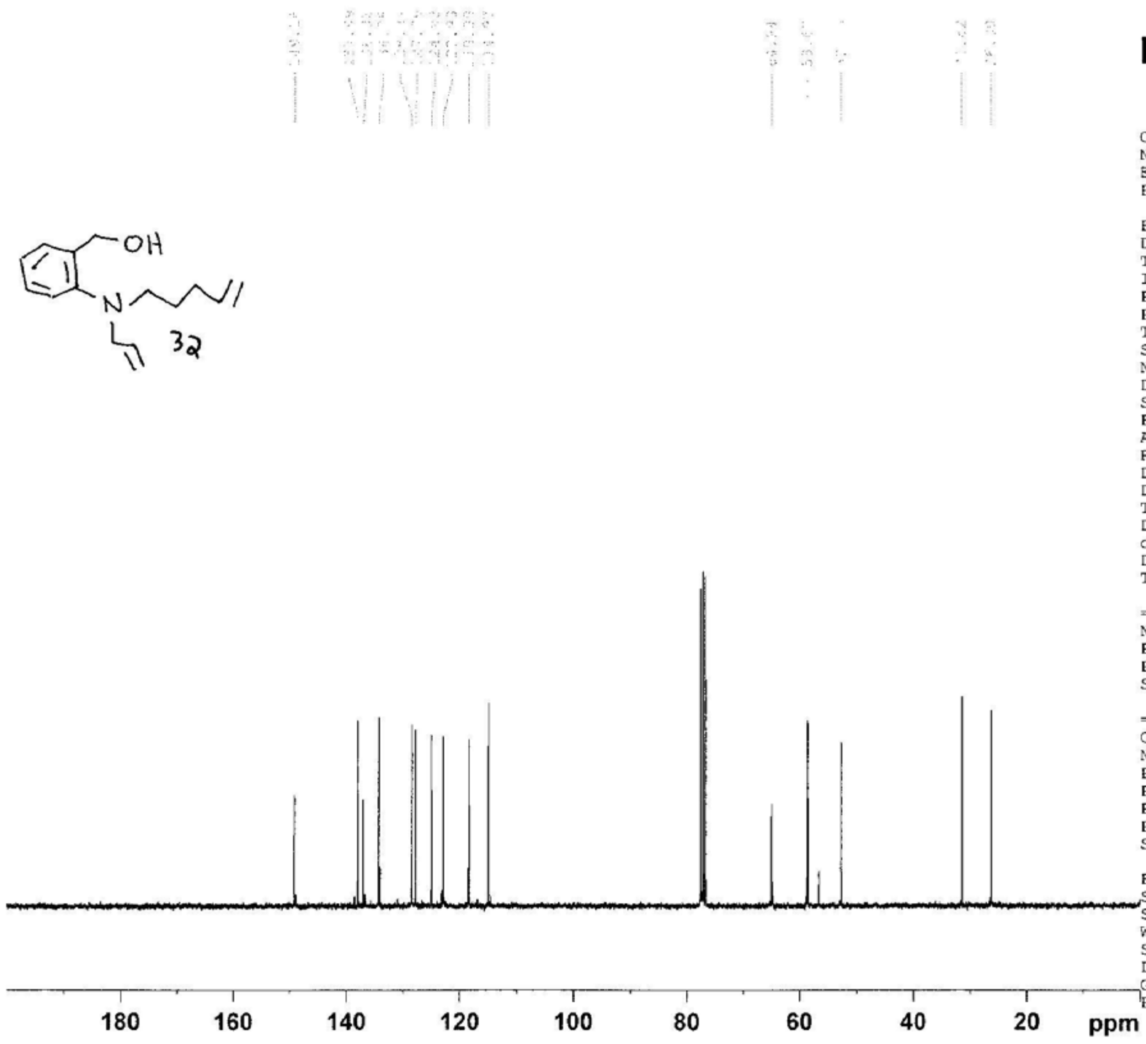


```
Current Data Parameters
NAME             KER-I-031
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090629
Time                 14.24
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                    90.5
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz

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



BRUKER

```
Current Data Parameters
NAME      KER-I-031carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20110427
Time               19.15
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                  6.00 usec
TE                 305.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2        300.1312005 MHz

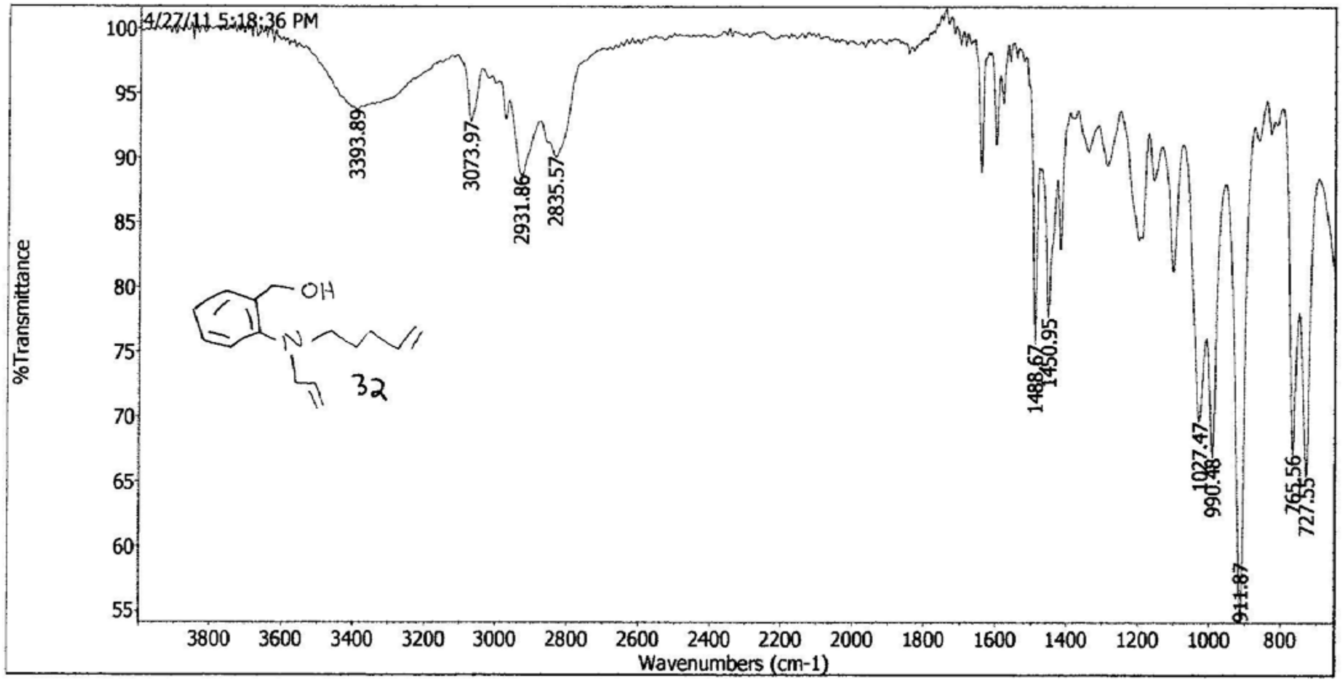
F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

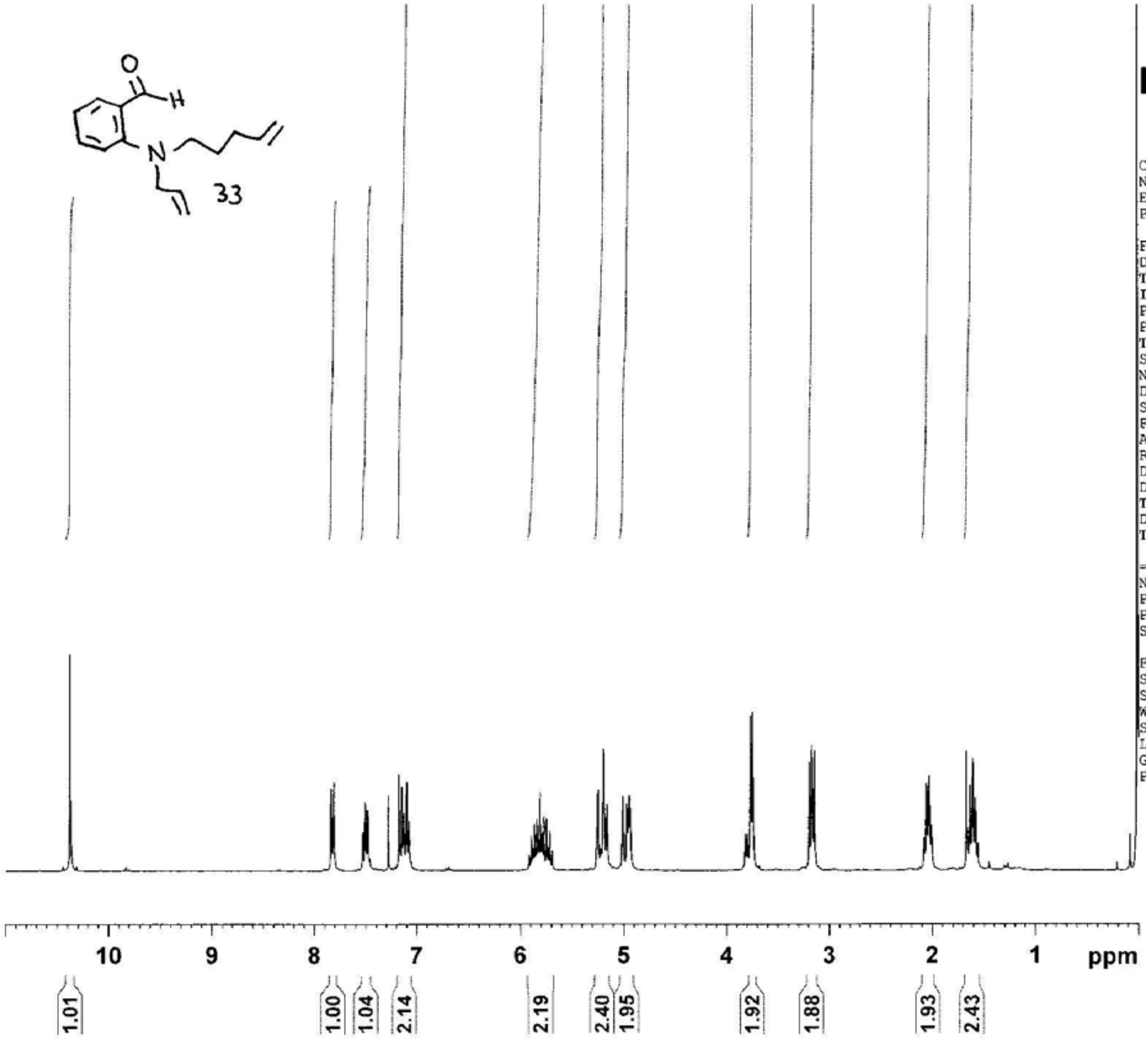
KER-I-031

Peak finding results for: 4/27/11 5:18:36 PM
Frequency: 656.29 - 3541.18, threshold: 70.556-98.819, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3393.89	3073.97	2931.86	2835.57	1488.67	1450.95	1027.47	990.48	911.87
Height	93.583	92.686	88.530	89.944	75.479	77.520	69.518	66.754	54.155

Peak#	10	11							
Position	765.56	727.55							
Height	66.974	65.310							



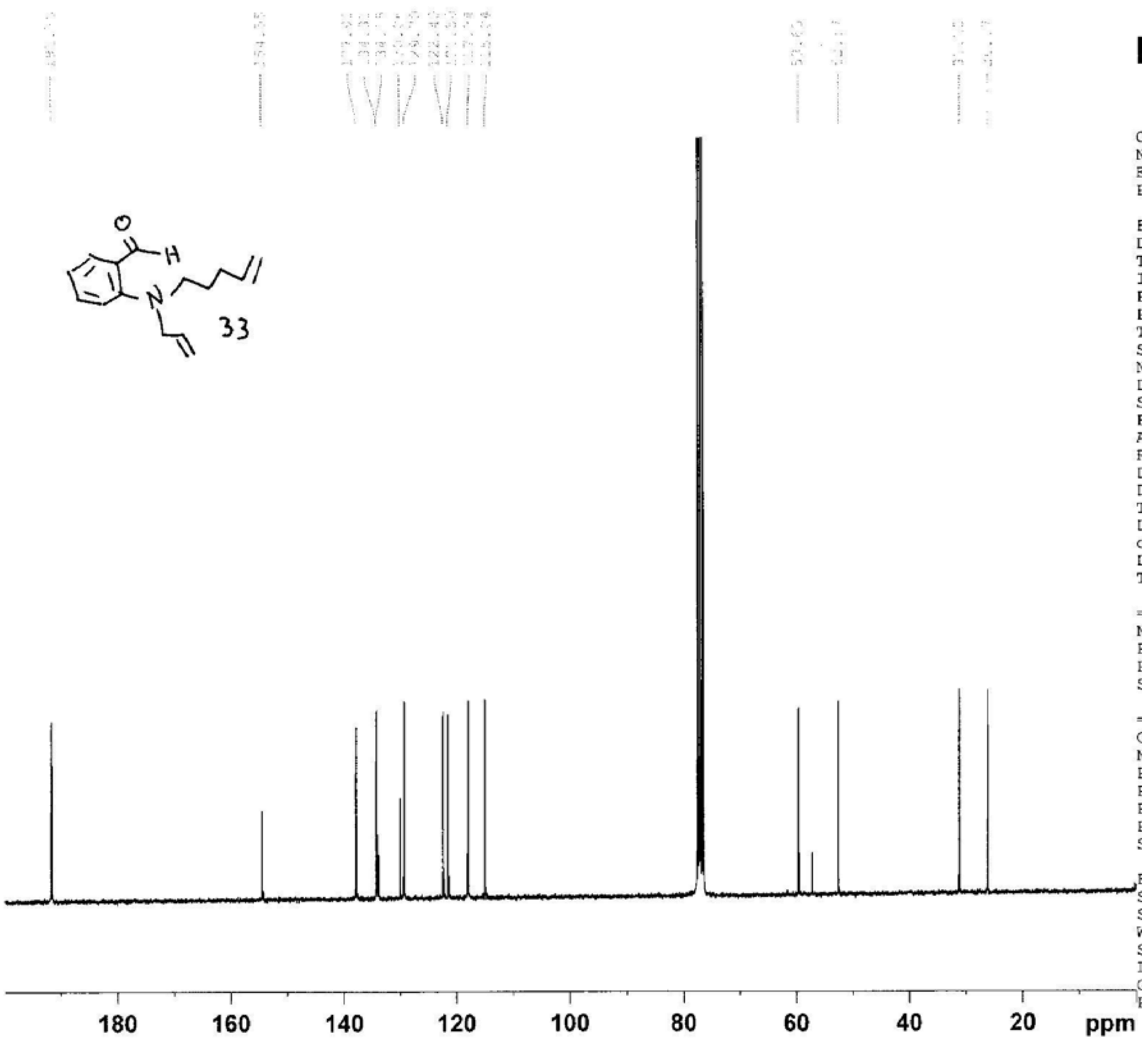


```
Current Data Parameters
NAME       KER-I-032(Post Column)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090701
Time_                9.04
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                  101.6
DW                 81.000 usec
DE                   6.00 usec
TE                  293.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



33

```
Current Data Parameters
NAME      KER-I-032(Carbon)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090702
Time_                  1.13
INSTRUM               spect
PROBHD    5 mm Multinucl
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    8192
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                    4096
DW                  27.800 usec
DE                    6.00 usec
TE                   295.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1           75.4752953 MHz

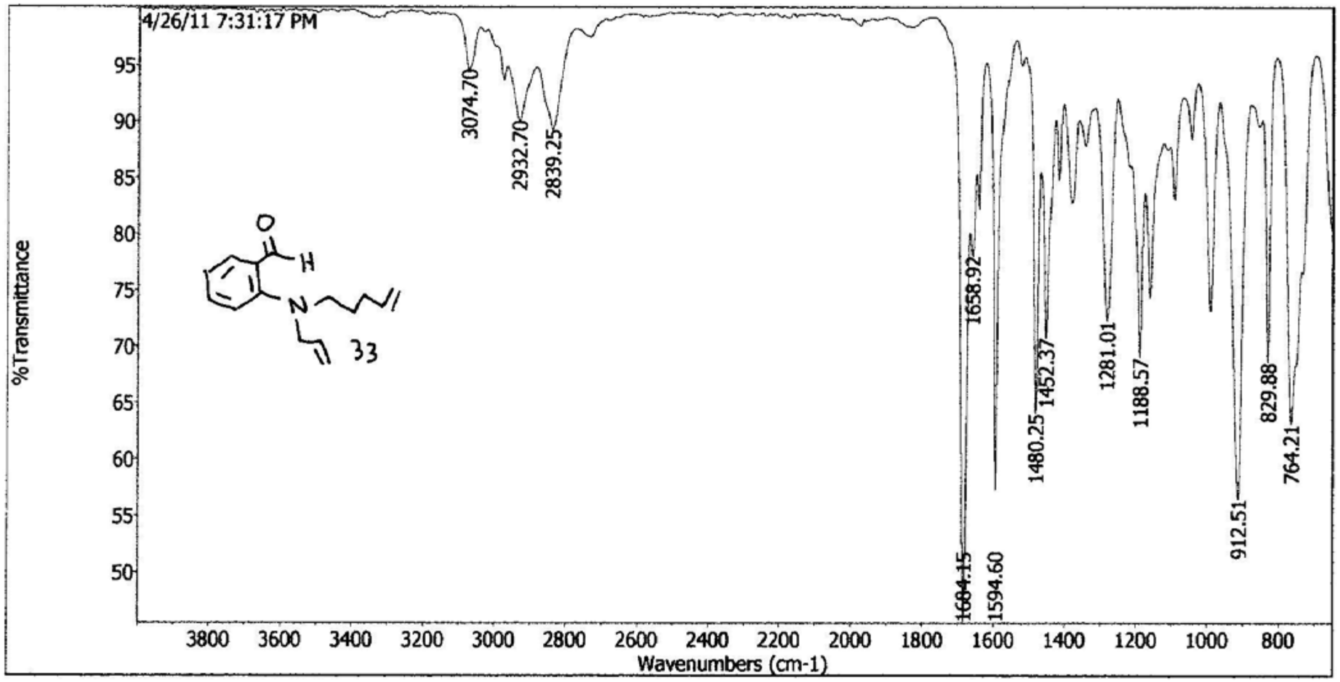
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2          300.1312005 MHz

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

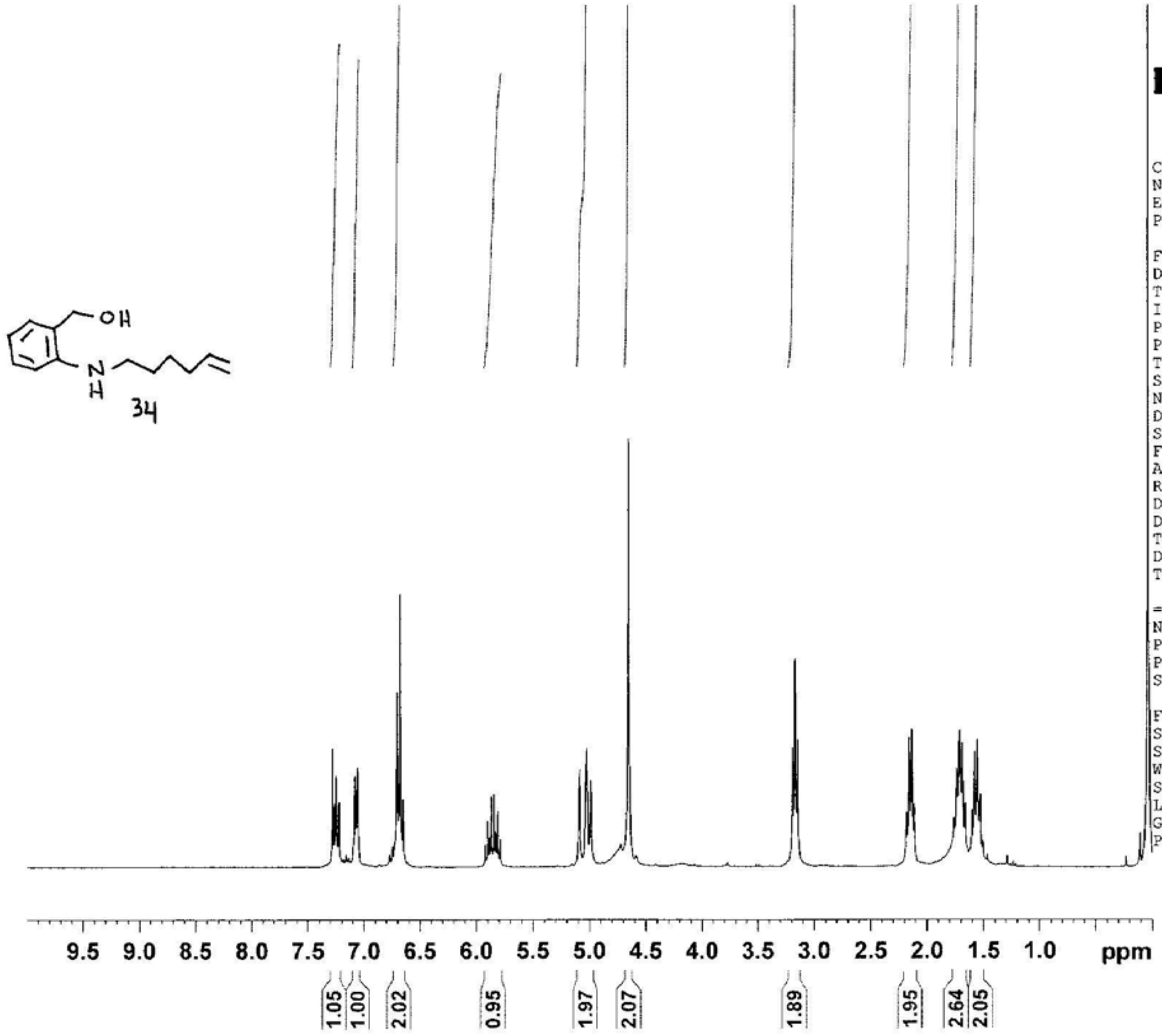
KER-I-032

Peak finding results for: 4/26/11 7:31:17 PM
Frequency: 687.71 - 3365.20, threshold: 67.681-98.056, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13
Position	3074.70	2932.70	2839.25	1684.15	1658.92	1594.60	1480.25	1452.37	1281.01	1188.57	912.51	829.88	764.21
Height	94.427	89.853	89.147	45.387	77.912	57.161	63.891	70.599	72.166	68.832	56.372	68.430	62.987



33



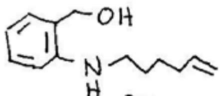
BRUKER

```
Current Data Parameters
NAME             KER-I-037
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090710
Time                 12.03
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                   80.6
DW                81.000 usec
DE                  6.00 usec
TE                 292.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



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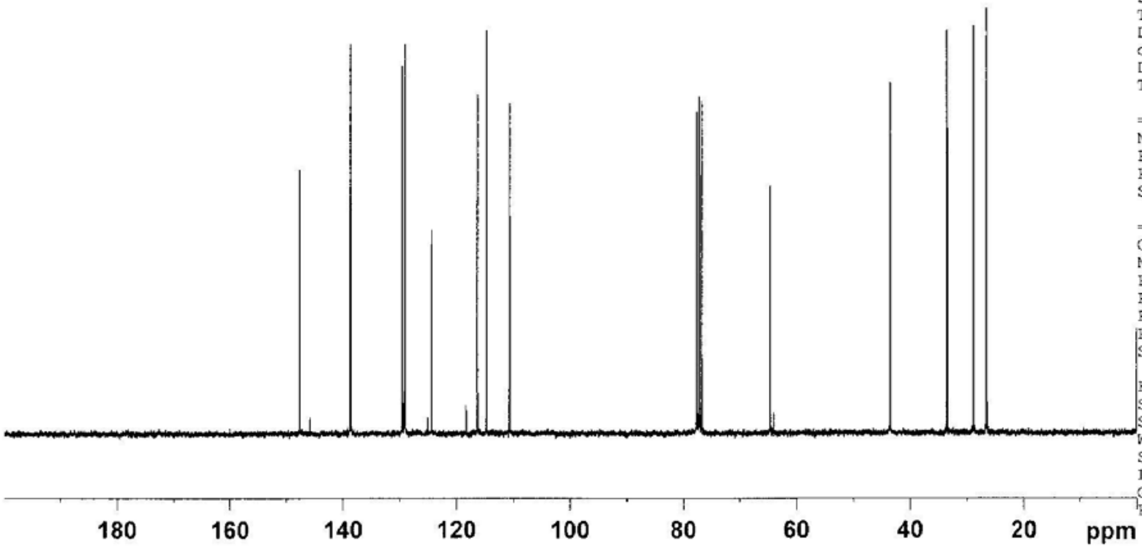


```
Current Data Parameters
NAME     KER-I-037carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110427
Time_              13.24
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  500
DS                    4
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ           1.8219508 sec
RG              9195.2
DW              27.800 usec
DE                6.00 usec
TE               300.2 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 7.10 usec
PL1               -1.50 dB
SFO1        75.4752953 MHz

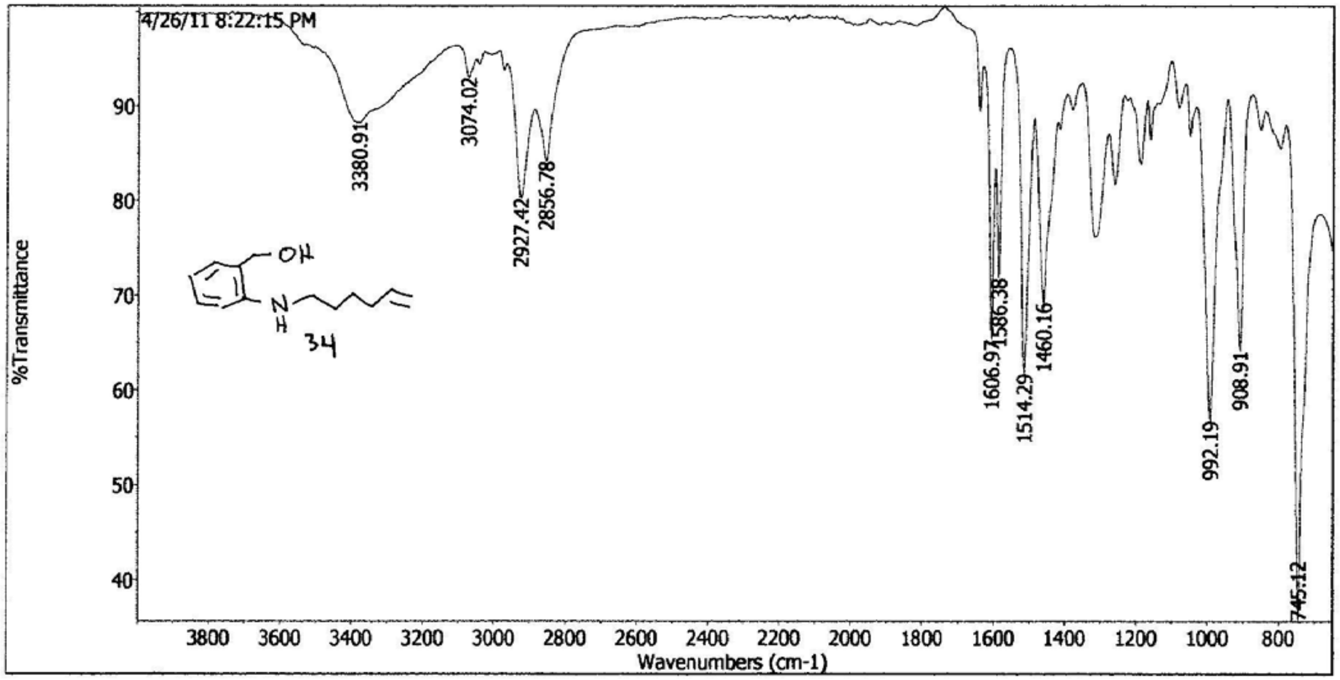
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              17.23 dB
PL13              19.00 dB
SFO2       300.1312005 MHz

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

KER-I-037

Peak finding results for: 4/26/11 8:22:15 PM
Frequency: 694.00 - 3484.62, threshold: 65.386-98.301, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11
Position	3380.91	3074.02	2927.42	2856.78	1606.97	1586.38	1514.29	1460.16	992.19	908.91	745.12
Height	88.112	92.876	80.127	84.049	65.109	71.677	61.566	69.045	56.647	64.008	35.447



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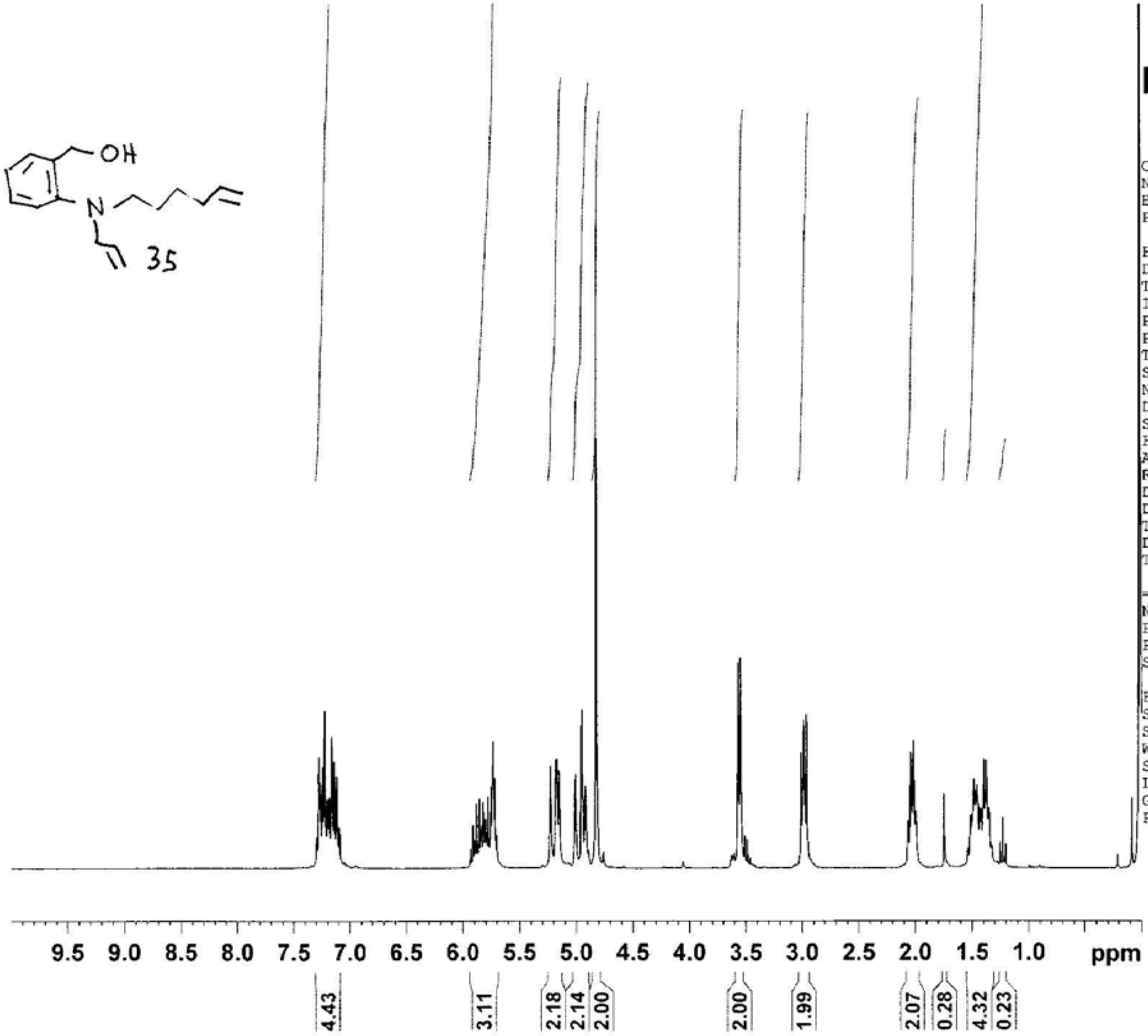
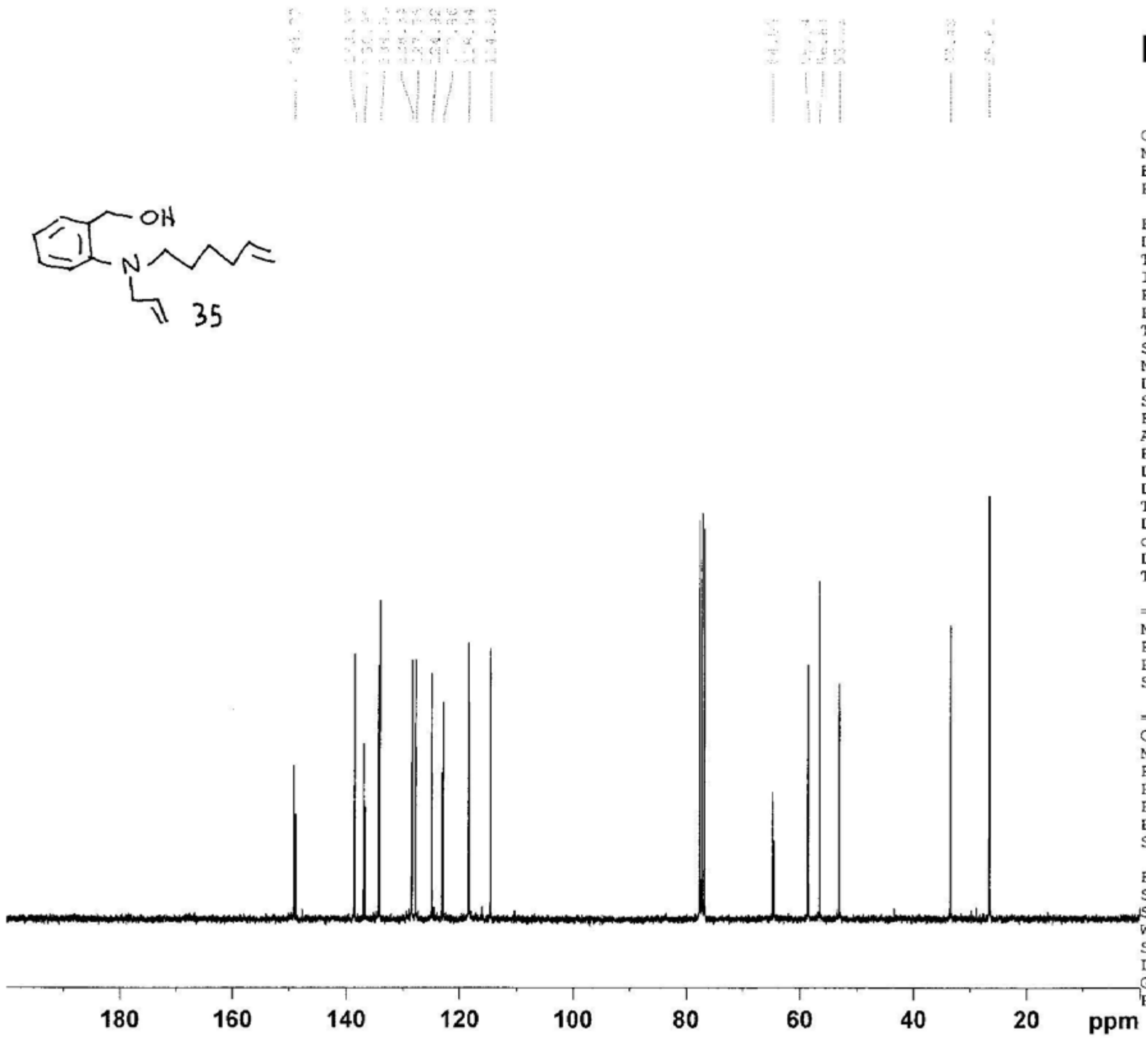


```
Current Data Parameters
NAME      KER-I-038(20-30Frac)
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_             20090713
Time                 16.26
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084660 sec
RG                    90.5
DW              81.000 usec
DE                6.00 usec
TE                 291.2 K
D1          1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1               11.00 usec
PL1                0.00 dB
SFO1       300.1318534 MHz

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



```
Current Data Parameters
NAME      KER-I-038carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110427
Time                22.50
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  6502
DW                27.800 usec
DE                  6.00 usec
TE                 319.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1          75.4752953 MHz

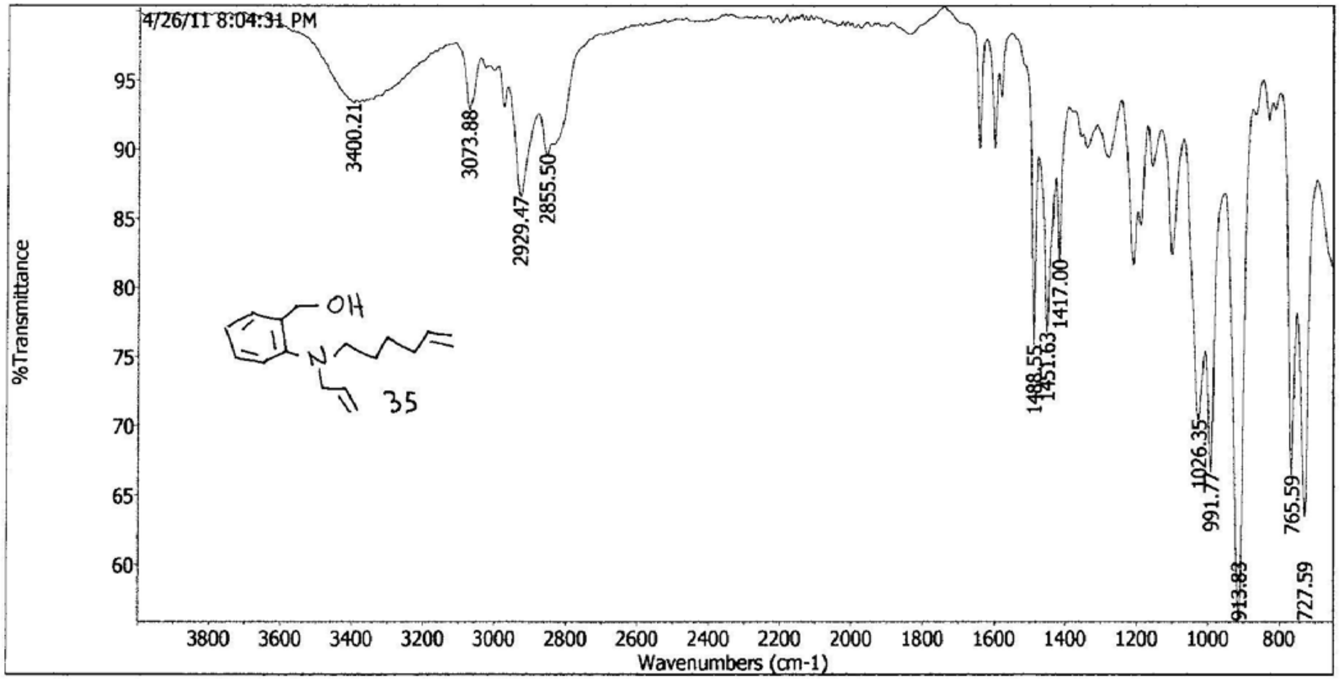
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2         300.1312005 MHz

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

KER-I-038

Peak finding results for: 4/26/11 8:04:31 PM
Frequency: 706.57 - 3622.89, threshold: 76.838-98.383, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12
Position	3400.21	3073.88	2929.47	2855.50	1488.55	1451.63	1417.00	1026.35	991.77	913.83	765.59	727.59
Height	93.269	92.763	86.499	89.537	75.747	76.666	81.911	70.360	66.585	55.908	66.382	63.398



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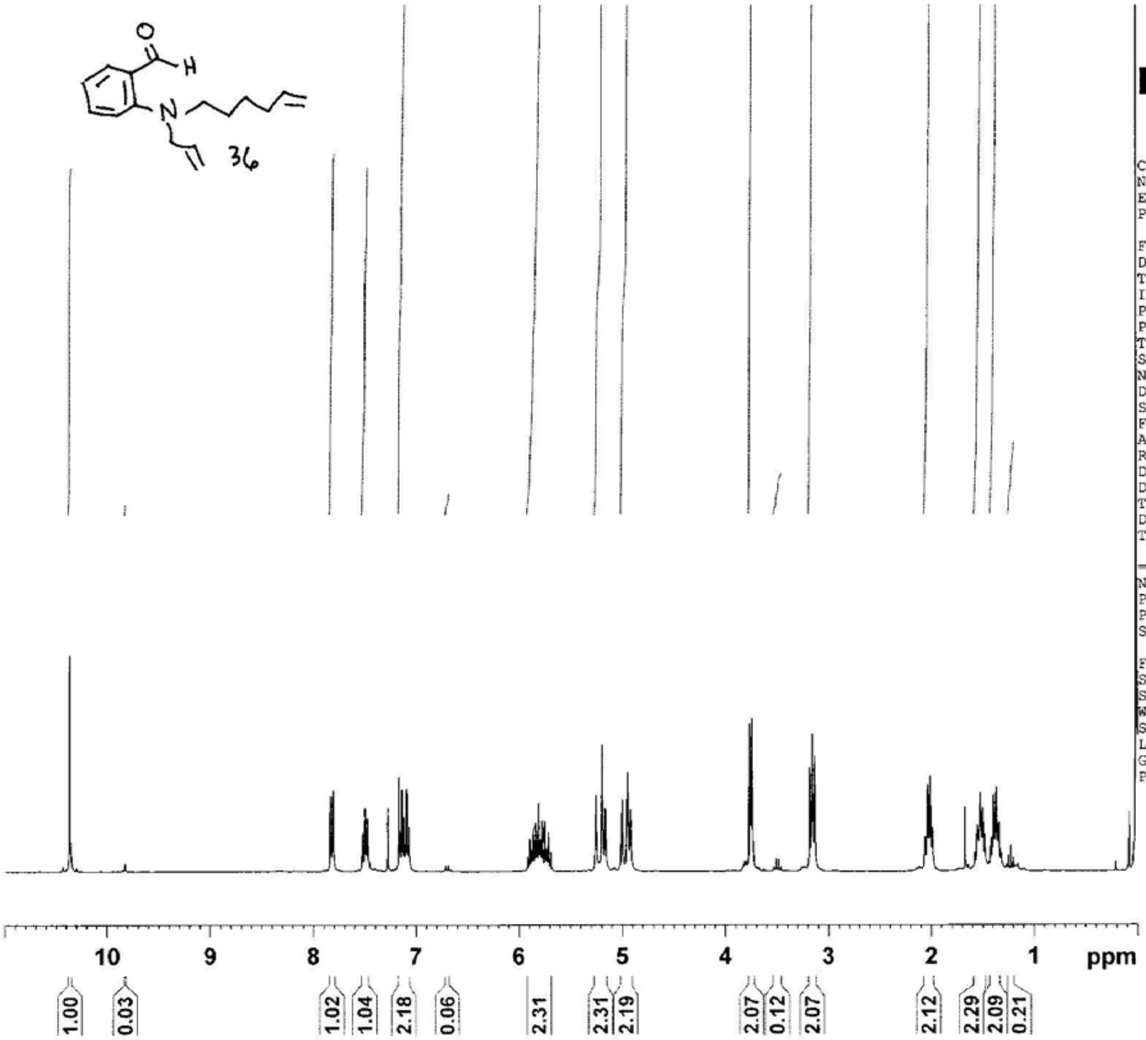
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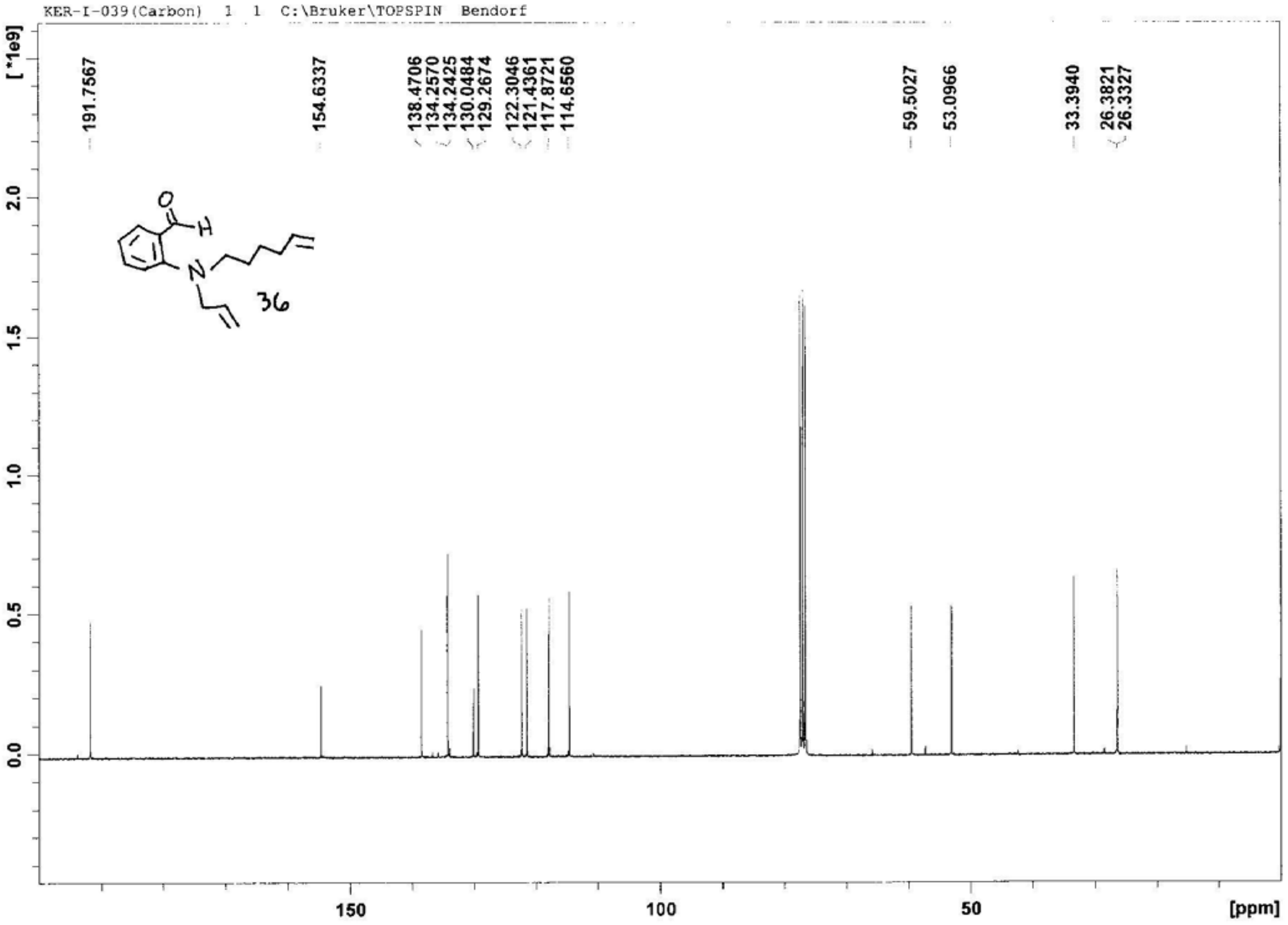
```
Current Data Parameters
NAME       KER-I-039(post column)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090714
Time                  15.39
INSTRUM               spect
PROBHD   5 mm Multinucl
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                5.3084660 sec
RG                     90.5
DW                   81.000 usec
DE                     6.00 usec
TE                    291.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1                    0.00 dB
SFO1            300.1318534 MHz

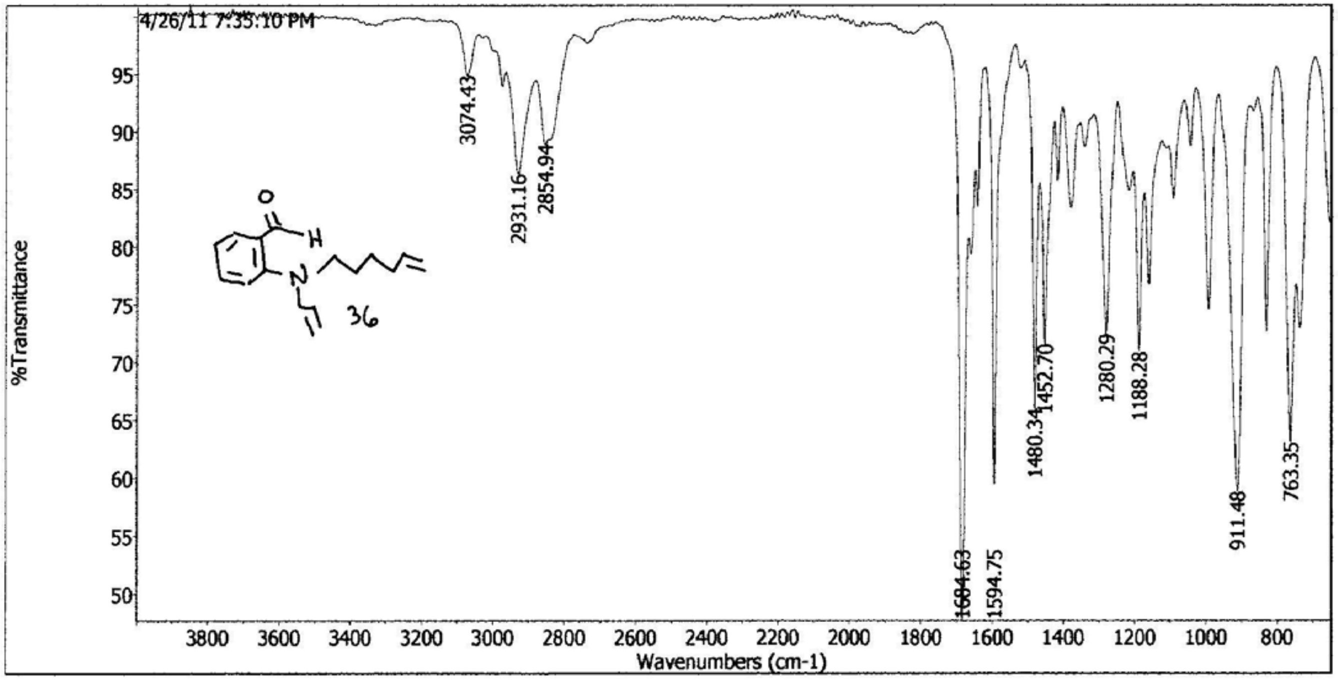
F2 - Processing parameters
SI                    32768
SF              300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

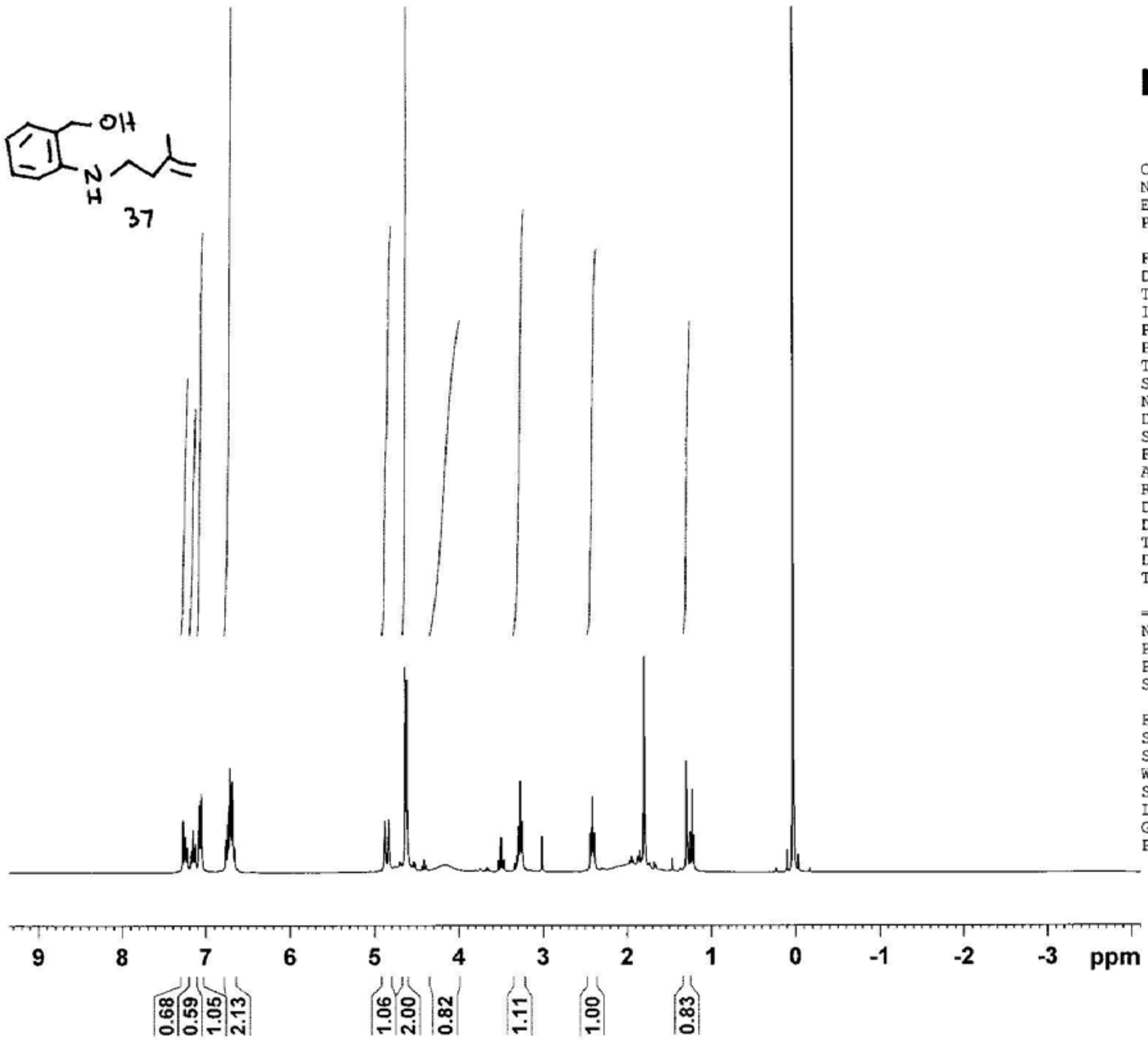
KER-I-039(Carbon) 1 1 C:\Bruker\TOPSPIN Bendorf
191.7567
154.6337
138.4706
134.2570
134.2425
130.0484
129.2674
122.3046
121.4361
117.8721
114.6560
59.5027
53.0966
33.3940
26.3821
26.3327
O
H
N
36
[*1e9]
2.0
1.5
1.0
0.5
0.0
150
100
50
[ppm]

KER-I-039

Peak finding results for: 4/26/11 7:35:10 PM
Frequency: 687.71 - 3365.20, threshold: 67.681-98.056, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11
Position	3074.43	2931.16	2854.94	1684.63	1594.75	1480.34	1452.70	1280.29	1188.28	911.48	763.35
Height	94.741	86.188	88.741	47.379	59.354	65.833	71.418	72.289	70.801	58.752	62.976





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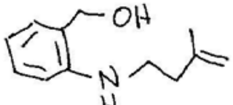
```
Current Data Parameters
NAME            KER-I-029
EXPNO                   1
PROCNO                  1

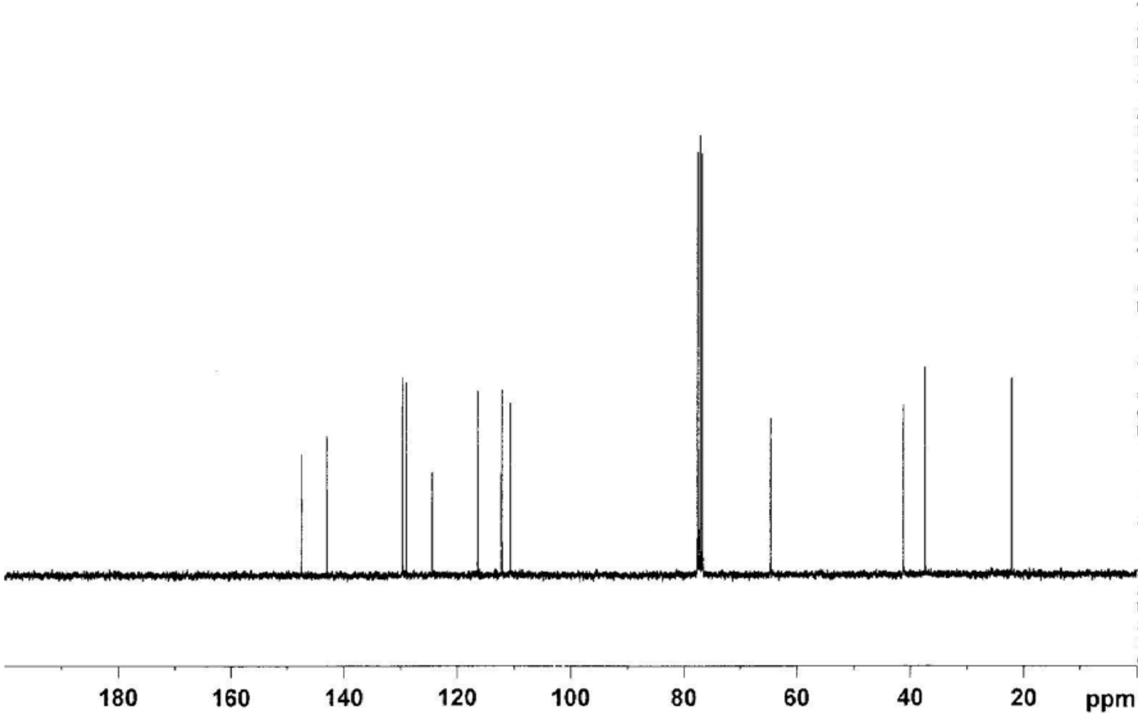
F2 - Acquisition Parameters
Date_            20090630
Time                 9.36
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                   80.6
DW                 81.000 usec
DE                   6.00 usec
TE                  292.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



37



```
Current Data Parameters
NAME        KER-I-029carbon
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20110427
Time_                 20.36
INSTRUM               spect
PROBHD    5 mm Multinucl
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     500
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                  4597.6
DW                  27.800 usec
DE                    6.00 usec
TE                   317.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1           75.4752953 MHz

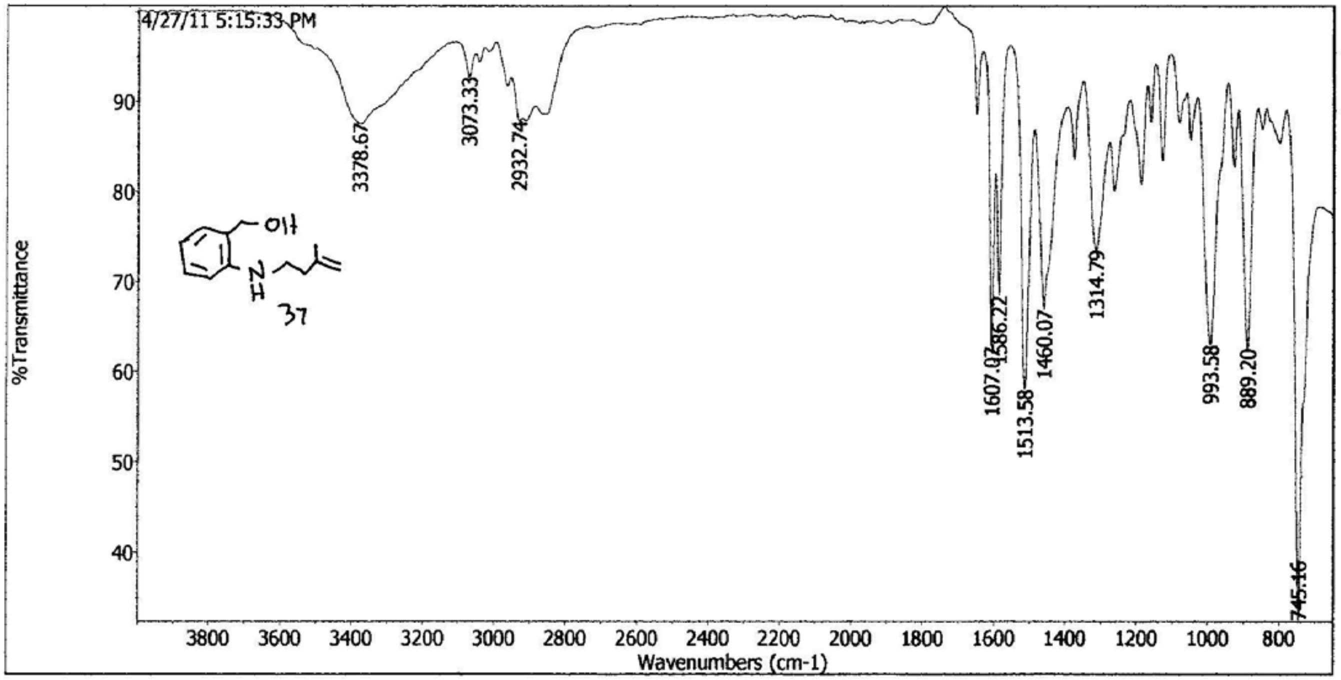
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2          300.1312005 MHz

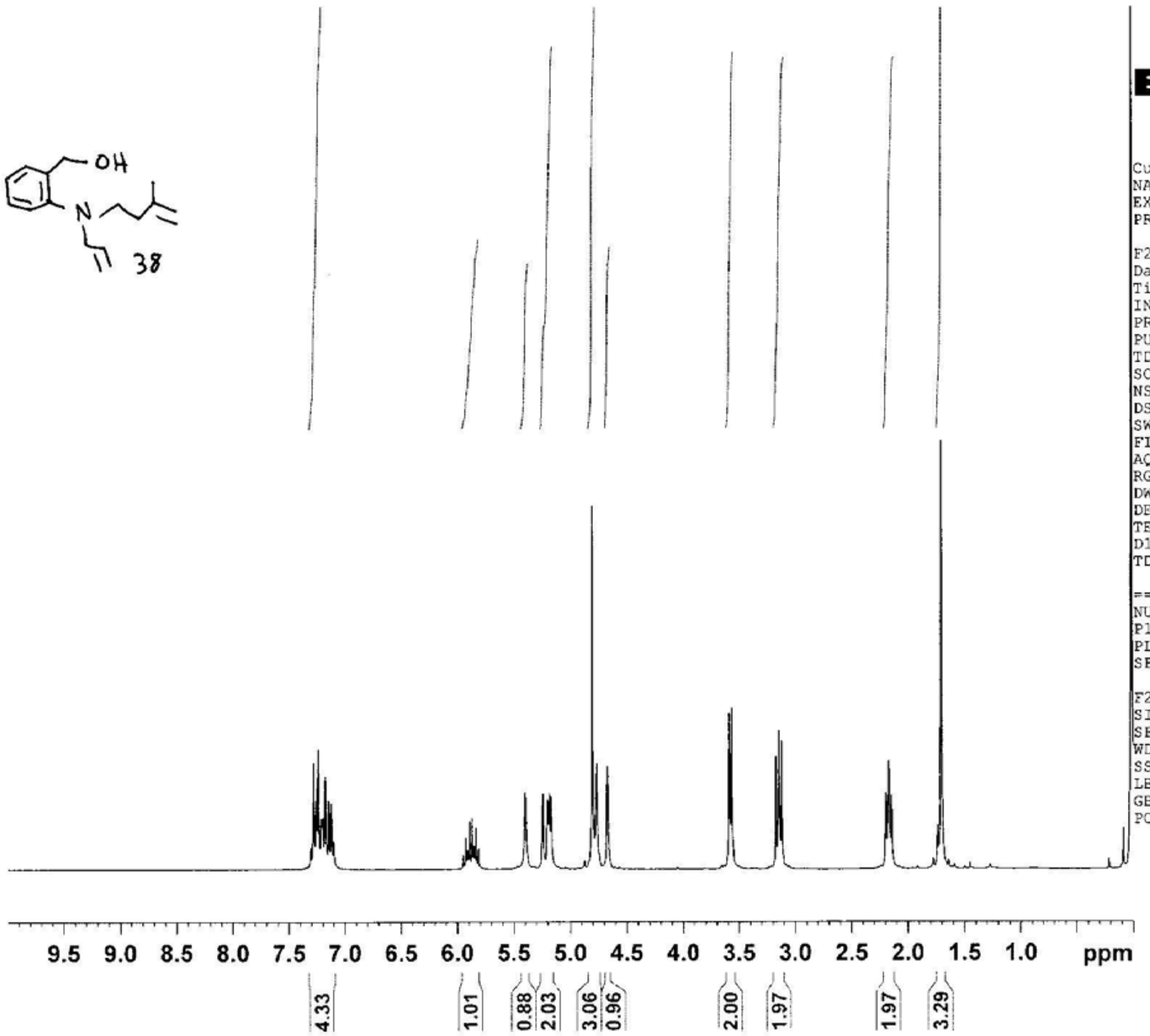
F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

KER-I-029

Peak finding results for: 4/27/11 5:15:33 PM
Frequency: 656.29 - 3541.18, threshold: 70.556-98.819, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11
Position	3378.67	3073.33	2932.74	1607.07	1586.22	1513.58	1460.07	1314.79	993.58	889.20	745.16
Height	87.378	92.567	87.631	62.537	68.279	57.886	66.698	73.316	62.806	62.358	32.066





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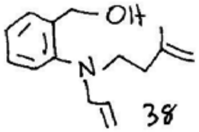
```
Current Data Parameters
NAME      KER-I-033(Pst. colm)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090707
Time                 13.40
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                    90.5
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1         300.1318534 MHz

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



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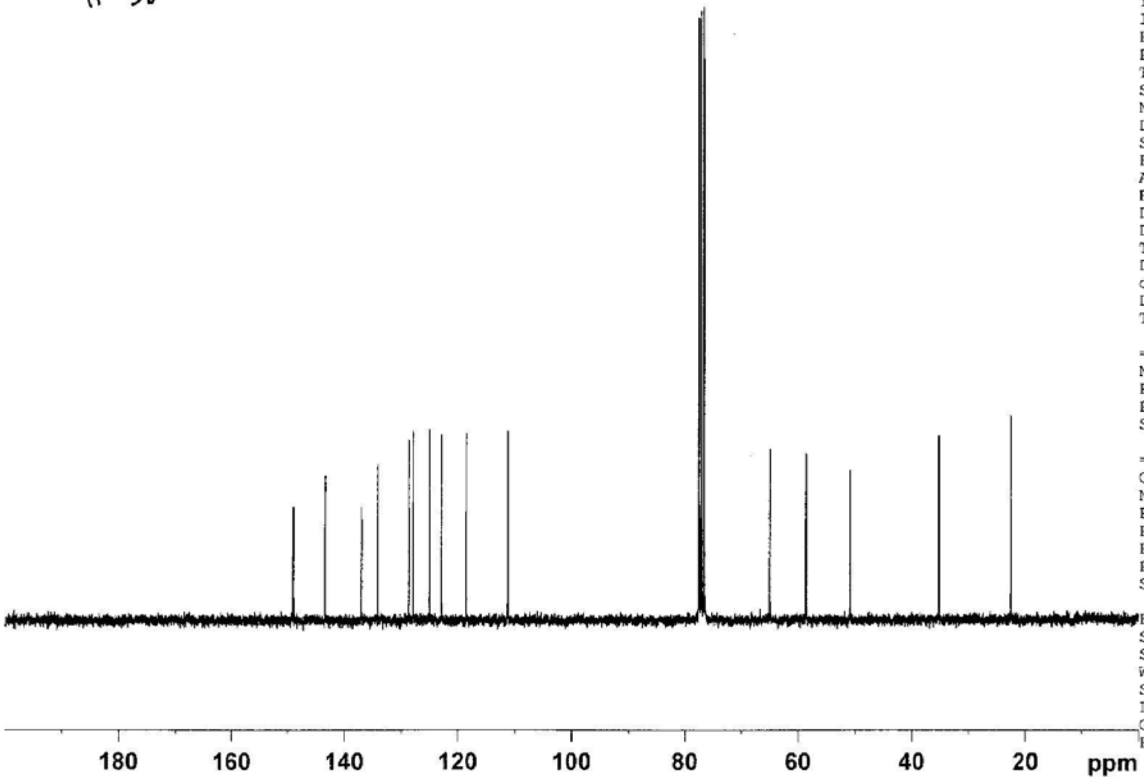


```
Current Data Parameters
NAME      KER-I-033carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110427
Time                21.12
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    500
DS                      4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 5792.6
DW                 27.800 usec
DE                   6.00 usec
TE                  316.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.10 usec
PL1                 -1.50 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL13                19.00 dB
SFO2        300.1312005 MHz

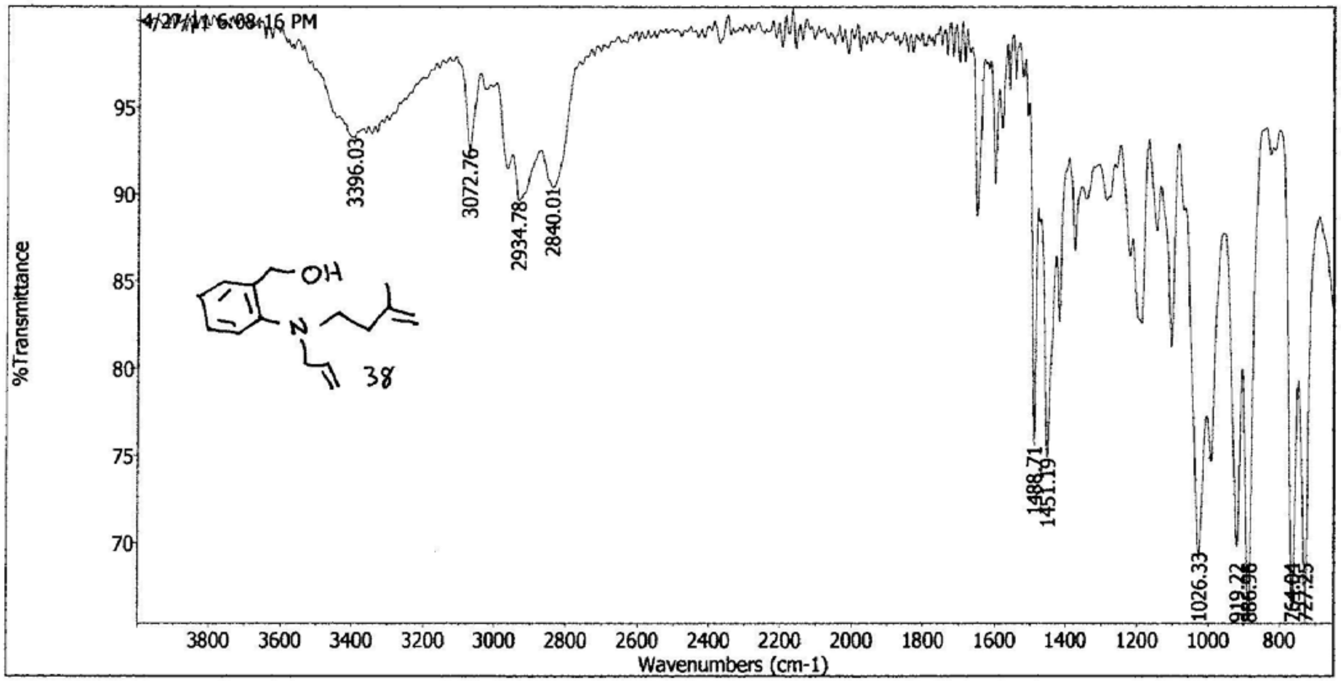
F2 - Processing parameters
SI                  32768
SF           75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

KER-I-033

Peak finding results for: 4/27/11 6:08:16 PM
Frequency: 656.29 - 3472.04, threshold: 70.608-97.635, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3396.03	3072.76	2934.78	2840.01	1488.71	1451.19	1026.33	919.22	886.96
Height	93.152	92.518	89.534	90.336	75.483	74.775	69.158	69.716	65.580

Peak#	10	11							
Position	764.04	727.25							
Height	66.112	65.393							



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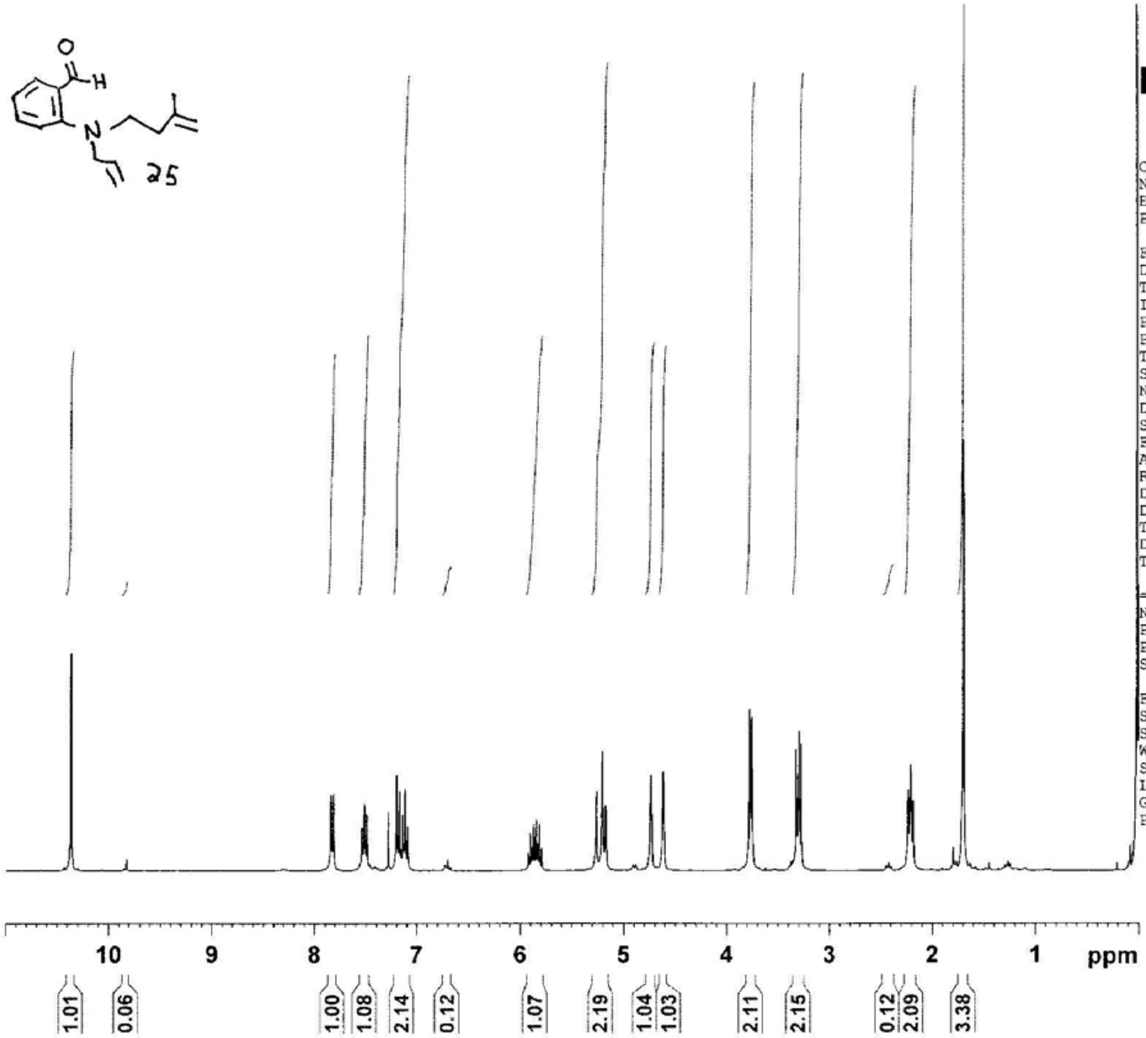
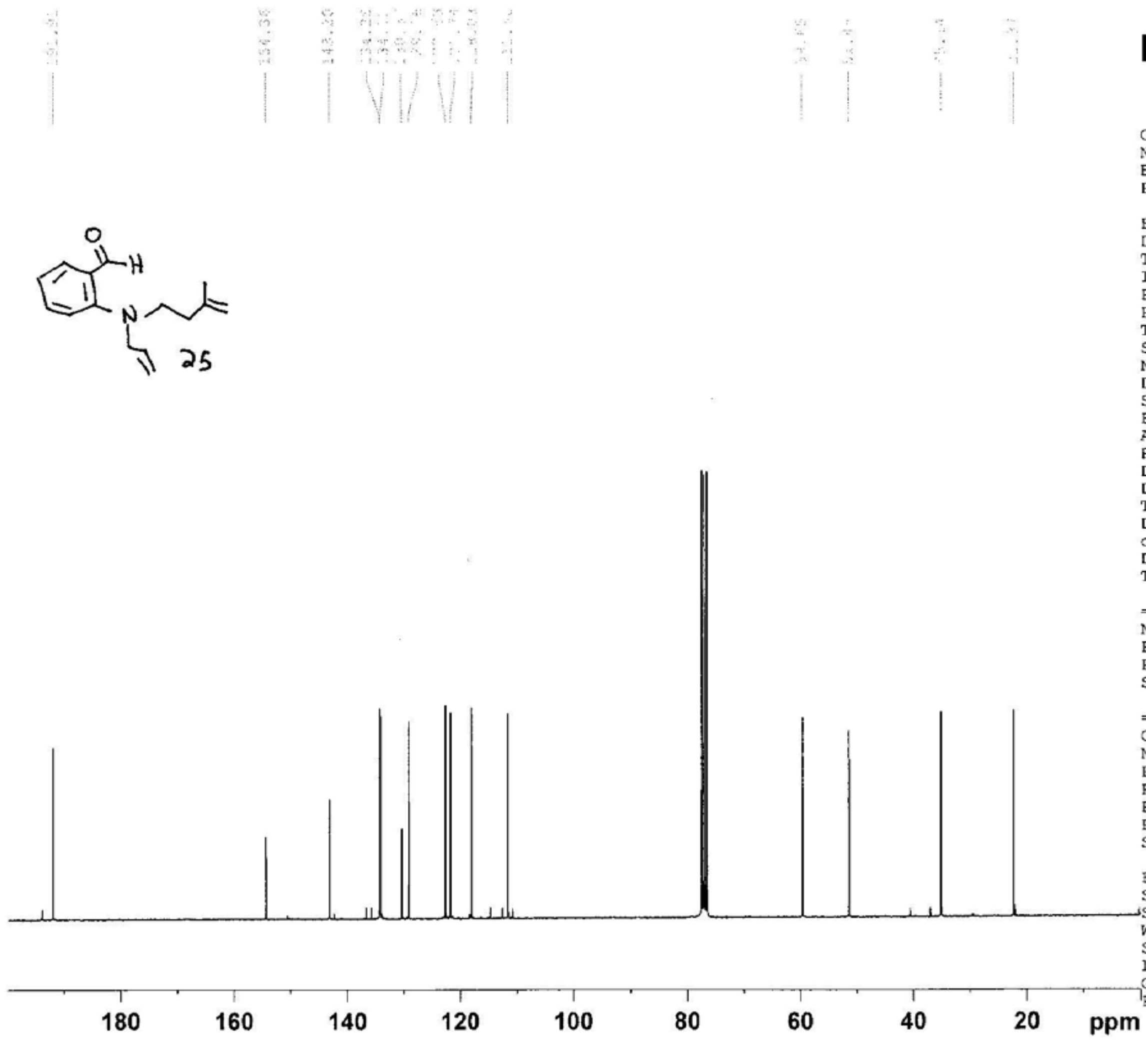


```
Current Data Parameters
NAME     KER-I-035(Pst. colm)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090708
Time                 16.35
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                    80.6
DW                81.000 usec
DE                  6.00 usec
TE                 291.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz

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



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```
Current Data Parameters
NAME     KER-I-035 carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090710
Time                 6.40
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                 12288
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  3251
DW                27.800 usec
DE                  6.00 usec
TE                 294.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2         300.1312005 MHz

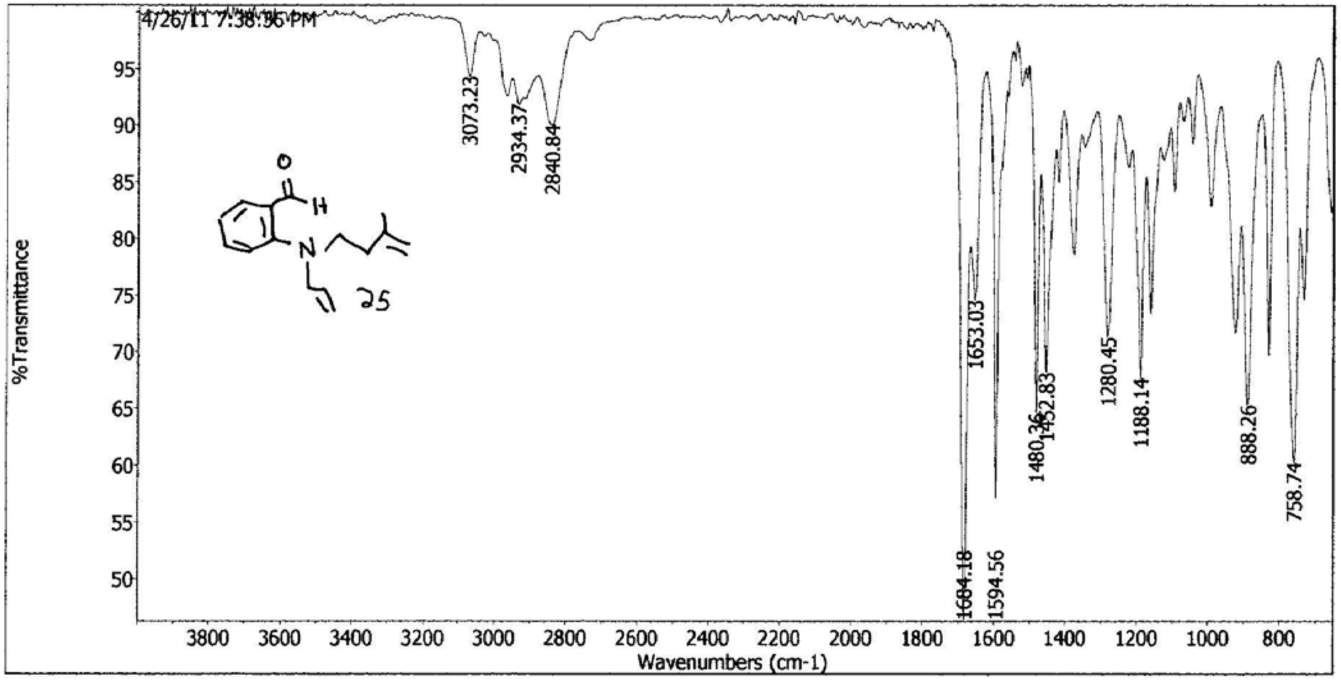
F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

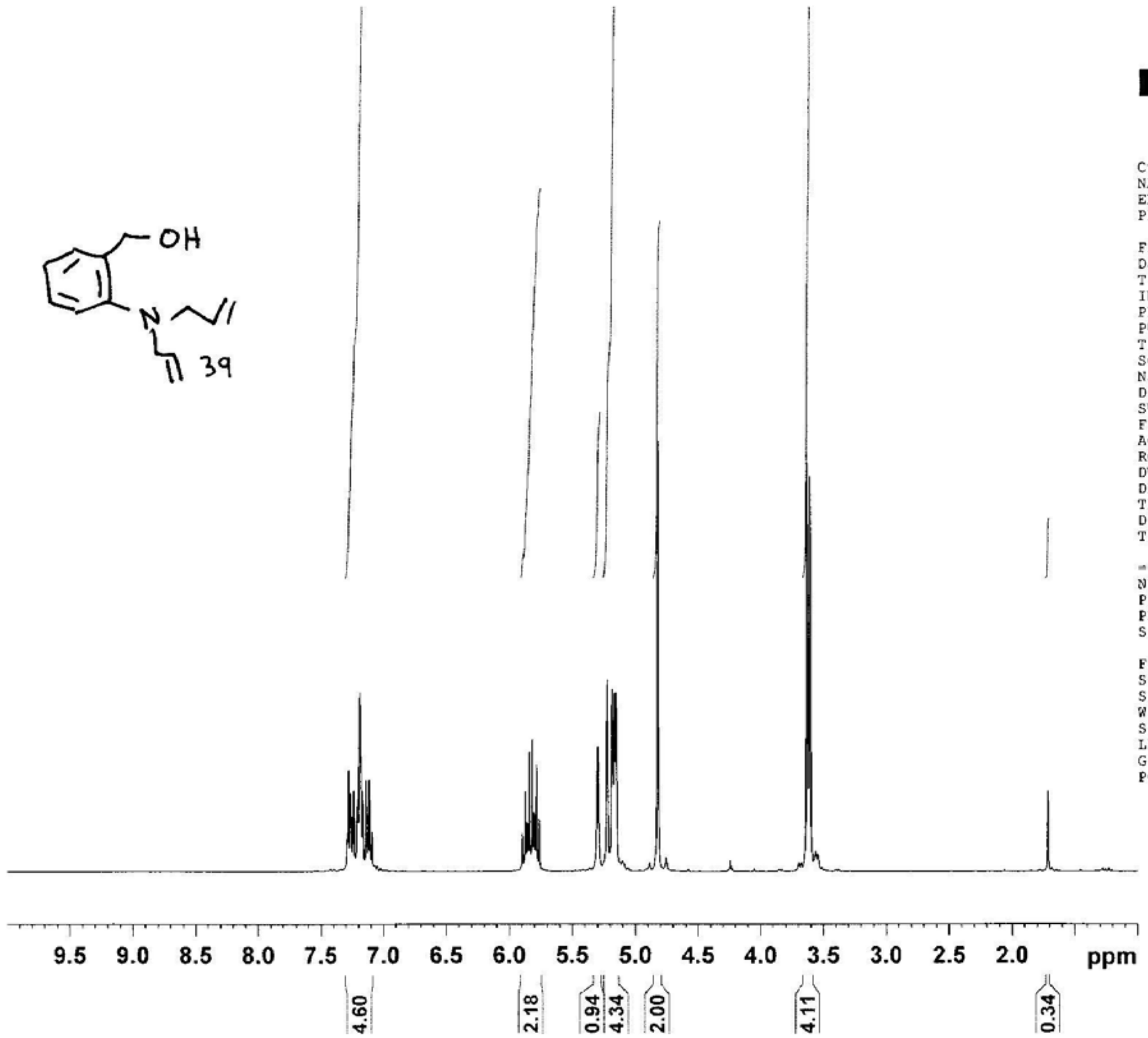
KER-I-035

Peak finding results for: 4/26/11 7:38:36 PM
Frequency: 687.71 - 3365.20, threshold: 67.681-98.056, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3073.23	2934.37	2840.84	1684.18	1653.03	1594.56	1480.36	1452.83	1280.45
Height	94.171	91.695	89.862	46.151	74.440	56.982	64.458	68.067	71.161

Peak#	10	11	12						
Position	1188.14	888.26	758.74						
Height	67.536	65.168	60.143						





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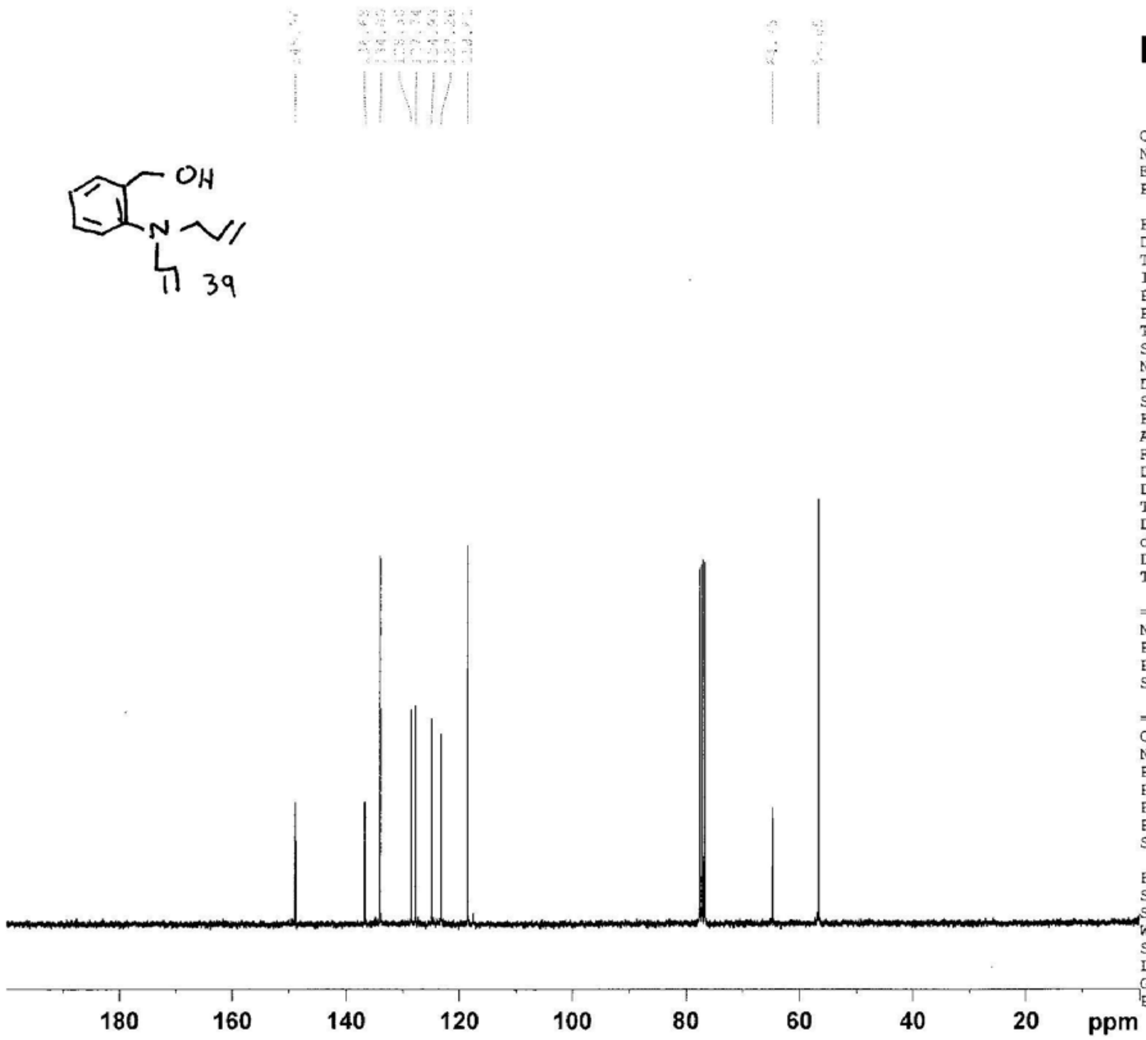
BRUKER

```
Current Data Parameters
NAME       KER-I-045(post Column)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090911
Time                 10.11
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                      16
DS                       2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                   101.6
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz

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



```
Current Data Parameters
NAME      KER-I-045carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110428
Time                 0.22
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    500
DS                      4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 2580.3
DW                 27.800 usec
DE                   6.00 usec
TE                  321.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.10 usec
PL1                 -1.50 dB
SFO1          75.4752953 MHz

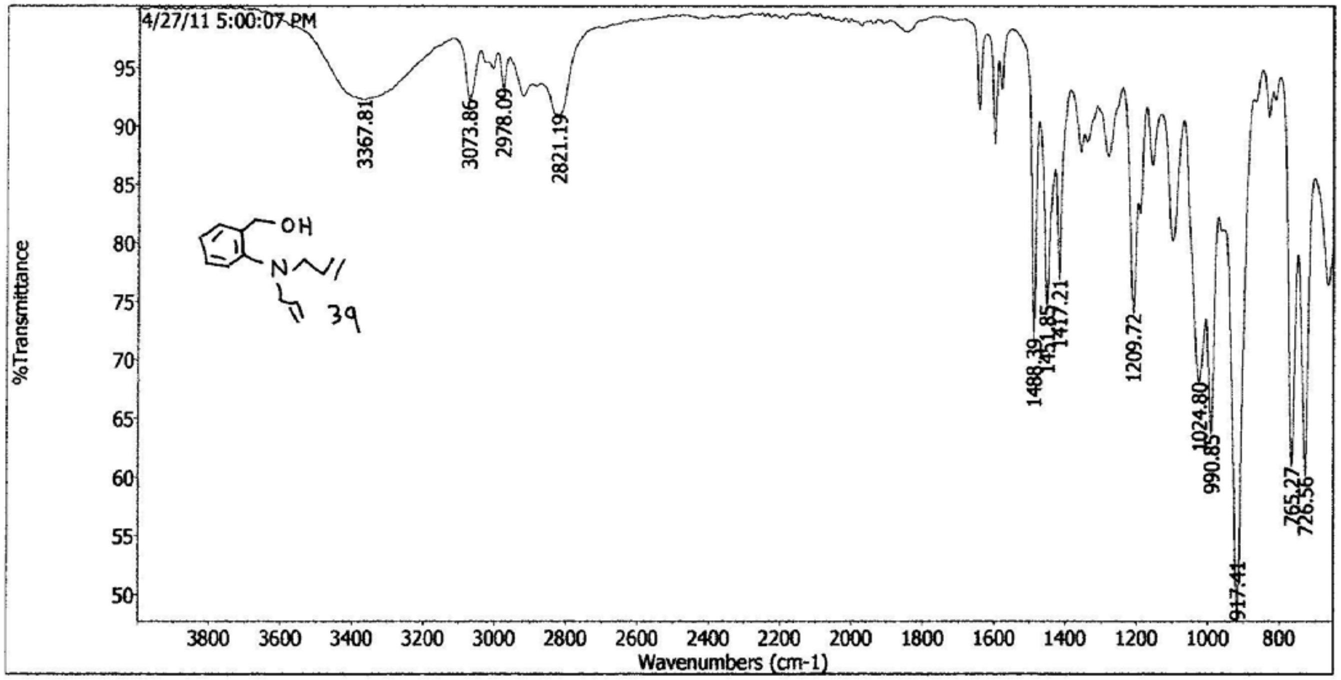
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL13                19.00 dB
SFO2         300.1312005 MHz

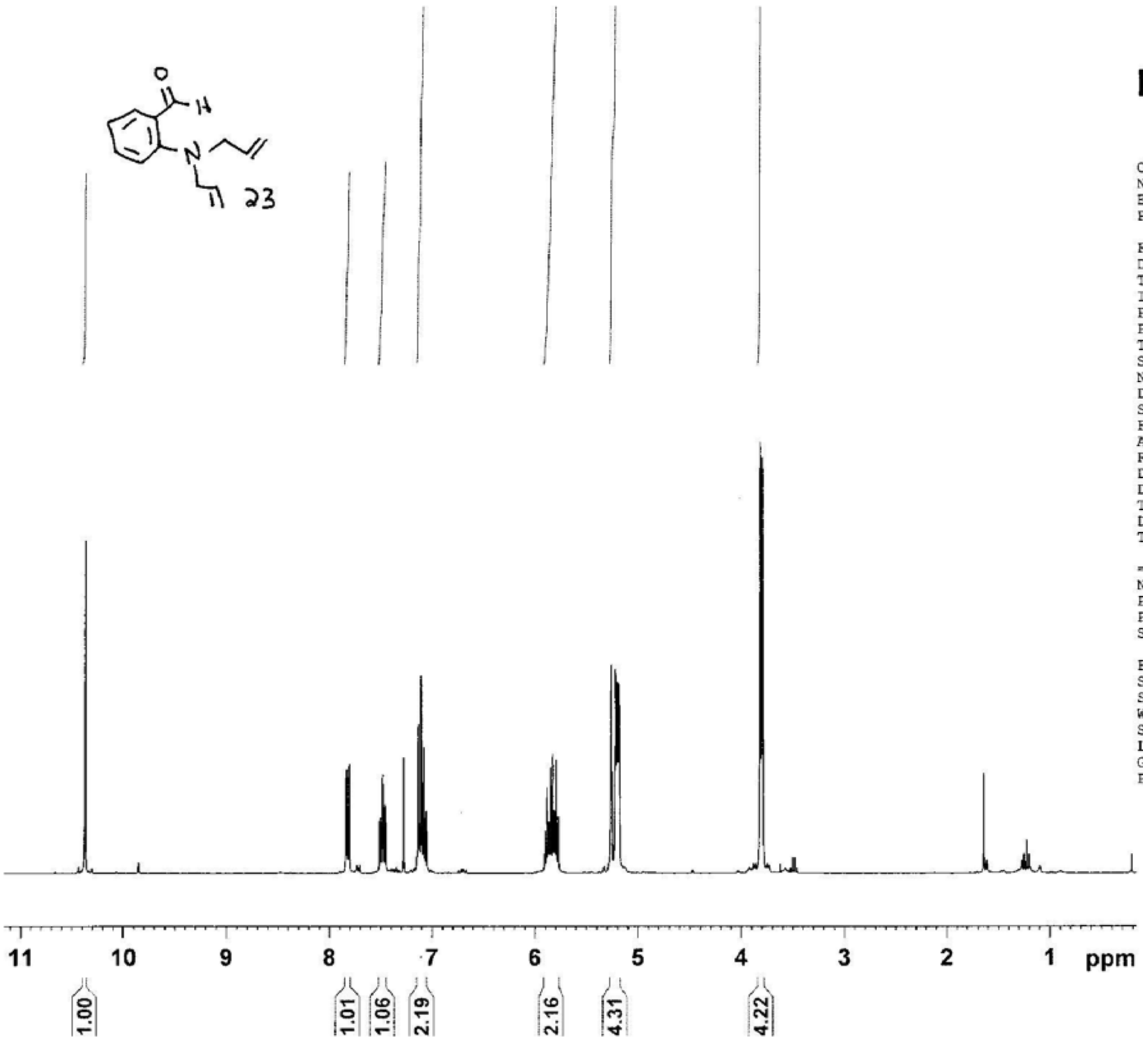
F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

KER-I-045

Peak finding results for: 4/27/11 5:00:07 PM
Frequency: 656.29 - 3541.18, threshold: 70.556-98.819, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13
Position	3367.81	3073.86	2978.09	2821.19	1488.39	1451.85	1417.21	1209.72	1024.80	990.85	917.41	765.27	726.56
Height	92.139	92.107	93.104	90.852	71.731	74.554	76.756	73.827	67.964	63.524	47.683	60.757	59.932



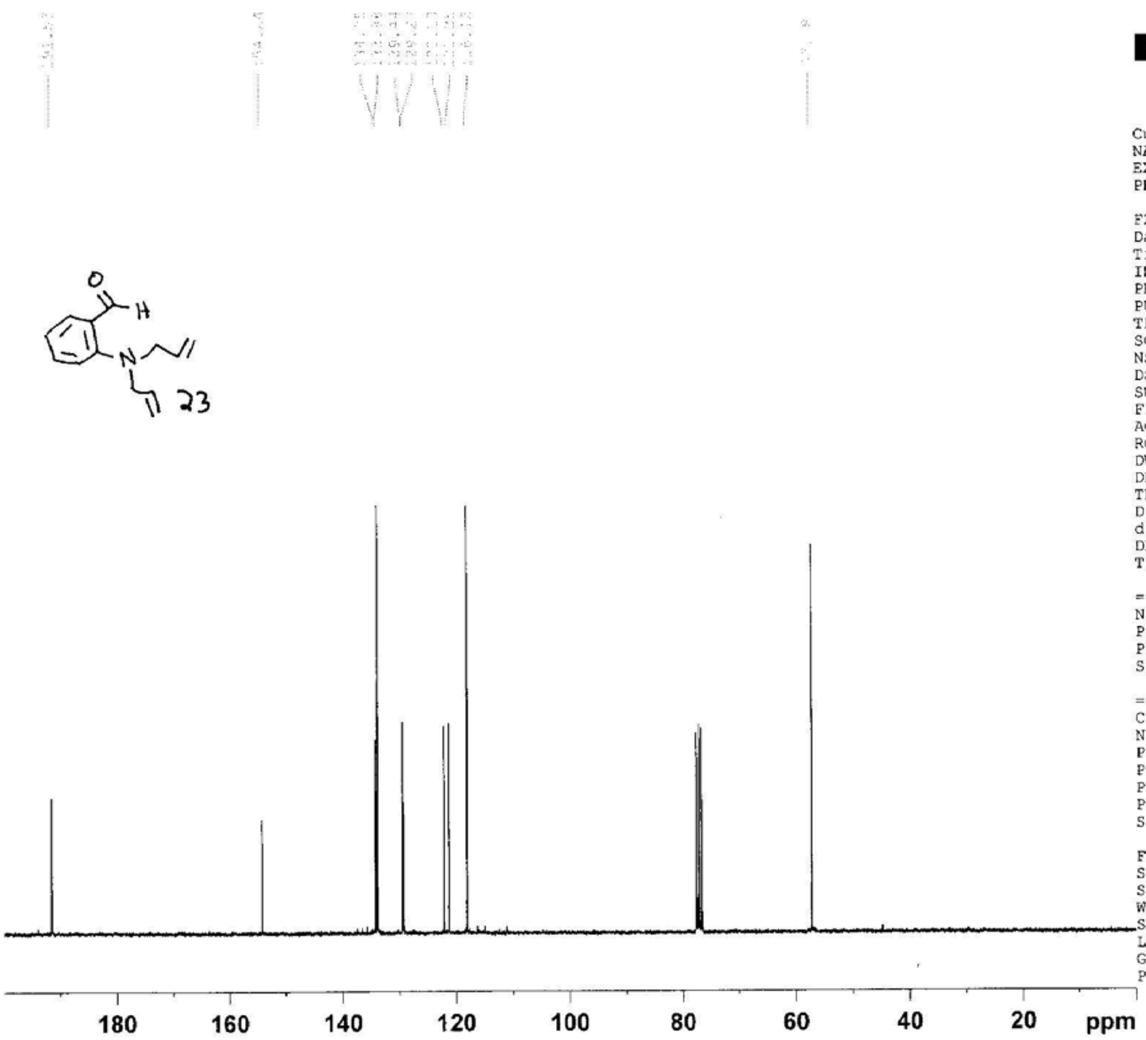


```
Current Data Parameters
NAME      KER-I-048(post Column)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090917
Time                 16.52
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                      16
DS                       2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                     114
DW                  81.000 usec
DE                    6.00 usec
TE                   293.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

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



23

```
Current Data Parameters
NAME      KER-I-048c13(500sns)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110426
Time                 20.50
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     500
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                    4096
DW                  27.800 usec
DE                    6.00 usec
TE                   296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1            75.4752953 MHz

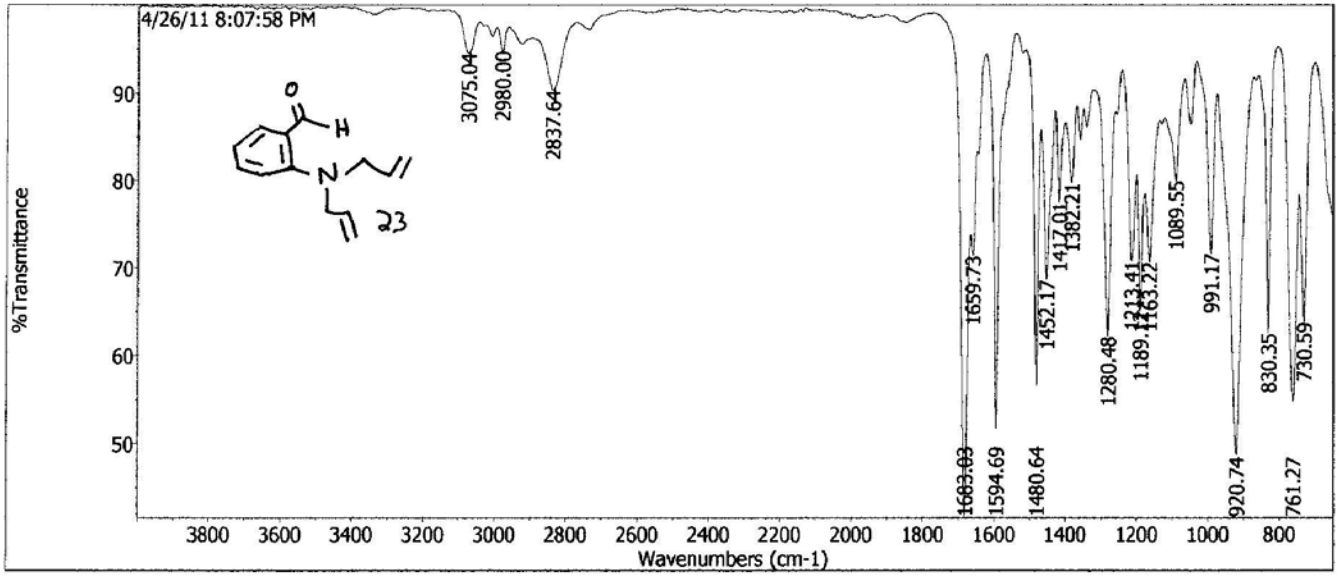
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2           300.1312005 MHz

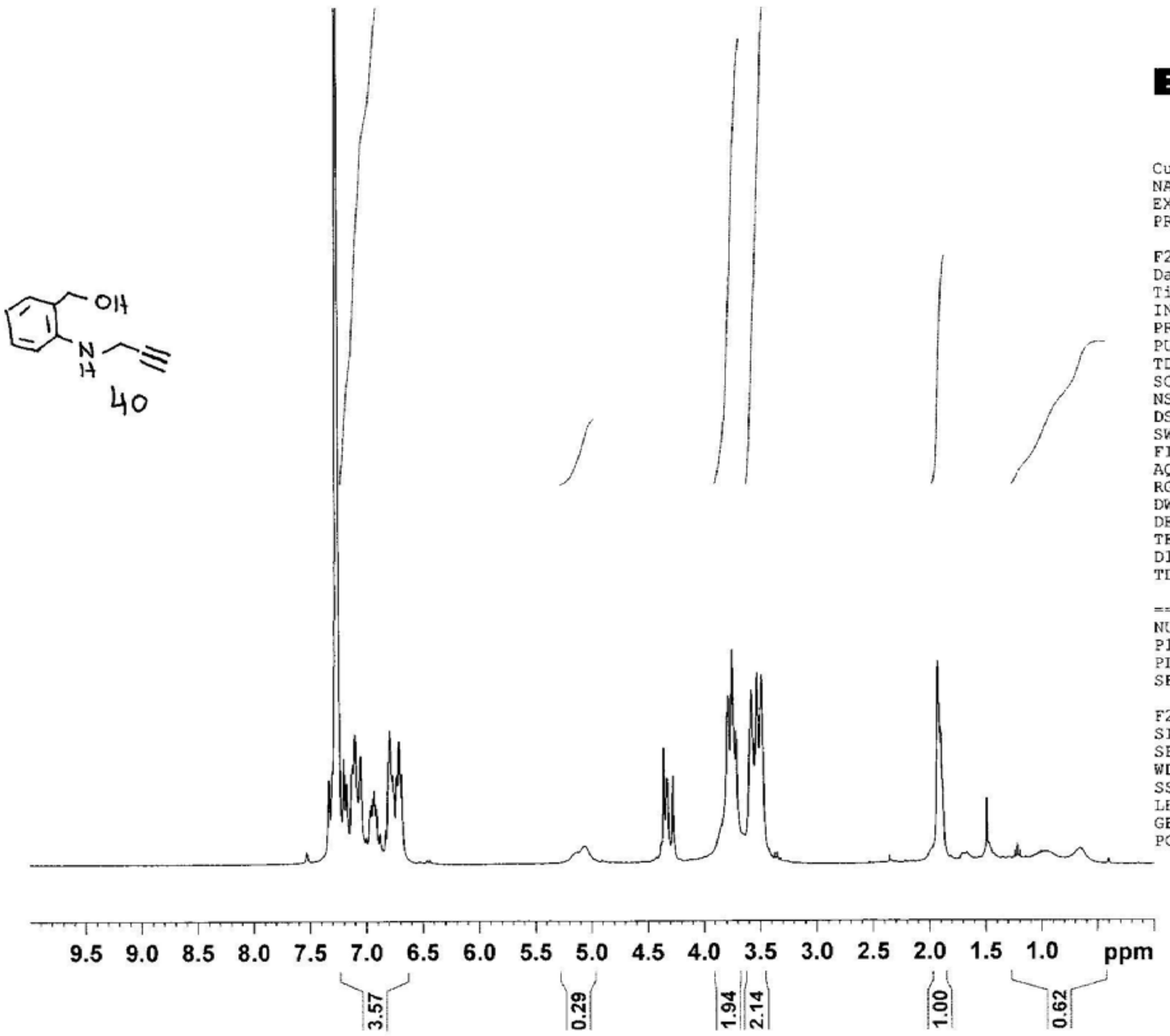
F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

KER-I-048

Peak finding results for: 4/26/11 8:07:58 PM
Frequency: 706.57 - 3289.77, threshold: 77.139-98.824, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Position	3075.04	2980.00	2837.64	1683.03	1659.73	1594.69	1480.64	1452.17	1417.01	1382.21	1280.48	1213.41	1189.12	1163.22	1089.55	991.17	920.74	830.35	761.27	730.59
Height	94.373	94.595	90.177	41.466	71.231	51.573	56.421	68.439	77.293	79.504	62.017	70.607	64.874	70.480	79.809	71.436	48.650	62.379	54.600	63.617





40

```
Current Data Parameters
NAME             KER-I-028
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090630
Time                  9.45
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                     128
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1              1.00000000 sec
TD0                      1

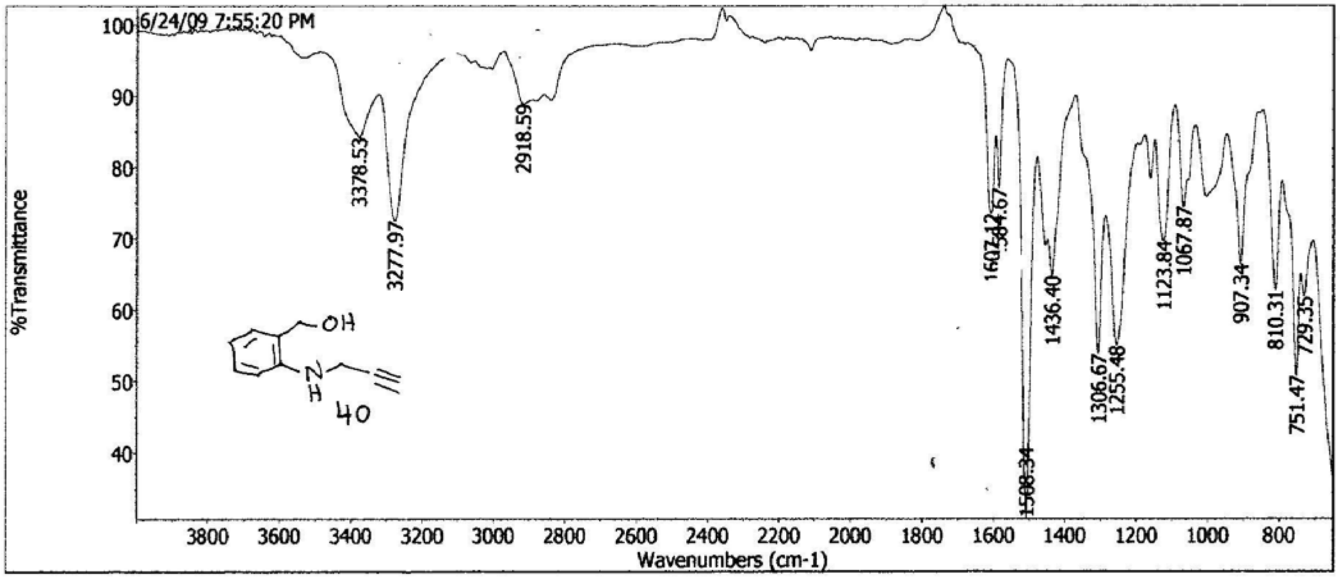
======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

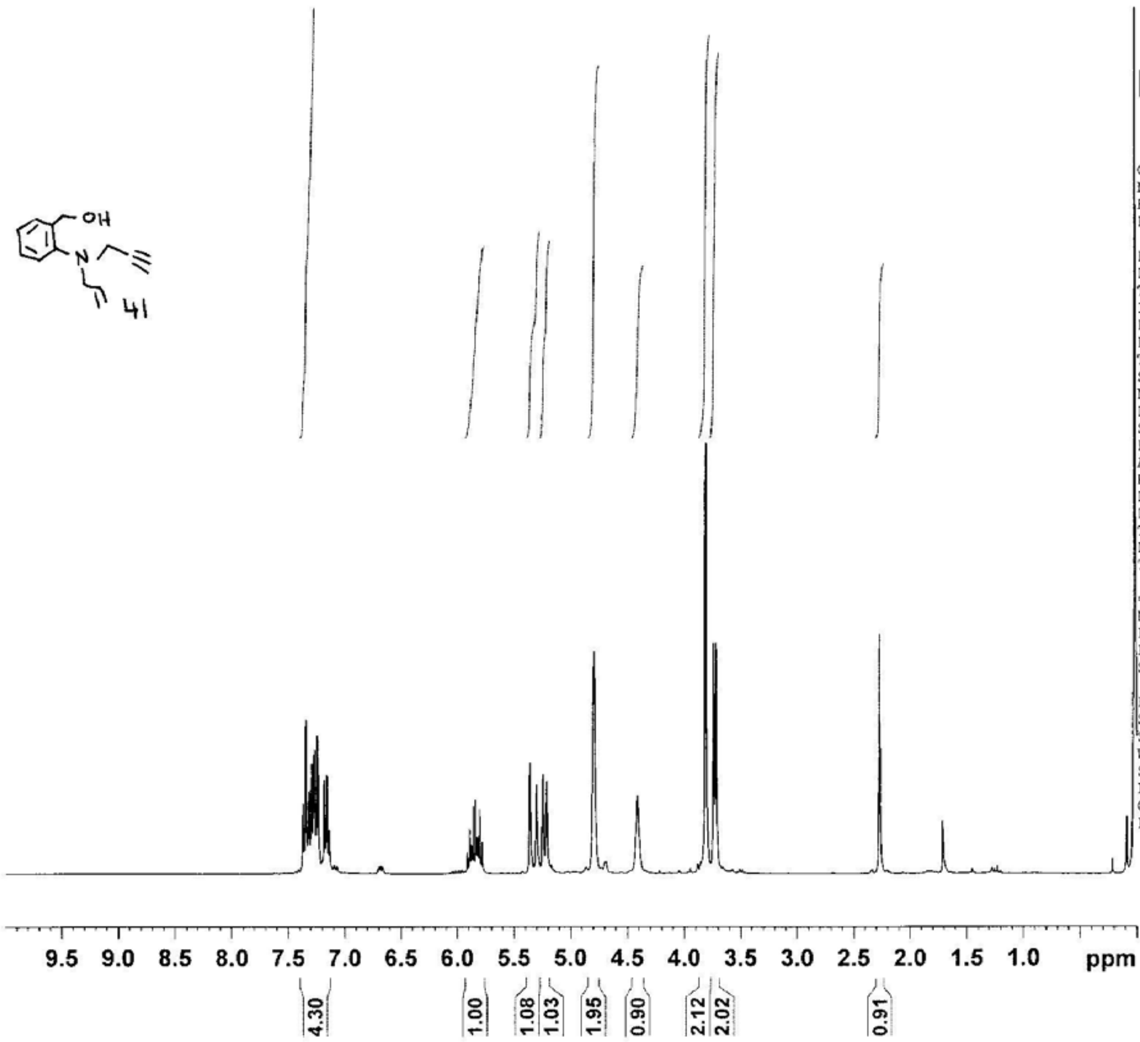
F2 - Processing parameters
SI                   32768
SF             300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

KER-I-028

Peak finding results for: 6/24/09 7:55:20 PM
Frequency: 668.86 - 3993.71, threshold: 71.868-97.204, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Position	3378.53	3277.97	2918.59	1607.12	1584.67	1508.34	1436.40	1306.67	1255.48	1123.84	1067.87	907.34	810.31	751.47	729.35
Height	83.949	72.241	88.637	73.242	76.786	30.757	64.445	53.531	54.743	69.329	74.159	66.071	62.438	50.527	61.629





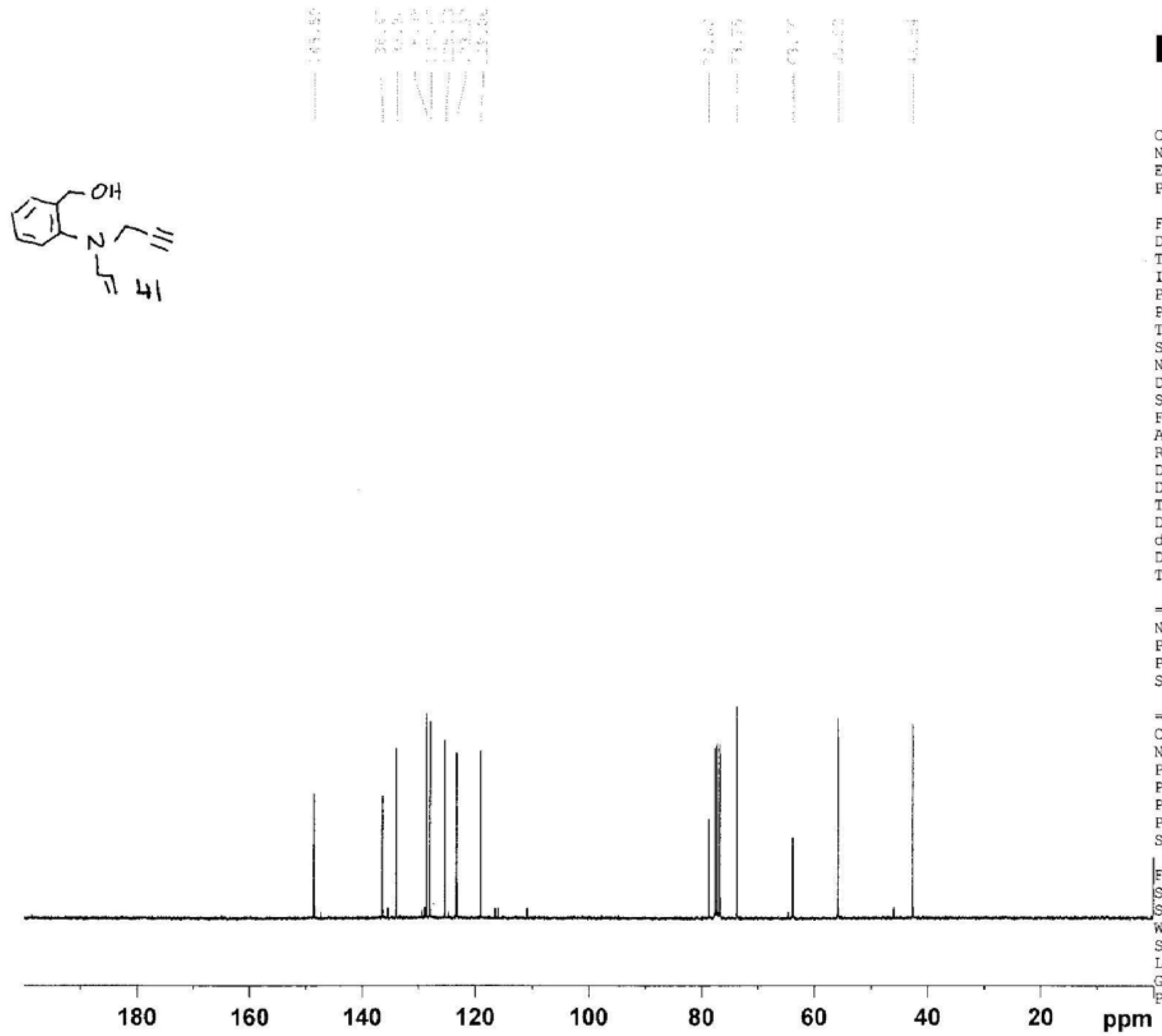
41

```
Current Data Parameters
NAME      KER-I-034(Pst. Colm)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20090707
Time                 14.44
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                   101.6
DW                  81.000 usec
DE                    6.00 usec
TE                   292.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

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



41

```
Current Data Parameters
NAME      KER-I-034carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110427
Time                18.33
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                2896.3
DW                27.800 usec
DE                  6.00 usec
TE                 302.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1         75.4752953 MHz

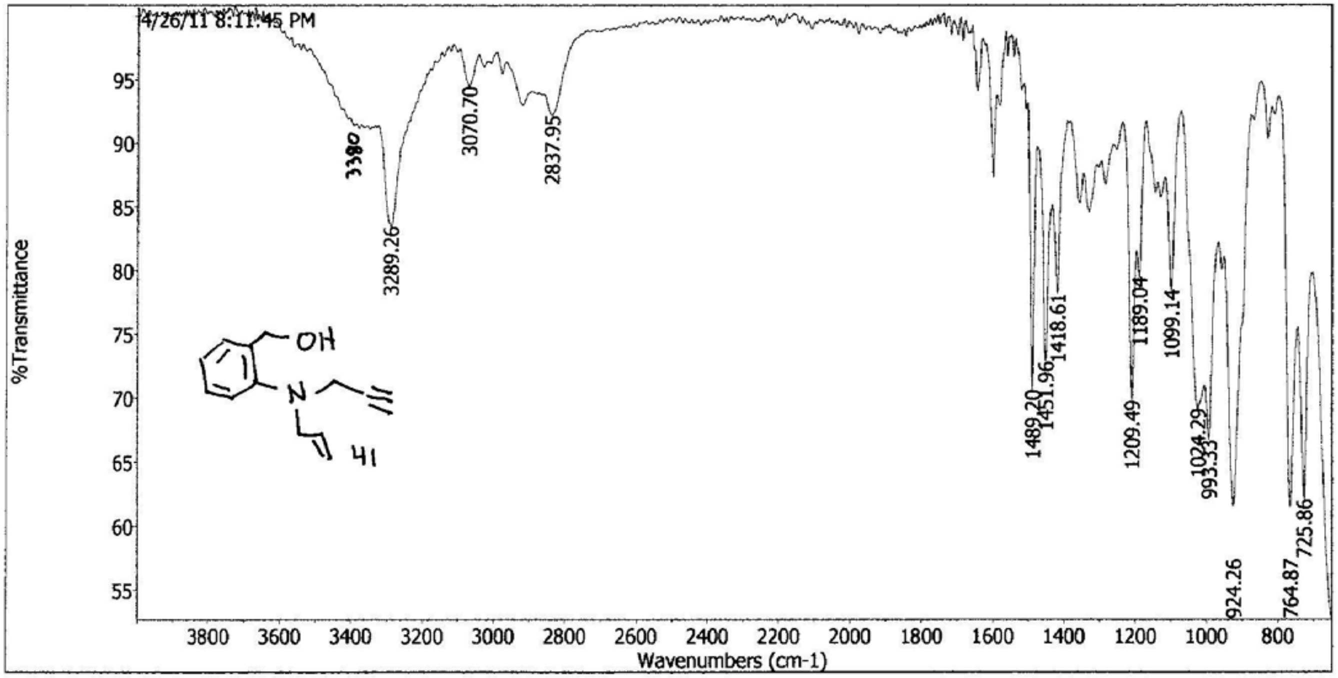
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2        300.1312005 MHz

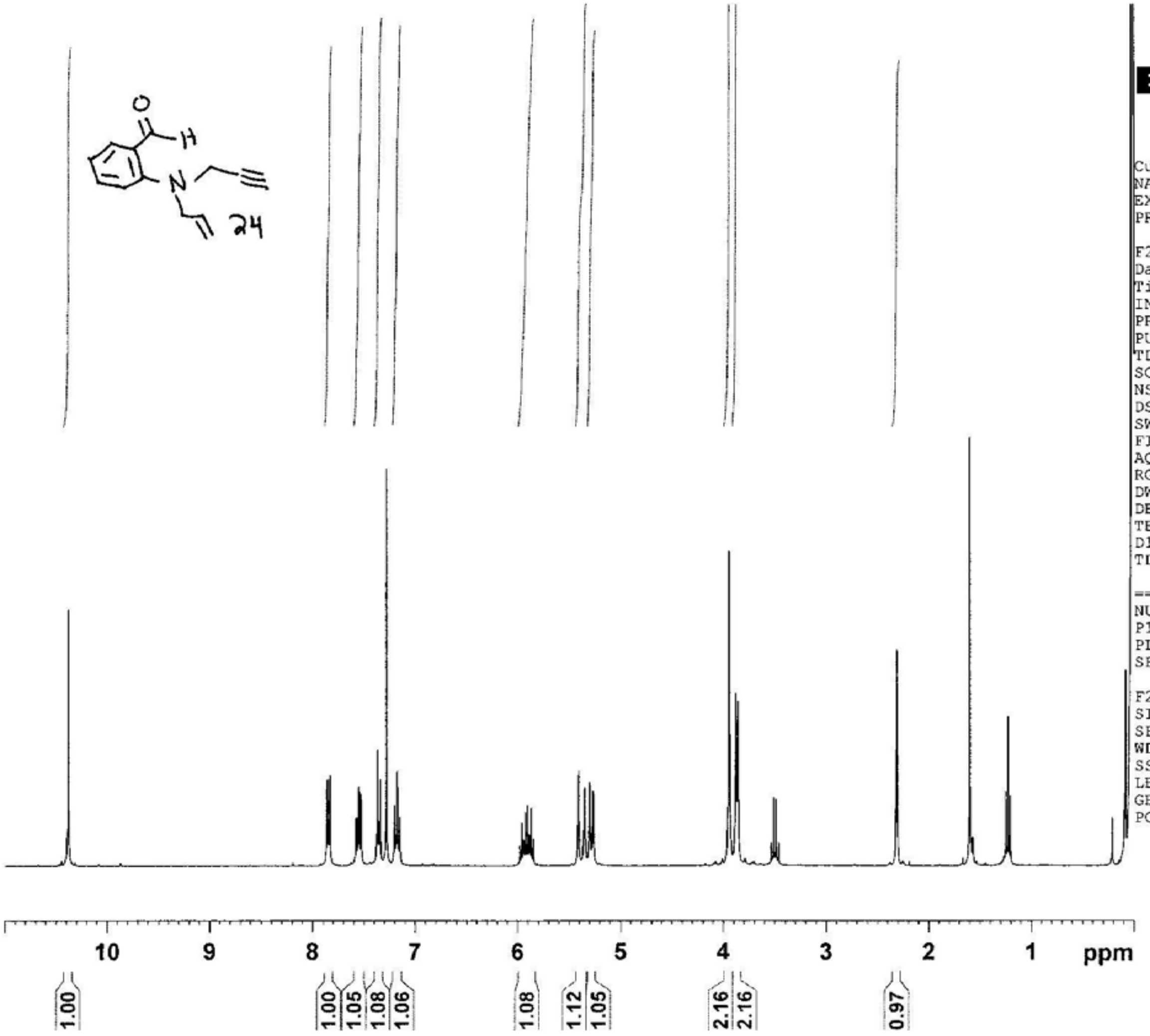
F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

KER-I-034

Peak finding results for: 4/26/11 8:11:45 PM
Frequency: 706.57 - 3472.04, threshold: 77.359-99.514, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Position	3289.26	3070.70	2837.95	1489.20	1451.96	1418.61	1209.49	1189.04	1099.14	1024.29	993.33	924.26	764.87	725.86
Height	83.342	94.309	92.080	70.506	72.727	78.040	69.725	79.329	78.369	69.084	66.610	61.396	61.281	61.974





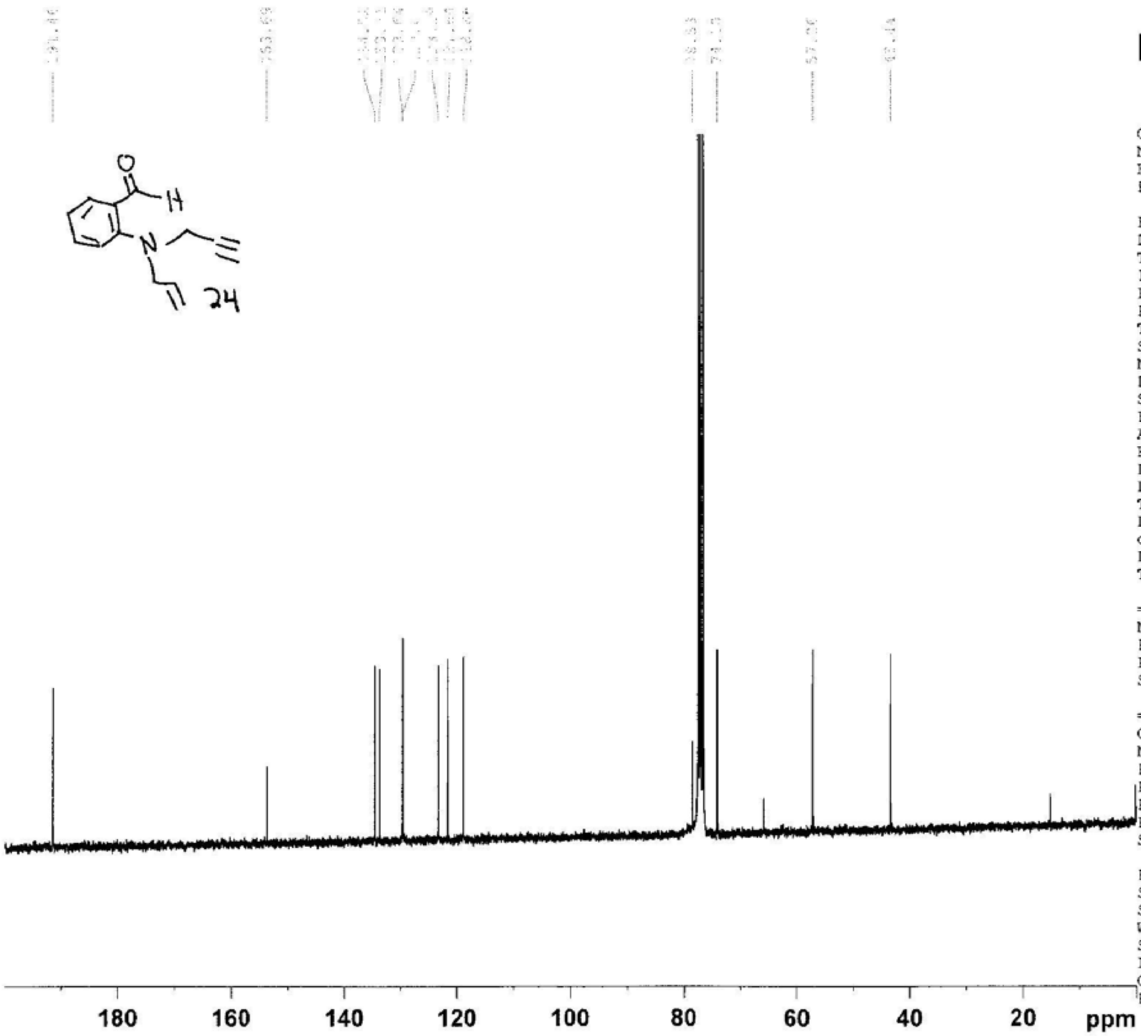
BRUKER

```
Current Data Parameters
NAME       KER-I-036(Pst. colm)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090708
Time                  15.42
INSTRUM               spect
PROBHD   5 mm Multinucl
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      256
DW                   81.000 usec
DE                     6.00 usec
TE                    291.2 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1                    0.00 dB
SFO1         300.1318534 MHz

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



```
Current Data Parameters
NAME     KER-I-036 carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090709
Time                 8.51
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  12288
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   4096
DW                 27.800 usec
DE                   6.00 usec
TE                  294.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.10 usec
PL1                 -1.50 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL13                19.00 dB
SFO2         300.1312005 MHz

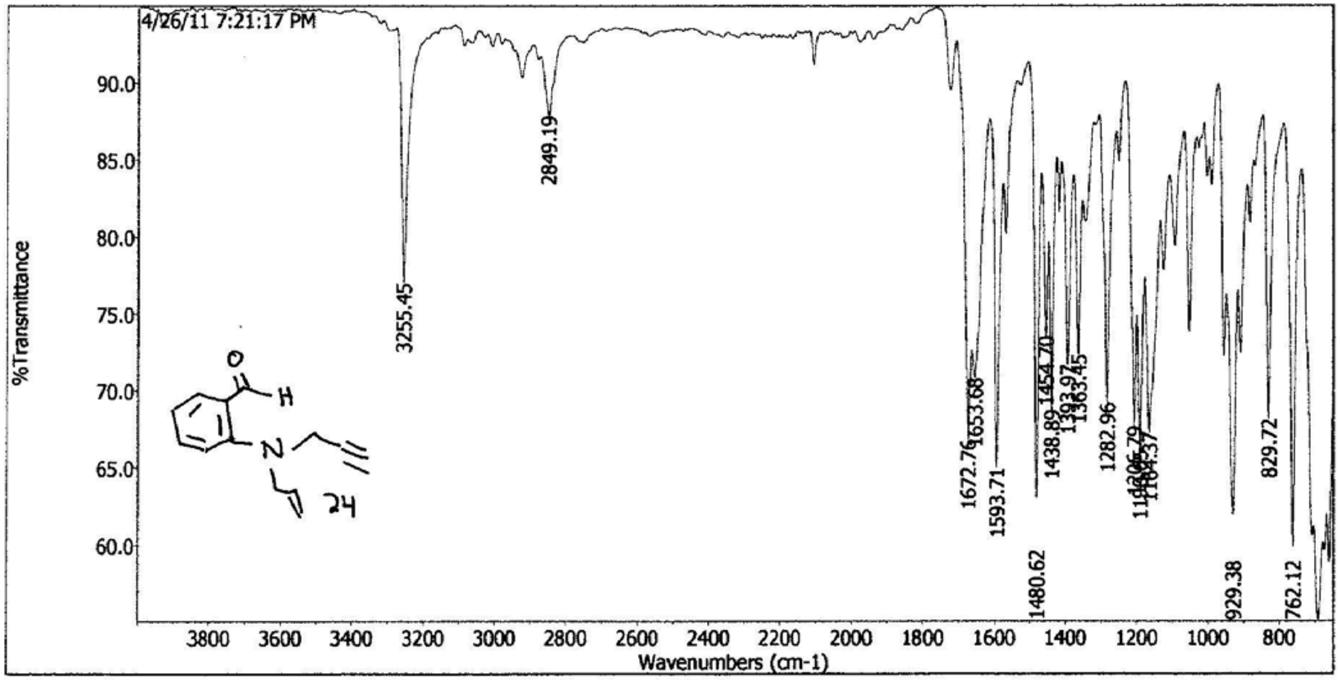
F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

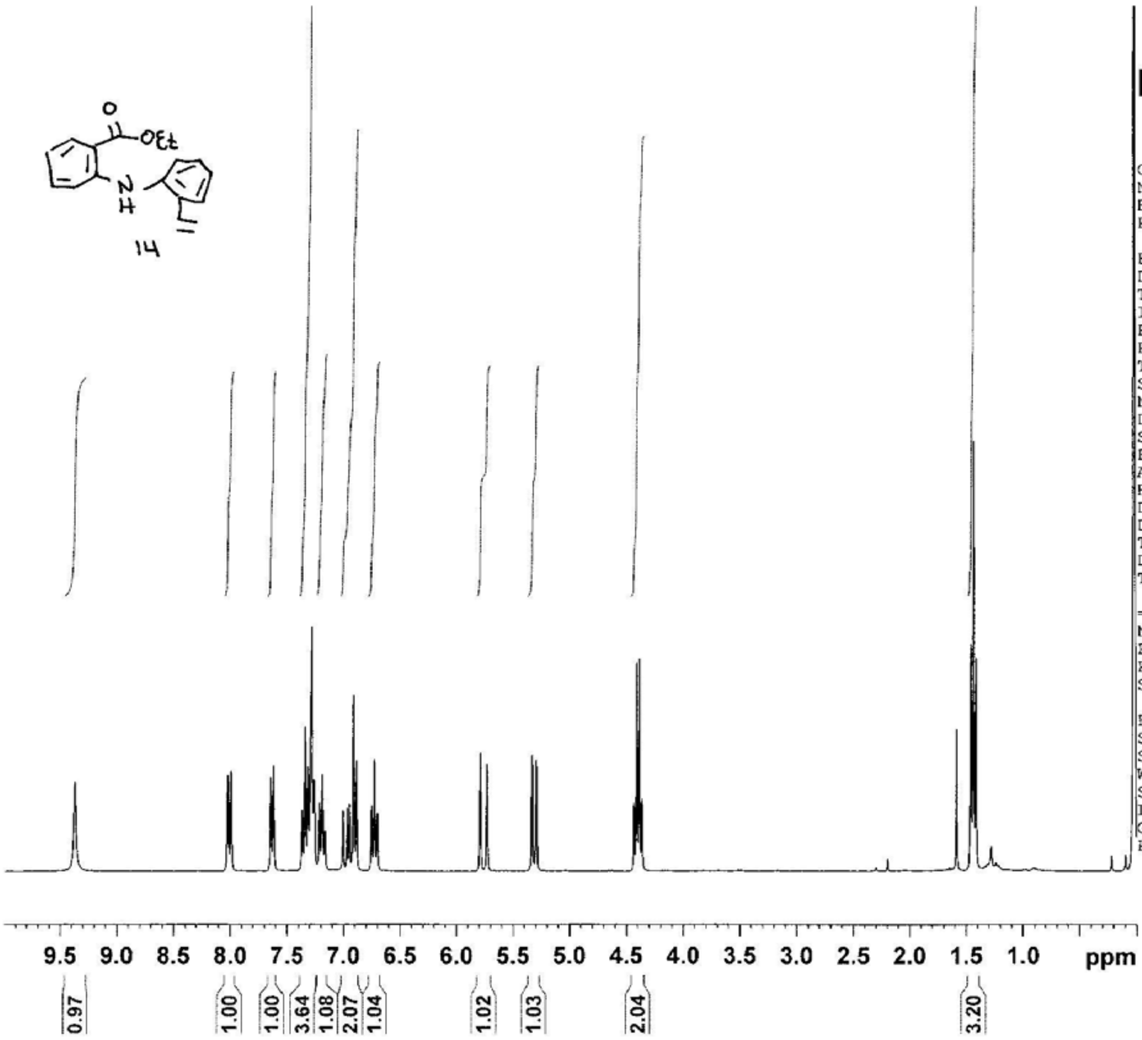
KER-I-036

Peak finding results for: 4/26/11 7:21:17 PM
Frequency: 687.71 - 3358.91, threshold: 67.670-93.673, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3255.45	2849.19	1672.76	1653.68	1593.71	1480.62	1454.70	1438.89	1393.97
Height	76.915	87.784	66.708	70.750	64.905	62.958	73.421	68.684	71.553

Peak#	10	11	12	13	14	15	16	17	
Position	1363.45	1282.96	1206.79	1190.65	1164.37	929.38	829.72	762.12	
Height	72.244	69.101	67.603	66.063	67.206	61.884	68.070	59.830	



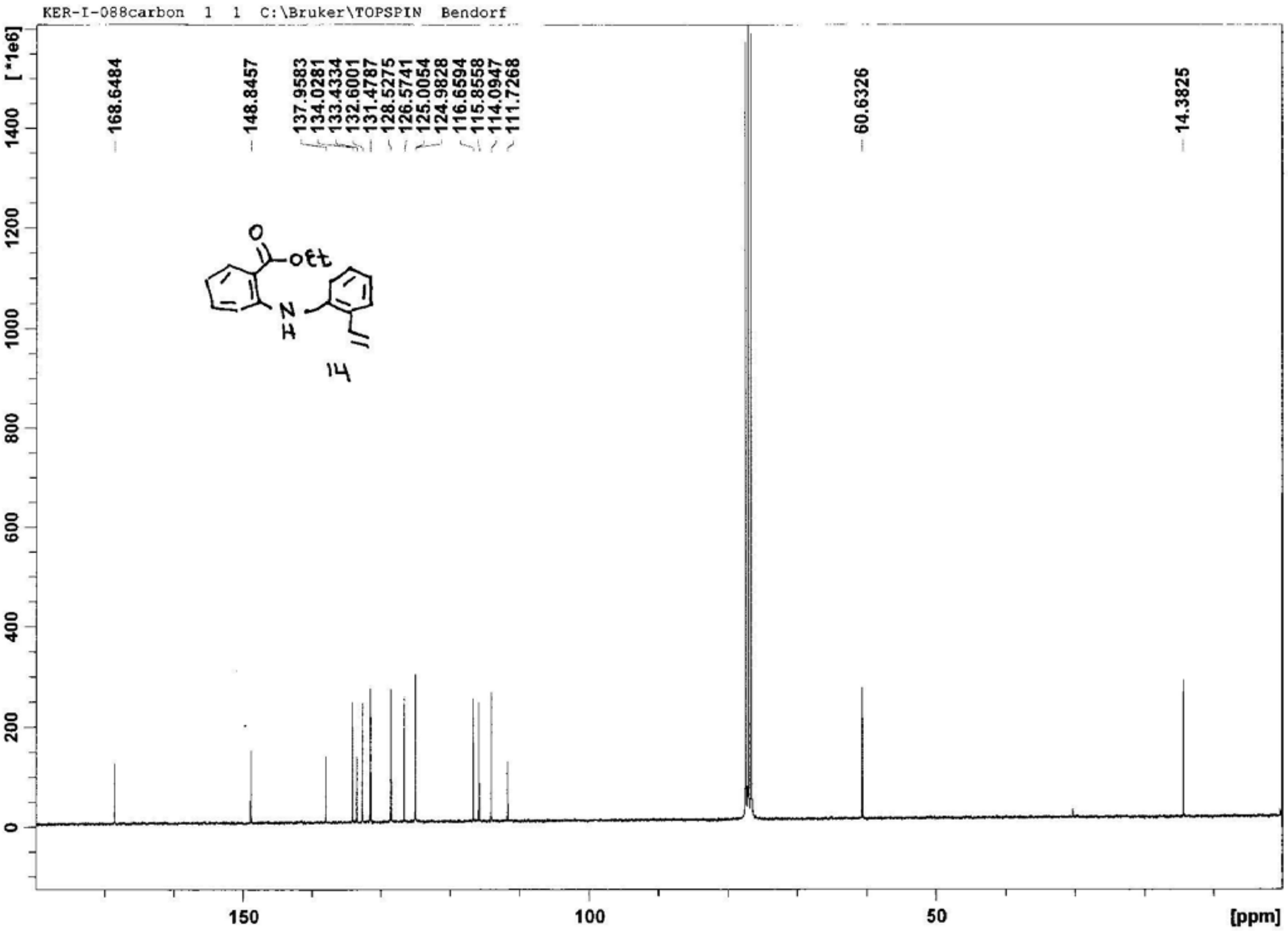


```
Current Data Parameters
NAME      KER-I-088retake
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20101210
Time_               16.39
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                  228.1
DW                 81.000 usec
DE                   6.00 usec
TE                  292.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

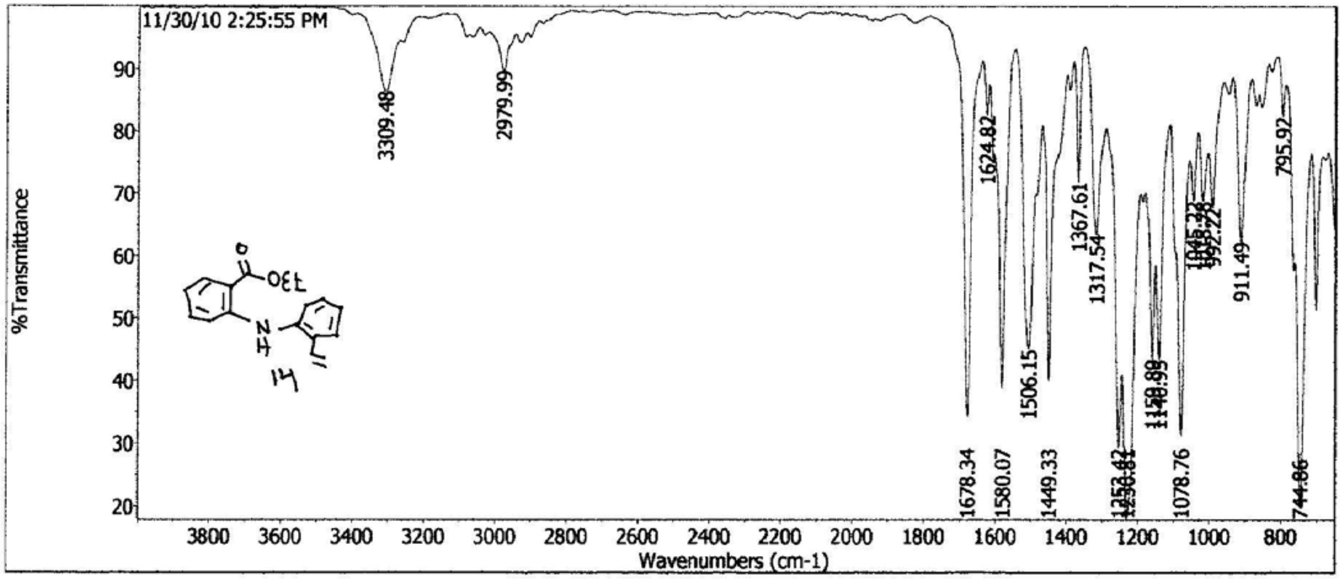
F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

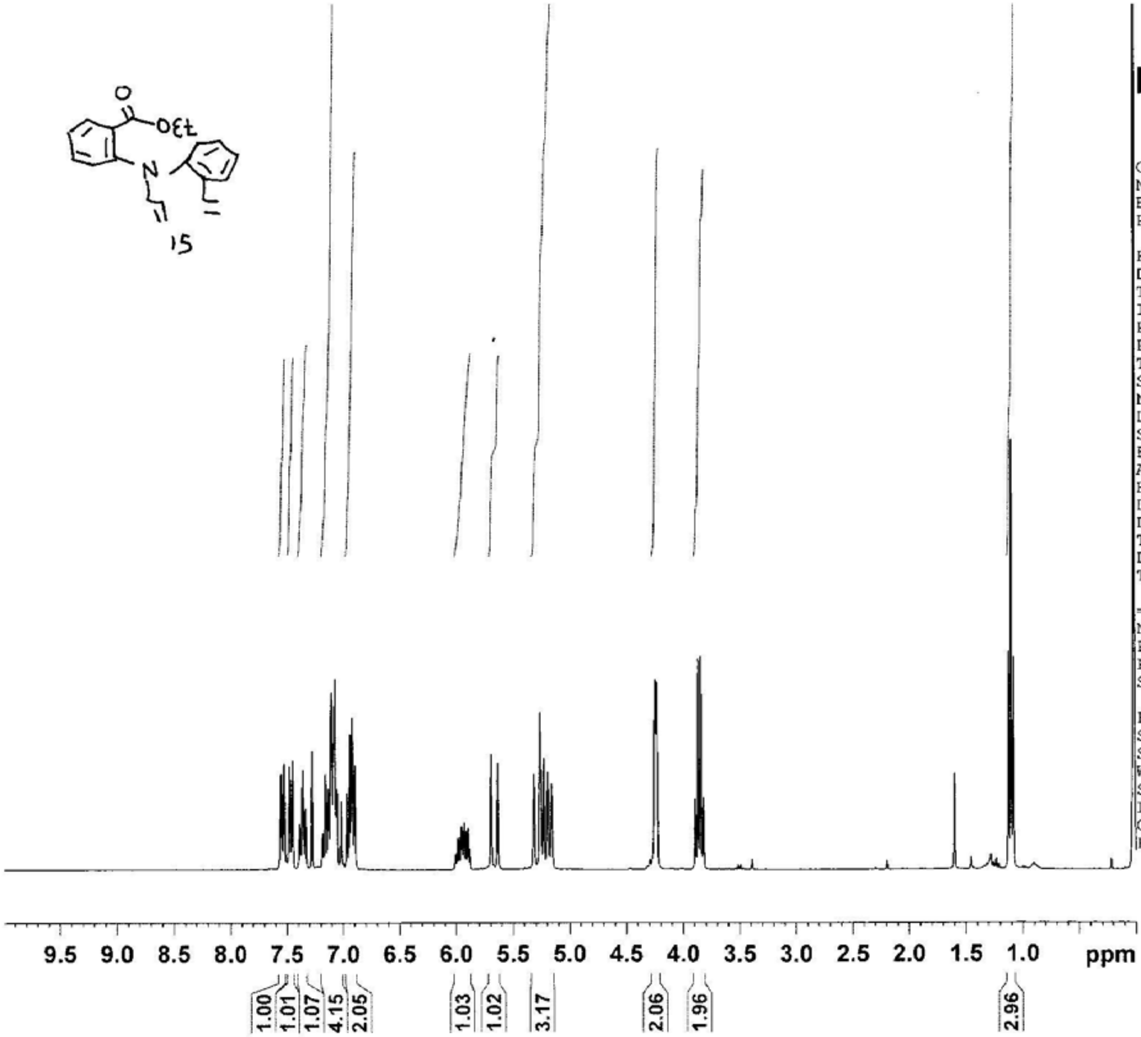

KER-I-088carbon 1 1 C:\Bruker\TOPSPIN Bendorf
168.6484
148.8457
137.9583
134.0281
133.4334
132.6001
131.4787
128.5275
126.5741
125.0054
124.9828
116.6594
115.8558
114.0947
111.7268
60.6326
14.3825
O
OEt
N
H
14
[*1e6]
1400
1200
1000
800
600
400
200
0
150
100
50
[ppm]

KER-I-088

Peak finding results for: 11/30/10 2:25:55 PM
Frequency: 706.57 - 4000.00, threshold: 82.574-96.341, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Position	3309.48	2979.99	1678.34	1624.82	1580.07	1506.15	1449.33	1367.61	1317.54	1253.42	1230.81	1159.89	1140.95	1078.76	1045.22	1018.78	992.22	911.49	795.92	744.86
Height	86.192	89.465	34.152	82.281	38.551	44.779	39.832	71.564	63.189	29.226	17.803	43.267	43.205	31.051	68.538	68.545	67.551	62.007	82.108	19.711



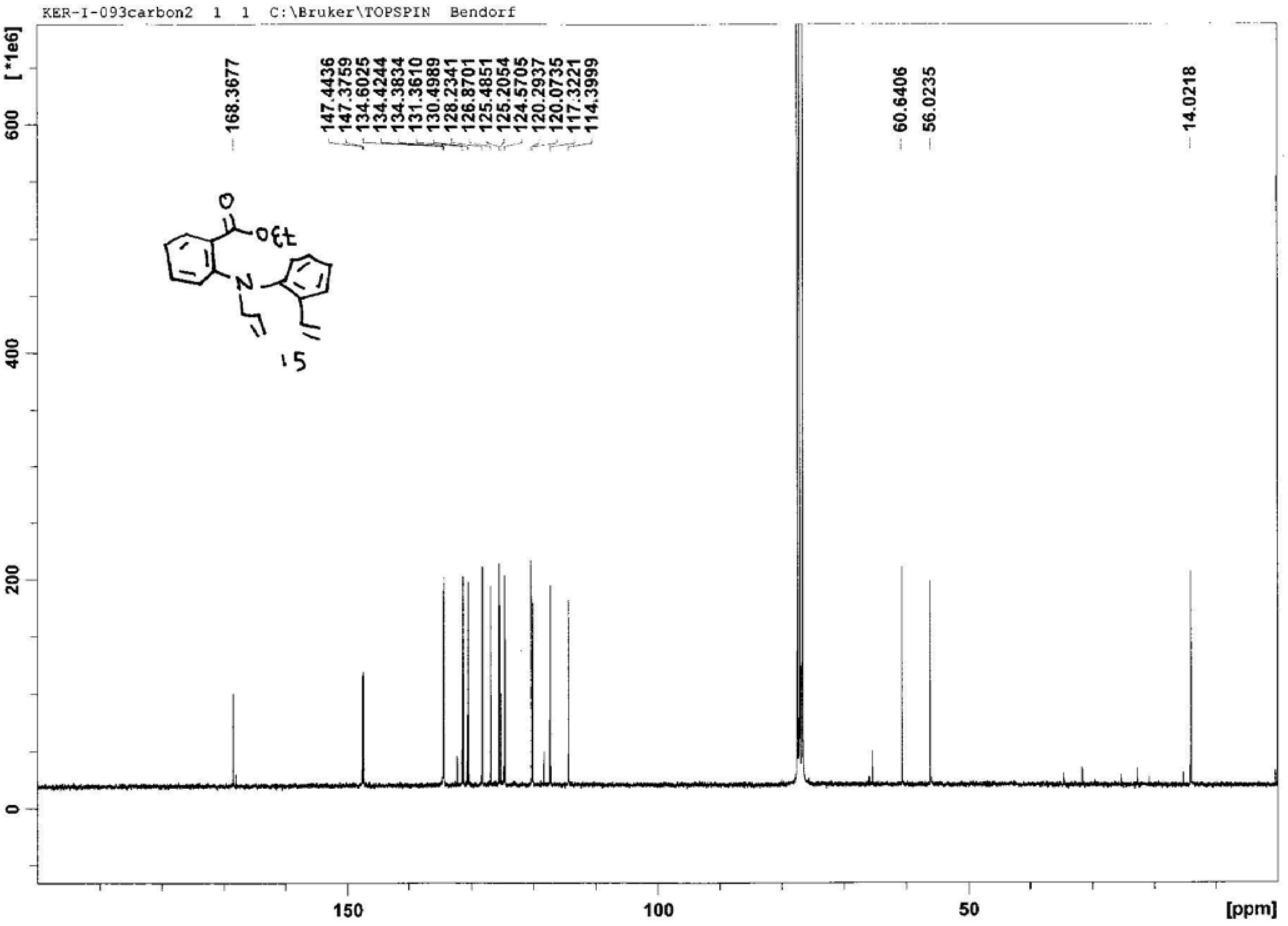


```
Current Data Parameters
NAME      KER-II-001frac13-16
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20101202
Time                16.05
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                    128
DW                 81.000 usec
DE                   6.00 usec
TE                  292.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

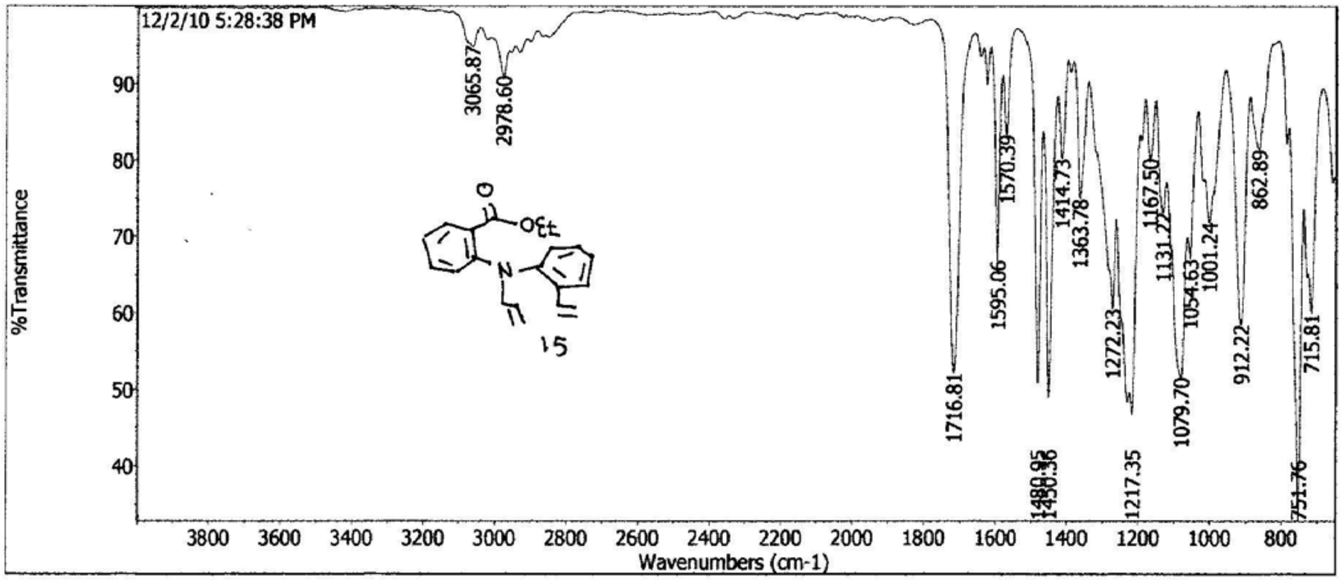
F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

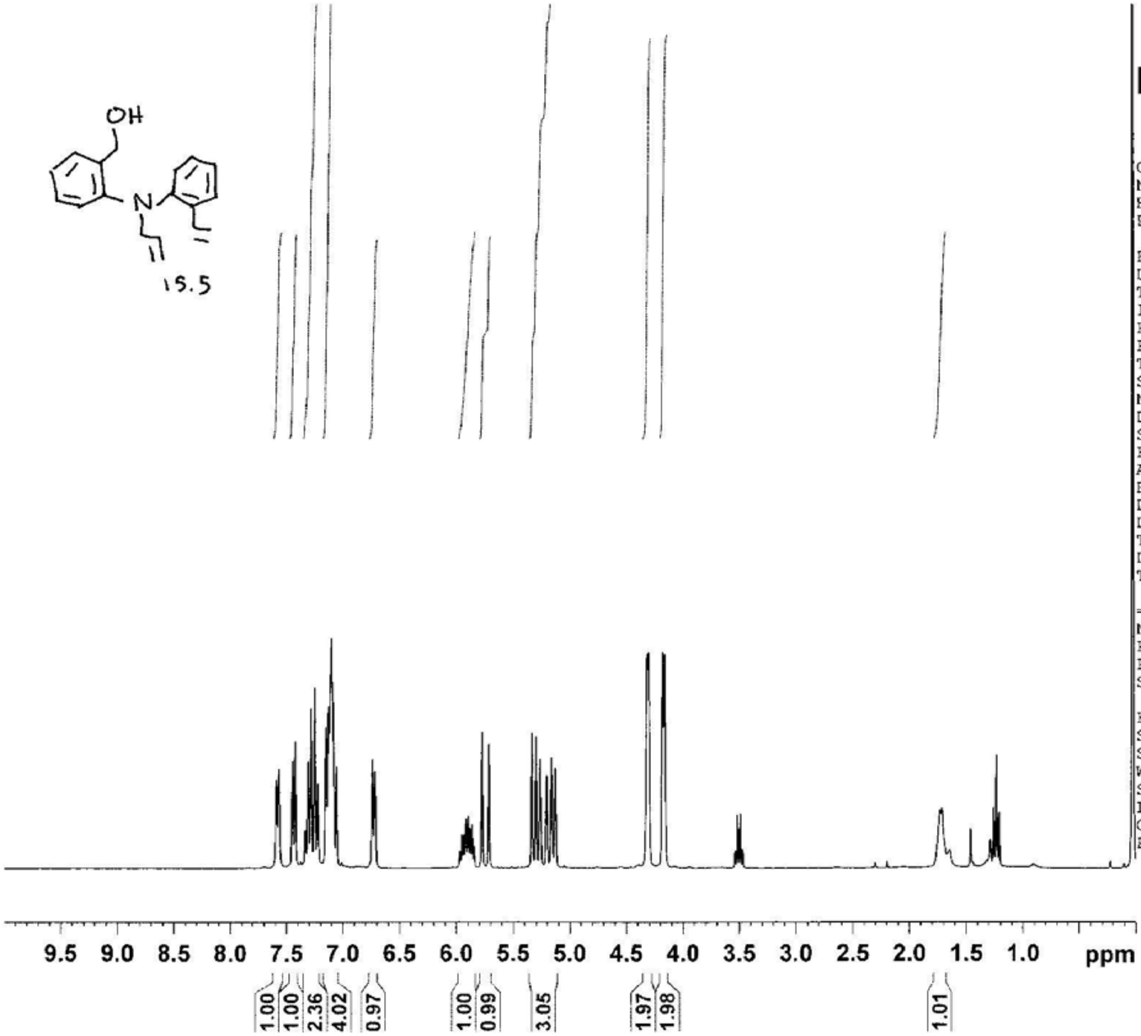

KER-I-093carbon2 1 1 C:\Bruker\TOPSPIN Bendorf
168.3677
147.4436
147.3759
134.6025
134.4244
134.3834
131.3610
130.4989
128.2341
126.8701
125.4851
125.2054
124.5705
120.2937
120.0735
117.3221
114.3999
60.6406
56.0235
14.0218
OEt
O
N
15
[*1e6]
600
400
200
0
150
100
50
[ppm]

Peak finding results for: 12/2/10 5:28:38 PM
Frequency: 662.57 - 4000.00, threshold: 84.630-99.119, sensitivity: 50.00
Peak finding result table:

KER-II-001

Peak#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Position	3065.87	2978.60	1716.81	1595.06	1570.39	1480.95	1450.36	1414.73	1363.78	1272.23	1217.35	1167.50	1131.22	1079.70	1054.63	1001.24	912.22	862.89	751.76	715.81
Height	94.726	90.763	51.966	66.607	83.159	50.750	48.644	79.944	74.723	60.341	46.567	79.925	72.918	51.370	66.850	71.598	58.310	81.179	32.780	59.707





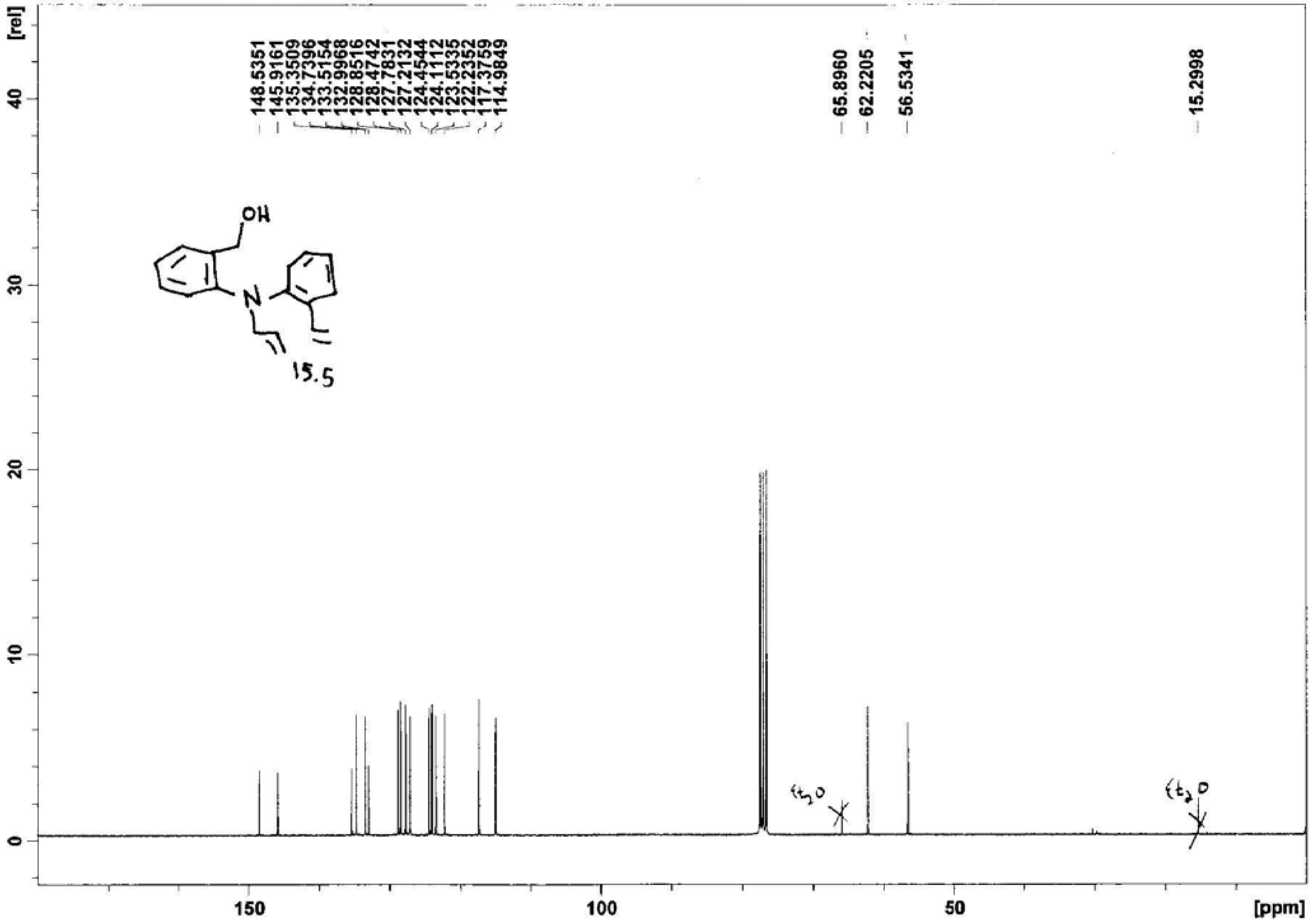
```
Current Data Parameters
NAME      KER-II-002crude
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20101209
Time                15.13
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                    114
DW                 81.000 usec
DE                   6.00 usec
TE                  292.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

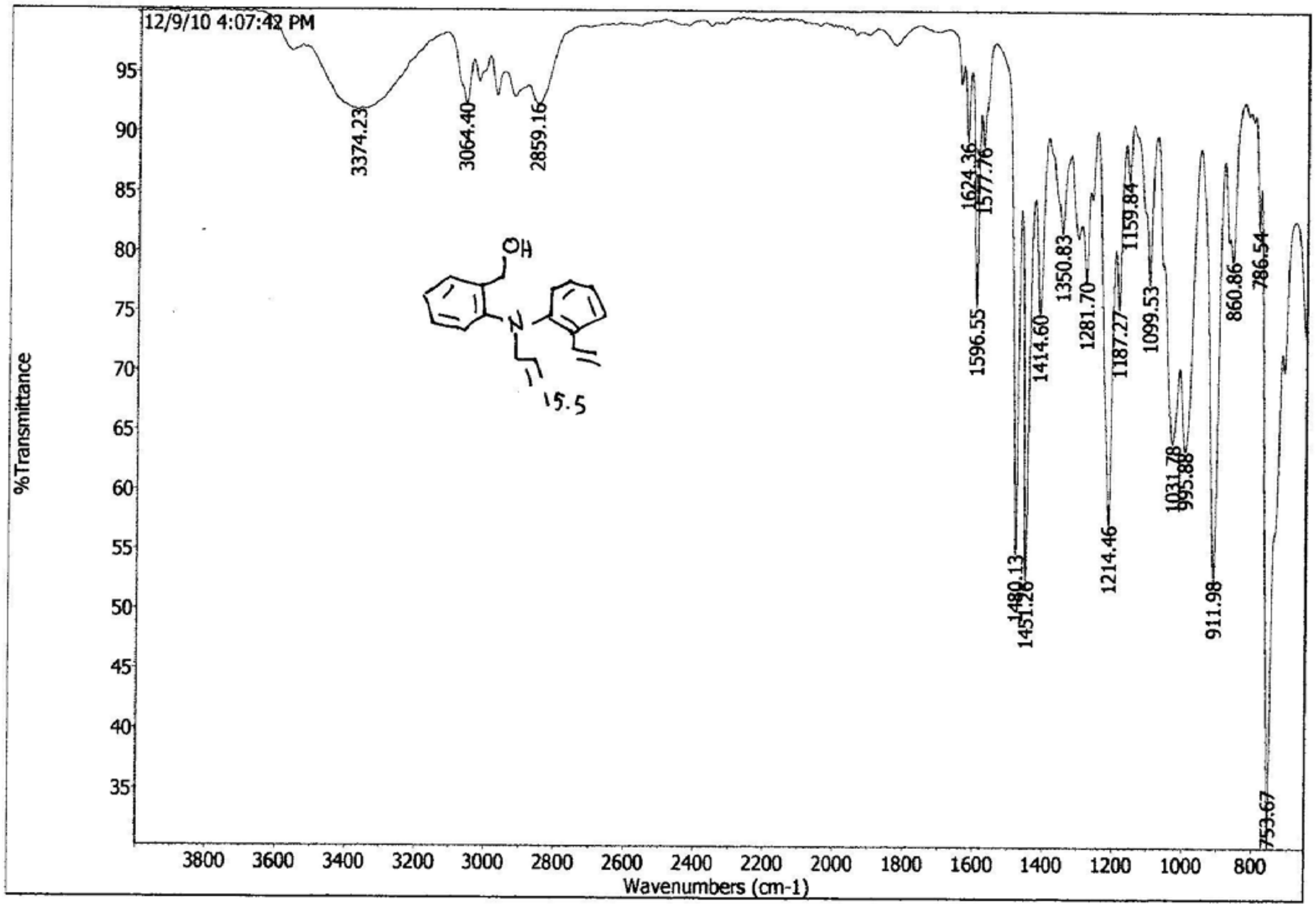
F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

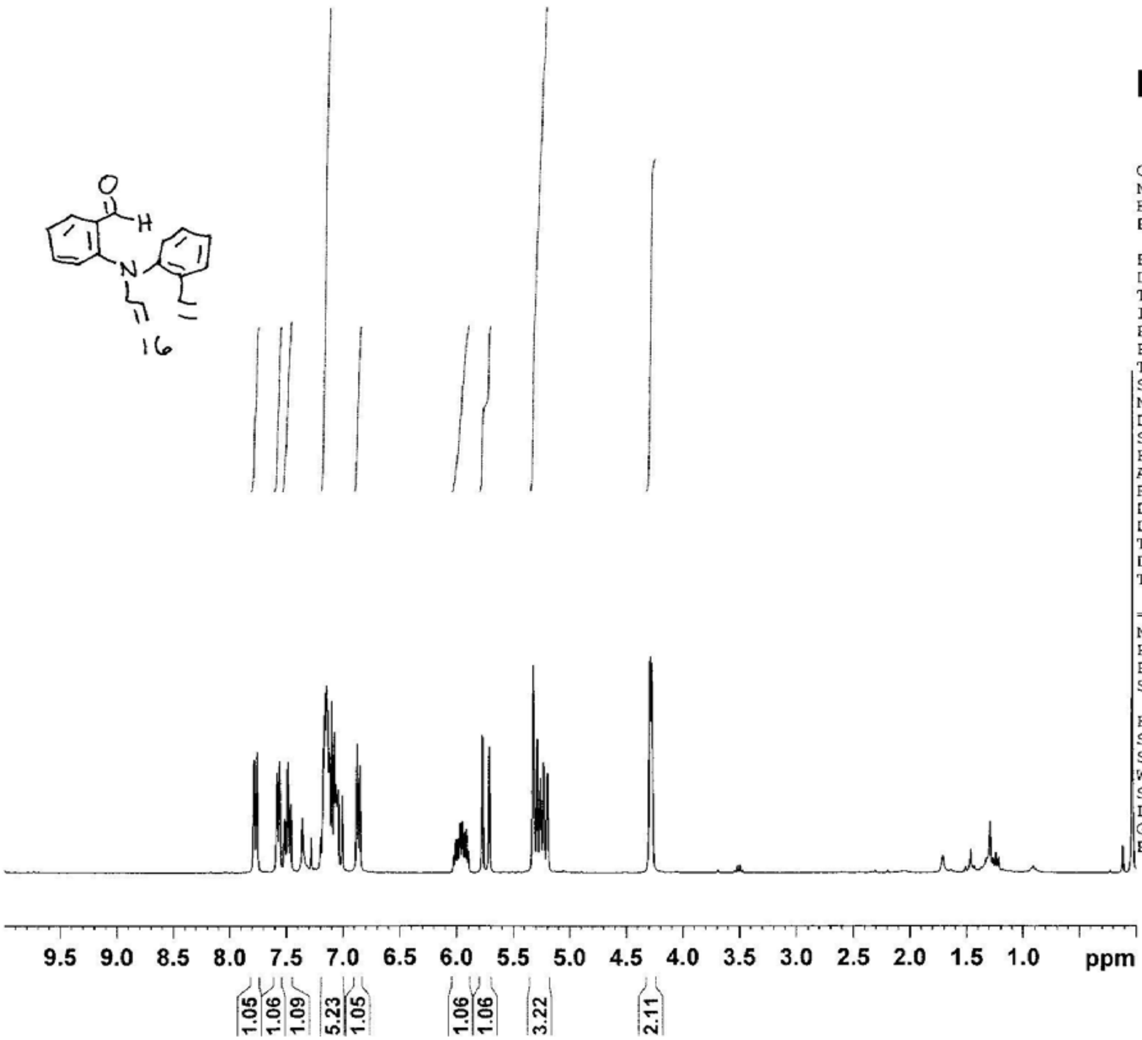
"KER 11-002 carbon" 1 1 C:\Bruker\TOPSPIN McDonald files from SiG O2



KER-II-002

Height	77.249	63.891	63.308	52.544	79.205	81.845	30.205



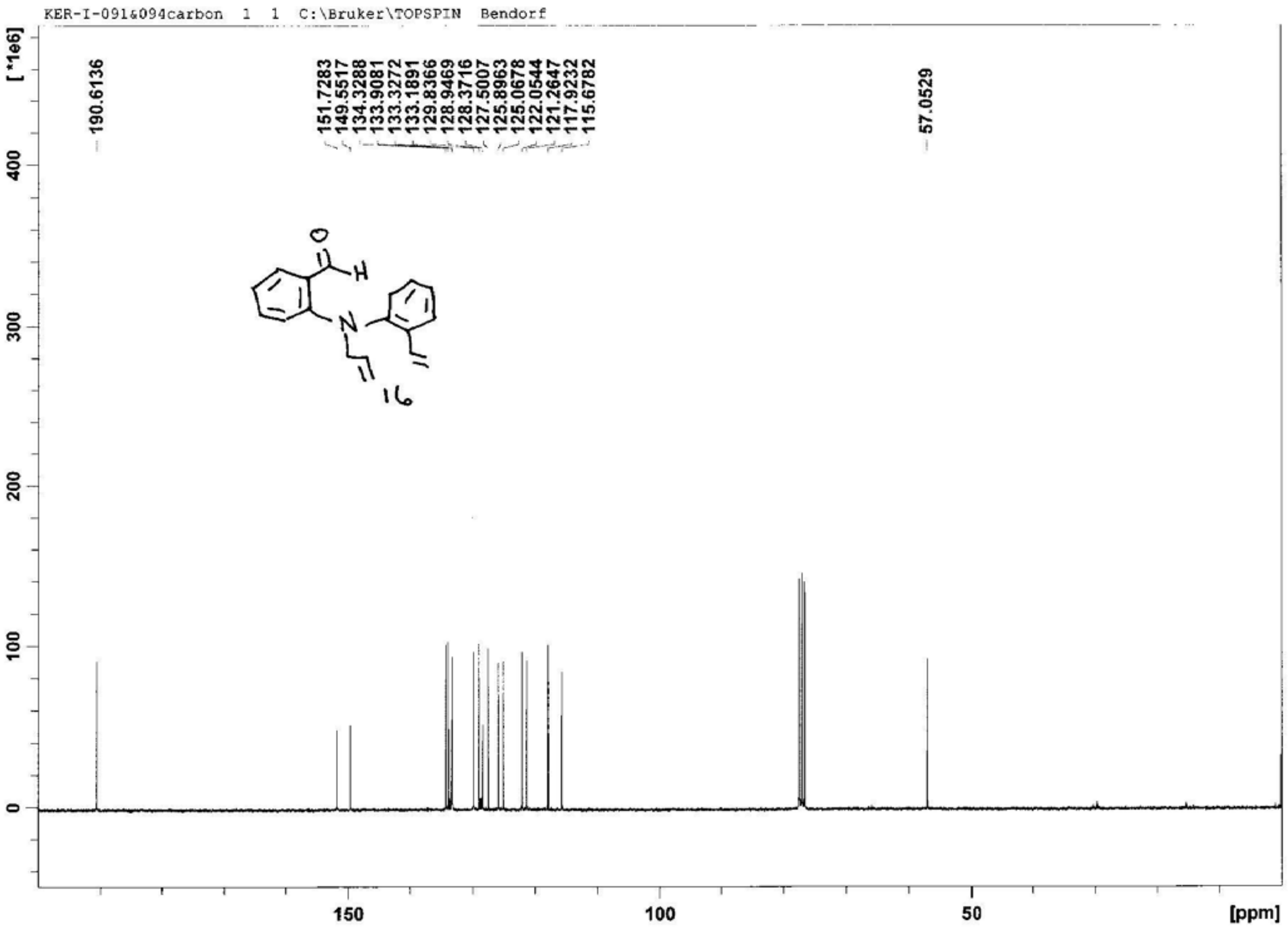


```
Current Data Parameters
NAME      KER-I-091&094check
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20101201
Time                 11.22
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                    71.8
DW                  81.000 usec
DE                    6.00 usec
TE                   293.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1        300.1318534 MHz

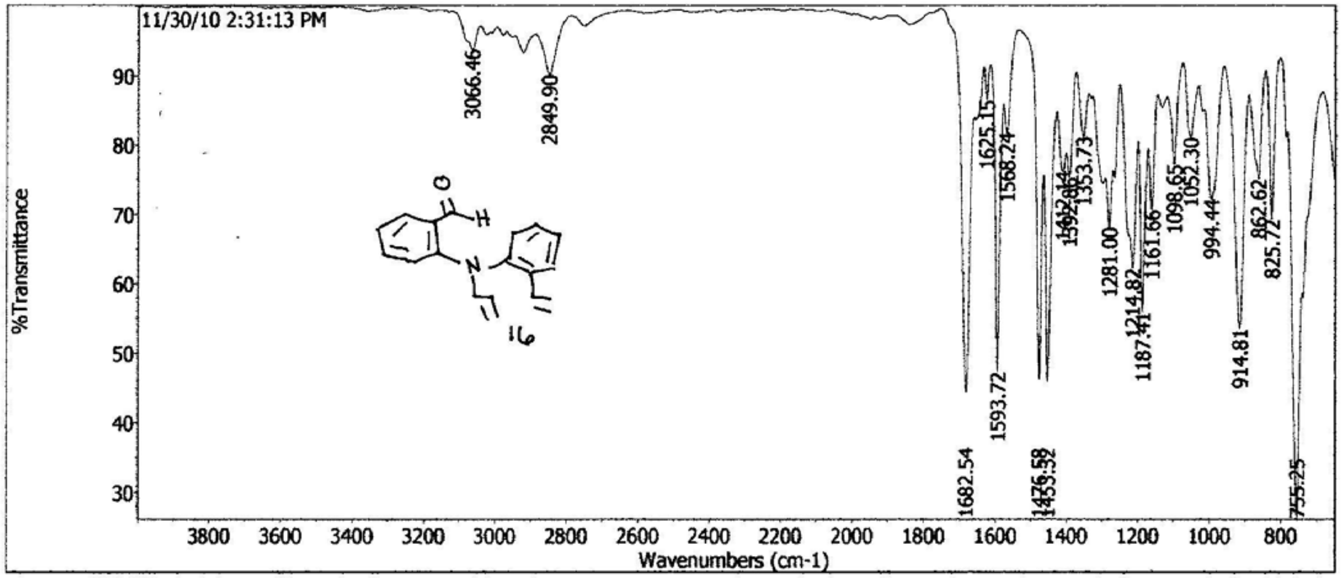
F2 - Processing parameters
SI                   32768
SF          300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

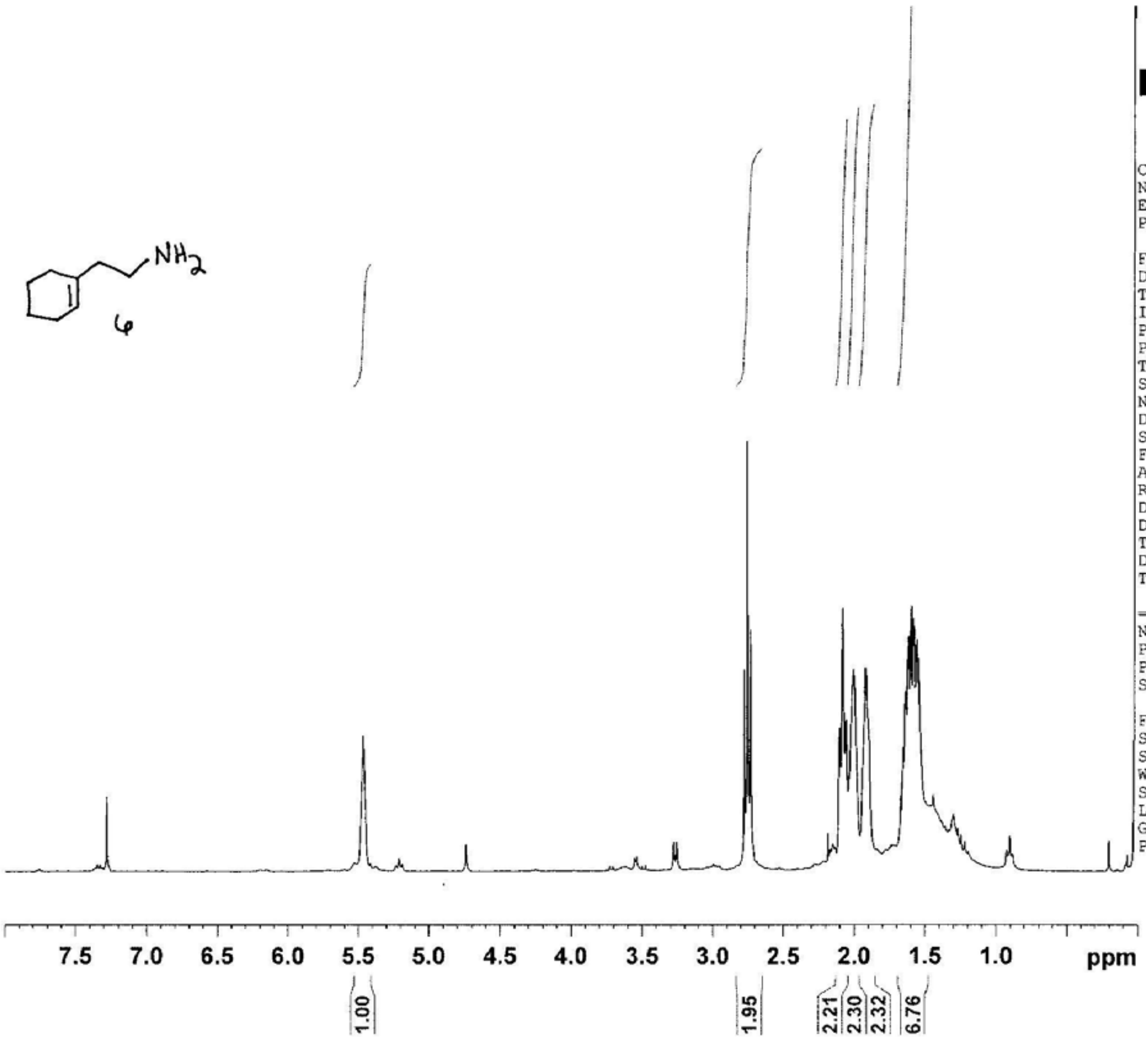

KER-I-091&094carbon 1 1 C:\Bruker\TOPSPIN Bendorf
190.6136
151.7283
149.5517
134.3288
133.9081
133.3272
133.1891
129.8366
128.9469
128.3716
127.5007
125.8963
125.0678
122.0544
121.2647
117.9232
115.6782
57.0529
O
H
N
16
[*1e6]
400
300
200
100
0
150
100
50
[ppm]

KER-I-091

Peak finding results for: 11/30/10 2:31:13 PM
Frequency: 706.57 - 3993.71, threshold: 82.650-99.471, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3066.46	2849.90	1682.54	1625.15	1593.72	1568.24	1476.58	1453.32	1412.14
Height	93.586	89.875	44.164	86.275	47.041	81.493	45.995	45.676	76.017
Peak#	10	11	12	13	14	15	16	17	18
Position	1392.86	1353.73	1281.00	1214.82	1187.41	1161.66	1098.65	1052.30	994.44
Height	75.109	80.933	67.888	61.946	55.671	70.400	76.963	80.841	71.952
Peak#	19	20	21	22					
Position	914.81	862.62	825.72	755.25					
Height	53.263	74.888	69.074	25.950					



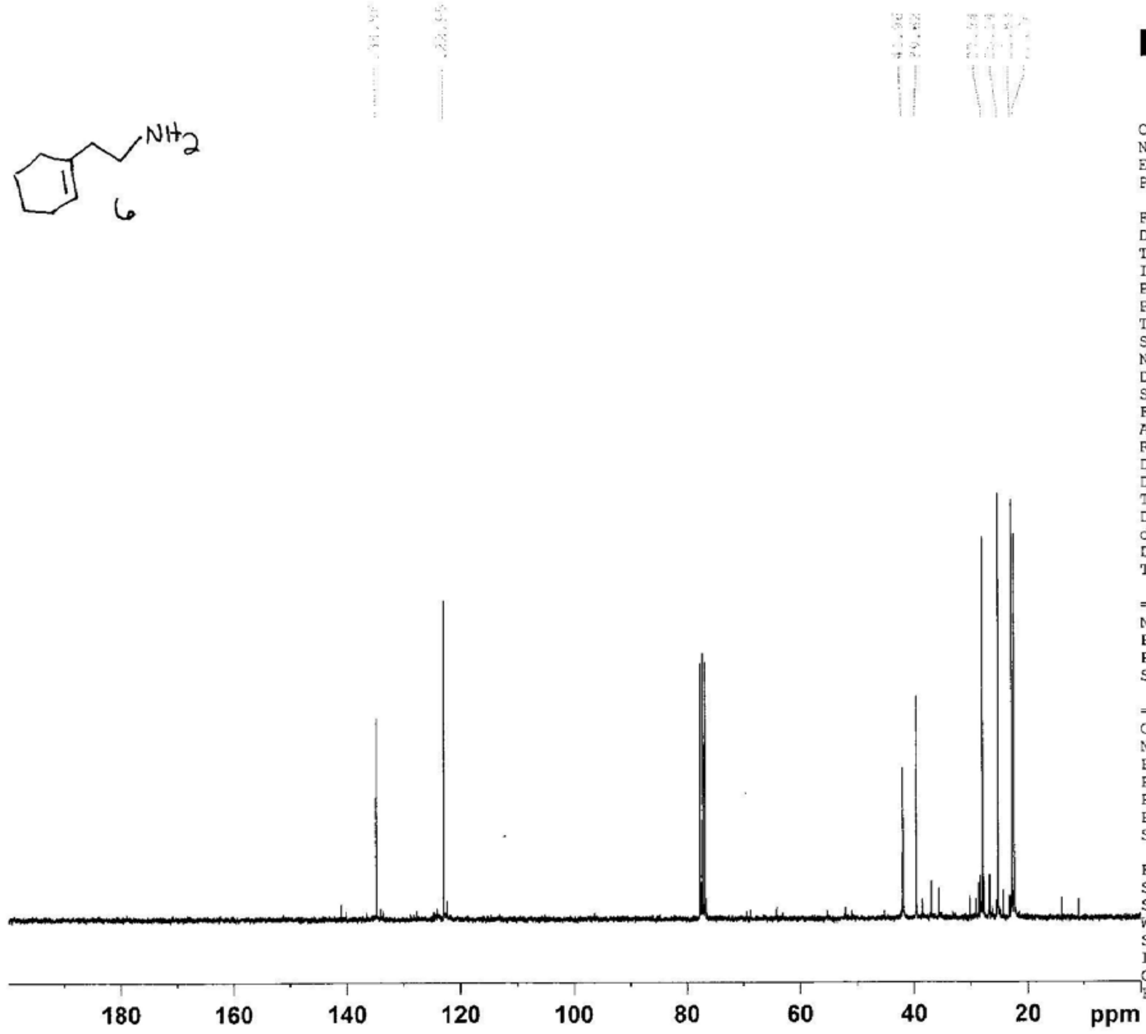


```
Current Data Parameters
NAME      KER-II-018crude2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110329
Time_                17.00
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                   161.3
DW                  81.000 usec
DE                    6.00 usec
TE                   305.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

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



```
Current Data Parameters
NAME     KER-II-018carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110427
Time                23.34
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                4597.6
DW                27.800 usec
DE                  6.00 usec
TE                 316.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.10 usec
PL1                -1.50 dB
SFO1          75.4752953 MHz

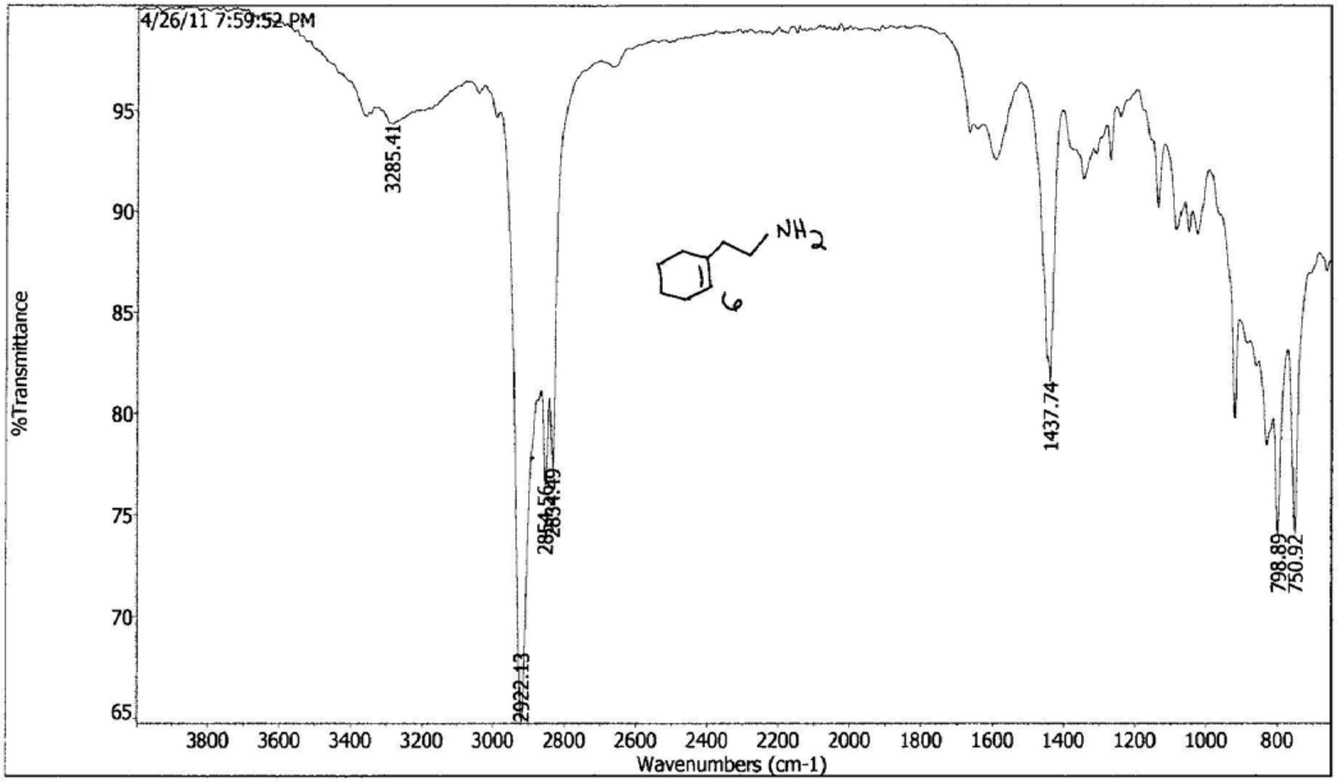
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL13               19.00 dB
SFO2         300.1312005 MHz

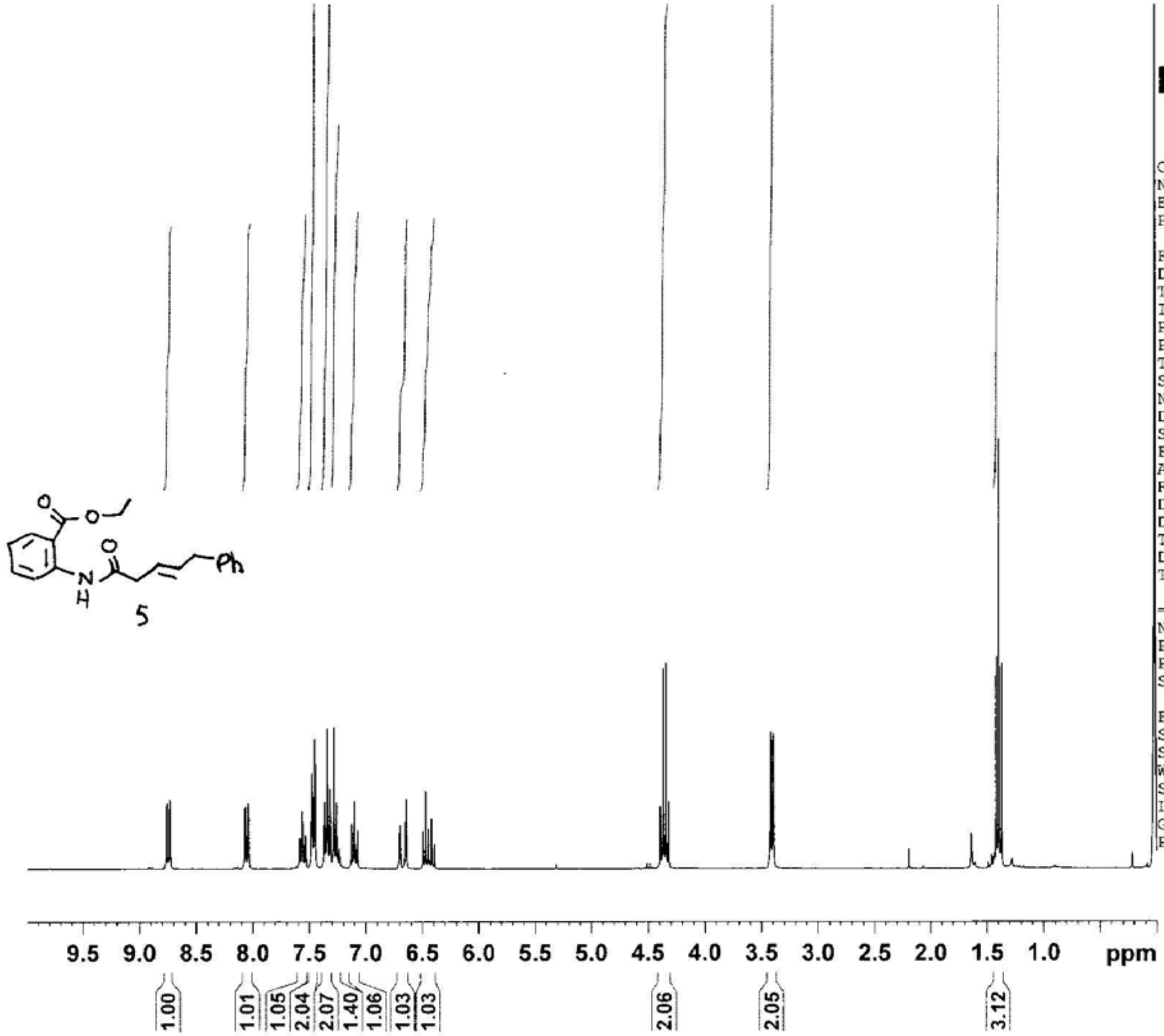
F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

KER-II-018

Peak finding results for: 4/26/11 7:59:52 PM
Frequency: 706.57 - 3428.05, threshold: 76.748-98.570, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7		
Position	3285.41	2922.13	2854.56	2834.49	1437.74	798.89	750.92		
Height	94.229	64.727	76.390	77.235	81.472	74.009	73.948		





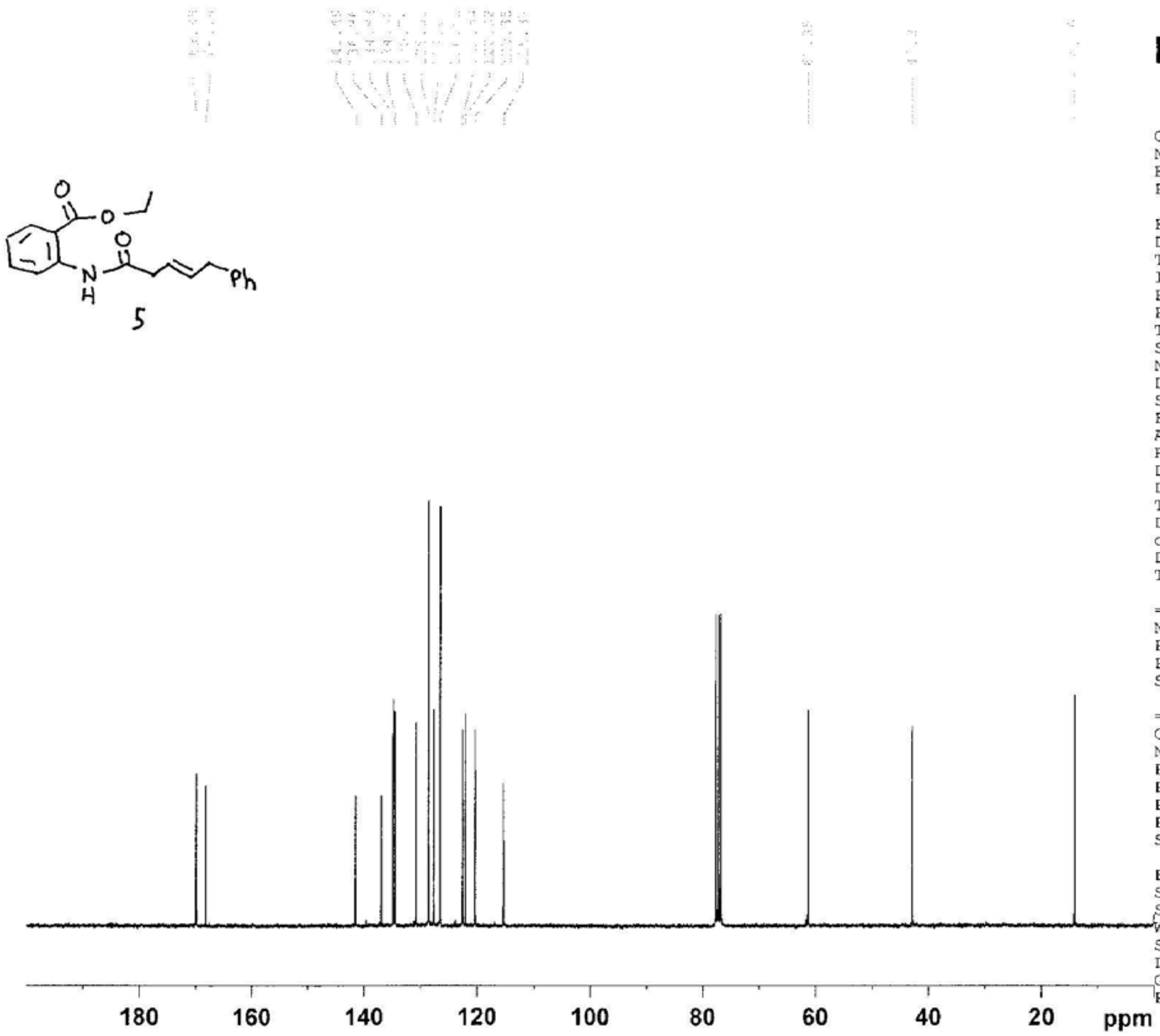
5

```
Current Data Parameters
NAME      KER-II-014highspt
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110329
Time                 17.15
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                     181
DW                  81.000 usec
DE                    6.00 usec
TE                   306.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

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



```
Current Data Parameters
NAME      KER-II-014carbon
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110427
Time                 14.51
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                    4096
DW                  27.800 usec
DE                    6.00 usec
TE                   302.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2          300.1312005 MHz

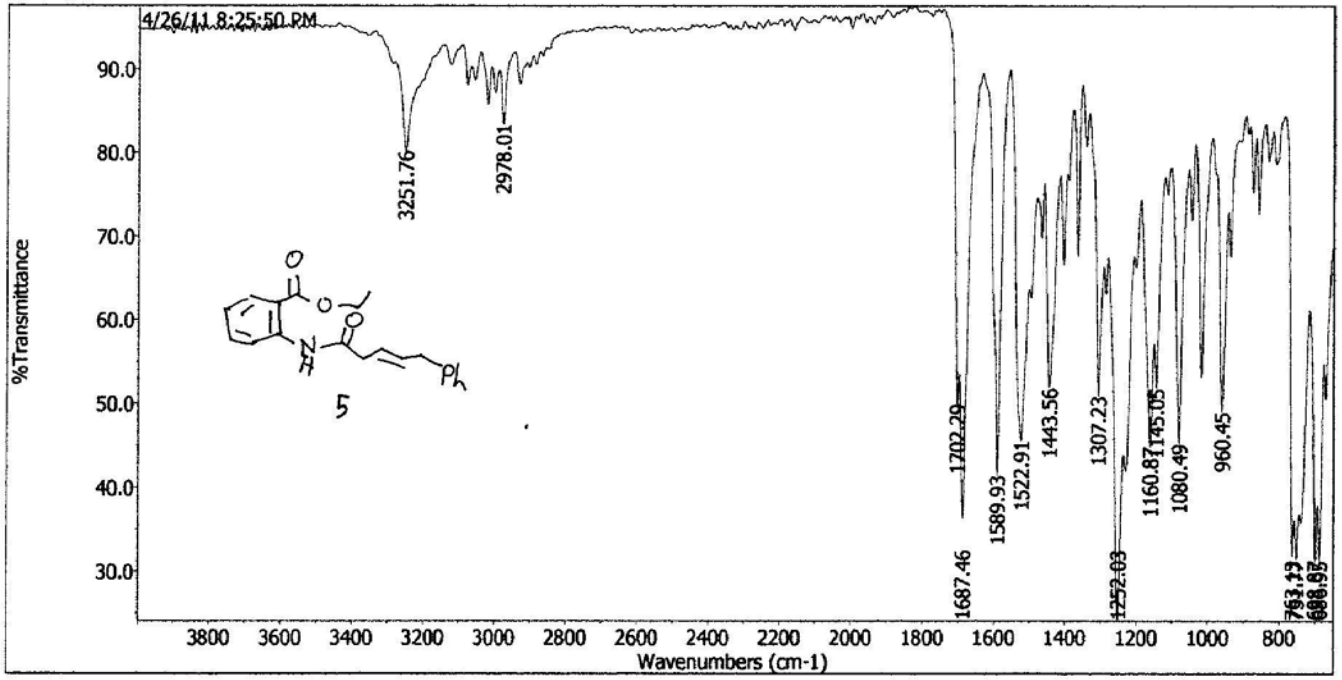
F2 - Processing parameters
SI                   32768
SF             75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

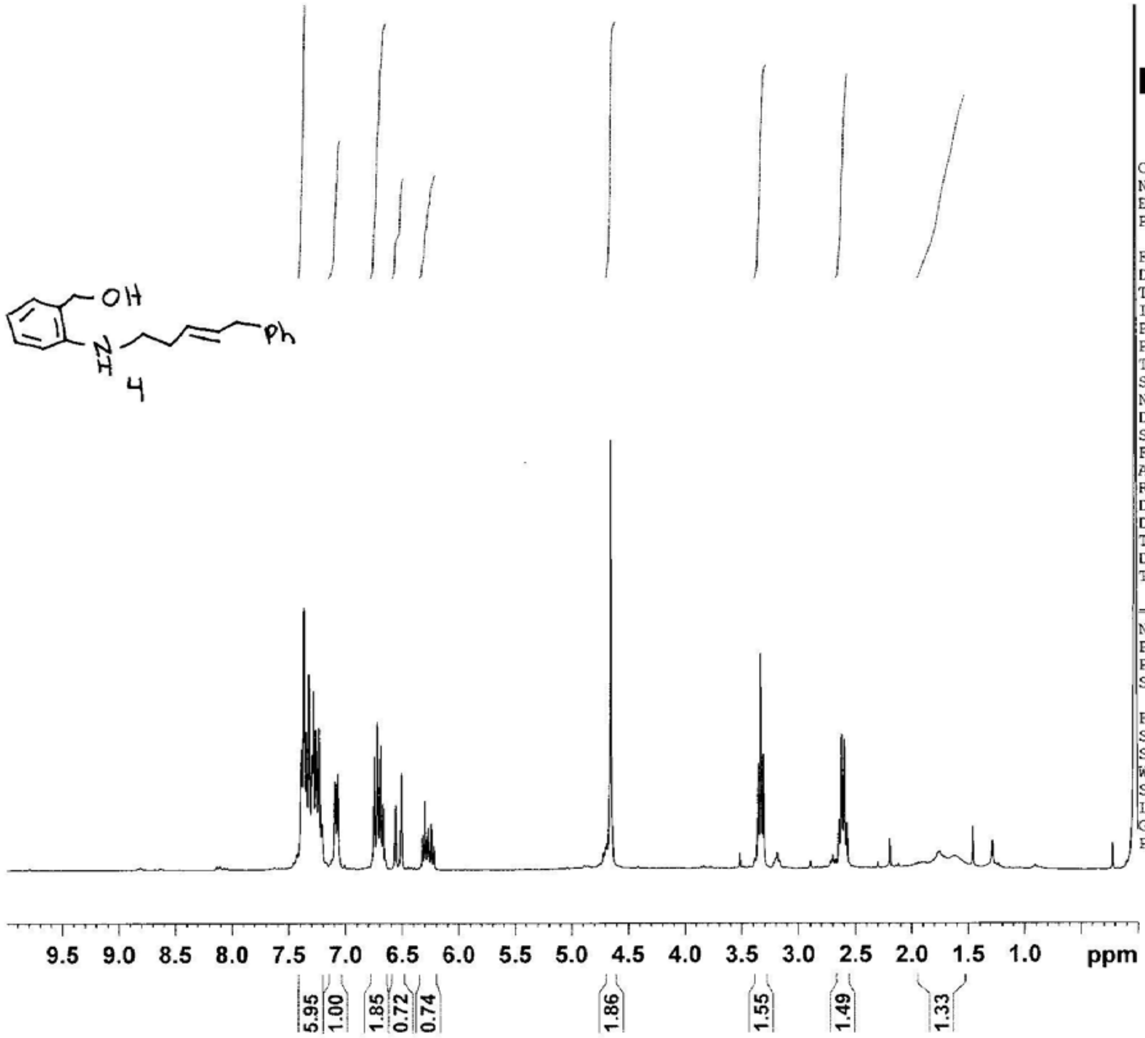
KER-II-014

Peak finding results for: 4/26/11 8:25:50 PM
Frequency: 656.29 - 3352.63, threshold: 45.496-90.284, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3251.76	2978.01	1702.29	1687.46	1589.93	1522.91	1443.56	1307.23	1252.03
Height	79.987	83.183	49.786	36.196	41.282	45.415	51.657	50.728	24.066

Peak#	10	11	12	13	14	15	16	17	
Position	1160.87	1145.05	1080.49	960.45	763.13	751.77	698.87	686.95	
Height	44.621	51.617	45.062	48.775	31.597	31.251	31.031	31.135	



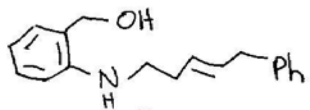


```
Current Data Parameters
NAME      KER-II-020crude
EXPNO                   1
PROCNO                  1

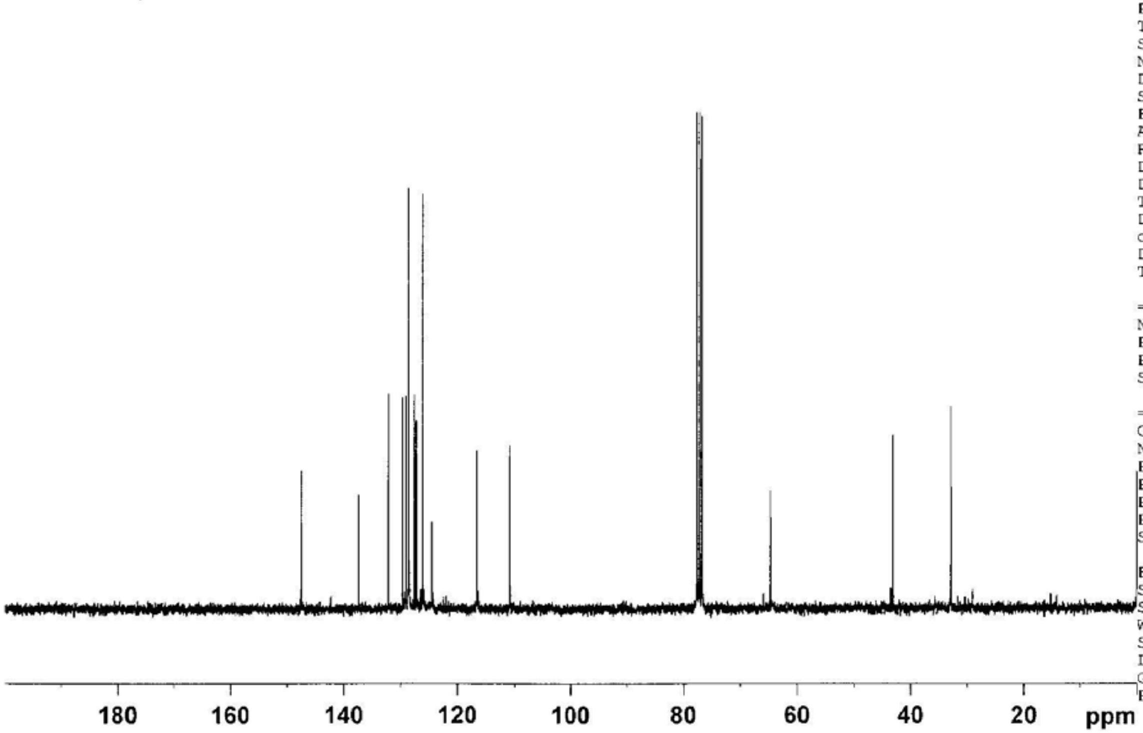
F2 - Acquisition Parameters
Date_            20110401
Time                12.44
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                  228.1
DW                 81.000 usec
DE                   6.00 usec
TE                  304.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



4



```
Current Data Parameters
NAME      KER-II-019carbon
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110427
Time_                22.05
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     500
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                  5792.6
DW                  27.800 usec
DE                    6.00 usec
TE                   320.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.10 usec
PL1                  -1.50 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 19.00 dB
SFO2           300.1312005 MHz

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

KER-II-019

Peak finding results for: 4/27/11 5:11:35 PM
Frequency: 656.29 - 3541.18, threshold: 70.556-98.819, sensitivity: 50.00
Peak finding result table:

Peak#	1	2	3	4	5	6	7	8	9
Position	3372.72	3024.32	2920.15	1606.25	1586.07	1513.61	1460.78	1311.36	992.77
Height	87.378	90.195	86.774	66.304	69.007	59.389	68.567	72.159	64.400

Peak#	10	11	12						
Position	964.14	743.09	691.91						
Height	54.614	31.649	40.368