Rhodium-Catalyzed Intramolecular Hydroacylation of Allyl Amine: Optimization and Scope

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

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Monday, April 22, 2013

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Honors Thesis

Dr. Bendorf

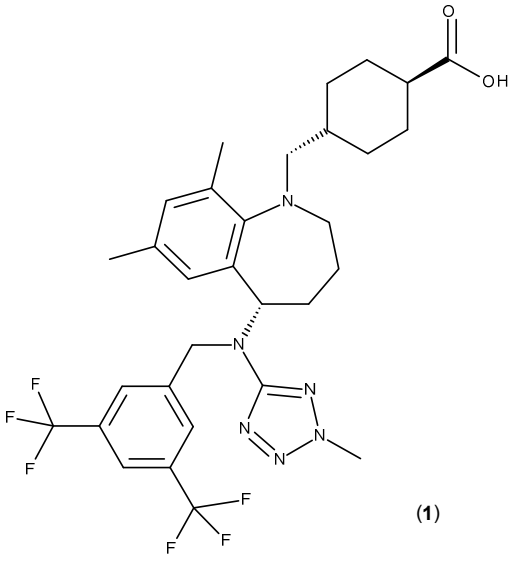
Abstract:

There are multiple compounds that are of pharmaceutical interest that contain a benzazepine core. Intramolecular hydroacylation of allylaminobenzaldehyde derivatives provide a route to synthesize benzazepines. The conditions for this hydroacylation have been optimized and a tandem hydroacylation-*in situ* deprotection of *N,N*-diallylaminobenzaldehyde has been developed. The allylaminobenzaldehydes were prepared in a 3-step synthesis from *N*-methylanthranilic acid and *N,N*-diallylaminobenzaldehyde was prepared in a 2-step synthesis from aminobenzylalcohol. Upon reaction with cationic rhodium catalyst these allylaminobenzaldehydes yielded benzazepines.

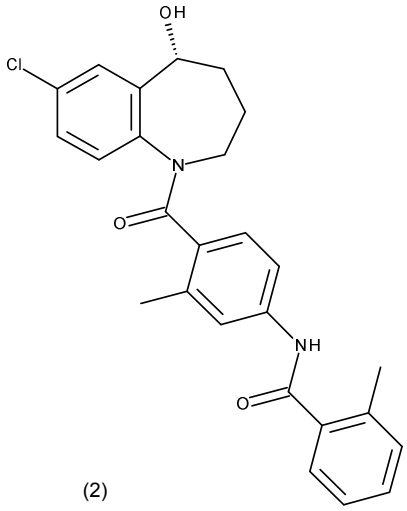
Introduction and Background:

Hydroacylation is defined as the addition of an aldehyde to an alkene. The intramolecular hydroacylation of a molecule containing both of these functional groups can be used to create a cyclized product. Ideally this would provide a wide range of cyclic products. However, intramolecular hydroacylation is limited with respect to the size of the rings that can be produced. Construction of medium-sized rings via intramolecular hydroacylation has proven to be difficult due to an unfavorable transition state during the cyclization process.[1] These medium-sized rings, specifically ones that contain a benzazepine core, are of interest because of the pharmaceutical applications they provide.[2,3] Examples of pharmaceutically active compounds that contain a benzazepine core include Evacetrapib, **1**, which is a cholesteryl ester transfer protein inhibitor and Tolvaptan, **2**, which increases sodium levels in the body.[2,3] Thus,

developing an intramolecular hydroacylation method to produce medium-sized rings is of interest.



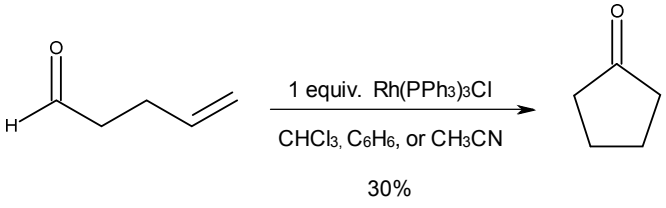
(**1**)



(2)

Intramolecular hydroacylation was initially used to prepare five-membered rings. Sakai first reported a rhodium-promoted hydroacylation in 1972. 4-Alkenals yielded cyclopentanones upon reaction with $Rh(PPh_3)_3Cl$, also known as Wilkinson's catalyst (Equation 1).[4]

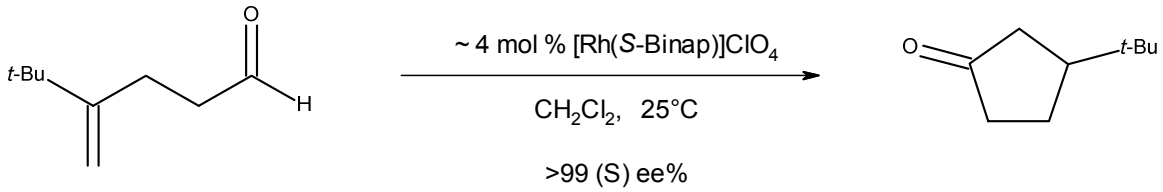
Equation 1.



Although Sakai's group was able to prepare cyclopentanones from 2- and 3- substituted 4-pentenals, stoichiometric amounts of Wilkinson's catalyst were required for the reaction to occur and the yields were relatively low.[4]

In 1980, Larock extended the scope of this cyclization. Larock found that by modifying the monodentate ligands on the catalyst he could obtain higher yields of cyclopentanones. However, the need for high amounts of catalyst still existed.[5] Later, Bosnich reported that cyclopentanones could be produced with high enantiomeric excess in almost quantitative yields and at low catalyst loading by using cationic rhodium catalysts (Equation 2).[6]

Equation 2.

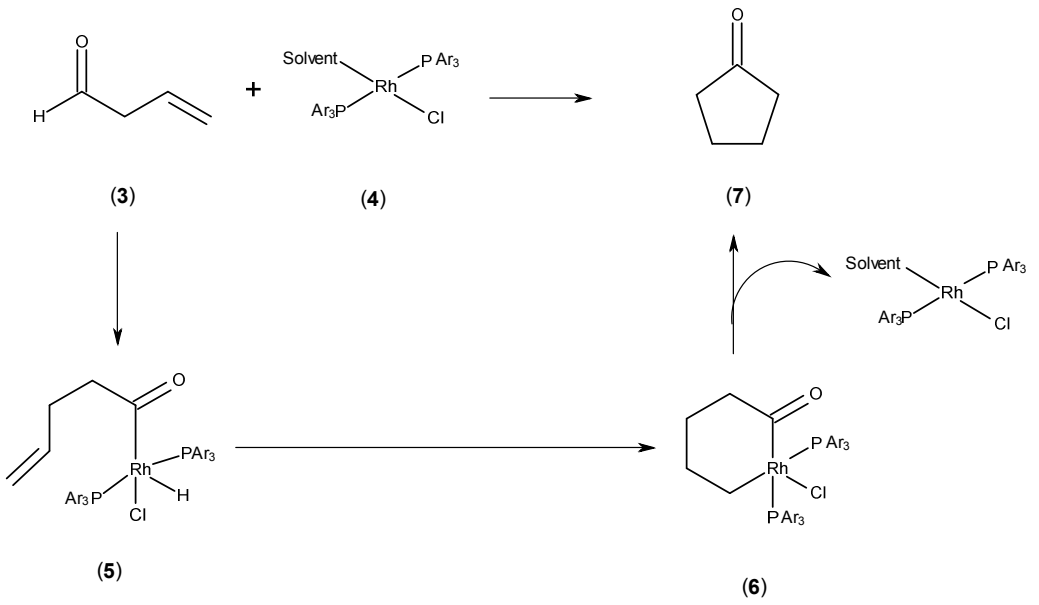


In his paper, Larock also suggested a mechanism for the intramolecular hydroacylation reaction (Scheme 1). The active catalytic complex, **4**, has a chloride and two phosphine ligands with a fourth site occupied by a coordinating solvent or ethylene.[5] The role of the ethylene is to help prevent decarbonylation by occupying a coordination site on the rhodium. The aldehyde, **3**, undergoes oxidative addition to the catalytic complex forming an acylhydridorhodium (III) complex, **5**. Insertion of the alkene into the rhodium hydride bond yields **6.** Reductive elimination produces the cyclized product **7**.[5]

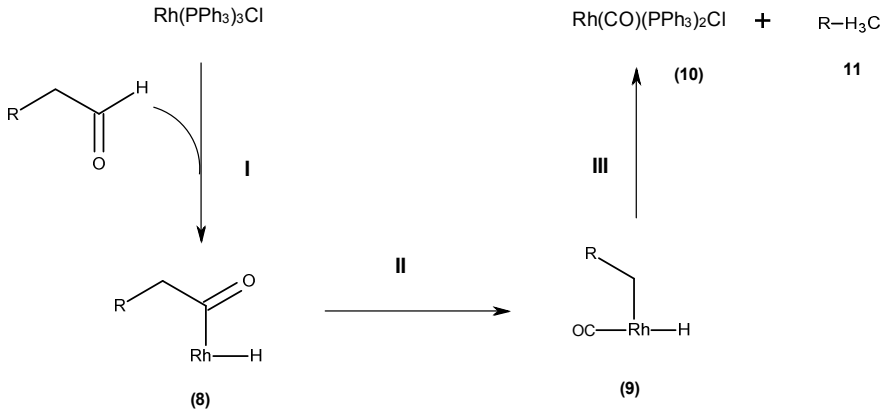
Bosnich also reported that because decarbonylation competes with hydroacylation, side reactions are possible. Decarbonylation, Scheme 2, occurs after oxidative addition of the aldehyde, step **I**. Next instead of an alkene insertion, there is a carbonyl deinsertion, step **II**, followed by a reductive elimination, step **III**. When this occurs the rhodium catalyst is no longer

active. To limit decarbonylation, he proposed the use of cationic catalysts what will favor hydroacylation.[6]

Scheme 1.



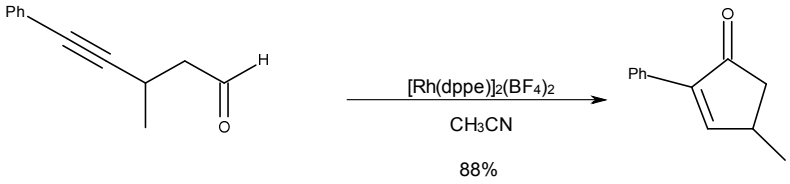
Scheme 2.



Bosnich predicted that a rhodium (I) complex a bidentate phosphine ligand would destabilize the formation of a carbonyl intermediate **9**, while stabilizing the hydrido-acyl

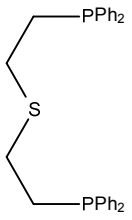
intermediate **8**. The bidentate phosphine ligand will do this by occupying the vacant site that would otherwise be open if monodentate ligands were used. Without the vacant site the carbonyl deinsertion cannot occur. This accelerates intramolecular hydroacylation over decarbonylation.[6] Bosnich also reported that having three sites open for the coordinating acyl hydride and alkene groups is ideal to increase the catalytic rate of the reaction. Without these vacancies, the catalytic rate would depend on the dissociation of the ligands. Coordinating solvents, such as acetone, help prevent the formation of the π-aryl dimer form of the rhodium catalytic complex, therefore increasing the catalytic activity.[6] Further supporting this hypothesis, Tanaka and Fu, in 2001, reported high yields of cyclopentenones using the bidentate ligand 1,2-bis(diphenylphosphanyl)ethane (dppe) in acetone (Equation 3).[7] At this time, Tanaka and Fu did not attempt to make the analogous six-membered ring.

Equation 3.



Another strategy to prevent decarbonylation was suggested by Willis and Weller. Here, they focused on intermolecular hydroacylation where the strategy for the prevention of decarbonylation is thought to be the same.[8] Originally, Willis and Weller hypothesized that the use of β-S-aldehydes with hemiliabile ligands, such as DPE-Phos, would help prevent decarbonylation. DPE-Phos protects the vacant site on the metal center that is needed to

accomadate the carbon monoxide ligand upon decarbonylation. The DPE-Phos ligand has oxygen in the middle of the bidentate backbone. The oxygen can then associate and dissociate readily to the vacant site. The tridentate ligands $(Ph_2PCH_2CH_2)_2X$ (X=S **12**, O **13**, PPh **14**) and methyl acrylate or vinyltrimethylsilane to make rhodium precursors, for oxidative addition of aldehydes (Equation 4).[8] Although, these precursors work with β-S-aldehydes, simple aldehydes do not react with the catalytic complexes in an appreciable amount of time. Willis suggests that the simple aldehyde cannot displace the alkene as well as β-S-aldehydes. The binding of β-sulfur aldehydes is more favorable due to the formation of a chelate allowing the displace the alkene from the complex for the oxidative addition of the aldehyde to occur.[8]



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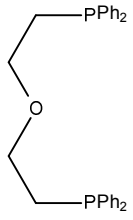

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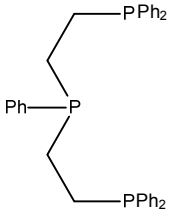

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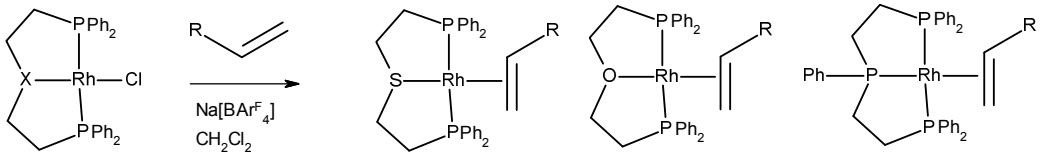
Equation 4.

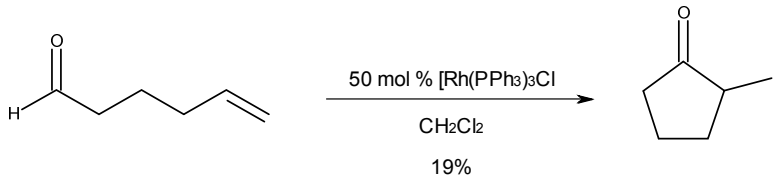


Along with the competing decarbonylation reaction, Larock reported that the reaction was sensitive to steric hindrance associated with the aldehydes. Initially, by varying the monodentate ligand he was able to produce the cyclopentanones of 4, 5 unsaturated

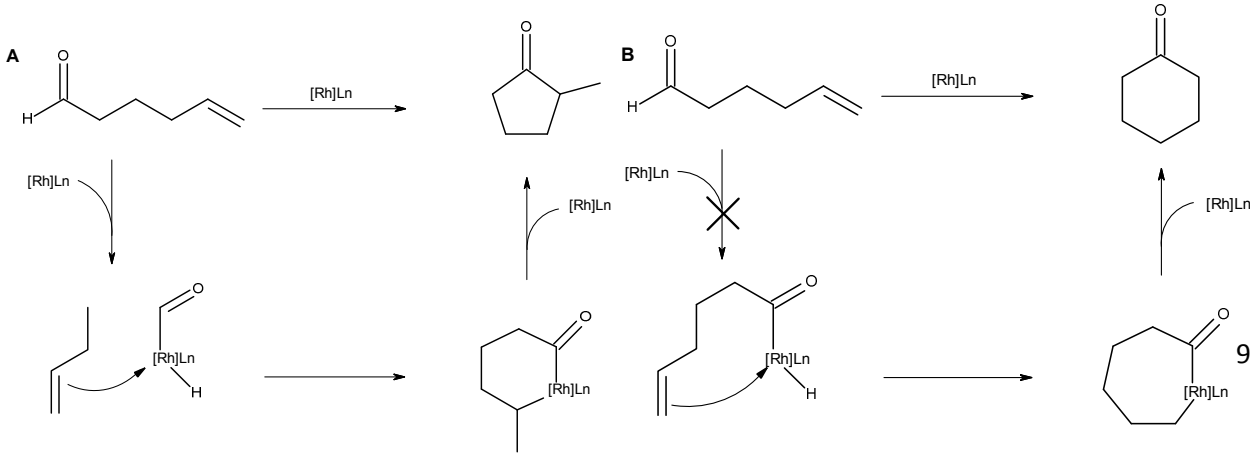
aldehydes, which were monosubstituted on the 2, 3, 4, or 5 position. When the 2 or 5 position was disubstituted, the substrate did not cyclize.[5] This is due to the sterics associated with disubstitution at those positions and the function of these positions in the mechanism. At the 2-position, the disubstitution is alpha to the aldehyde. Substitution here may prevent oxidative addition of the aldehyde in the mechanism. Disubstitution at the 5-position may inhibit the insertion of the alkene into the rhodium-hydride bond due to steric hindrance.

With 5,6-unsaturated aldehydes, the intended cyclohexanone product was not observed; Instead 2-methylcyclopentanone was produced (Equation 5).[5] Here, the 5,6-unsaturated aldehyde underwent exo-cyclization, path **A**, as opposed to endo-cyclization, path **B**, which was observed for 4-pentenal (Scheme 3). This suggests that the distance between the aldehyde and the alkene plays an important role in intramolecular hydroacylation and highlights the difficulty in creating rings larger than cyclopentanone.[5]

Equation 5.

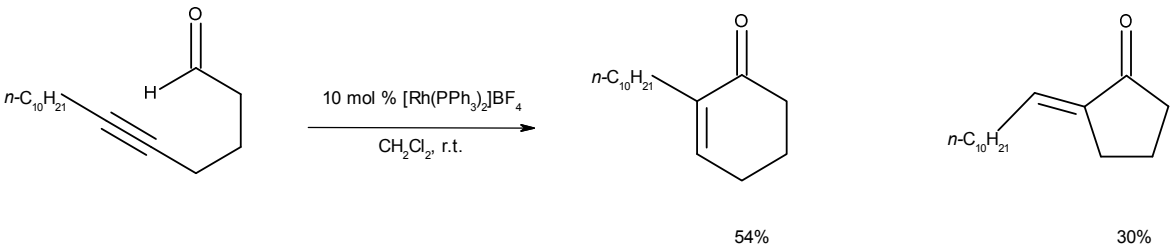


Scheme 3.

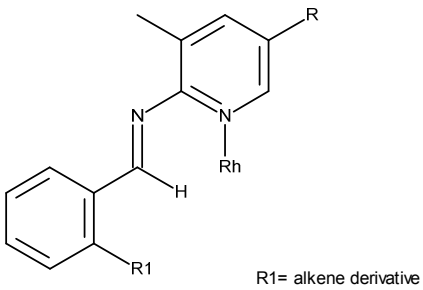


Tanaka has also developed a method for direct hydroacylation of alkynes to make cyclopentanones and cyclohexenones (Equation 6).[9] Two cationic rhodium catalysts with monodentate phosphine ligands, typically $P(OPh)_3$ or PPh_3, were studied. The use of triphenylphosphine ligands favored the formation of the cyclohexenone product over the cyclopentanone. Other monodentate ligands with different electronic and steric characteristics lowered the yields and bidentate ligands with large natural bite angles led to the formation of the cyclopentanone product. Bidentate ligands with small natural bite angles did not produce either product.[9]

Equation 6.



One method to produce medium-sized rings with direct hydroacylation was proposed by Douglas and co-workers.[10] Their method included using a cocatalyst to generate an imine intermediate and eliminate the possibility of decarbonylation. The imine intermediate does not have a carbonyl so it cannot decarbonylate. Douglas forms the imine *in situ* from the aldehyde by reacting it with aniline and benzyl alcohol. The reaction used for optimization is displayed in Equation 7.



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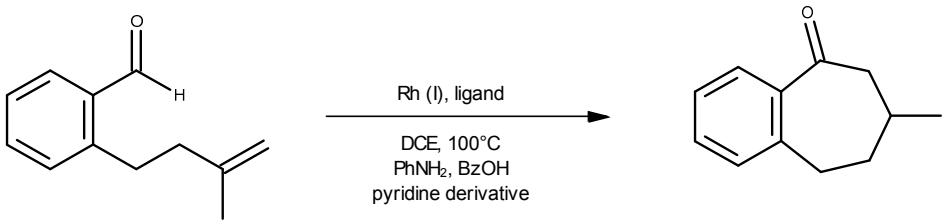
Equation 7.

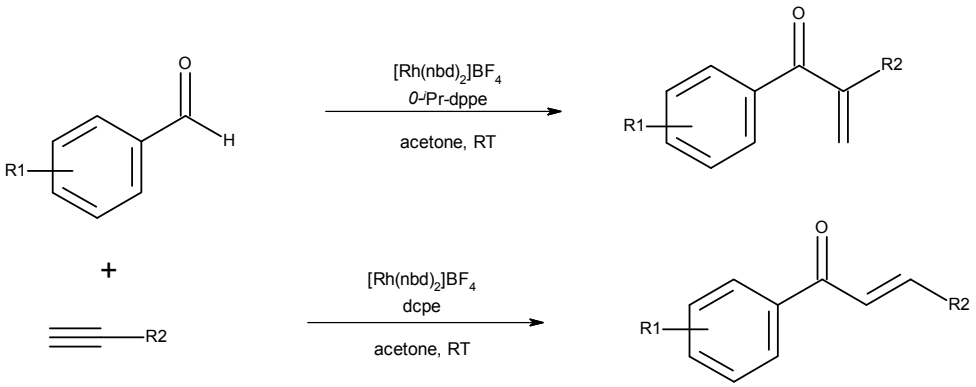


The reaction rate can be influenced by varying the solvent. The reaction is fastest in $PhCF_3$ as compared to DCE. Under the optimized conditions a reduction in the amount of cocatalyst from 120 mol% to 10 mol% was possible.[10] The reason for this was unclear; the solvents tested did not follow trends in solvent polarity or Lewis basicity. Triphenylphosphine was the optimal ligand for the reaction. Sterically demanding ligands, such as tri-*ortho*-toyl phosphine, suppressed the imine formation while mixed alkyl/aryl phosphine ligands decreased the efficiency of the catalytic complex.[10]

Willis and Weller found that the regiochemistry of intermolecular hydroacylation products can be affected by varying the ligand on the catalyst (Equation 8).[11] Branched products are favored by the use of *o*-^{i}Pr-dppe as the ligand on rhodium. To favor the formation of linear-products, electron-rich diphosphine ligands can be used. The ligand dcpe showed

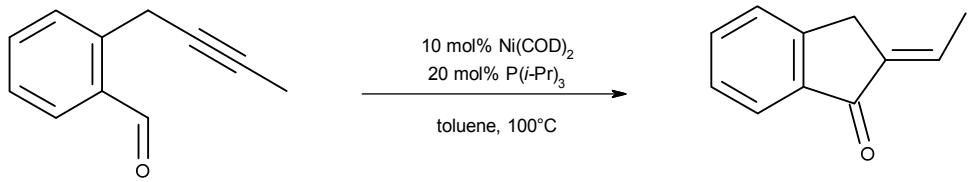
excellent catalytic activity and allowed for the reduction in the amount of catalyst from 10 mol% to 1 mol%.[11]

Equation 8.



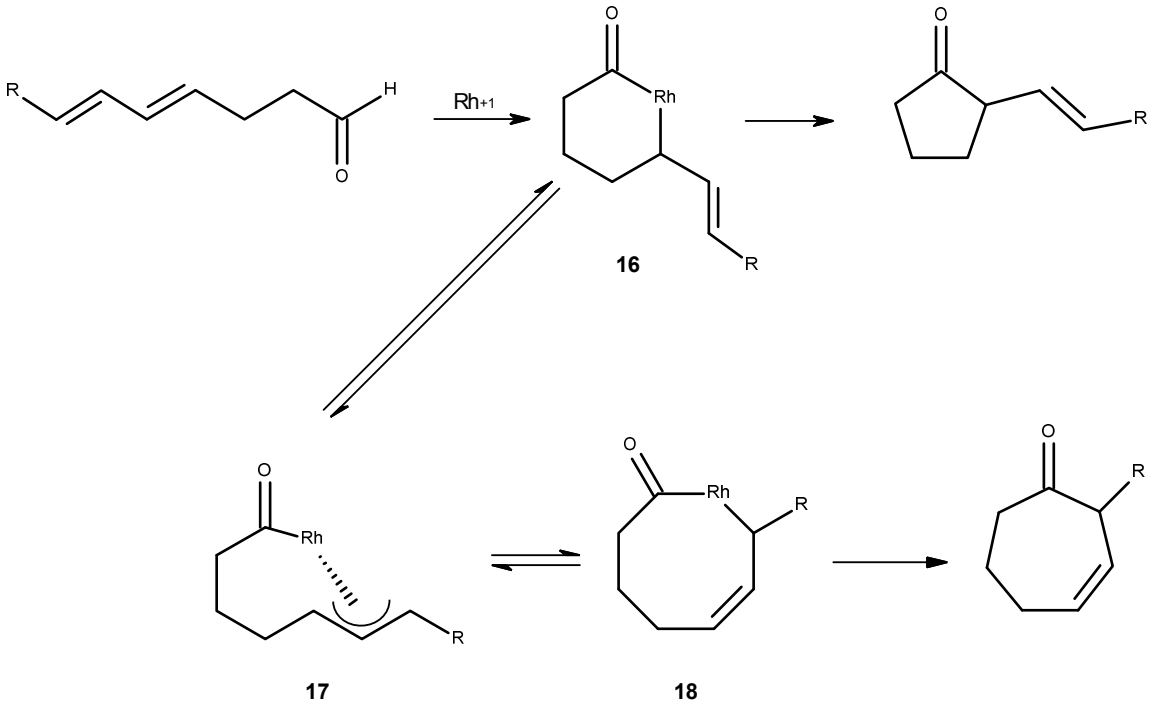
Yamamoto and co-workers examined the effect of the ligands on the nickel-catalyzed intramolecular hydroacylation of alkynes (Equation 9).[12] Initial investigations showed that the reaction failed when $Ni(COD)_2$ was used as the catalyst in the absence of phosphine ligands. As a result, a series of phosphine ligands were tested. Of the ligands tested, $P(i\text{-}Pr)_3$ proved to be optimal in terms of electronics and sterics. Phosphine ligands with more or less steric hindrance, such as PCy_3 and PMe_3, exhibited lower yields for the reaction. Also, by changing the monodentate ligand to a bidentate ligand, there was a lower yields were observed. Therefore, having both a strong electron-donor property and adequate bulkiness is needed for the reaction to occur.[12]

Equation 9.



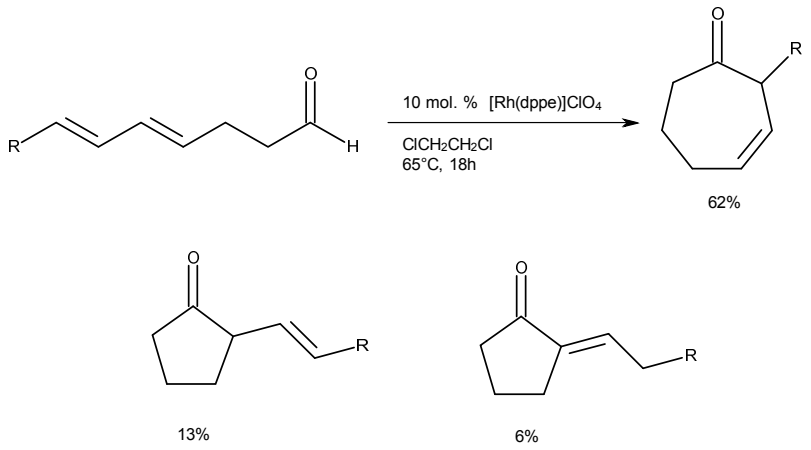
In 2002, Sato reported that cycloheptenones could be produced by the hydroacylation of 4,6-dienals via a ring-expansion (Scheme 4). Oxidative addition of the aldehyde to the rhodium is followed by the insertion of the alkene to produce rhodium metallacyle **16**. The η^1-allyl intermediate **16** can isomerizes to η^1-allyl **18** via η^3-allyl intermediate **17**. The reductive elimination of **18** yields the cycloheptenone product.[1]

Scheme 4.



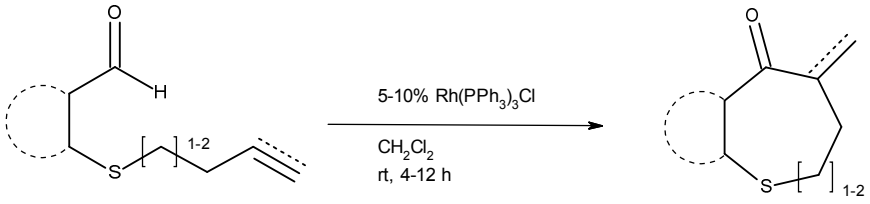
A variety of substituted cycloheptenones were produced using this reaction, an example is shown in Equation 10.[1] However, when the 6-alkene was in the *Z* conformation, cyclization did not occur. Sato reasoned that rhodium coordinated to the latter alkene before reductive elimination to form the cycloheptenone product. This is not favorable in the *Z* conformation because it does not position the second alkene in the right alignment for the ring expansion.[1]

Equation 10.



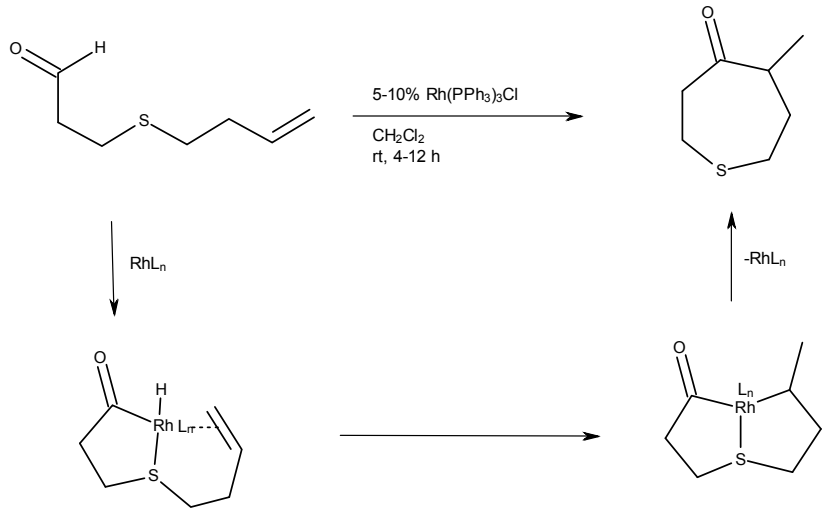
In 2002, Bendorf published her work on chelation-assisted intramolecular hydroacylation which resulted in medium-ring heterocycles.[13] She was able to react ω-alkenals and alkynals containing a Lewis basic sulfur tether atom with Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, to produce seven- or eight-membered heterocycles. Use of a sulfur tether atom promoted cyclization; however, the use of oxygen or CH_2 as tether atoms did not (Equation 11).[13] These results indicate that the tether atom is necessary for hydroacylation to occur and that basicity of the tether atom also plays a role.

Equation 11.



The key to this reaction is the sulfur atom, which is positioned three carbons from the aldehyde. Sulfur is able to coordinate to rhodium, which may help promote the oxidative addition of rhodium. The mechanism for hydroacylation is illustrated in Scheme 5.[13] The promotion of oxidative addition may also prevent decarbonylation, because the 4-membered metallacyle produced by this side reaction would be too strained.

Scheme 5.

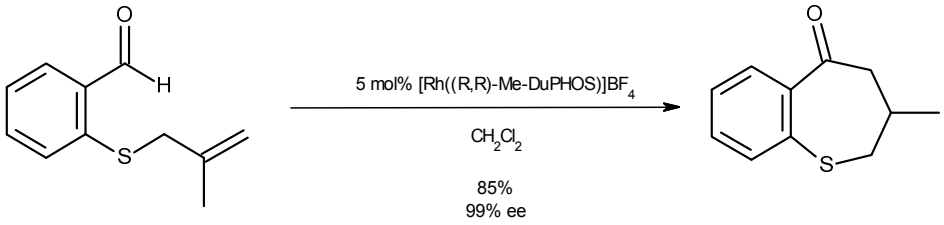


The distance between the aldehyde, alkene and the sulfur tether atom is critical. The sulfur tether atom needs to be β to the aldehyde; if sulfur is closer or further away from the

alkene hydroacylation does not occur.[13] When the aldehyde is α or γ to sulfur, the complex is not able to place the aldehyde in a favorable position where it can undergo oxidative addition even with prior chelation to sulfur. Hydroacylation also does not occur if the distance between the sulfur and alkene is more than three carbons, because the alkene is not able to insert into the rhodium hydride bond.[13]

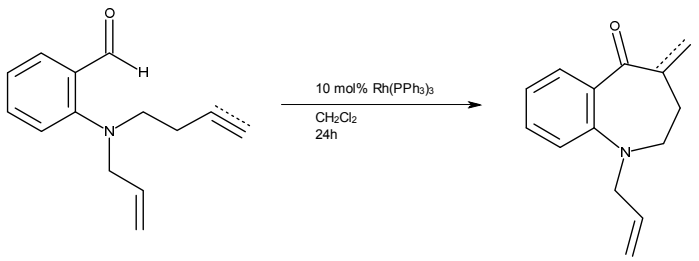
In 2009, Dong published a paper on asymmetric olefin hydroacylation with results that complement Bendorf's.[14] Allyl sulfides were cyclized when the catalyst [Rh((R,R)-Me-DuPHOS)]BF_4 was used (Equation 12). These heterocycles were produced with high regioselectivity and enantioselectivity.

Equation 12.

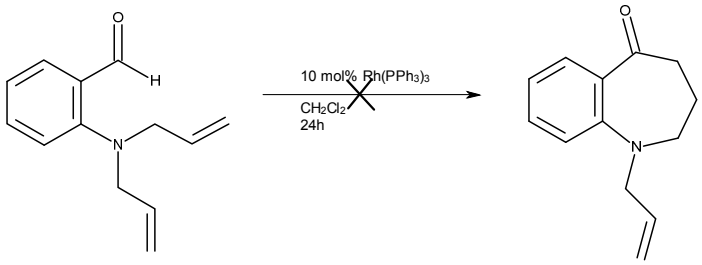


In 2012, Bendorf reported the production of nitrogen heterocycles using Wilkinson's catalyst.[15] 3-Butenyl or 3-butynyl substituted allyl amines formed heterocycles via exo-hydroacylation and in high yield (Equation 13). When both groups on the nitrogen were allyl groups, the predicted endo-hydroacylation did not occur (Equation 14).[15]

Equation 13.



Equation 14.

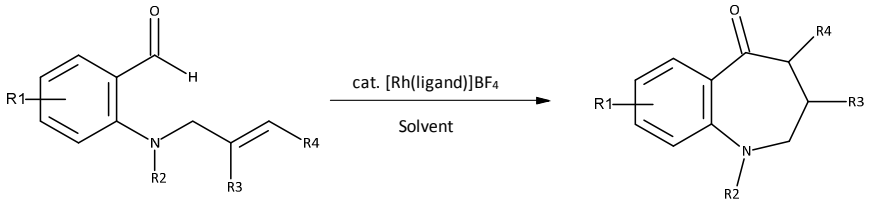


Currently, research in the Bendorf lab is focused on the hydroacylation of *N*-allyl groups. Ideally, the substituted *N*-allyl groups will allow us to vary the substituents α and β to the ketone on the heterocycle. Using the butenyl or butynyl group always results in a substituent α to the ketone. Furthermore, allyl groups are easier to install on the nitrogen than butenyl groups via an S_N2 reaction. There is also a wide variety of allyl groups commercially available. Since Wilkinson's catalyst did not work for these cyclizations, a cationic rhodium (I) catalyst was examined and, based on research described earlier, the [Rh(dppe)]BF_4 cationic catalyst was chosen. Research thus far has included the preparation of substrates, examination of the effect of allyl substitution on hydroacylation, and optimization of catalyst. With respect to the catalyst, one aspect of particular interest is the effect of the ligand; how changing the ligand's electronic and steric characteristics affect the catalysts' reactivity.

Results and Discussion:

The general reaction and conditions that the cyclizations occur under are illustrated in Equation 15. A range of benzazepines can be prepared by varying the R-groups on the substrate. Variation of the ligand and solvent can help to optimize the reaction.

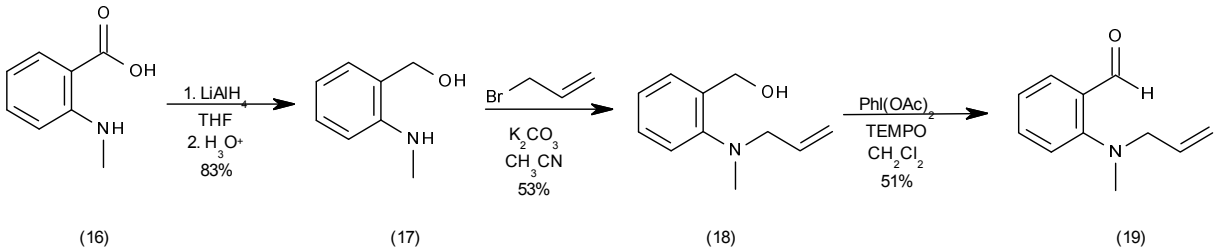
Equation 15.



Initial Experiments and Optimization:

A representative synthesis of a hydroacylation substrate, **19**, is shown in Scheme 6. *N*-methyl anthranilic acid, **16**, is reduced by lithium aluminum hydride to produce 2-(methylamino)benzenemethanol, **17**. This compound is alkylated with allyl bromide. Initial attempts of the *N*-alkylation were conducted with freshly distilled allyl bromide. However, the absence of the radical inhibitor in allyl bromide led to polymerization in the reaction vessel which in turn lowered the yield and purity of **18**. To prevent polymerization, undistilled allyl bromide and sodium iodide were added to the reaction. Once these changes were made, the reaction proceeded as expected. The 2-(methylamino)benzenemethanol, **18**, was oxidized to an aldehyde **19** using TEMPO and diacetyliodobenzene.

Scheme 6.

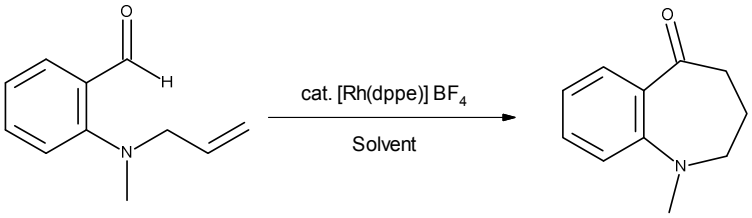


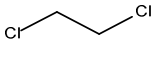
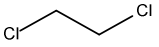
(16) (17) (18) (19)

The conditions for the hydroacylation reaction were optimized with respect to the solvent and amount of catalyst (Table 1). Reducing the equivalents of the catalyst from 0.10 to 0.05 had no effect on the yield of the reaction (entries 1-4). Higher yields were observed in coordinating solvents, such as acetone. This is because the catalyst can exist as a π-aryl dimer in non-coordinating solvent, such as dichloroethane. However, in coordinating solvents the catalyst exists as the more reactive monomer due to the solvent's ability to coordinate to the complex.[6]

We were concerned that the product may coordinate to the rhodium complex and that as a result, some product would be lost during purification. To determine if this would happen, triethylamine was added to the reaction after hydroacylation was complete (Table 1, Entry 5). It was hoped that triethylamine would displace any product still bound to the catalyst. The yield of the product was unchanged, which suggests that this concern was unfounded. These results led to the optimized conditions of using 5 mol % of the catalyst in acetone at room temperature for the cyclization reactions. Once optimized conditions of the hydroacylation reaction were identified, multiple substrates could be screened for this reaction.

Table 1.

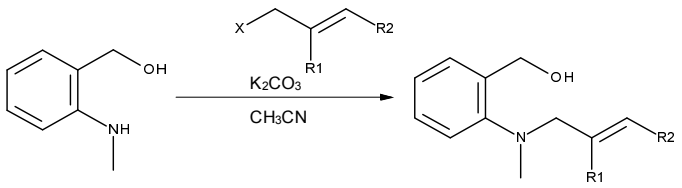


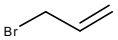
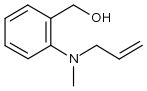
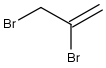
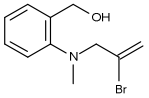
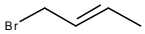
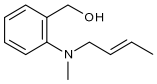
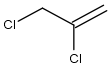
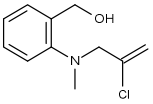
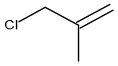
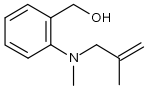
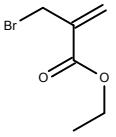
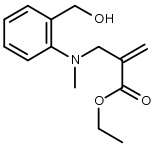
Entry	Equivalents of Catalyst	Temperature	Solvent	Yield
1	0.05	Reflux		85%
2	0.1	Reflux		83%
3	0.1	Room Temperature		92%
4	0.05	Room Temperature		93%
5	0.05	1. Room Temperature 2. NEt_3		93%

Synthesis of Substrates:

The allyl halides that were chosen for the substrate were done so to provide a wide range of information on the scope and limitations of hydroacylation reaction. Substrates were prepared for cyclization in a manner analogous to that of compound **19**. First, the compounds were alkylated by a variety of allyl halides (Table 2). We believe the increase in yields from entry 2 to 3 was due to the addition of 10% NaOH in the workup of the reaction to ensure the product was not dissolved in the aqueous layer during extraction.

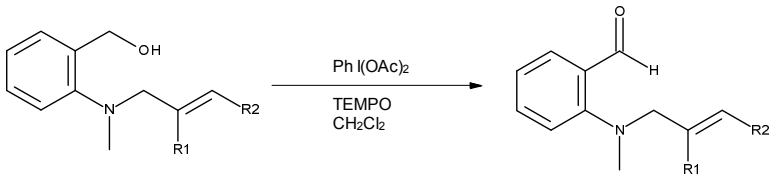
Table 2.

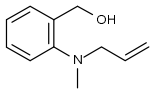
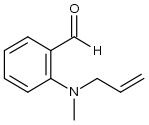
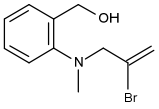
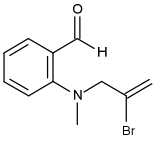
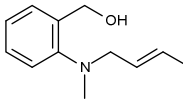
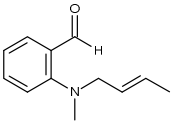
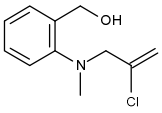
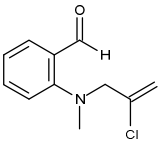
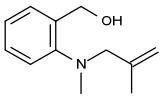
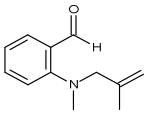
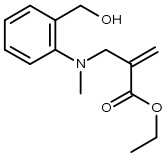
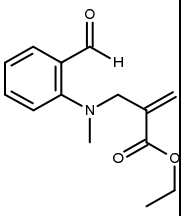


Entry	Allyl Halide	Product	Yield	Entry	Allyl Halide	Product	Yield
1			92%	4			94%
2			76%	5			91%
3			89%	6			70%

The amino-alcohols were oxidized to the aldehyde using a TEMPO oxidation (Table 3). An increase in yield from entry 2 to entry 3 was thought to be due to improvement of technique over time.

Table 3.

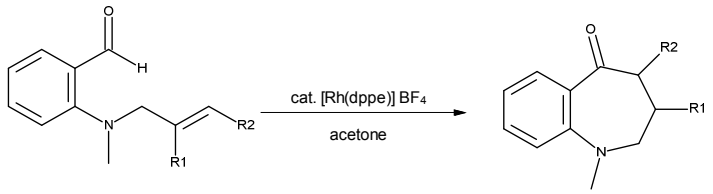


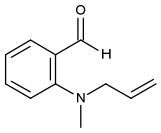
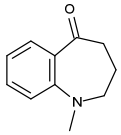
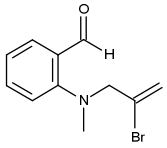
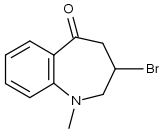
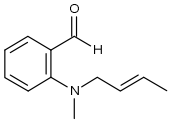
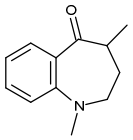
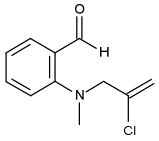
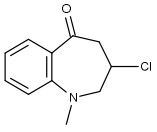
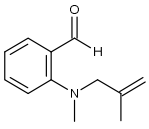
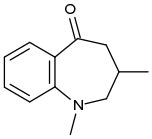
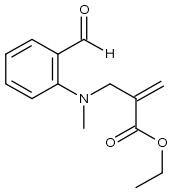
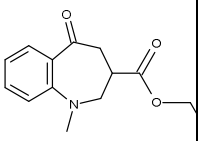
Entry	Substrate	Product	Yield	Entry	Substrate	Product	Yield
1			92%	4			95%
2			59%	5			89%
3			89%	6			88%

Substrate Screening:

As seen in Table 4 the aminoaldehydes were treated with [Rh(dppe)]BF_4 using the optimized conditions that were determined previously (Table 1)**.**

Table 4



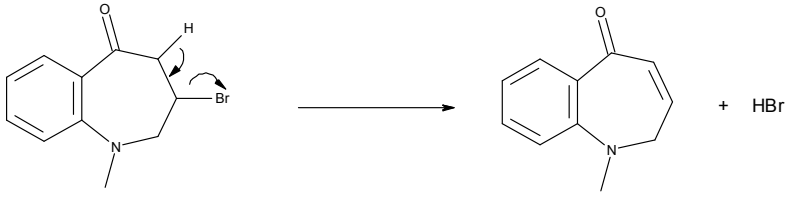
Entry	Substrate	Product	Yield	Entry	Substrate	Product	Yield
1			93%	4[a]			0%
2[a]			0%	5[a]			0%
3			91%	6[a]			45%

Reaction Conditions: 5 mol% [Rh(dppe)]BF_4, 0.1M of substrate in acetone, room temperature.
a. Reaction ran at reflux.

The allyl amine substrate (Table 4, entry 1) underwent hydroacylation in high yields. However, the crotyl analog, entry 2, failed to cyclize. This is likely due to steric strain associated with the insertion of the alkene into the rhodium hydride bond. On the other hand, if the alkyl substituent is on the internal carbon of the allyl alkene the substrate proceeds to cyclize, (entry 3). The vinyl ester yields an approximate 1:1 ratio of starting material to product (entry 6). The ester group decreases the alkene's electron density, therefore making the coordination of the alkene less likely to occur during the reaction.

Vinyl halides failed to cyclized (entries 4 and 5). We suggest that this may be due to an elimination reaction that could occur after a small amount of product is initially formed (Equation 16)**.** Elimination of HBr would liberate acid which could deactivate the catalyst or protonate the *N*-tether atom. To prevent this from happening, a base could be added to the reaction to neutralize the acid.

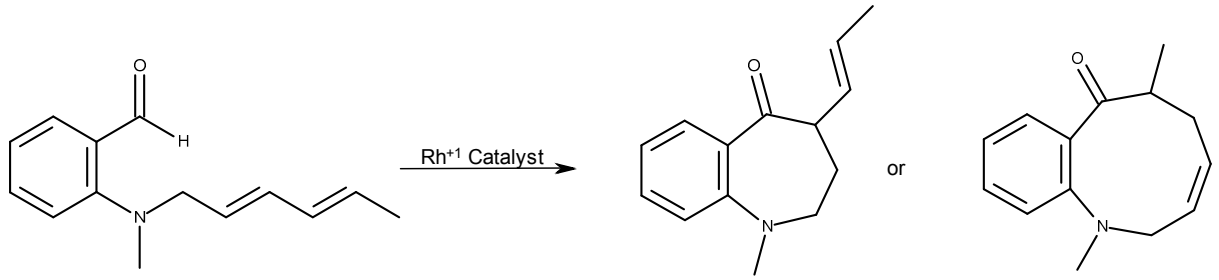
Equation 16



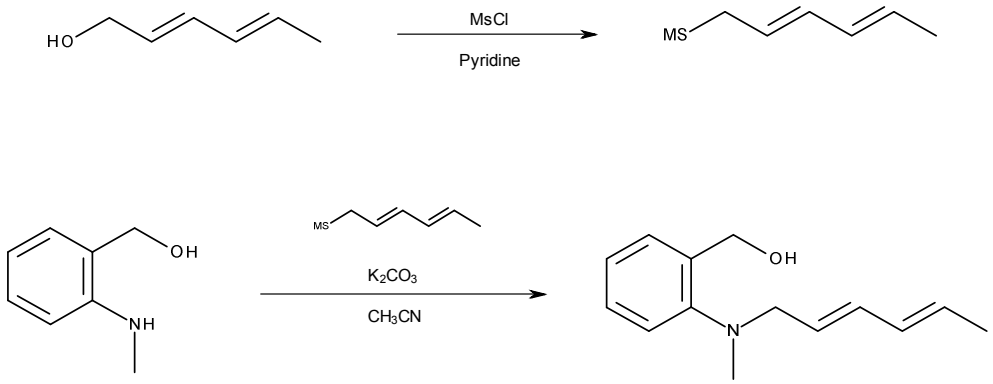
Addition of potassium carbonate to the reaction vessel had no apparent effect on the reaction. Only trace amounts of product were seen. This was surprising because the reason for the failure to cyclize is not thought to be due to steric hindrance; due to the equally bulky methyl-substituted substrate results (Table 4, entry 3). However, halides have both electron-donating (via resonance) and electron-withdrawing (via induction) characteristics. Therefore failure of the reaction may be due to an electronic effect. To further understand the reasoning for the halide's failure, a wider variety of substituted allyl substrates need to be examined. This will allow for the results of the halo- and ester-substituted allyl substrates to be put into perspective. A good allyl-group to screen would be the analogous vinyl ether. Vinyl ethers donate electron density to the alkene and would give further insight to the reaction, and whether this is the reason the halides fail to cyclize.

Another substrate of interest is a conjugated allyl diene (Equation 17). This substrate can potentially perform a ring-expansion during the coordination of the alkene to the rhodium complex, similar to Sato's work (Scheme 4).[1] The ring-expansion would allow for the production of a 9-membered heterocycle.

Equation 17.



Scheme 7.

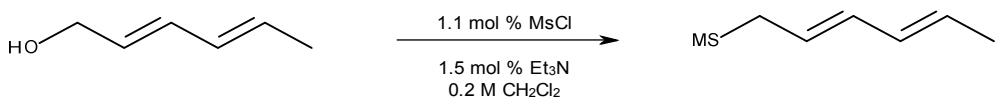


This substrate was expected to be prepared from the mesylate via Scheme 7; a route similar to that shown in Scheme 6. However, the formation of the mesylate has been proven to be difficult. Initially, the mesylate was then added to the reaction vessel, Scheme 7**.** This method did not produce any diene product that could to be characterized by ^{1}H NMR. The

product is thought to be a highly reactive compound due to the presence of the conjugated diene. This high reactivity may make the mesylate unstable at room temperature. Therefore, in the second attempt, the mesylate was prepared at 0°C with a shorter reaction time. The mesylate was kept at 0°C and with no workup the amine was added directly into the reaction vessel. However, this did not produce any product which we could visualize by Thin-Layer chromatography due to the pyridine present in the reaction vessel. ^{1}H NMR showed no evidence of product. Having pyridine present is a problem because it smears on the TLC-plate making it difficult to interpret the TLC results. Also, the pyridine is difficult to remove from the reaction mixture in later steps.

A different procedure which used triethylamine, which, unlike pyridine can be removed under vaccum was looked into (Equation 18).[16] Two experiments were conducted, the first experiment involved the mesylate being added directly to the methylaminobenzyl alcohol without a prior workup. In the second experiment, the mesylation was worked up prior to addition to the amine. However, neither experiments worked; further optimization of this reaction is still in progress.

Equation 18.



Optimization of Catalyst:

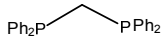
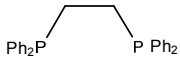
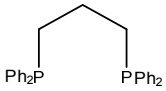
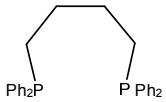
Optimization of the catalyst was pursued to improve the yields of products. Bidentate ligands with diverse bite angles were screened on the rhodium catalyst. Different bite angles, or the angle between the two phosphines, allow for different orientations of ligands on the rhodium metal. This is significant because in order for the insertion and reductive elimination step of hydroacylation to take place, the functional groups need to be oriented *cis* to one another.

Casey and co-workers propose that the key intermediate in the hydroformylation mechanism of is a five-coordinate bis(phosphine)rhodium complex analogous to compound **5** in Scheme 1.[17] This complex allows insertion and reductive elimination to occur the functional groups need to be *cis* to each other. A way that may help position the functional groups *cis* to each other is to have a ligand that is also coordinated *cis* on the rhodium. It is suggested that chelating ligands with a bite angle close to 90° would more selectively add in a *cis* manner in apical and equatorial sites in a trigonal bypyramid geometry. Therefore, the bite angle of the phosphine ligand is of interest to look into in order to enhance the likelihood for insertion and reductive elimination to occur.[17]

We wanted to see how minor differences in bite angle would affect the catalytic activity before making larger changes such as with DPEphos, which has a bite angle of about 102 degrees as well as different electronic properties. The ligands 1,2-bis(diphenylphosphanyl)methane dppm, 1,2-bis(diphenylphosphanyl)ethane dppe, 1,2-bis(diphenylphosphanyl)propane dppp, and 1,2-bis(diphenylphosphanyl)butane dppb were

chosen to see if small variations in the bite angle would influence the outcome of the reaction. Bite angles for these ligands were found, by the source, doing molecular modeling while using rhodium atom as the center, these are shown in **Table 5.**[18] It is assumed that the these angles are fairly close to those that are actually on a rhodium center.

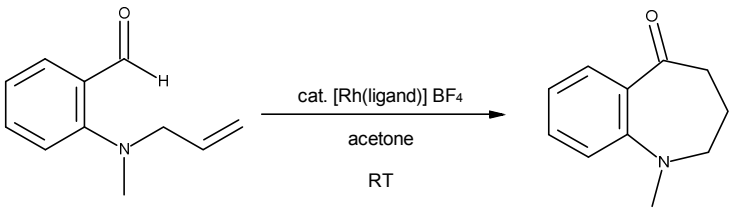
Table 5.

Ligand	Bite Angle
dppm 	72°
dppe 	85°
dppp 	91°
dppb 	98°

The substrates chosen for this study were the allyl benzaldehyde, **19**, and the ester-substituted allyl benzaldehyde, **20**. Allyl substrate **19** was chosen to insure that the catalyst worked and it allowed further insight into the reactivity of the catalyst (Equation 19). The ester-

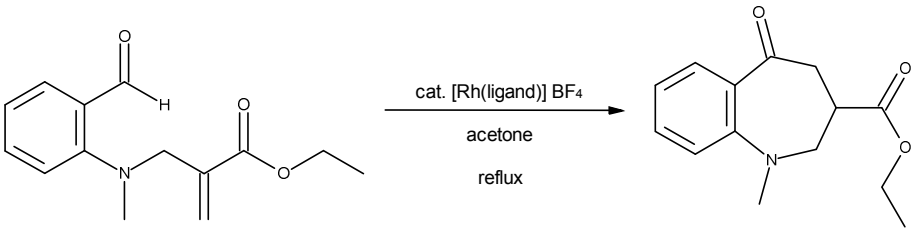
substituted allyl substrate **20** was chosen because its reactivity with [Rh(dppe)]BF_4 was lower than that of the other substrates that cyclized (Equation 20).

Equation 19.



(21)

Equation 20.

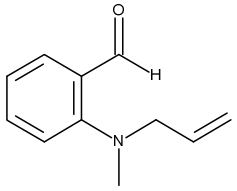
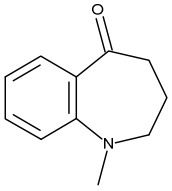
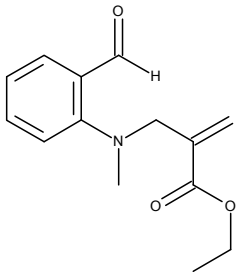
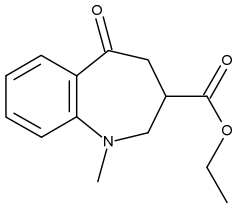
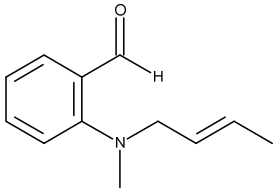
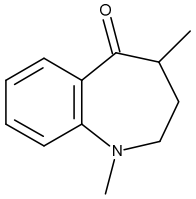


(20)

The results of these experiments suggest that the bite angle of the diphosphine ligand has an effect on the outcome of the hydroacylation reaction (Table 6). Initial screening experiments used dppe as the ligand entries 2 and 6. The allyl substrate worked best with dppe as the ligand. While using dppm the allyl substrate had to react for twenty-four hours and still produced a lower yield than with dppe (entry 1). Also, while using dppp with the allyl substrate, after two hours entry 3 showed no starting material via TLC, however, only a modest yield of product was isolated. With dppb as the ligand the allyl substrate also showed a decrease in

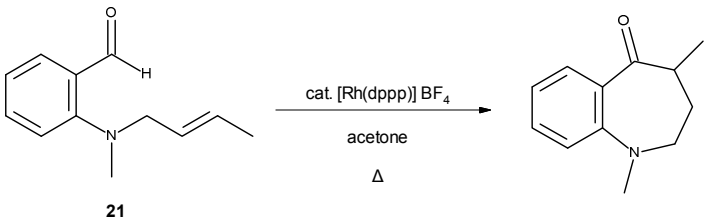
reactivity. As for the ester substrate there was an improved yield with dppp as the ligand from dppe. This is opposite of what is seen with the allyl substrate. Using dppm as the ligand did not cyclize any product for the ester substrate. The ligand dppb only produced a low yield of isolated product. The crotyl substrate, Table 4, entry 2, was also tested with dppp, and although dppp worked well with the other substrates it did not cyclize the crotyl substrate (Equation 21).

Table 6.

Entry	Substrate	Product	Ligand	Bite Angle	Time	Yield
1			dppm	72	24 hours	88%
2			dppe	85	2 hours	93%
3			dppp	91	2 hours	74%
4			dppb	98	1.5 hours	74%
5			dppm	72	24 hours	0%
6			dppe	85	24 hours	45%
7			dppp	91	2 hours	95%
8			dppb	98	24 hours	37%
9			dppp	91	24 hours	0%

Reaction Conditions: 5mol% of [Rh(ligand)]BF_4, 0.1 M substrate in acetone. For substrate **19** reactions were ran at room temperature; substrate **20** at reflux.

Equation 21.

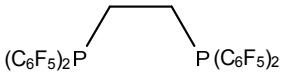
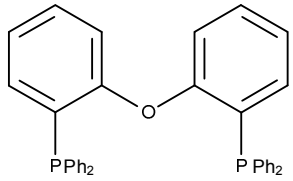
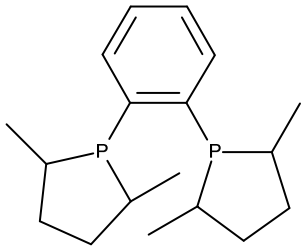
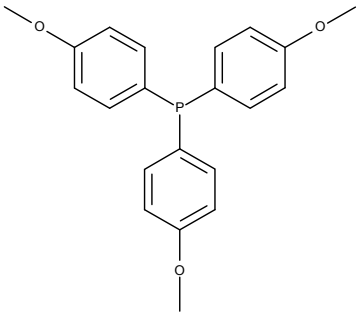


21

The results of varying the bite angle of the ligand showed an increase in reactivity of the catalyst for those ligands whose bite angle was within five degrees of 90°. This supports the initial theory that ligands that will be more likely to coordinate in a *cis* fashion to the rhodium complex will increase the likelihood of reductive elimination. This will, theoretically, increase the reaction rate. Dppm, whose bite angle is 72°, showed a decrease in reactivity. This may be because the bite angle is so small the functional groups involved in the reductive elimination are more likely to spread out on the catalytic complex slowing down in step in the mechanism. Dppb whose bite angle is 98° also showed a decrease in the formation of product. This is thought to be due to the large bite angle forcing the functional groups involved in the reductive elimination step closer together hindering the reductive elimination of the product.

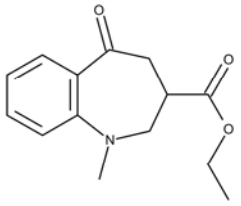
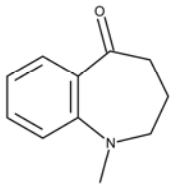
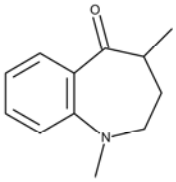
Ligands that have a broader range of electronic properties and bite angles were examined (Table 6). The ligands examined were DPE-Phos, 1, 2 Bis(dipentafluorophenylphosphino) ethane (dfppe), (R, R)-MeDUPHOS, and Tris(4-methoxyphenyl) phosphine, $P(PhOMe)_3$. Since $P(PhOMe)_3$ is a monodentate ligand it does not have a bite angle. These ligands vary not only by their bite angle, but they also have different electronics properties.[18] These ligands were tested under the same conditions as the previous group of ligands with the allyl, ester, and crotyl substrates. These results are shown in Table 7.

Table 6.

Ligand	Bite angle
dfppe 	*85
DPE-Phos 	102°
(R, R)-Me DUPHOS 	83°
$P(PhOMe)_3$ 	---

*The ligand, dfppe, is estimated to have the approximately the same bite angle as dppe.

Table 7.

Entry	Product	Ligand	Bite Angle	Time	Yield
1[a]		dfppe	*85	24 hours	0%
2		DPE-Phos	102	24 hours	13%
3		(R, R)-Me DUPHOS	83	24 hours	0%
4		$P(PhOMe)_3$	---	24 hours	0%
5		dfppe	*85	24 hours	0%
6		(R, R)-Me DUPHOS	83	24 hours	80%
7		DPE- Phos	102	24 hours	0%
8		$P(PhOMe)_3$	---	24 hours	0%

Reaction Conditions: 5mol% of [Rh(ligand)]BF_4, 0.1 M substrate in acetone. For substrate **19** and **21** reactions were run at room temperature; substrate **20** at reflux. *a* was run at refux.

When dfppe was used as a ligand, the reaction ceased (entries 1 and 5). This could be due to the dfppe ligand being a poor σ-donor because of the fluorinated phenyl groups attached to the phosphorous. This creates a deficiency of electron-density towards the metal. The less electron-rich rhodium may be sluggish as a result.

With DPE-Phos there was a decrease in the reactivity of the rhodium complex (entries 2 and 7). This may be due to the oxygen in the backbone of the ligand. As mentioned before Willis and Weller looked into DPE-Phos as a ligand for their intermolecular hydroacylation reaction with simple aldehydes.[9] The found that, DPE-Phos was attractive because of the oxygen's ability to associate and dissociate off of the rhodium complex. However, for the

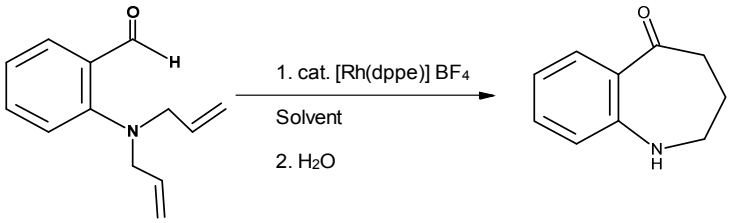
analogous intramolecular hydroacylation reaction with the chelating nitrogen this could have the complete opposite effect. The fact that the oxygen can associate and dissociate off of the complex might actually disfavor the oxidative addition and the reductive elimination steps of the reaction. Both of which are essential for the cyclization of product. Another reason could also be due to the larger bite angle. As seen with the other set of ligand screenings, as the bite angle increased over 90° the reactivity of the catalyst decreased.

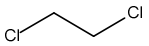
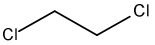
As for (R, R)-MeDUPHOS, there is a slight decrease in the reactivity of the catalyst with the allyl substrate, while no product was seen for the ester substrate. This may be due to the bite angle of the ligand which is 83°. As mentioned before with the first testing of ligands, the hydroacylation reaction was favored by ligands whose bite angles were within 5° of 90° to help with the reductive elimination step. One other reason for the decrease in the formation of product may be due to steric hindrance of the backbone. With (R, R)-MeDUPHOS there is now an aryl group in the backbone. There is also steric hindrance associated with the methyl groups on the phospholane rings that could hamper the reaction.

The monodentate ligand $P(PhOMe)_3$ was screened with the crotyl substrate instead of the allyl substrate. Yamamoto used monodentate ligands on his nickel hydroacylation catalyst. He found that bulky, strongly electron-donating ligands led to the best catalysts. His promising results led to the use of this ligand in our ligand studies. In our case , the monodentate ligand did not show these promising results; neither substrate cyclized. Monodentate phosphine ligands are not ideal, possibly because they are labile. This can be problematic because it can hinder the *cis* geometry needed for the reductive elimination step.

An overview of all the ligand studies shows the need for the ligands bite angle to be as close to 90° as possible in order to promote the reductive elimination of the product from the rhodium complex. Sterically hindered ligands are not ideal on the catalyst for this reaction. Furthermore, electron-withdrawing ligands are not ideal for this reaction because they slow the initial oxidative addition of the aldehyde into the rhodium complex. Lastly, monodentate ligands are not ideal due to the ease with which they can dissociate.

Table 9.



Entry	Equivalents of Catalyst	Temperature	Added Reagents	Solvent	Yield
1	0.05	Reflux	———		47%
2	0.1	Reflux	9:1 $CH_3CN:H_2O$ After 3.5 h		72%
3	0.05	Room Temperature	———		60%
4	0.05	Room Temperature	H_2O After 3h		88%

An *in situ* hydroacylation-deprotection reaction was also investigated for cyclization of *N,N*-diallylaminoaldehyde. The deprotection of the amine allows for subsequent modification at the amine (Table 9)**.** This reaction was run in both non-coordinating and coordinating solvents.

Similar to previous results, higher yields were observed with coordinating solvents. Yields of the deprotected product were also increased by the addition of water after hydroacylation.

Conclusions:

In conclusion, hydroacylation reactions are optimally run in coordinating solvents such as acetone. Success of the reaction depends on the substitution on the allyl substituents. Substitution on the internal alkene carbon by alkyl and ester groups is tolerated; however, lower yields are obtained for the ester substrate. Vinyl halides do not undergo hydroacylation. Substitution on the terminal alkene carbon blocks hydroacylation. Studies on the catalyst show that dppe and dppp ligands provide the highest yield of products. The bite angle of the ligand needs to be within 5° of 90° otherwise the reaction will decrease in reactivity. Poor σ-donor ligands are not effective in for this type of intramolecular hydroacylation. Lastly, an *in situ* hydroacylation-deprotection reaction has been developed.

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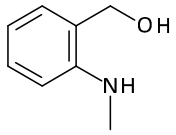
Experimental:

General Methods:

All reactions were carried out under nitrogen or argon atmosphere, using oven-dried glassware unless otherwise noted. Methylene chloride and acetonitrile were distilled from calcium hydride. Anhydrous acetone and tetrahydrofuran (THF) were used as received. 2-amino benzyl alcohol was recrystalized from hexand and toluene. All other reagents were used as received. The catalyst, [Rh(ligand)]BF_4, were prepared according to literature methods.[1] All reactions were monitored using thin layer chromatography (TLC) or gas chromatography. Thin layer chromatography was performed using Analtech, silica gel-GF, 250 microns, glassed-back plates and visualized by using ultraviolet (UV) light and iodine. Gas chromatography was done using a Hewlett Packard 5890A Gas Chromatograph. Products were purified using column chromatography with 70-230 mesh silica gel (Merck, 60 grade) and specified proportions of hexane and ethyl acetate as the mobile phase. Infrared (IR) spectra were obtained using a Thermo Electron IR100 equipped with an ATR device. Nuclear Magnetic Resonance spectra, ^1H and ^{13}C, were obtained using a Bruker Avance DPX-300 NMR Spectrometer. NMR spectra were taken using $CDCl_3$ as the solvent and TMS as the reference.

Preparations of Substrates:

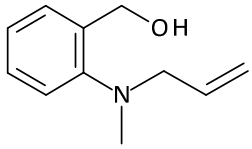
A. 2-(methylamino)benzenemethanol (KAW-I-039)



A 250-mL round bottom flask equipped with a dropping funnel was charged with lithium aluminum hydride (1.5781 g, 0.04158 mol). The flask was cooled to 0 °C and THF (30 mL) was

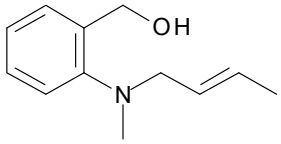
added via syringe into the dropping funnel then drop-wise into the flask. An Erlenmeyer flask was charged with a dark purple solution of *n*-methylanthranilic acid (3.1495 g, 0.02084 mol) and THF (30 mL). The *N*-methylanthranilic acid solution was added to the dropping funnel, and was added drop-wise to the 0 °C reaction mixture over 40 minutes. The reaction fizzed and turned blue-green. The reaction was warmed to room temperature and THF (20 mL) was added. The reaction was heated to reflux overnight then cooled to 0°C and diluted with ether (40 mL). Water (1.58 mL), 10% sodium hydroxide (2.4 mL), and water (4.75 mL) were added slowly. The reaction was warmed to room temperature, stirred 15 minutes and anhydrous magnesium sulfate (approximately 1.5 g, 0.12 mol) was added. After stirring for 15 minutes, the reaction was filtered through celite with ether (100 mL). The filtrate was washed sequentially with 10% sodium hydroxide (2x30 mL), water (30 mL), and brine (40 mL), and then dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product that was purified by column chromatography using hexane: ethyl acetate (90:10). This yielded the pale yellow oil title compound (2.3535 g, 0.01716 mol, 82%). IR (neat, cm^{-1}): 3399.9, 2869.5, 2813.3, 1606.8, 1585.7, 1512.4, 1456.3, 1308.3, 1166.3, 989.9, 745.5. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.25 (m, 1H, phenyl H), 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H, phenyl H), 6.64 (m, 2H, phenyl H), 4.61 (s, 2H, C**H$_2$**OH), 2.85 (s, 3H, C**H$_3$**NH). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 148.5 (phenyl C), 129.7 (phenyl C), 128.9 (phenyl C), 124.3 (phenyl C), 116.4 (phenyl C), 110.1 (phenyl C), 64.69 (**C**H_2OH), 30.3 (**C**H_3NH).

B. 2-[(methyl)(2-propen-1-yl)amino]benzenemethanol (KAW-I-040)

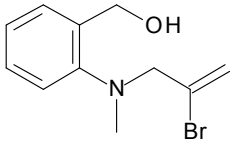


A 50-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.4481 g, 3.337 mmol) and acetonitrile (12 mL). Potassium carbonate (0.9307 g, 6.734 mmol) was added and a condenser attached. Allyl bromide (0.306 mL, 3.54 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (3 mL). The reaction was refluxed overnight and the color of the solution changed from clear to brown. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded the title compound as a pale yellow oil (0.2535 g, 1.430 mmol, 42.5%). IR (neat, cm^{-1}): 3397.80, 3072.00, 2846.34, 2793.03, 1643.56, 1490.03, 1451.16, 1026.61, 917.55, 763.73, 725.24. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.26 (m, 1H, phenyl H), 7.21 (m, 2H, phenyl H), 7.12 (m, 1H, phenyl H), 5.88 (ddt, *J* = 16.6, 10.2, 6.5 Hz, 1H, C**H**=CH_2), 5.46 (s, 1H, O**H**), 5.21 (m, 2H, CH=C**H_2**), 4.81 (s, 2H, C**H_2**OH), 3.54 (dt, *J*= 6.5, 1.2 Hz, 2H, C**H_2**CH), 2.69 (s, 3H, C**H_3**N). ^{13}C NMR experiment KAW-I-087 (75 MHz, $CDCl_3$ δ): 151.3 (phenyl C), 135.78 (phenyl C), 134.40(alkene C), 128.52 (phenyl C), 128.11 (phenyl C), 124.71 (phenyl C), 121.46 (phenyl C), 118.46 (alkene C), 64.91 (**C**H_2OH), 64.10 (N**C**H_2CH=CH_2), 41.54 (**C**H_3NH).

C. 2-[(methyl)(2-buten-1-yl)amino]benzenemethanol (KAW-I-044)



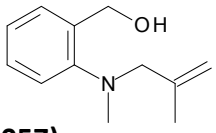
A 100-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.5061 g, 3.670 mmol) and acetonitrile (25 mL). Potassium carbonate (1.0289g, 7.4444 mmol) was added and a condenser attached. Crotyl bromide (0.456 mL, 4.43 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (5 mL). The reaction was refluxed overnight and the color of the solution changed from colorless to dark yellow. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was made basic to about pH 9. The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded a mixture of the cis and trans isomers of the title compound as a pale yellow oil (0.5337 g, 2.790 mmol, 76%). ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.26 (m, 1H, phenyl H), 7.20 (m, 1H, phenyl H), 7.14 (m, 2H, phenyl H), 5.77 (s, 1H, CH_2O**H**), 5.63 (m, 1H, CH=C**H**CH_3), 5.54 (m, 1H, C**H**=$CHCH_3$), 4.81 (s, 2H, C**H$_2$**OH), 3.44 (d, *J* = 6.5 Hz, 2H, C**H$_2$**CH=CH), 2.66 (s, 3H, C**H$_3$**N), 1.71 (m, 3H, CH=CHC**H$_3$**).



D. 2-[(methyl)(2-bromo-2-propen-1-yl)amino]benzenemethanol (KAW-I-049)

A 50-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.2771 g, 2.020 mmol) and acetonitrile (15 mL). Potassium carbonate (0.5602 g, 4.053 mmol) was added and a condenser attached. 2,3-Dibromopropene (.4925 g, 2.464 mmol) was added to a test

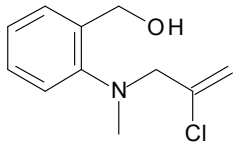
tube and dissolved with acetonitrile (2 mL). The solution was added to the reaction flask under nitrogen flush. The test tube was rinsed and transferred with acetonitrile (3x1 mL). The reaction was refluxed overnight and the color of the solution changed from colorless to pinkish brown. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was made basic to about pH 9. The solution was extracted with ether (3x30 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded the pale yellow-orange oil title compound (0.3807 g, 1.762 mmol, 87.2%). IR (neat, cm^{-1}): 3378.12, 2950.74, 2851.16, 2798.38, 1629.63, 1598.84, 1490.53, 1451.29, 1233.38, 1172.53, 1086.11, 1023.58, 939.91, 897.26, 764.86. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.26 (m, 2H, phenyl H), 7.18 (m, 1H, phenyl H), 7.13 (m, 1H, phenyl H), 5.93 (dt, *J*= 1.76, 1.18 Hz, 1H, BrC=C**H$_2$**), 5.67 (d, *J*= 1.76, 1H, BrC=C**H$_2$**), 4.81 (s, 2H, C**H$_2$**OH), 4.36 (s, 1H, CH_2O**H**), 3.73 (s, 2H, **CH$_2$**BrC=CH_2), 2.68 (s, 3H, C**H$_3$**N). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 151.1 (phenyl C), 136.27 (phenyl C), 130.78 (phenyl C), 129.18 (phenyl C), 128.51 (phenyl C), 125.07 (phenyl C), 121.45 (alkene C), 119.92 (alkene C), 65.31 (N**C**H_2CBr=CH_2), 64.10 (**C**H_2OH), 41.59 (**C**H_3NH).



E. 2-[(methyl)(2-methyl-2-propen-1-yl)amino]benzenemethanol (KAW-I-057)

A 25-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.3578 g, 2.609 mmol) and acetonitrile (7 mL). Potassium carbonate (0.7224 g, 5.227 mmol) was added and a condenser attached. 2-methyl-3-chloropropene (0.306 mL, 3.13 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (6 mL). The reaction was

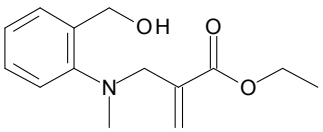
refluxed overnight and the color of the solution changed from colorless to pinkish purple. Sodium iodide (0.5875 g, 3.917 mmol) was added to the reaction and was allowed to reflux overnight again. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was made basic to about pH 9. The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded the title compound as a beige oil (.4439 g, 2.321 mmol, 89%). IR (neat, cm^{-1}): 3361.48, 3072.03, 2942.21, 2844.68, 2793.94, 1489.97, 1450.14, 1025.64, 895.87, 761.81, 725.81. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.27 (m, 1H, phenyl H), 7.22 (m, 2H, phenyl H), 7.11 (m, 1H, phenyl H), 5.06 (s, 1H, $CH_2O\mathbf{H}$), 5.01 (s, 1H, $CH_2C(CH_3)=C\mathbf{H_2}$), 4.96 (s, 1H, $CH_2C(CH_3)=C\mathbf{H_2}$), 4.82 (s, 2H, $C\mathbf{H_2}OH$), 3.44 (s, 2H, $C\mathbf{H_2}C(CH_3)=CH_2$), 2.61 (s, 3H, $C\mathbf{H_3}N$), 1.81 (s, 3H, $CH_2C\mathbf{H_3}C=CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 152.05 (phenyl C), 141.86 (alkene C), 135.69 (phenyl C), 128.55 (phenyl C), 128.26 (phenyl C), 124.63 (phenyl C), 121.25 (phenyl C), 114.20 (alkene C), 64.62 ($N\mathbf{C}H_2CCH_3=CH_2$), 64.13 ($\mathbf{C}H_2OH$), 41.56 ($\mathbf{C}H_3NH$).



F. 2-[(methyl)(2-chloro-2-propen-1-yl)amino]benzenemethanol (KAW-I-073)

A 25-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.2180 g, 1.589 mmol) and acetonitrile (5 mL). Potassium carbonate (.4428 g, 3.204 mmol) was added and a condenser attached. 2,3-dichloropropene bromide (0.175 mL, 1.900 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (5 mL). The reaction was refluxed overnight and the color of the solution changed from clear to dark yellow. The reaction

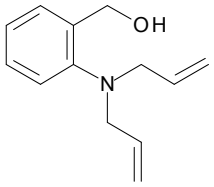
solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was made basic to about pH 9. The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (98:2). This yielded the title compound as a beige oil (0.3063 g, 1.447 mmol, 91%). IR (neat, cm^{-1}): 3389.44, 2950.96, 2851.20, 1634.88, 1490.86, 1451.38, 1088.79, 1024.16, 941.50, 891.31, 765.49. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.28 (m, 2H, phenyl H), 7.19 (m, 1H, phenyl H), 7.14 (m, 1H, phenyl H), 5.47 (q, *J*= 1.13 Hz, 1H, $CH_2CCl=C\mathbf{H_2}$), 5.41 (d, *J*= 1.13, 1H, $CH_2CCl=C\mathbf{H_2}$), 4.80 (s, 2H, $C\mathbf{H_2}OH$), 4.48 (s, 1H, $CH_2O\mathbf{H}$), 3.69 (s, 2H, $C\mathbf{H_2}CCl=CH_2$) , 2.69 (s, 3H, $C\mathbf{H_3}N$). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 151.13 (phenyl C), 138.98 (phenyl C), 136.28 (phenyl C), 129.12 (phenyl C), 128.49 (phenyl C), 125.11 (alkene C), 121.47 (phenyl C), 115.63 (alkene C), 64.23 ($N\mathbf{C}H_2CCl=CH_2$), 63.53 ($\mathbf{C}H_2OH$), 41.58 ($\mathbf{C}H_3NH$).



G. 2-[(methyl)(2-ethylpropanoate-2-propen-1-yl)amino]benzenemethanol (KAW-I-065)

A 50-mL round bottom flask was charged with 2-(methylamino)benzenemethanol (0.2062g, 1.503 mmol) and acetonitrile (10 mL). Potassium carbonate (.4155 g, 3.006 mmol) was added and a condenser attached. Ethyl 2-(bromomethyl) acrylate (0.249 mL, 1.803 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (5 mL). The reaction was refluxed overnight and the color of the solution changed from clear to milky white. More ethyl 2-(bromomethyl) acrylate (0.2915 mL, 2.111 mmol) and sodium iodine (0.2262 g, 1.509 mmol) was added. The color of the solution turned yellow. The reaction was refluxed overnight and

the color of the solution changed from yellow to milky yellow. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). The solution was made basic to about pH 9. The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x20 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded the title compound as a beige oil (0.2611 g, 1.047 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.29 (m, 1H, phenyl H), 7.22 (ddd, *J*= 7.55, 4.32, 1.59 Hz, 1H, phenyl H), 7.12 (m, 1H, phenyl H), 6.34 (d, *J*= 1.32 Hz, 1H, $CH_2C(COOCH_2CH_3)=C\mathbf{H_2}$), 5.78 (q, *J*= 1.32, 1H, $CH_2C(COOCH_2CH_3)=C\mathbf{H_2}$), 4.73 (s, 2H, $C\mathbf{H_2}OH$), 4.64 (s, 1H, $CH_2O\mathbf{H}$), 4.22 (q, *J*= 7.13 Hz, 2H, $CH_2C(COO\mathbf{CH_2}CH_3)=CH_2$) , 3.78 (s, 2H, $C\mathbf{H_2}C(COOCH_2CH_3)=CH_2$), 2.65 (s, 3H, $C\mathbf{H_3}N$), 1.29 (t, *J*= 7.13 Hz, 3H, $CH_2C(COOCH_2C\mathbf{H_3})=CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 166.65 (**C**=O), 151.60 (phenyl C), 136.86 (phenyl C), 136.55 (phenyl C), 129.08 (alkene C), 128.39 (alkene C), 128.24 (phenyl C), 124.96 (phenyl C), 121.60 (phenyl C), 64.13 ($\mathbf{C}H_2OH$), 61.11 ($N\mathbf{C}H_2C(COOCH_2CH_3)=CH_2$), 57.88 ($COO\mathbf{C}H_2CH_3$), 42.41 ($\mathbf{C}H_3NH$), 14.14 ($(COOCH_2\mathbf{C}H_3$).

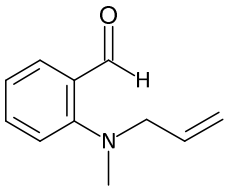


H. 2-[(diallyl)amino]benzenemethanol (KAW-I-004)

A 250-mL round bottom flask was charged with 2-aminobenzylalcohol (1.5448g, 12.54 mmol) and acetonitrile (40 mL). Potassium carbonate (5.2240 g, 37.80 mmol) followed by sodium iodide (4.7482 g, 31.68 mmol). Allyl bromide (3.4 mL, 39.06 mmol) was added via syringe and afterwards the condenser was rinsed with acetonitrile (5 mL). The reaction was left at room temperature over the weekend and the color of the solution changed from golden to

red-brown. The reaction solution was transferred with ether (3x5 mL) then with water (10 mL). Sodium bicarbonate (20 mL) was added to the solution. The solution was extracted with ether (3x20 mL). The ether extract was washed with brine (3x30 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and purified using column chromatography in hexane: ethyl acetate (95:5). This yielded the title compound as a yellow oil (2.2200 g, 10.92 mmol, 87%). IR (neat, cm^{-1}): 3392.21, 3074.25, 2978.30, 2821.96, 1641.81, 1598.44, 1593.78, 1488.37, 1451.89, 1417.19, 1209.71, 1025.01, 990.81, 917.39. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.25 (m, 1H, phenyl H), 7.17 (m, 2H, phenyl H), 7.09 (m, 1H, phenyl H), 5.82 (ddt, *J*= 17.1, 10.3, 6.5 Hz, 2H, C**H**=CH_2), 5.27 9 (s, 1H, **OH**), 5.17 (m, 4H, CH=C**H$_2$**), 4.80 (s, 2H, C**H$_2$**OH), 3.61 (d *J*= 6.5 Hz, 4H, C**H$_2$**CH=CH_2). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 148.94 (phenyl C), 136.66 (phenyl C), 133.97 (alkene 2C), 128.49 (phenyl C), 127.72 (phenyl C), 124.91 (phenyl C), 123.25 (phenyl C), 118.60 (alkene 2C), 64.76 (**C**H_2OH), 56.63 (N**C**H_2CH=CH_2, 2C).

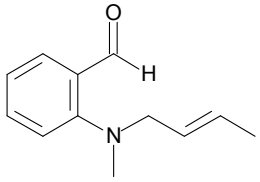
I. 2-[(methyl)(2-propen-1-yl)amino]benzaldehyde (KAW-I-041)



A 25-mL round bottom flask was charged with 2-[(methyl)(2-propen-1-yl)amino]benzenemethanol (0.2365 g, 1.330 mmol) and methylene chloride (7 mL). TEMPO (0.0417 g, 0.2660 mmol) and iodobenzene diactetate (0.5141 g, 1.596 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to red-brown. The solution transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (25 mL). The solution was extracted with ether (3x15 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20

mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded the title compound as bright yellow oil (0.1189 g, 0.6786 mmol, 51%). IR (neat, cm^{-1}): 3070.29, 2981.32, 2853.47, 2789.32, 1680.99, 1595.12, 1481.78, 1452.21, 1280.49, 1180.26, 921.90, 830.11, 758.96. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.27 (s, 1H, C**H**O), 7.78 (dd, *J*= 7.7, 1.7 Hz, 1H, phenyl H), 7.48 (ddd, *J*= 8.3, 7,2, 1.7 Hz, 1H, phenyl H), 7.10 (m, 2H, phenyl H), 5.87 (ddt, *J*= 17.1, 10.2, 5.9 Hz, 1H, C**H**=CH_2), 5.26 (m, 2H, CH=C**H$_2$**), 3.73 (d, *J*= 5.9 Hz, 2H, C**H$_2$**CH=CH_2), 2.86 (s, 3H, C**H$_3$**N).

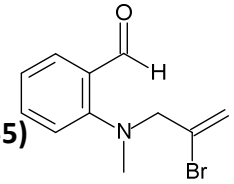
J. 2-[(methyl)(2-buten-1-yl)amino]benzaldehyde (KAW-I-046)



A 50-mL round bottom flask was charged with 2-[(methyl)(2-buten-1-yl) amino]benzenemethanol (0.5184 g, 2.711 mmol) and methylene chloride (15 mL). TEMPO (0.0855 g, 0.547 mmol) and iodobenzene diactetate (1.0515 g, 3.2646 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to dark brown. The solution transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (25 mL). The solution was extracted with ether (3x15 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded a mixture of *cis* and *trans* title compound as a bright yellow oil (0.3005 g, 1.588 mmol, 59%). IR (neat, cm^{-1}): 2938.61, 2852.92, 2724.50, 1681.93, 1594.71, 1481.62, 1451.17, 1276.27, 1188.83,

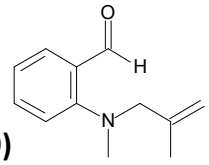
965.24, 934.58, 830.65, 760.73. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.25 (s, 1H, C**H**O), 7.79 (dd, *J*= 7.7, 1.8 Hz, 1H, phenyl H), 7.47 (m, 1H, phenyl H), 7.09 (m, 2H, phenyl H), 5.66 (m, 1H, C**H**=CH_2), 5.58 (m, 1H, CH=C**H**CH_3), 3.66 (d, *J*= 6.0 Hz, 2H, C**H$_2$**CH=$CHCH_3$), 2.83 (s, 3H, C**H$_3$**N), 1.73 (dq, *J*= 6.0, 1.24 Hz, 3H, CH=CHC**H$_3$**). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.48 (H**C**=O), 155.69 (phenyl C), 134.50 (phenyl C), 130.10 (phenyl C), 129.34 (alkene C), 127.77 (phenyl C), 126.83 (alkene C), 121.01 (phenyl C), 118.86 (phenyl C), 61.63 (N**C**H_2CH=$CHCH_3$), 42.41 (**C**H_3NH), 14.14 (NCH_2CH=CH**C**H_3).

K. 2-[(methyl)(2-bromo-2-propen-1-yl)amino]benzaldehyde (KAW-I-055)



A 25-mL round bottom flask was charged with 2-[(methyl)(2-bromo-2-propen-1-yl)amino]benzenemethanol (0.2143 g, 0.9919 mmol) and methylene chloride (5 mL). TEMPO (0.0318 g, 0.204 mmol) and iodobenzene diactetate (0.3892 g, 1.208 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to dark orange. The solution transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (15 mL). The solution was extracted with ether (3x15 mL). The ether extract was washed with sodium thiosulfate (3x15 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded the title compound as a bright yellow oil (0.1973 g, 0.9217 mmol, 73%). IR (neat, cm^{-1}): 2853.49, 2723.89, 1680.47, 1594.57, 1482.52, 1452.49, 1278.00, 1183.38, 1082.00, 898.55, 830.24, 759.80. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.33 (s, 1H, C**H**O), 7.79 (d, *J*= 1.8 Hz, 1H, phenyl H), 7.50 (ddd, *J*= 8.3, 7.2, 1.8 Hz, 1H, phenyl H), 7.12 (m, 2H, phenyl H), 5.91 (q, *J*= 1.7 Hz, 1H, CBr=C**H$_2$**),

5.65 (dt, *J*= 1.7, 0.94 Hz, 1H, CBr=C**H$_2$**), 3.99 (s, 2H, C**H$_2$**CBr=CH$_2$), 2.93 (s, 3H, C**H$_3$**N). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.33 (H**C**=O), 154.45 (phenyl C), 134.68 (phenyl C), 130.61 (phenyl C), 129.89 (alkene C), 127.92 (phenyl C), 121.89 (phenyl C), 119.46 (phenyl C), 118.82 (alkene C), 65.58 (N**C**H$_2$CBr=CH$_2$), 41.86 (**C**H$_3$NH).

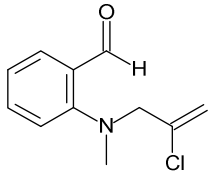


L. 2-[(methyl)(2-methyl-2-propen-1-yl)amino]benzaldehyde (KAW-I-059)

A 50-mL round bottom flask was charged with 2-[(methyl)(2-methyl-2-propen-1-yl)amino]benzenemethanol (0.2646 g, 1.383 mmol) and methylene chloride (8 mL). TEMPO (0.0432 g, 0.276 mmol) and iodobenzene diactetate (0.5350 g, 1.661 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from light orange to red orange. The solution was combined with KAW-I-060. The solution transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (20 mL). The solution was extracted with ether (3x20 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded the title compound as a bright yellow oil (0.3961 g, 2.093 mmol, 89%). IR (neat, cm^{-1}): 3072.53, 2851.41, 2702.67, 1681.42, 1657.41, 1595.11, 1483.15, 1446.44, 1283.75, 1183.63, 898.85, 829.99, 758.99. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.28 (s, 1H, C**H**O), 7.77 (dd, *J*= 7.7, 1.8 Hz, 1H, phenyl H), 7.47 (ddd, *J*= 8.3, 7.2, 1.8 Hz, 1H, phenyl H), 7.10 (dd, *J*= 8.3, 0.79 Hz, 1H, phenyl H), 7.02 (m, 1H, phenyl H), 5.03 (s, 1H, CCH$_3$=C**H$_2$**), 4.96 (s,1H, CCH$_3$=C**H$_2$**), 3.67 (s, 2H, C**H$_2$**CCH$_3$=CH$_2$), 2.84 (s, 3H, C**H$_3$**N),

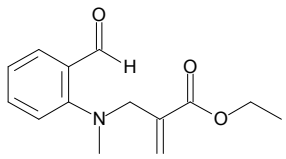
1.72 (s, 3H, CC**H$_3$**=CH$_2$). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.46 (H**C**=O), 155.96 (phenyl C), 141.46 (phenyl C), 134.57 (phenyl C), 129.89 (phenyl C), 127.58 (alkene C), 120.99 (phenyl C), 118.72 (phenyl C), 112.87 (alkene C), 64.64 (N**C**H$_2$CCH$_3$=CH$_2$), 41.95 (**C**H$_3$NH), 20.35 (NCH$_2$C**C**H$_3$=CH$_2$).

M. 2-[(methyl)(2-chloro-2-propen-1-yl)amino]benzaldehyde (KAW-I-074)



A 25-mL round bottom flask was charged with 2-[(methyl)(2-chloro-2-propen-1-yl)amino]benzenemethanol (0.2578 g, 1.218 mmol) and methylene chloride (7 mL). TEMPO (0.0381 g, 0.244 mmol) and iodobenzene diactetate (0.4715 g, 1.475 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to red-orange. The solution transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (20 mL). The solution was extracted with ether (3x15 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded the title compound as bright yellow oil (0.2280 g, 1.088 mmol, 89%). IR (neat, cm^{-1}): 2854.95, 2709.76, 1680.95, 1595.10, 1482.66, 1452.94, 1281.24, 1184.61, 1157.66, 830.31, 759.80. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.31 (s, 1H, C**H**O), 7.78 (dd, *J*= 7.7, 1.8 Hz, 1H, phenyl H), 7.50 (ddd, *J*= 8.3, 7.2, 1.8 Hz, 1H, phenyl H), 7.10 (m, 2H, phenyl H), 5.45 (q, *J*= 1.5 Hz, 1H, CCl=C**H$_2$**), 5.40 (dt, *J*= 1.4, 0.78 Hz, 1H, CBr=C**H$_2$**), 3.93 (s, 2H, C**H$_2$**CCl=CH$_2$), 2.93 (s, 3H, C**H$_3$**N). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.92 (H**C**=O), 154.58 (phenyl C), 138.45(phenyl C), 134.68(phenyl C), 130.63

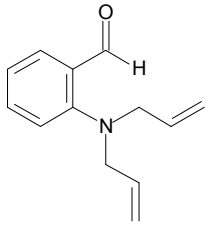
(phenyl C), 127.91 (alkene C), 121.87 (phenyl C), 119.39 (phenyl C), 114.53 (alkene C), 64.12 (N**C**H_2CBr=CH_2), 41.55 (**C**H_3NH).



N. 2-[(methyl)(2-ethylpropan-oate-2-propen-1-yl)amino]benzaldehyde (KAW-I-067)

A 25-mL round bottom flask was charged with 2-[(methyl)(2-ethylpropanoate-2-propen-1-yl)amino]benzenemethanol (0.1737 g, 0.6968 mmol) and methylene chloride (7 mL). TEMPO (0.0225 g, 0.144 mmol) and iodobenzene diactetate (0.2700 g, 0.8383 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to dark orange. The solution transferred with ether (3x5 mL). The solution was extracted with ether (3x20 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (98:2). This yielded the title compound as a bright yellow oil (0.1524 g, 0.6163 mmol, 88%). IR (neat, cm^{-1}): 2982.20, 2855.33, 2699.54, 1712.90, 1681.42, 1595.56, 1483.12, 1292.68, 1147.89, 1110.71, 1084.68, 760.88. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.23 (s, 1H, C**H**O), 7.78 (dd, *J*= 7.7, 1.8 Hz, 1H, phenyl H), 7.47 (ddd, *J*= 8.2, 7.2, 1.8 Hz, 1H, phenyl H), 7.11 (d, *J*= 8.2, 1H, phenyl H), 7.05 (t, *J*= 7.2 Hz, 1H, phenyl H), 6.37 (q, *J*= 1.4 Hz, 1H, C(-OCH_2CH_3)=C**H_2**), 5.83 (q, *J*= 1.4 Hz, 1H, C(-OCH_2CH_3)=C**H_2**), 4.17 (q, *J*= 7.1 Hz, 2H, C(-OC**H_2**CH_3)=CH_2), 4.05 (s, 2H, C**H_2**C(-OCH_2CH_3)=CH_2), 2.88 (s, 3H, C**H_3**N), 1.25 (t, *J*= 7.1 Hz, 3H, C(-OCH_2C**H_3**)=CH_2). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.92 (H**C**=O), 166.27 (CH_2C(**C**OOCH_2CH_3)=CH_2), 155.28 (phenyl C), 136.31

(phenyl C), 134.63 (phenyl C), 130.25 (phenyl C), 127.85 (alkene C), 126.36 (phenyl C), 121.46 (phenyl C), 119.08 (alkene C), 64.12 ($NCH_2C(COO\mathbf{C}H_2CH_3)=CH_2$), 58.77 ($N\mathbf{C}H_2C(COOCH_2CH_3)=CH_2$), 41.99 ($\mathbf{C}H_3NH$), 14.11 (($NCH_2C(COOCH_2\mathbf{C}H_3)=CH_2$).



O. 2-[(diallyl)amino]benzaldehyde (KAW-I-003)

A 100-mL round bottom flask was charged with 2-[(diallyl)amino]benzenemethanol (0.7270 g, 3.576 mmol) and methylene chloride (18 mL). TEMPO (0.1111 g, 0.7110 mmol) and iodobenzene diactetate (1.4037 g, 4.358 mmol) were added to the flask. The reaction was stirred at room temperature overnight; and the color of the solution changed from orange to brown-orange. The solution was transferred with ether (3x5 mL) and made slightly basic with saturated sodium bicarbonate (20 mL). The solution was extracted with ether (3x20 mL). The ether extract was washed with sodium thiosulfate (3x20 mL) and brine (3x20 mL) sequentially and dried over sodium sulfate. The solvent was removed *in vacuo.* The crude product was purified using column chromatography in hexane: ethyl acetate (99:1). This yielded the title compound as bright yellow oil (0.3997g, 1.985 mmol, 55%). IR (neat, cm^{-1}): 3075.10, 2979.91, 2836.65, 2723.98, 1683.08, 1594.90, 1480.92, 1280.55, 920.18, 762.00. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 10.34 (s, 1H, C**H**O), 7.82 (dd, *J*= 6.5, 1.3 Hz, 1H, phenyl H), 7.47 (m, 1H, phenyl H), 7.09 (m, 2H, phenyl H), 5.85 (m, 2H, $C\mathbf{H}=CH_2$), 5.20 (m, 4H, $CH=C\mathbf{H_2}$), 3.79 (dd *J*= 5.9, 1.1 Hz, 4H, $C\mathbf{H_2}CH=CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$ δ): 191.64 (H**C**=O), 154.25 (phenyl C), 134.25 (phenyl C), 133.88 (alkene 2C), 129.46 (phenyl C), 129.28 (phenyl C), 122.11 (phenyl C), 121.25 (phenyl C), 118.13 (alkene 2C), 57.30 ($N\mathbf{C}H_2CH=CH_2$).

Hydroacylation reactions:

A. [Rh(dppe)]BF_4 (KAW-I-062):

A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0235 g, 0.0628 mmol) and 1,2-bis(diphenylphosphanyl)ethane, dppe, (0.0251 g, 0.0628 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (6.3 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[dppe]BF_4 was then used for hydroacylation experiments.

B. [Rh(dppm)]BF_4 (KAW-II-001):

A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0230 g, 0.0615 mmol) and 1,2-bis(diphenylphosphanyl)methane, dppm, (0.0231 g, 0.0601 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (6.15 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[dppm]BF_4 was then used for hydroacylation experiments.

C. [Rh(dppp)]BF_4 (KAW-II-006):

A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0206 g, 0.0551 mmol) and 1,2-bis(diphenylphosphanyl)propane, dppp, (0.0230 g, 0.0558 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (5.51 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[dppp]BF_4 was then used for hydroacylation experiments.

D. [Rh(dppb)]BF_4 (KAW-II-014):

A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0175 g, 0.0467 mmol) and 1,2-bis(diphenylphosphanyl)butane, dppb, (0.0201g, 0.0471 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (4.70 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[dppb]BF_4 was then used for hydroacylation experiments.

E. [Rh(DPE-Phos)]BF_4 (KAW-II-024):

A 10-mL Schlenk flask was charged with pre-catalyst [Rh$(NBD)_2$]BF_4 (0.0189 g, 0.0505 mmol) and (Oxydi-2,1-phenylene)bis(diphenylphosphine), DPE-Phos, (0.0268g, 0.0498 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (5.00 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[DPE-Phos]BF_4 was then used for hydroacylation experiments.

F. [Rh(dfppe)]BF_4 (KAW-II-028):

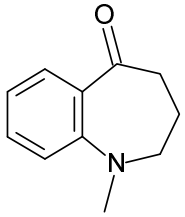
A 10-mL Schlenk flask was charged with pre-catalyst [Rh$(NBD)_2$]BF_4 (0.0199g, 0.0532 mmol) and 1,2-Bis[bis(pentafluorophenyl)phosphino]ethane, dfppe, (0.0399g, 0.0526 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (5.25 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of Rh[dfppe]BF_4 was then used for hydroacylation experiments.

G. [Rh{(R, R)-Me-DuPhos}]BF_4 (KAW-II-037):

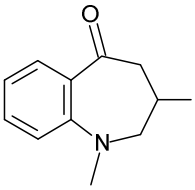
A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0187g, 0.0500 mmol) and (−)-1,2-Bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene, (R, R)-Me-DuPhos, (0.0153g, 0.0499 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (5.00 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of [Rh{(R, R)-Me-DuPhos}]$BF_4$was then used for hydroacylation experiments.

H. [Rh{P(PhOMe)$_3$}]BF_4 (KAW-II-037):

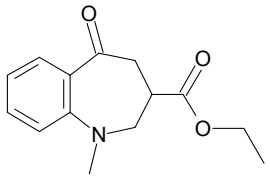
A 10-mL Schlenk flask was charged with pre-catalyst [Rh(NBD)$_2$]BF_4 (0.0131g, 0.0350 mmol) and (−)-1,2-Bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene, P(PhOMe)$_3$, (0.0251g, 0.0712 mmol). The flask was evacuated and backfilled with argon three times. Dry, degassed acetone (3.50 mL, 0.01M substrate) was added via syringe to the flask to yield a bright orange solution. Hydrogen gas was bubbled through the solution (via needle) for 5 minutes, during this time, the solution became pale orange. The solution was freeze-thawed degassed three times to remove the hydrogen then backfilled with argon. The solution of [Rh{P(PhOMe)$_3$}]BF_4 was then used for hydroacylation experiments.

I. 1,2,3,4-tetrahydro-1-methyl-5H-1-benzazepin-5-one (KAW-I-064): 

A 10-mL Schlenk flask fitted with a condenser was charged with 2-[(2-propen-1-yl)(methyl)amino]benzaldehyde(0.0764 g, 0.4360 mmol). The flask was evacuated and backfilled with argon three times. Degassed acetone (4.4 mL, 0.1M substrate) was added to the flask via syringe. The $[Rh(dppe)]BF_4$ (2.18 mL, 0.01M in acetone, 0.0218 mmol) was added to the flask via syringe. The solution went from golden yellow to orange stirring overnight. The solution was concentrated over celite using *in vacuo* and purified by column chromatography in hexane: ethyl acetate (99:1). This title compound as a yellow oil (0.0709 g, 0.4047 mmol, 93%). The product turns solid once placed in refrigerator. IR (neat, cm^{-1}): 2928.51, 2862.02, 1661.72, 1595.25, 1488.58, 1441.37, 1339.77, 1296.82, 1162.99, 947.79, 750.64. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.75 (dd, *J*= 7.8, 1.8 Hz, 1H, phenyl H), 7.34 (ddd, *J*= 8.6, 7.1, 1.8 Hz, 1H, phenyl H), 6.88 (d, *J*= 8.6 Hz, 1H, phenyl H), 6.82 (ddd, *J*= 7.8, 7.1, 1.0 Hz, 1H, phenyl H), 3.24 (t, *J*= 6.7 Hz, 2H, C=OC**H$_2$**), 3.12 (s, 3H, C**H$_3$**N), 2.78 (t, *J*= 7.1 Hz, 2H, C**H$_2$**N), 2.24 (tt, *J*= 7.1, 6.75 Hz, 2H, CH_2C**H$_2$**CH_2). ^{13}C NMR (75 MHz, $CHCl_3$ δ): 203.2 (ketone C), 154.2 (phenyl C), 132.5 (phenyl C), 129.8 (phenyl C), 127.00 (phenyl C), 116.0 (phenyl C), 113.8 (phenyl C), 57.3 (C=O**C**H$_2$), 40.9 (CH_2**C**H_2CH_2), 40.1 (**C**H_2N), 31.1 (**C**H_3N).

J. 1,2,3,4-tetrahydro-1,3-dimethyl-5H-1-benzazepin-5-one (KAW-I-061): 

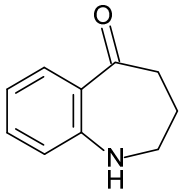
A 10-mL Schlenk flask fitted with a condenser was charged with 2-[(methyl)(2-methyl-2-propen-1-yl)amino]benzaldehyde (0.0875 g, 0.462 mmol). The flask was evacuated and backfilled with argon three times. Degassed acetone (2.4 mL, 0.2M substrate) was added to the flask via syringe. The [Rh(dppe)]BF_4 (2.31 mL, 0.01M in acetone, 0.0231 mmol) was added to the flask via syringe. The solution went from golden yellow to light orange stirring overnight. The solution was concentrated over celite using *in vacuo* and purified by column chromatography in hexane: ethyl acetate (98:2). This title compound as a pale yellow oil (0.0795g, 0.420 mmol, 91%). IR (neat, cm^{-1}): 2957.56, 2870.15, 1661.73, 1595.81, 1489.29, 1442.82, 1353.57, 1298.44, 1196.54, 1164.23, 1112.76, 1004.67, 750.10, 735.17. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.76 (dd, *J*= 7.8, 1.8 Hz, 1H, phenyl H), 7.33 (ddd, *J*= 8.5, 7.0, 1.8 Hz, 1H, phenyl H), 6.87 (d, *J*= 8.5 Hz, 1H, phenyl H), 6.81 (ddd, *J*= 7.8, 7.0, 1.0 Hz, 1H, phenyl H), 3.31 (dd, *J*= 14.2, 6.5 Hz, 1H, C=OC**H$_2$**), 3.14 (s, 3H, C**H$_3$**N), 2.94 (dd, *J*= 14.2, 6.5 Hz, 1H, C=OC**H$_2$**), 2.83(dd, *J*= 10.5, 6.5 Hz, 1H, C**H$_2$**N), 2.63 (tq, *J*= 14.2, 6.5 Hz, 2H, CH_2C**H** (CH_3) CH_2), 2.52 (dd, *J*= 10.5, 6.5 Hz, 1H, C**H$_2$**N), 1.14 (d, *J*= 6.5 Hz, 3H, (CH_2CH (C**H$_3$**) CH_2) . ^{13}C NMR (75 MHz, $CHCl_3$ δ): 201.9 (ketone C), 154.4 (phenyl C), 132.4 (phenyl C), 129.8 (phenyl C), 126.5 (phenyl C), 117.7(phenyl C), 113.3 (phenyl C), 64.4 (C=O**C**H_2), 48.62 (**C**H_3N), 40.9 (**C**H_2N), 38.8 (CH_2**C**H(CH_3)CH_2), 18.7 (CH_2**C**H(CH_3)CH_2).



K. 1,2,3,4-tetrahydro-1-methyl-3-ethylpropanoate-5H-1-benzazepin-5-one (KAW-I-069):

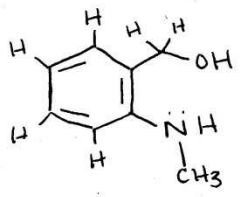
A 10-mL Schlenk flask fitted with a condenser was charged with 2-[(methyl)(2-ethylpropan-oate-2-propen-1-yl)amino]benzaldehyde (0.0629 g, 0.254 mmol). The flask was evacuated and backfilled with argon three times. Degassed acetone (2.55 mL, 0.1M substrate) was added to the flask via syringe. The $[Rh(dppe)]BF_4$ (1.27 mL, 0.01M in acetone, 0.0127 mmol) was added to the flask via syringe. The solution went from golden yellow to light orange stirring overnight. The solution was concentrated over celite using *in vacuo* and purified by column chromatography in hexane: ethyl acetate (98:2). This title compound as a pale yellow oil (0.0282g, 0.114 mmol, 45%). IR (neat, cm^{-1}): 2980.9, 2875.09, 1718.85, 1660.14, 1598.29, 1495.47, 1443.86, 1203.46, 1173.25, 1161.84, 1113.31, 1073.80, 1015.64, 758.14. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.78 (dd, *J*= 7.8, 1.7 Hz, 1H, phenyl H), 7.35 (ddd, *J*= 8.5, 7.0, 1.7 Hz, 1H, phenyl H), 6.86 (m, 2H, phenyl H), 4.24 (q, *J*= 7.2, 1.0 Hz, 2H, OC**H$_2$**CH_3), 4.23 (q, *J*= 7.2, 1.0 Hz, 2H, OC**H$_2$**CH_3), 3.80 (d, *J*= 13.5 Hz, 1H, C=OC**H$_2$**), 3.32 (m, 1H, C**H$_2$**N), 3.20 (m, 2H, C**H$_2$**N, C=OC**H$_2$**), 2.92 (m, 1H, CH_2C**H**(-OCH_2CH_3)CH_2), 1.31 (t, *J*= 7.2 Hz, 3H, OCH_2C**H$_3$**). ^{13}C NMR (75 MHz, $CHCl_3$ δ): 200.2 (ketone C), 173.0 (ester C), 154.3 (phenyl C), 132.8 (phenyl C), 129.9 (phenyl C), 126.2 (phenyl C), 118.3(phenyl C), 113.6 (phenyl C), 61.2 (O**C**H_2CH_3), 59.0 (**C**H_2N), 48.28 (**C**H_3N), 42.8 (C=O**C**H_2), 40.3 (CH_2**C**H(-OCH_2CH_3)CH_2), 14.2 (OCH_2**C**H_3).

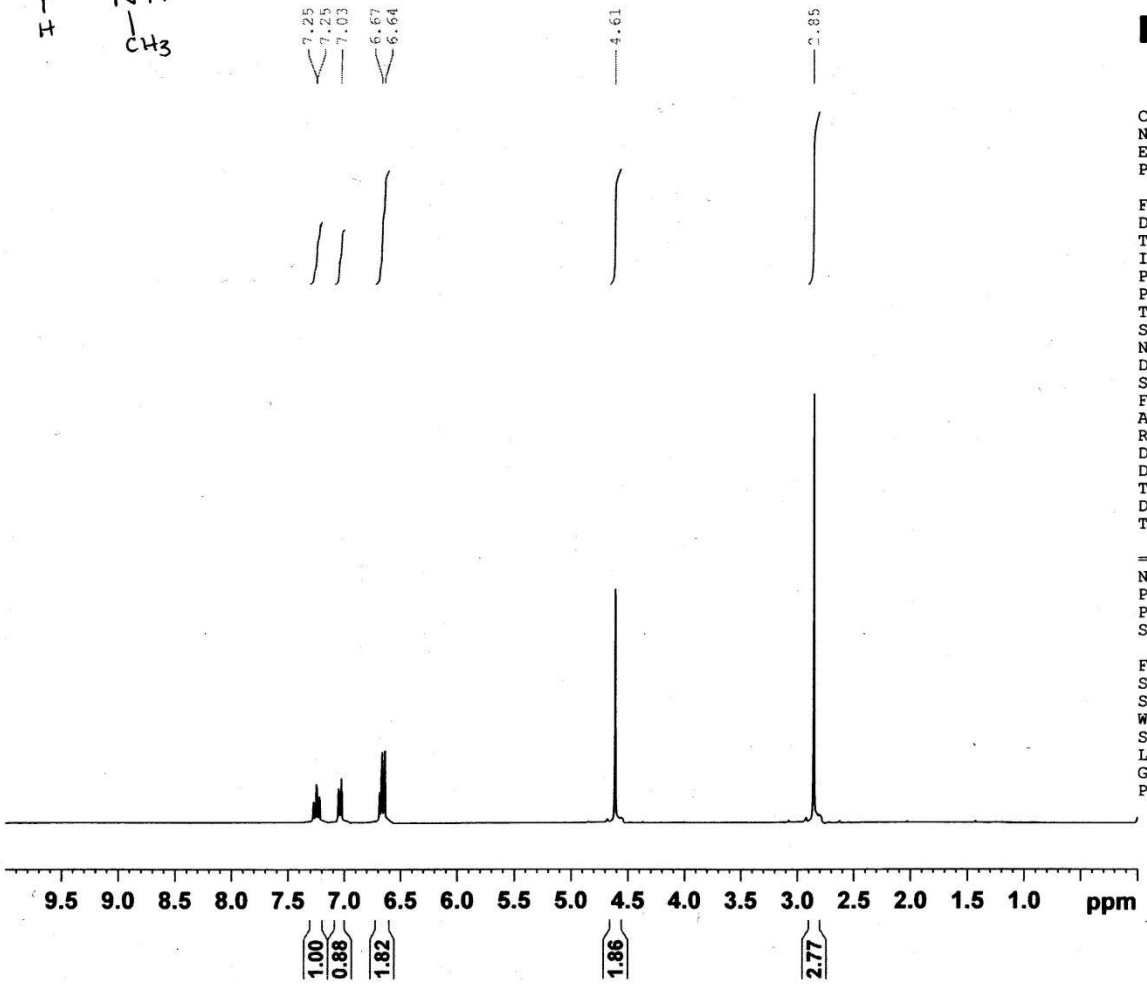
L. 1,2,3,4-tetrahydro-1-benzazepin-5-one (KAW-I-052):



A 10-mL Schlenk flask fitted with a condenser was charged with 2-[diallylamino]benzaldehyde(0.0788 g, 0.391 mmol). The flask was evacuated and backfilled with argon three times. Degassed acetone (3.91 mL, 0.1M substrate) was added to the flask via syringe. The [Rh(dppe)]BF_4 (1.96mL, 0.01M in acetone, 0.0196 mmol) was added to the flask via syringe. The solution went from light orange to a darker orange stirring for 3 hours. After 3 hours 100µL of deionzed water sparged with nitrogen was added and was allowed to stir overnight. The solution was concentrated over celite using *in vacuo* and purified by column chromatography in hexane: ethyl acetate (90:10). This title compound as a pale yellow oil (0.0554 g, 0.344 mmol, 88%). The product turns solid once placed in refrigerator. IR (neat, cm^{-1}): 3385.12, 3369.03, 2925.78, 1648.44, 1597.20, 1479.89, 1333.92, 1295.07, 1231.56, 1154.57, 754.71. ^{1}H NMR (300 MHz, $CDCl_3$ δ): 7.72 (ddd, *J*= 7.9, 1.7, 0.3 Hz, 1H, phenyl H), 7.24 (ddd, *J*= 8.1, 7.0, 1.7 Hz, 1H, phenyl H), 6.82 (ddd, *J*= 7.9, 7.0, 1.0 Hz, 1H, phenyl H), 6.76 (ddd, *J*= 8.1, 1.0, 0.3 Hz, 1H, phenyl H), 4.6 (s, 1H, **NH**), 3.26 (t, *J*= 7.1 Hz, 2H, C**H$_2$**N), 2.82 (t, *J*= 7.1 Hz, 2H, C=OC**H$_2$**), 2.18 (q, *J*= 7.1 Hz, 2H, CH_2C**H$_2$**CH_2). ^{13}C NMR (75 MHz, $CHCl_3$ δ): 202.8 (ketone C), 153.6 (phenyl C), 132.4 (phenyl C), 129.5 (phenyl C), 125.4 (phenyl C), 118.7 (phenyl C), 117.6(phenyl C), 47.96 (C=O**C**H_2), 41.21 (**C**H_2N), 31.42 (CH_2**C**$H_2$$CH_2$).

KAW-i-039

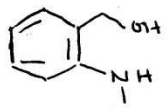


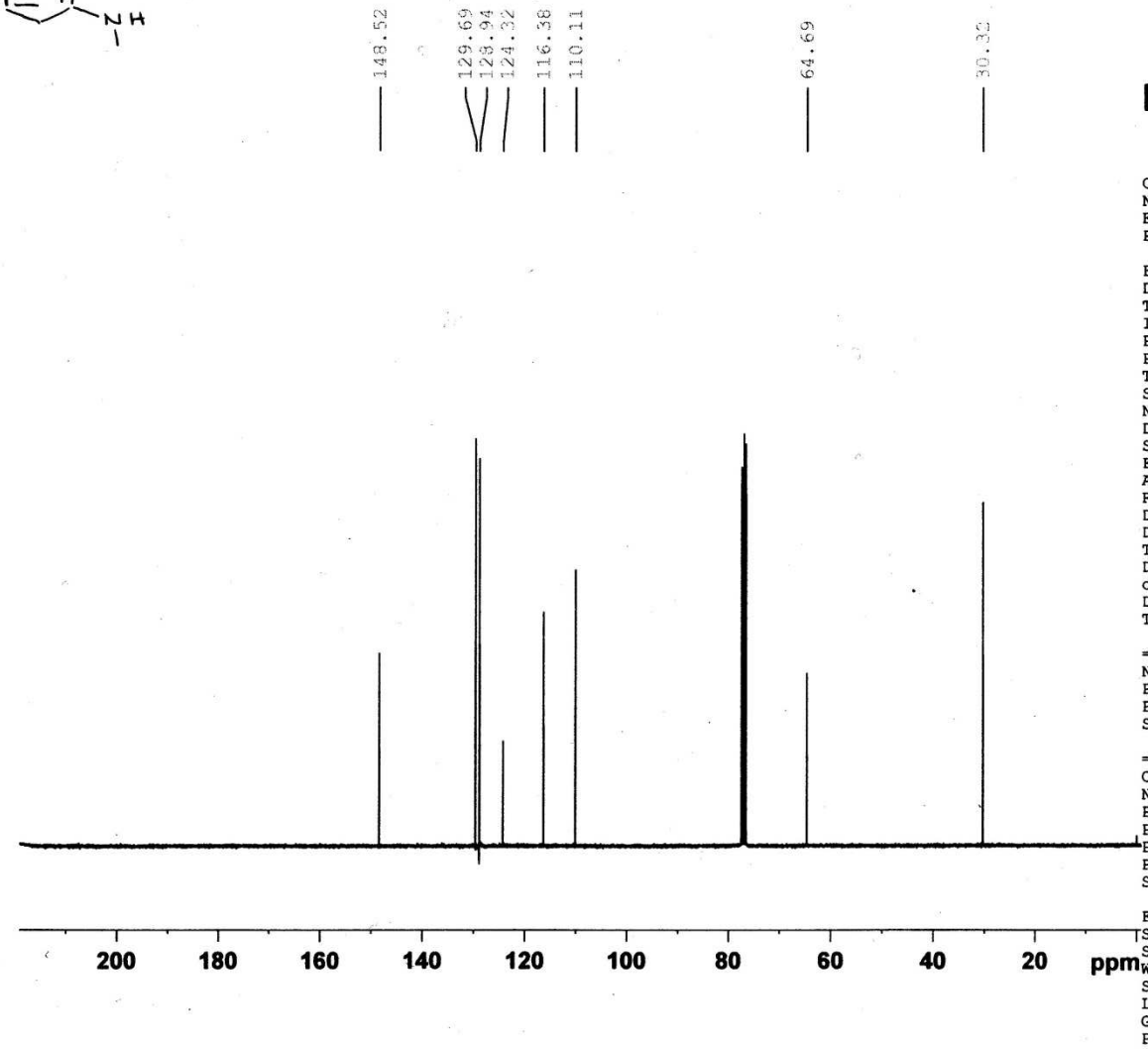


BRUKER

```
Current Data Parameters
NAME      KAW-1-039 pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120620
Time               9.52
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              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          300.1300117 MHz
WDW                  no
SSB                   0
LB              0.00 Hz
GB                    0
PC                 1.00
```

KAW-I-039





BRUKER

Current Data Parameters
NAME KAW-I-039 C13
EXPNO 1
PROCNO 1

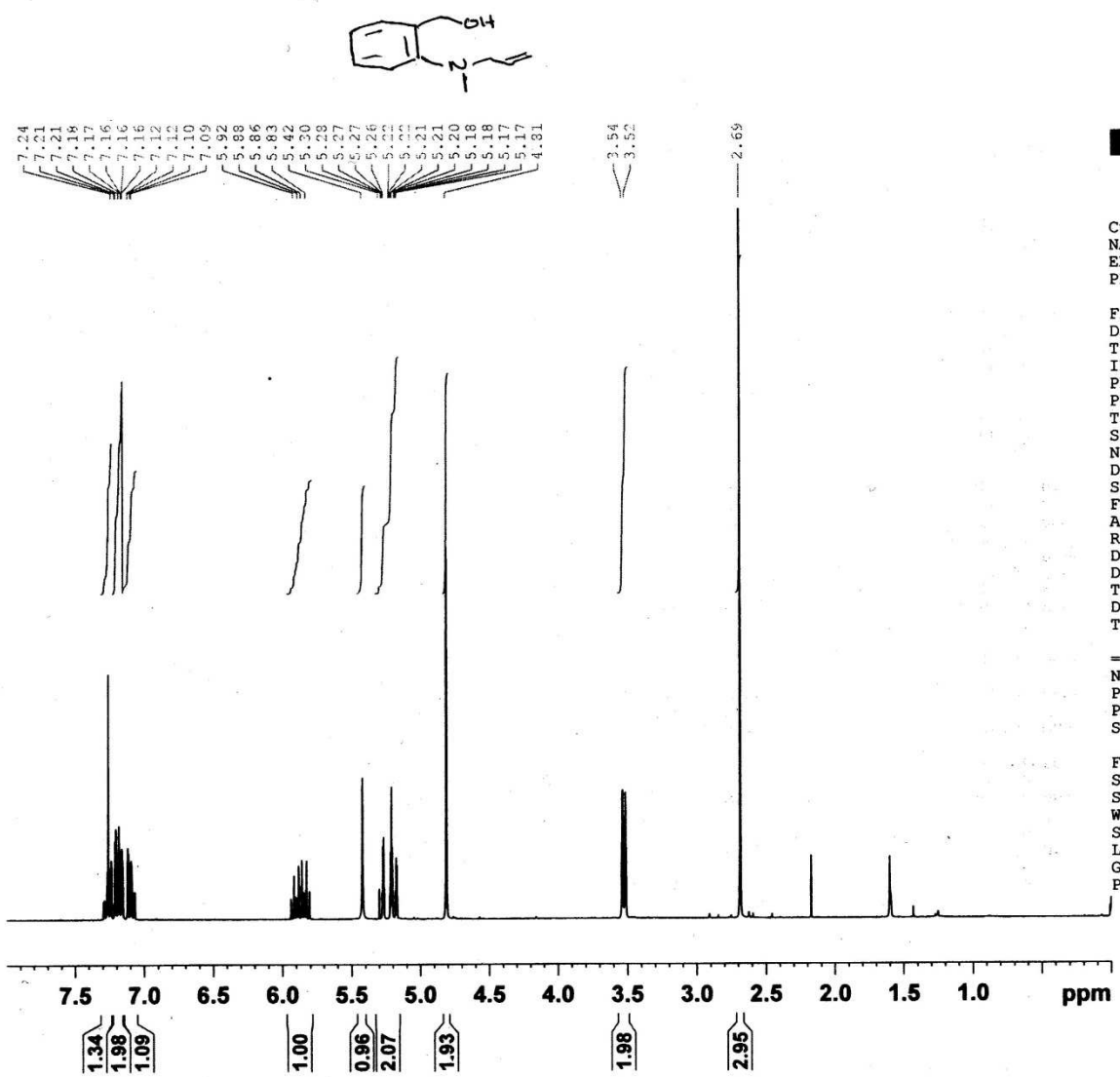
F2 - Acquisition Parameters
Date_ 20120622
Time 1.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2580.3
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 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 75.4677521 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-1-087



BRUKER

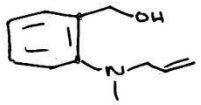
Current Data Parameters
NAME KAW-I-087
EXPNO 1
PROCNO 1

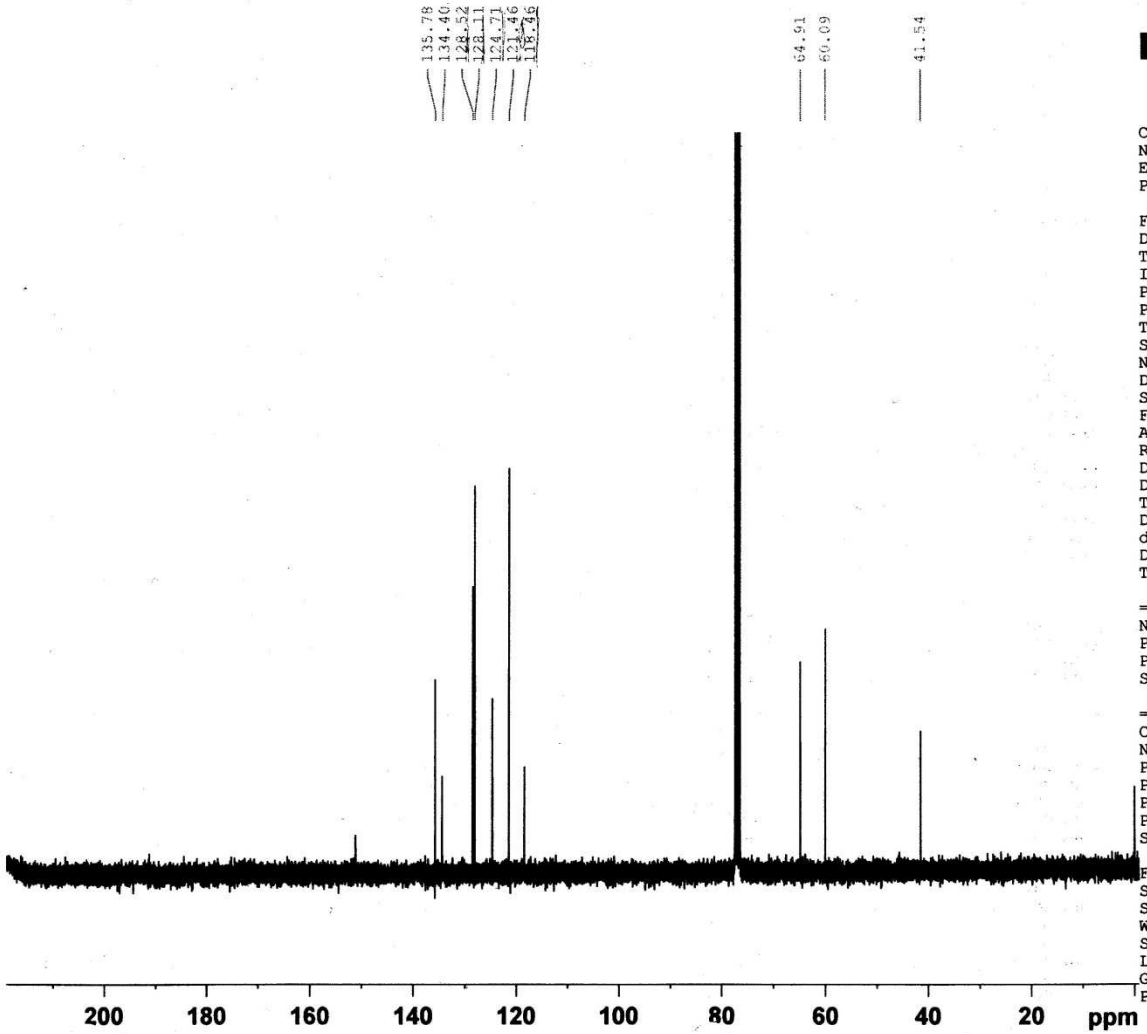
F2 - Acquisition Parameters
Date_ 20121024
Time 10.55
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300059 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-1-087





BRUKER

Current Data Parameters
NAME KAW-I-087 c13
EXPNO 1
PROCNO 1

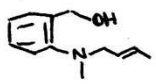
F2 - Acquisition Parameters
Date_ 20121025
Time 9.18
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

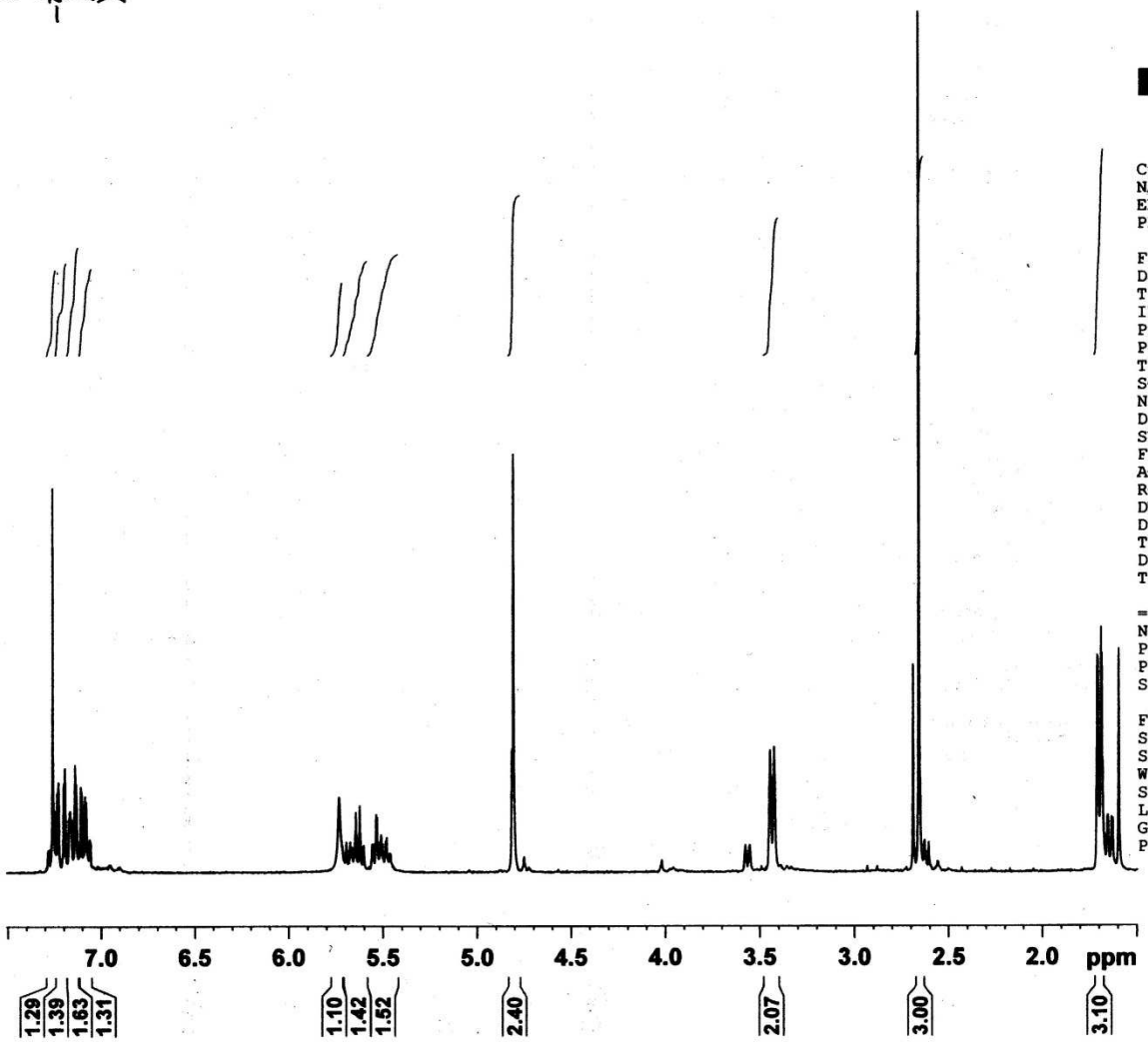
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-II-027 & 032

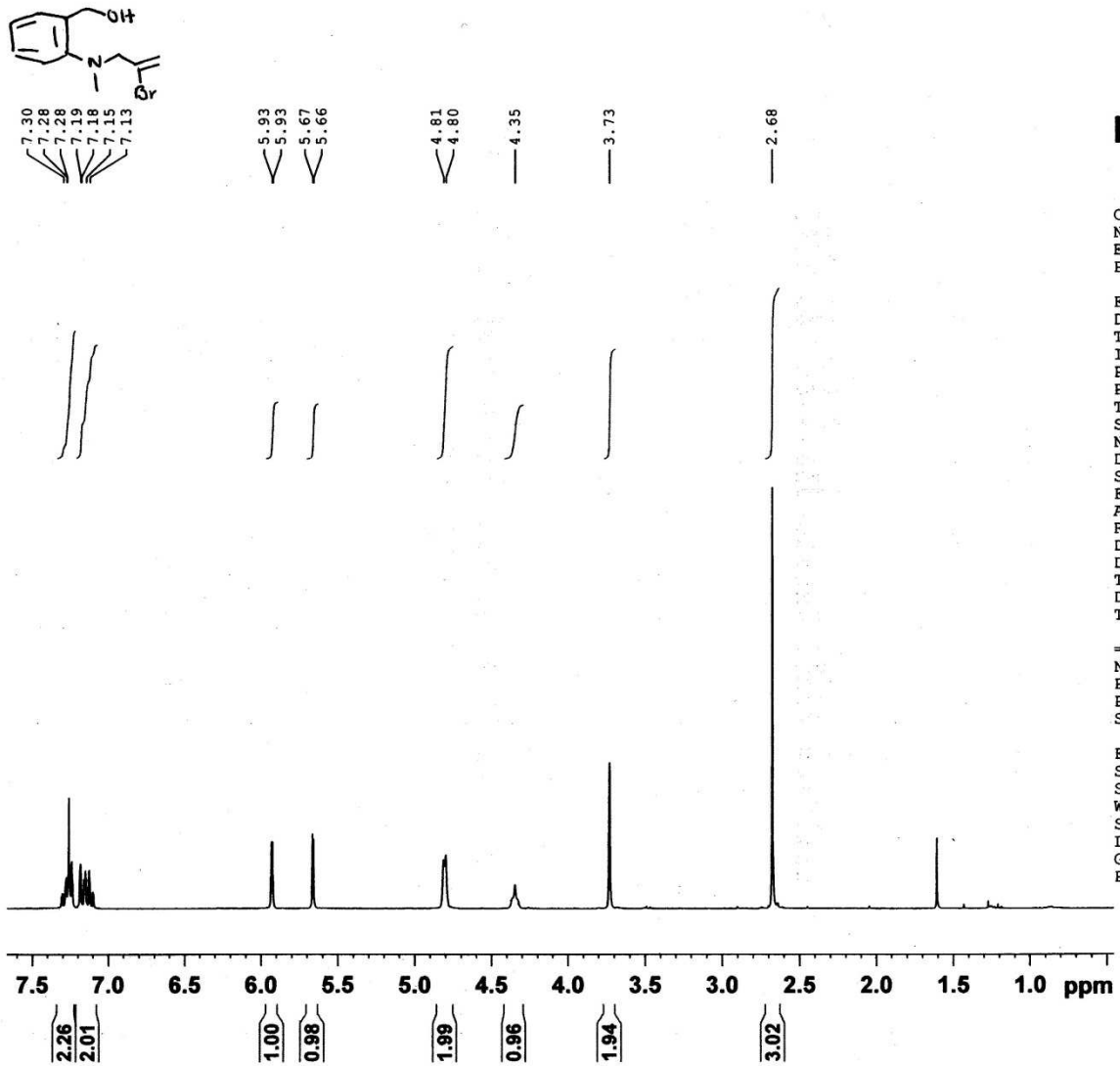




BRUKER

```
Current Data Parameters
NAME      KAW-II-027 and 032
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130222
Time                 14.05
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                   574.7
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            300.1300060 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

KAW-II-021+022



BRUKER

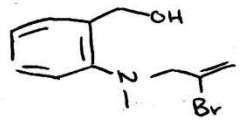
Current Data Parameters
NAME KAW-II-021&022
EXPNO 1
PROCNO 1

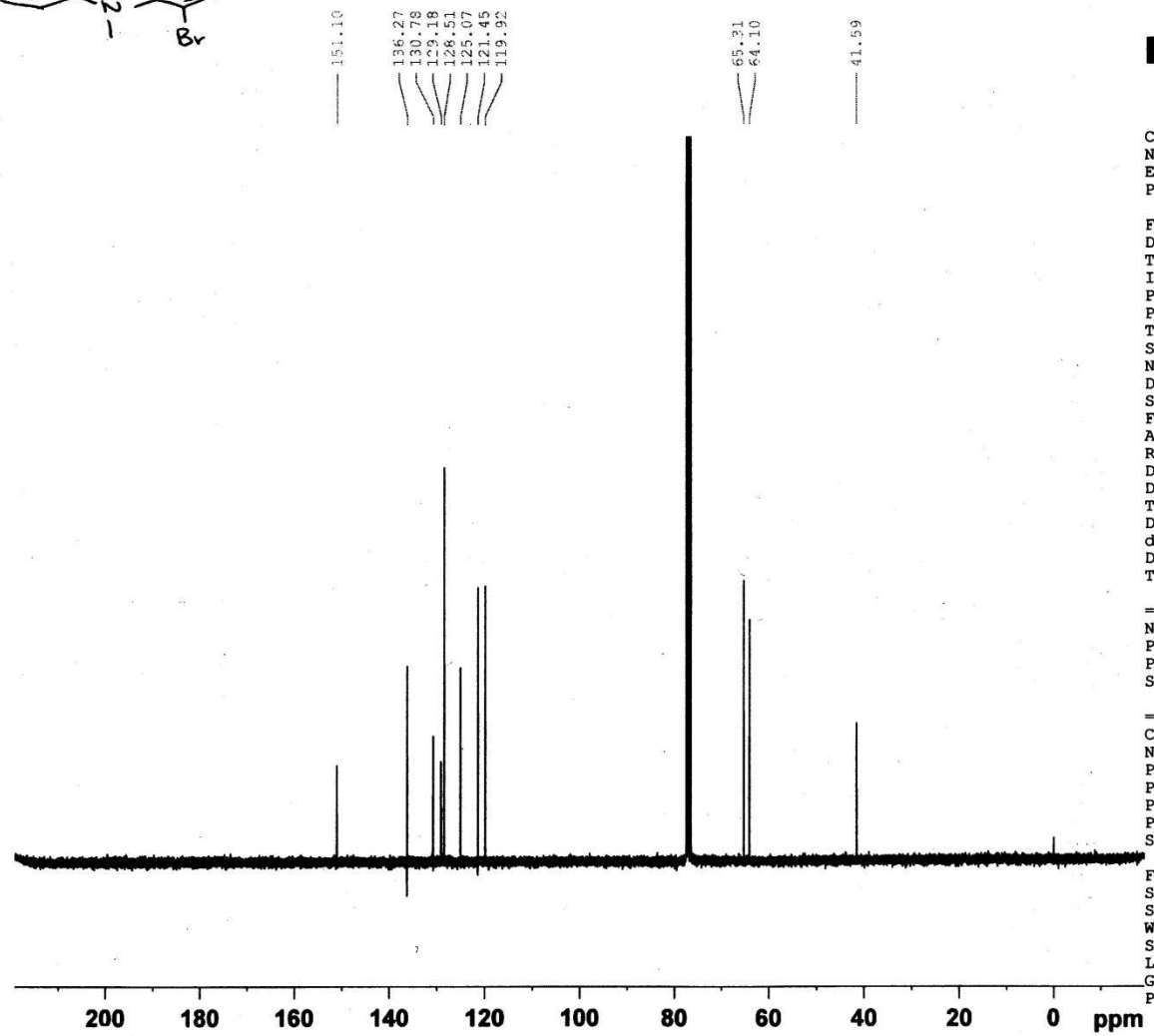
F2 - Acquisition Parameters
Date_ 20130208
Time 14.18
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 512
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-I-49





BRUKER

Current Data Parameters
NAME KAW-I-049 C13
EXPNO 1
PROCNO 1

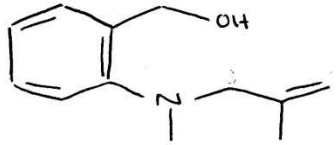
F2 - Acquisition Parameters
Date_ 20120729
Time 8.19
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2896.3
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

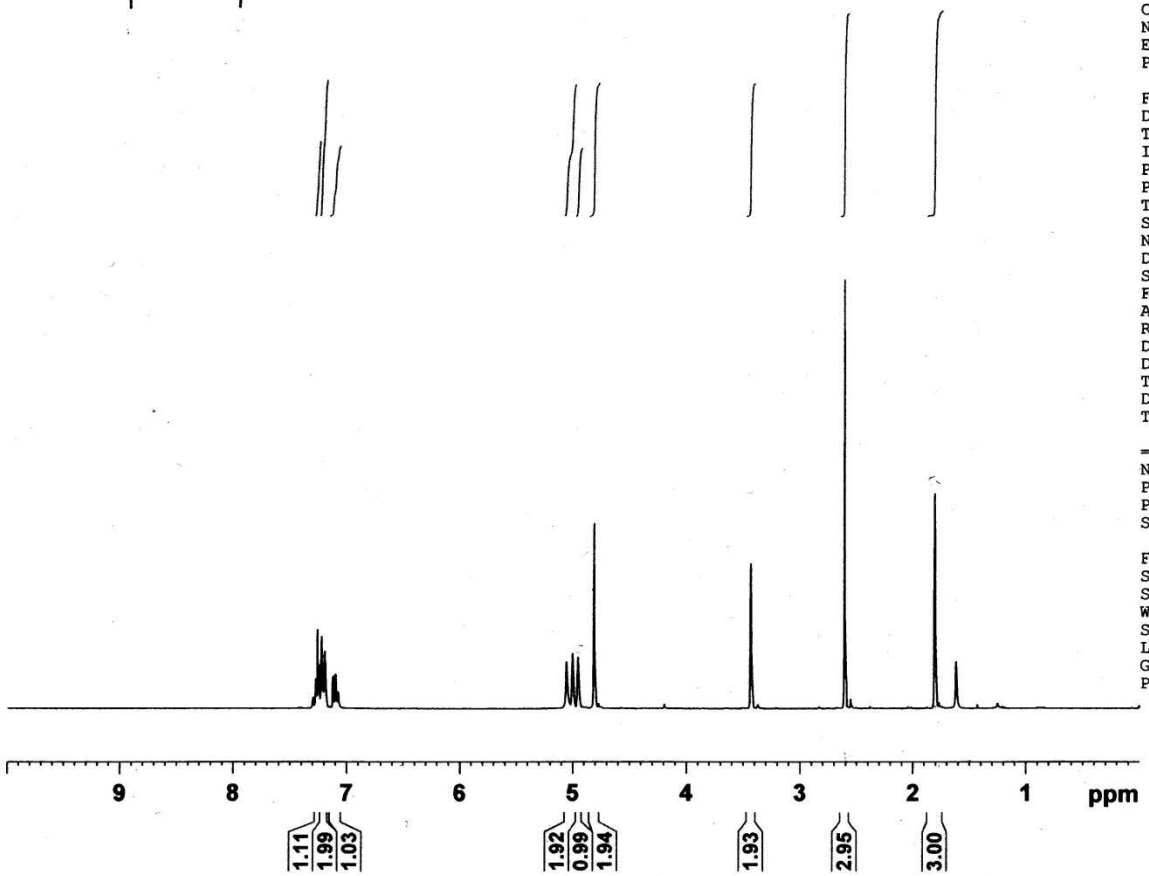
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 75.4677499 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-1-057





BRUKER

Current Data Parameters

NAME	KAW-I-057
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120713
Time	11.12
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	456.1
DW	81.000 usec
DE	6.00 usec
TE	293.2 K
D1	1.00000000 sec
TD0	1

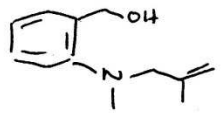
======== CHANNEL f1 ========

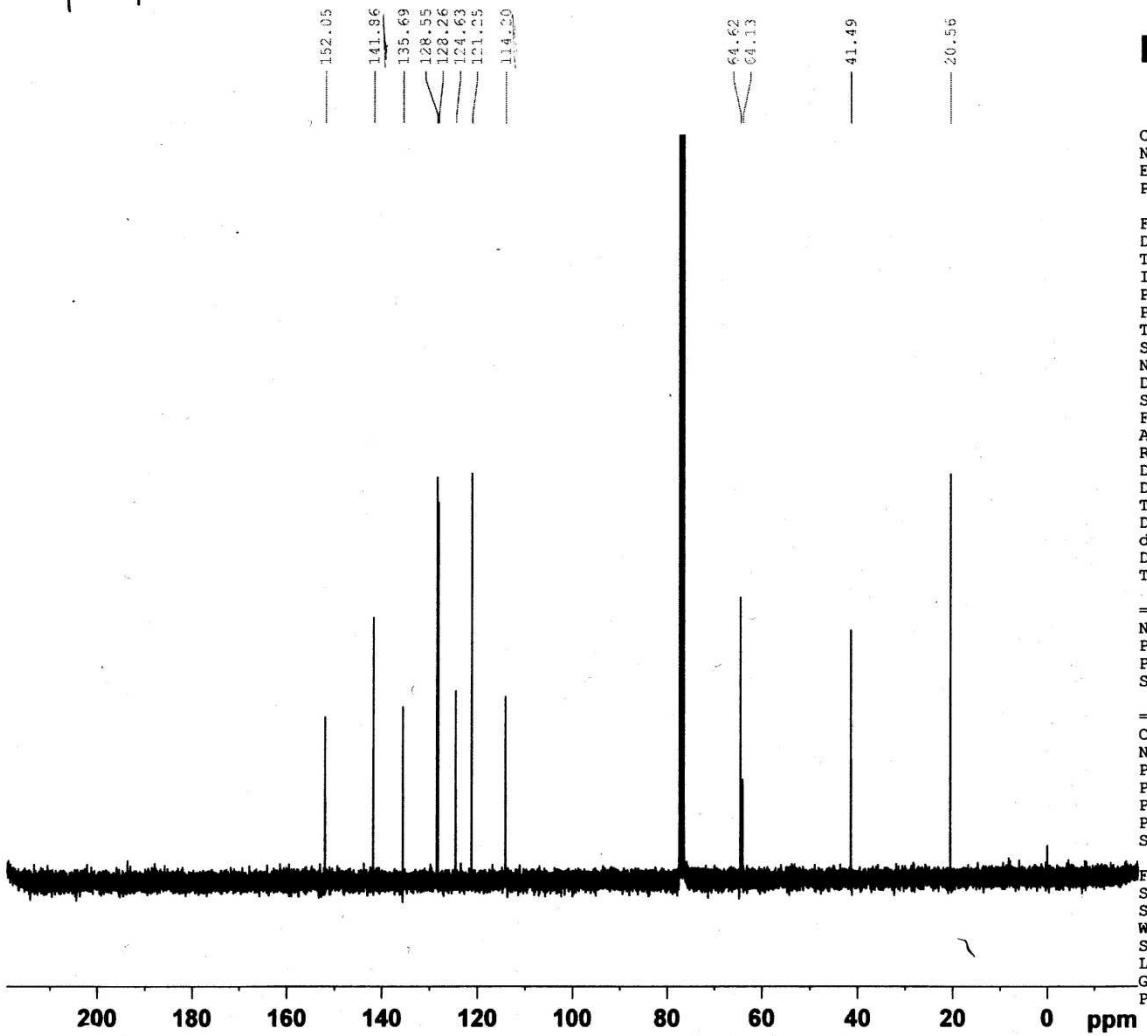
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300065 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

KAW-I-057





BRUKER

Current Data Parameters
NAME KAW-I-057 C13
EXPNO 1
PROCNO 1

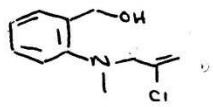
F2 - Acquisition Parameters
Date_ 20120730
Time 4.23
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2896.3
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

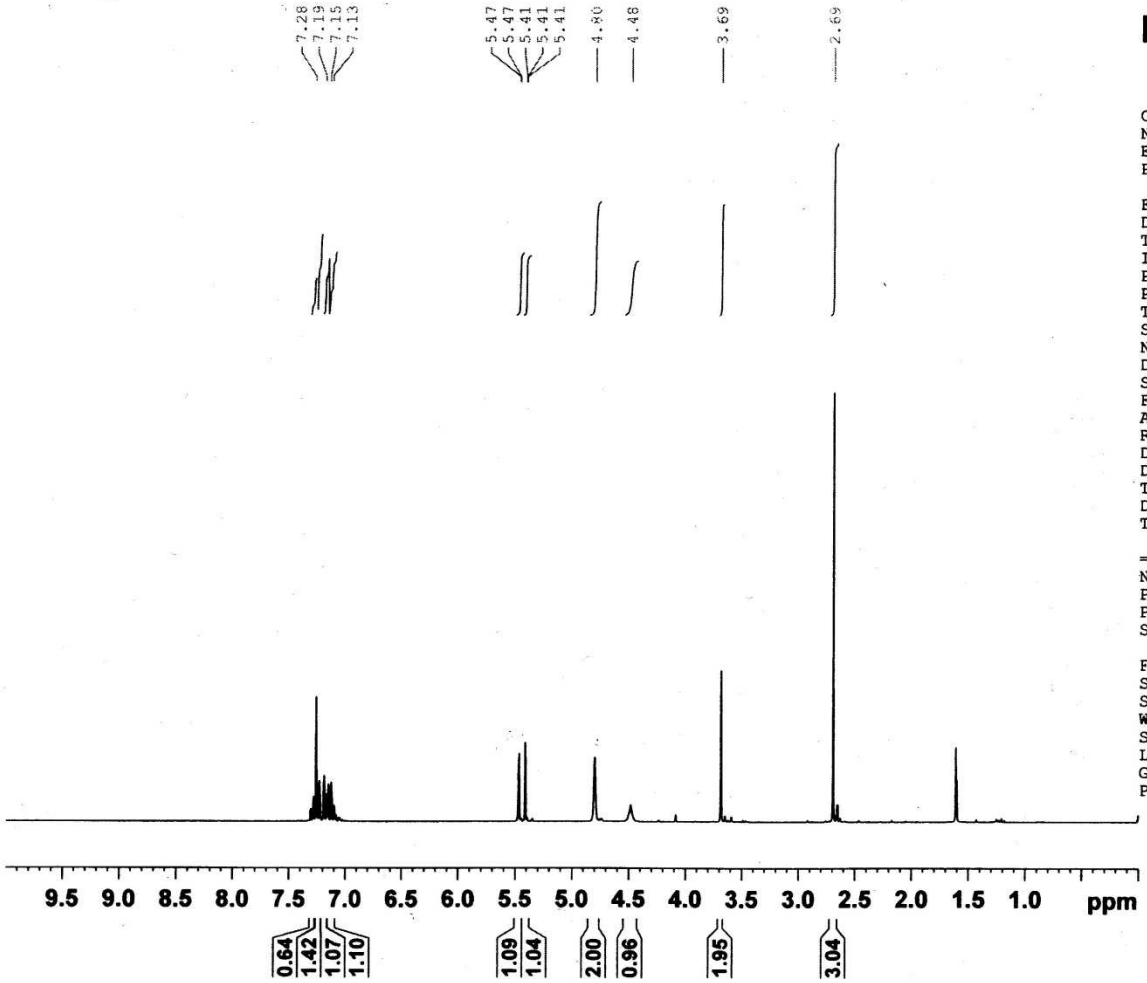
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-073





BRUKER

Current Data Parameters

NAME	KAW-I-073
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120801
Time	16.49
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	574.7
DW	81.000 usec
DE	6.00 usec
TE	293.2 K
D1	1.00000000 sec
TD0	1

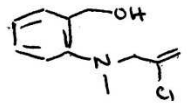
======== CHANNEL f1 ========

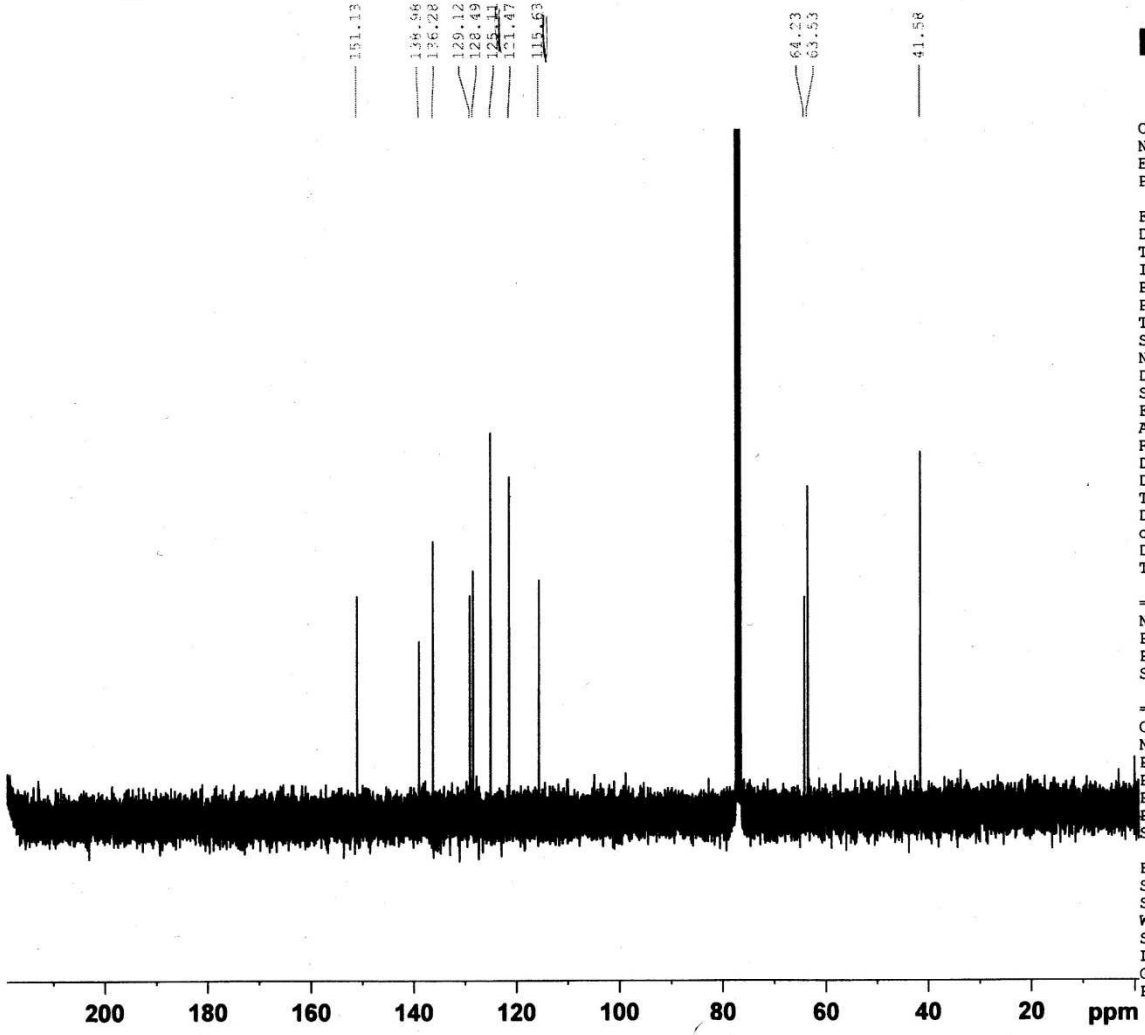
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300058 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

KAW-I-073





BRUKER

Current Data Parameters

NAME	KAW-i-075
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120829
Time	5.55
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	7000
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	293.2 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

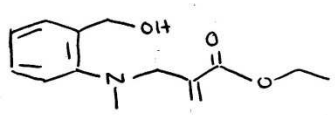
======== CHANNEL f2 ========

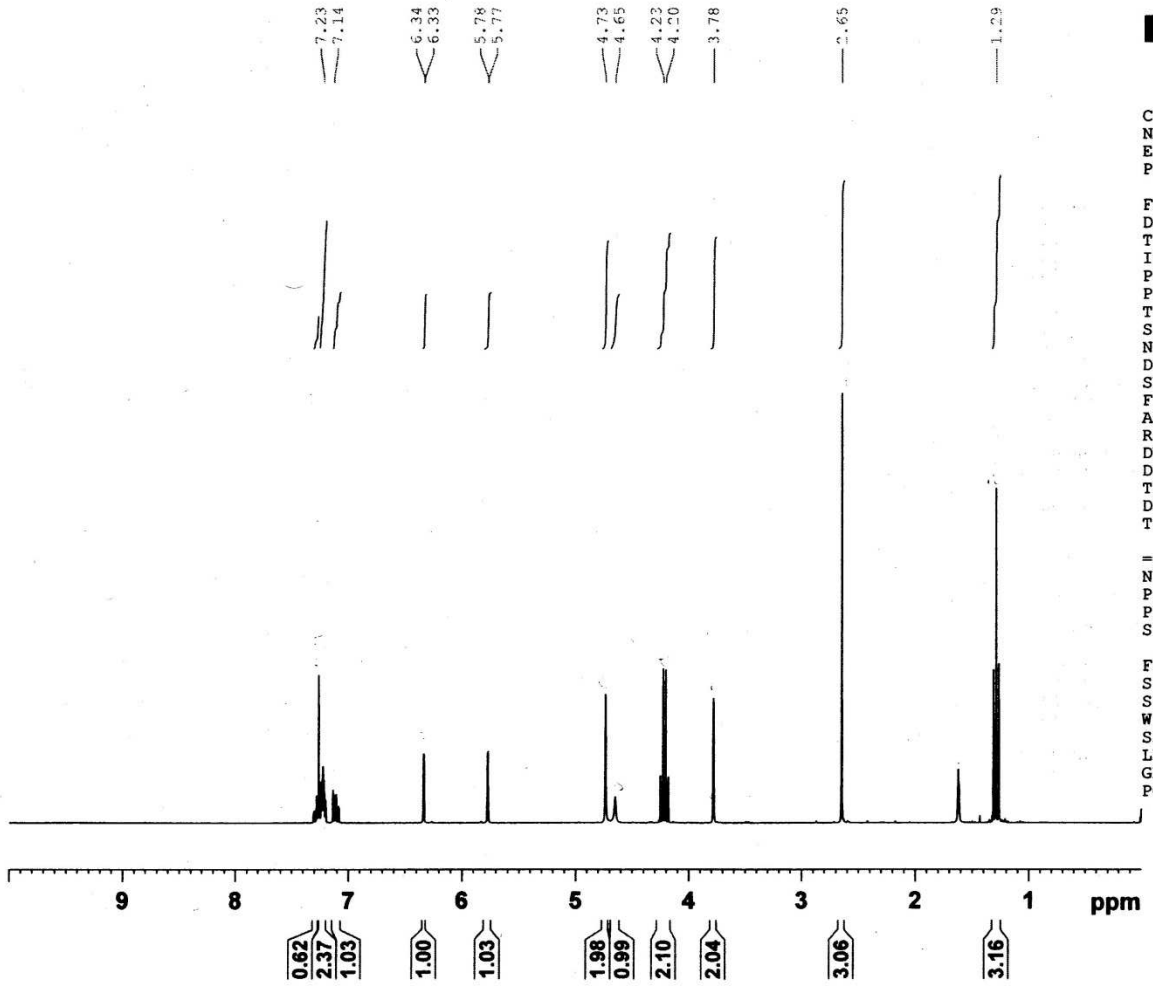
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL13	19.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677490 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

KAW-I-065 Pure

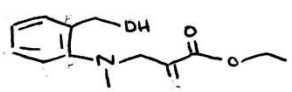


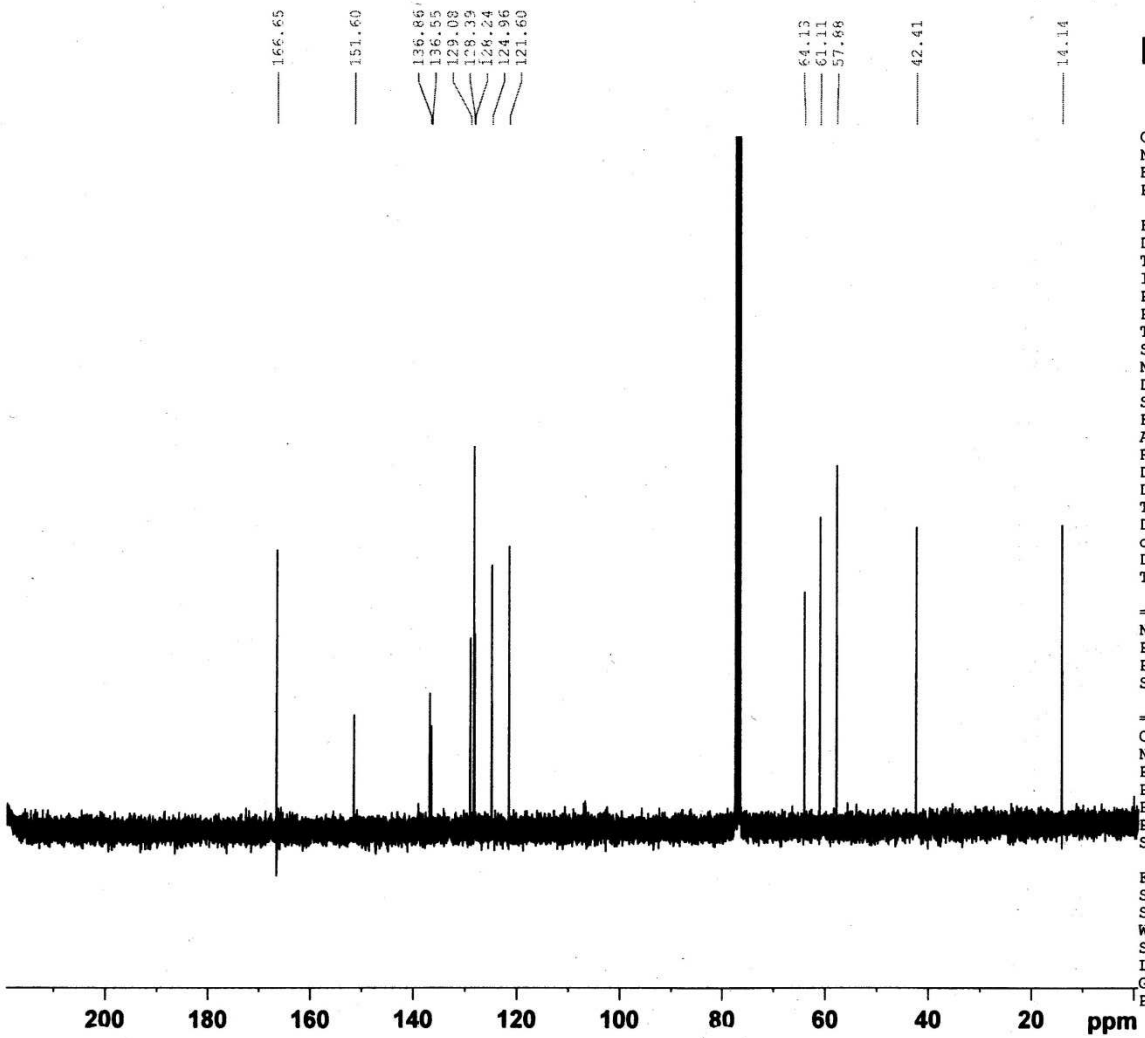


BRUKER

```
Current Data Parameters
NAME      KAW-I-065 Pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120725
Time               16.21
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                574.7
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          300.1300054 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                  1.00
```

KAW-1-065

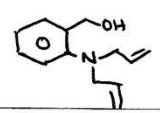




BRUKER

```
Current Data Parameters
NAME       KAW-i-065 C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120726
Time               1.04
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                8000
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                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                1.40
```

KAW-i-004



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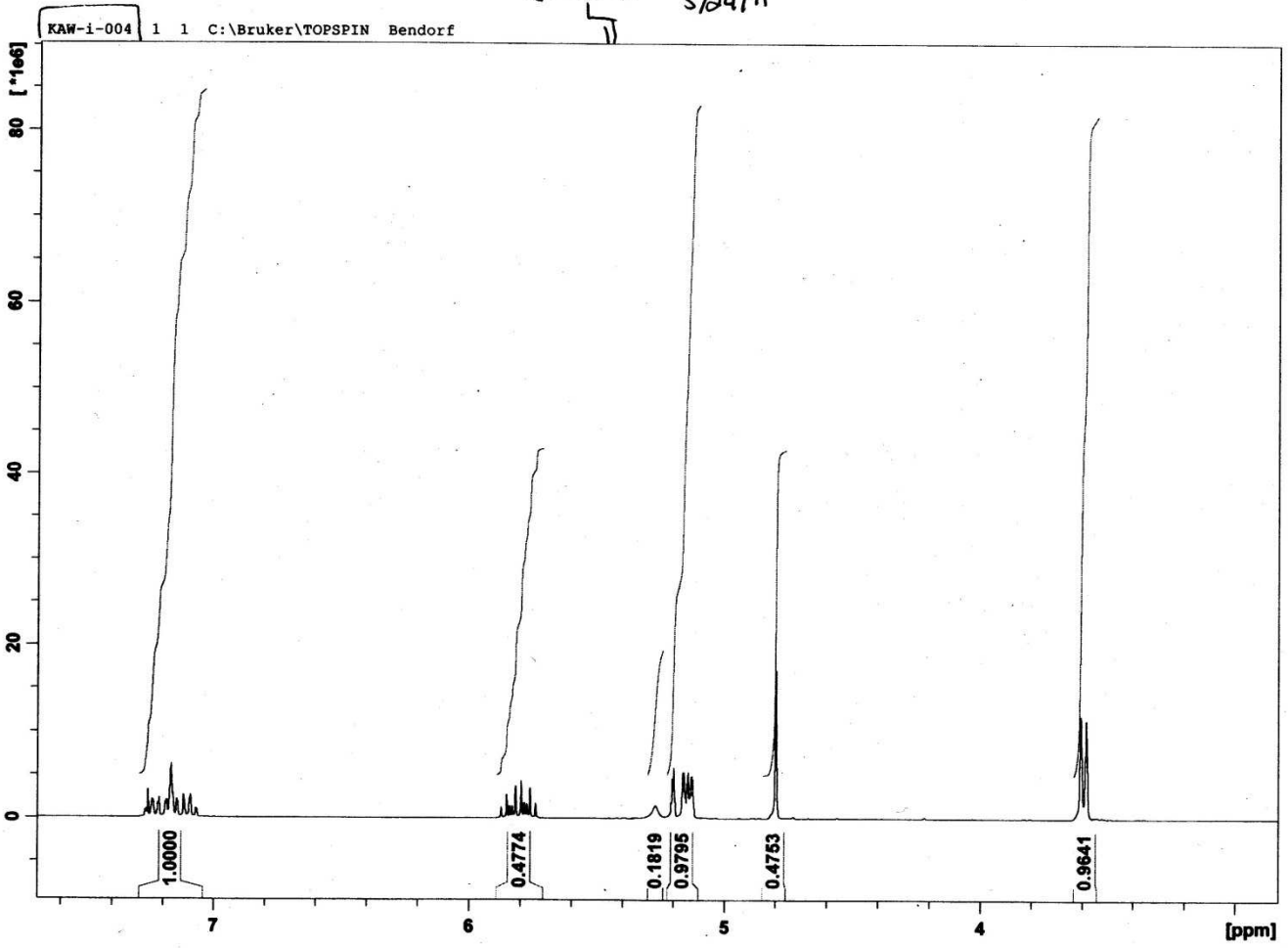
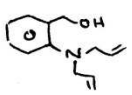


KAW-i-004



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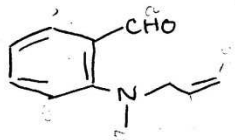
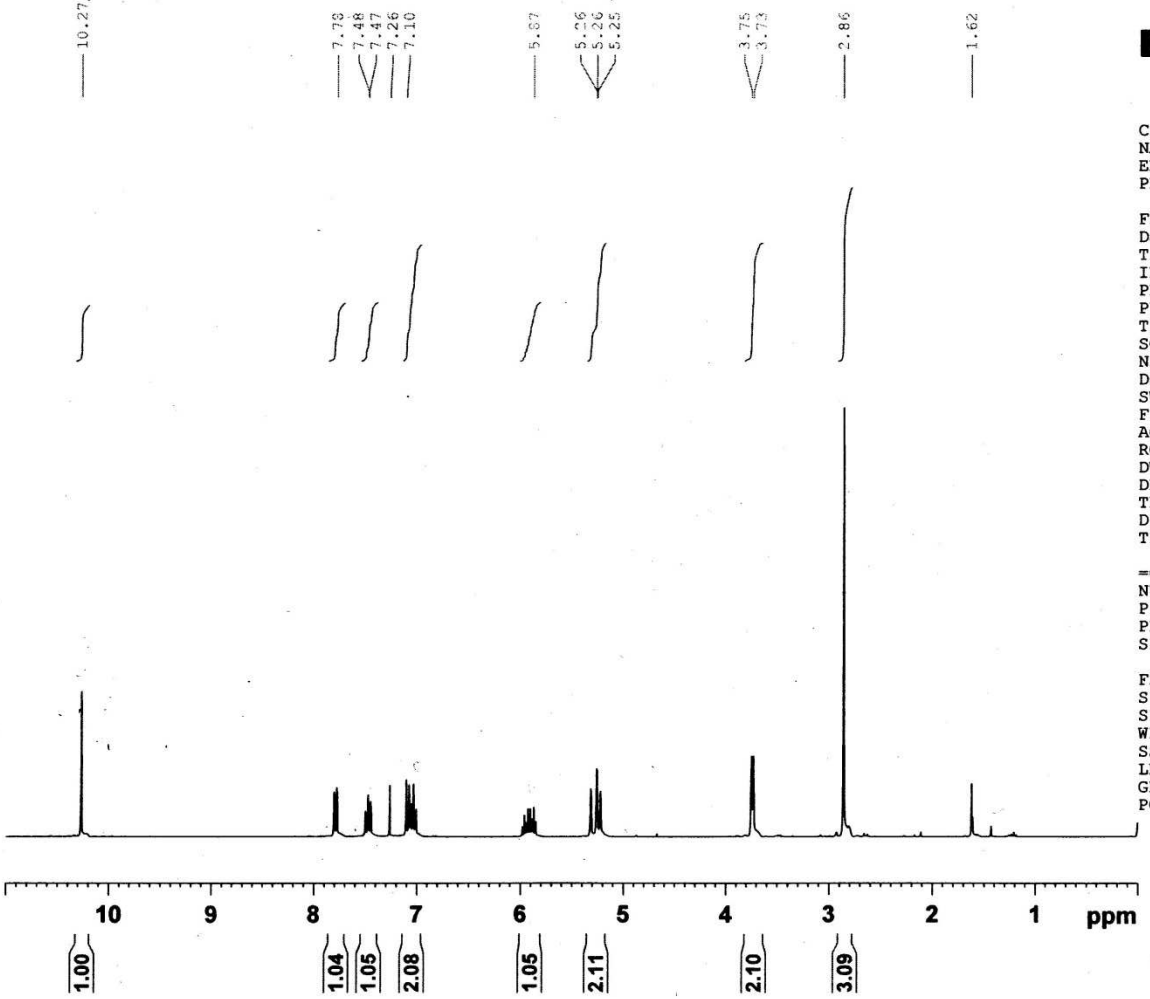
BRUKER

```
Current Data Parameters
NAME      KAW-i-004 13Cb
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110526
Time              12.36
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                 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           75.4677504 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

KAW-I-041

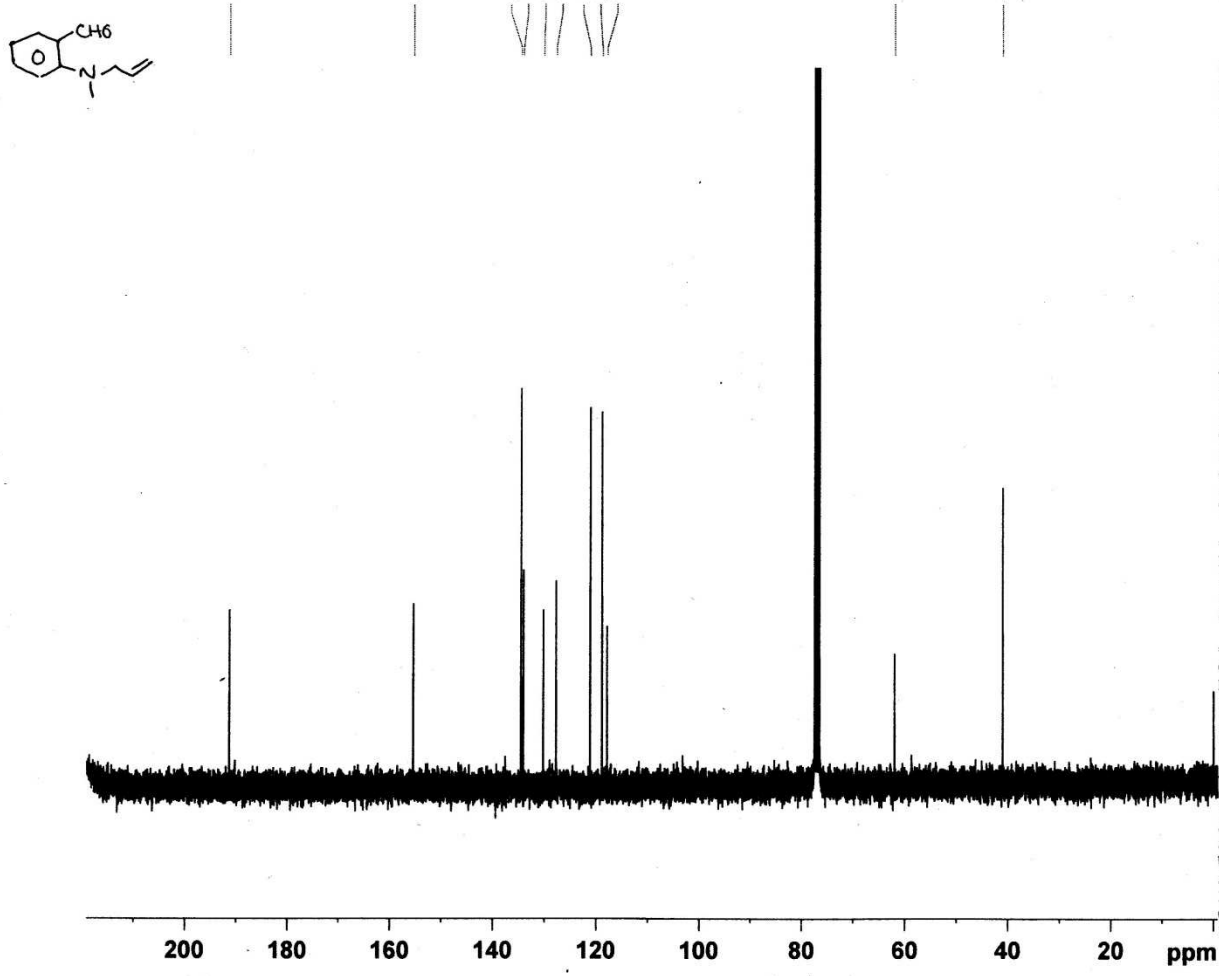




BRUKER

```
Current Data Parameters
NAME                  KAW-I-041
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20120621
Time                      10.19
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                        406.4
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             300.1300051 MHz
WDW                          no
SSB                           0
LB                      0.00 Hz
GB                            0
PC                         1.00
```

KAW-i-015 6/16/11



BRUKER

Current Data Parameters
NAME KAW-i-015 c13
EXPNO 1
PROCNO 1

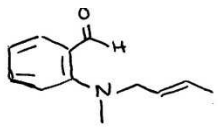
F2 - Acquisition Parameters
Date_ 20110617
Time 0.24
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8192
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2896.3
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

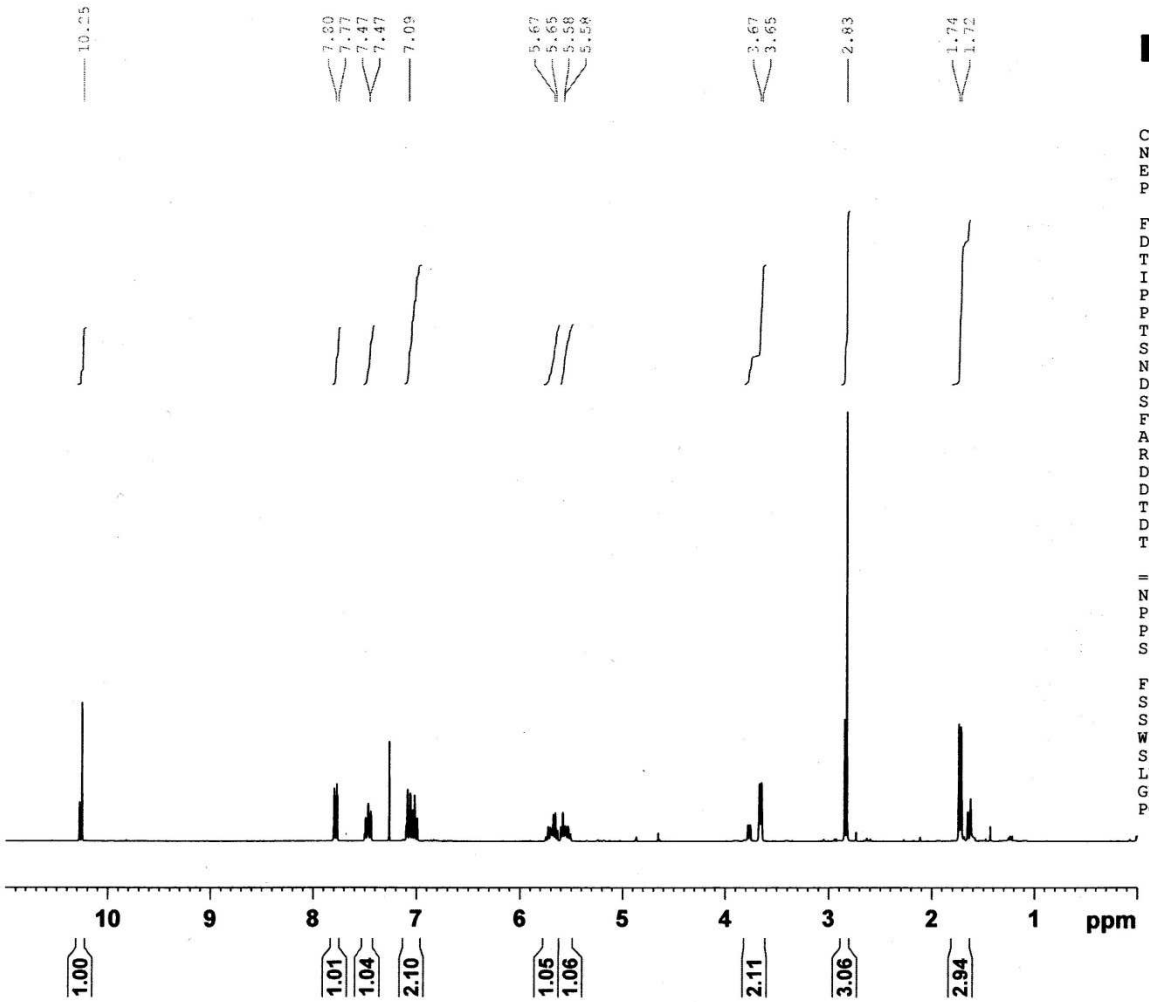
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 75.4677493 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-046

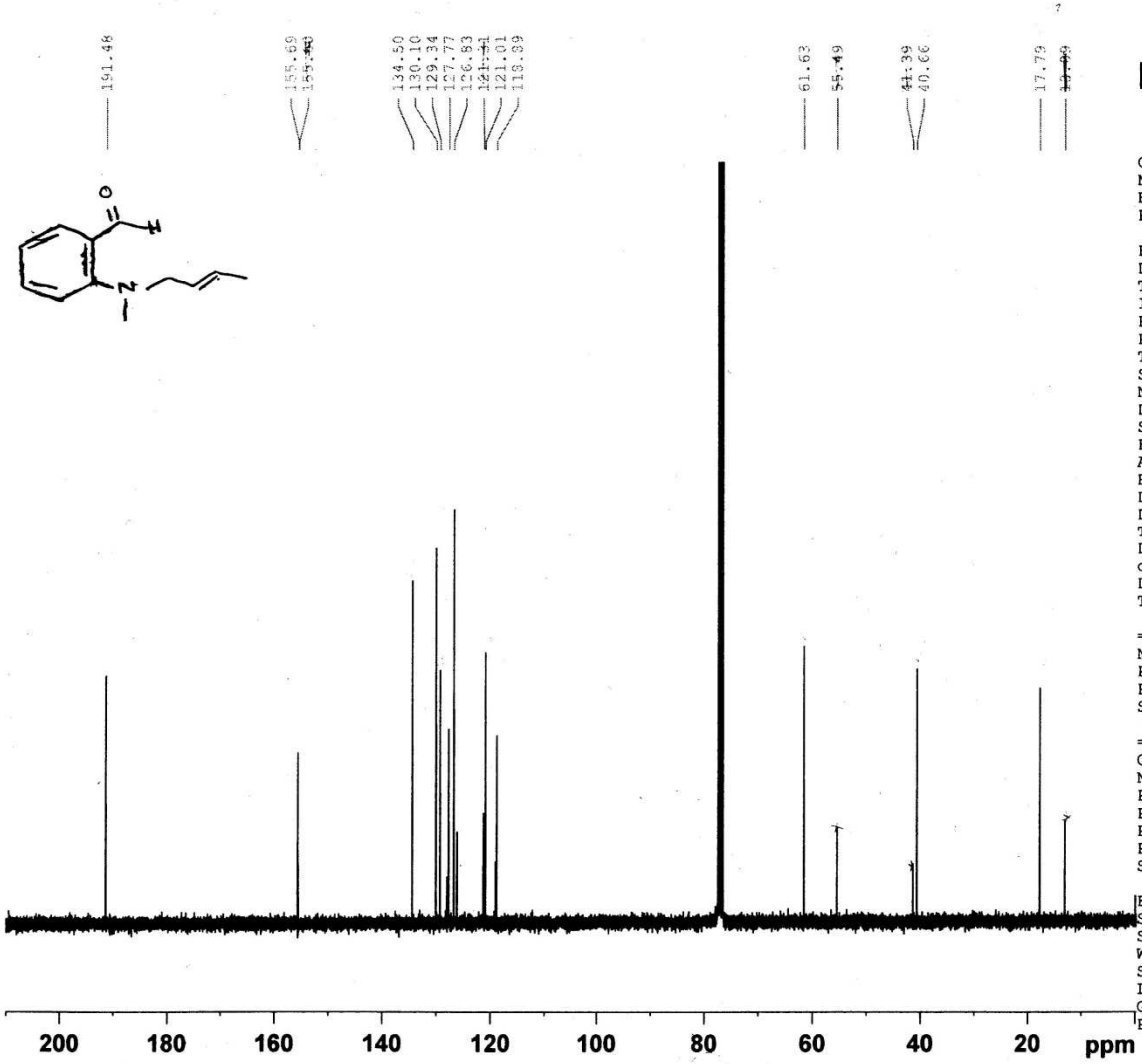




BRUKER

```
Current Data Parameters
NAME                  KAW-I-046
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20120628
Time                      10.17
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                       287.4
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               300.1300052 MHz
WDW                         no
SSB                          0
LB                      0.00 Hz
GB                           0
PC                        1.00
```

KAW-1-046



BRUKER

Current Data Parameters
NAME KTcule
EXPNO 1
PROCNO 1

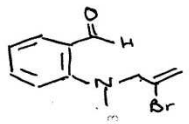
F2 - Acquisition Parameters
Date_ 20120701
Time 3.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3649.1
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

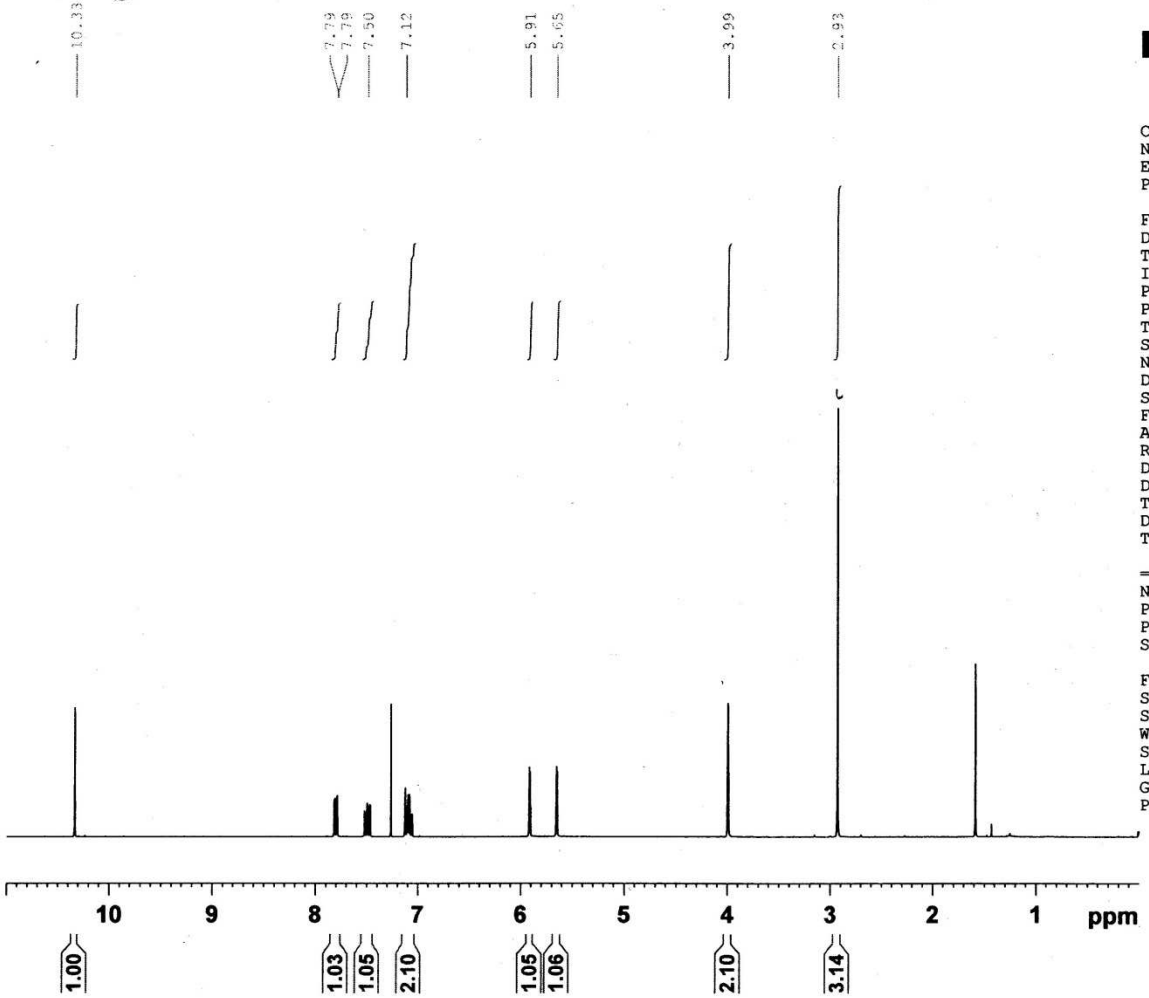
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-055





BRUKER

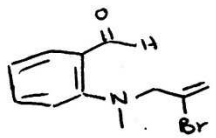
Current Data Parameters
NAME KAW-I-055
EXPNO 1
PROCNO 1

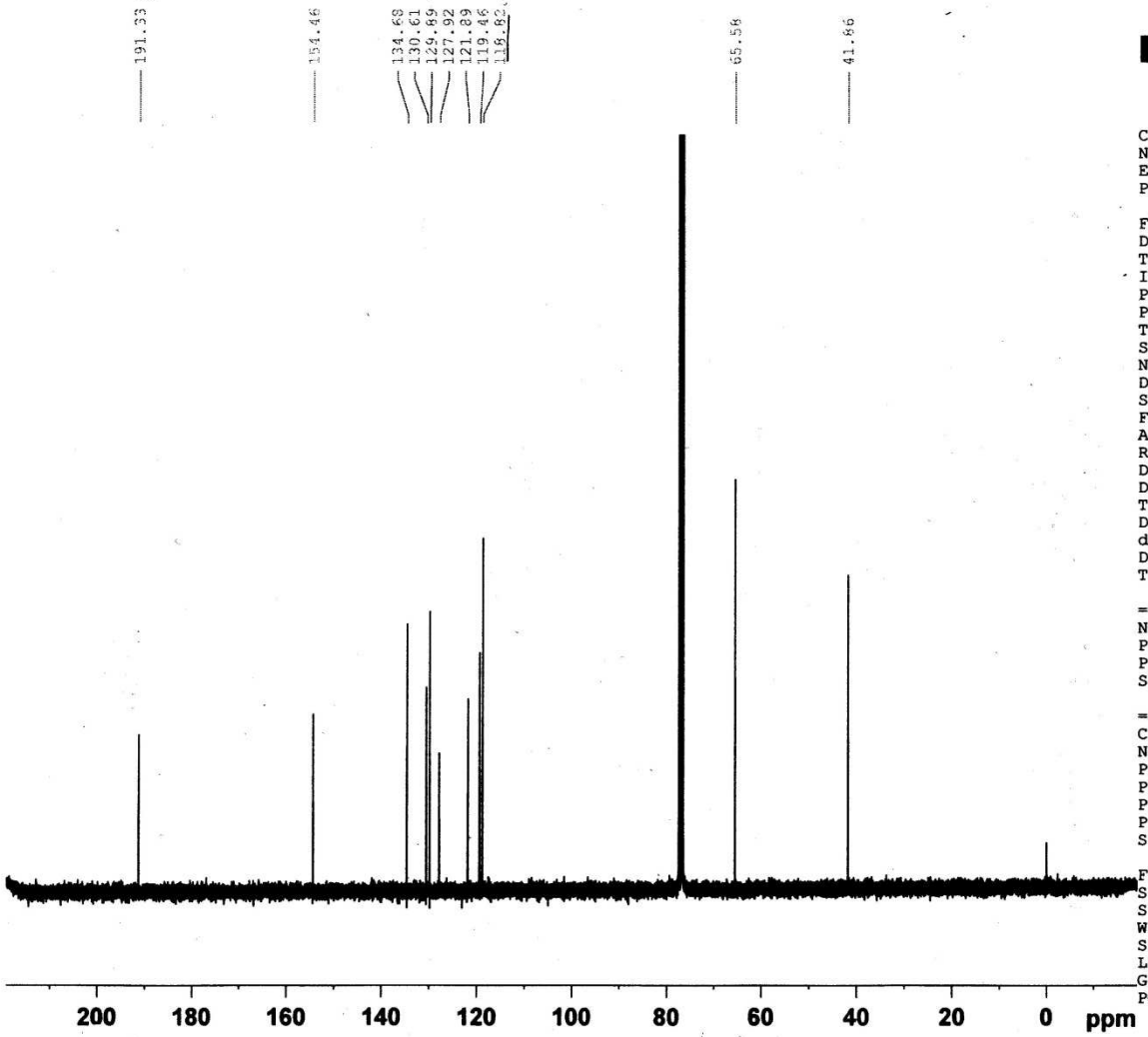
F2 - Acquisition Parameters
Date_ 20120710
Time 8.48
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300051 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-I-055





BRUKER

Current Data Parameters

NAME	KAW-I-055 C13
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120729
Time	19.38
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8000
DS	4
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	1824.6
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

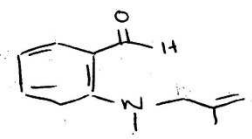
======== CHANNEL f2 ========

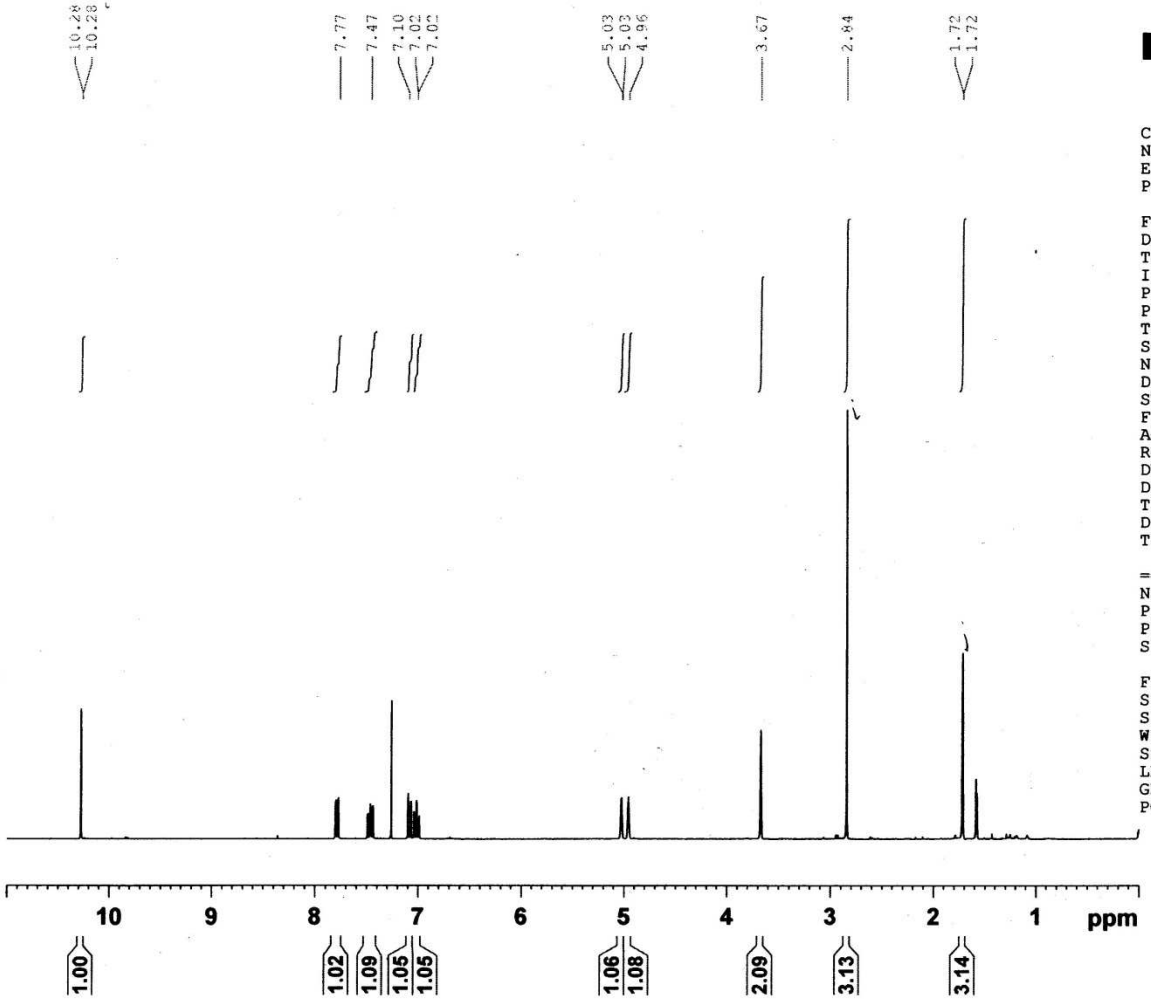
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL13	19.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677490 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

KAW-I-059 & 060





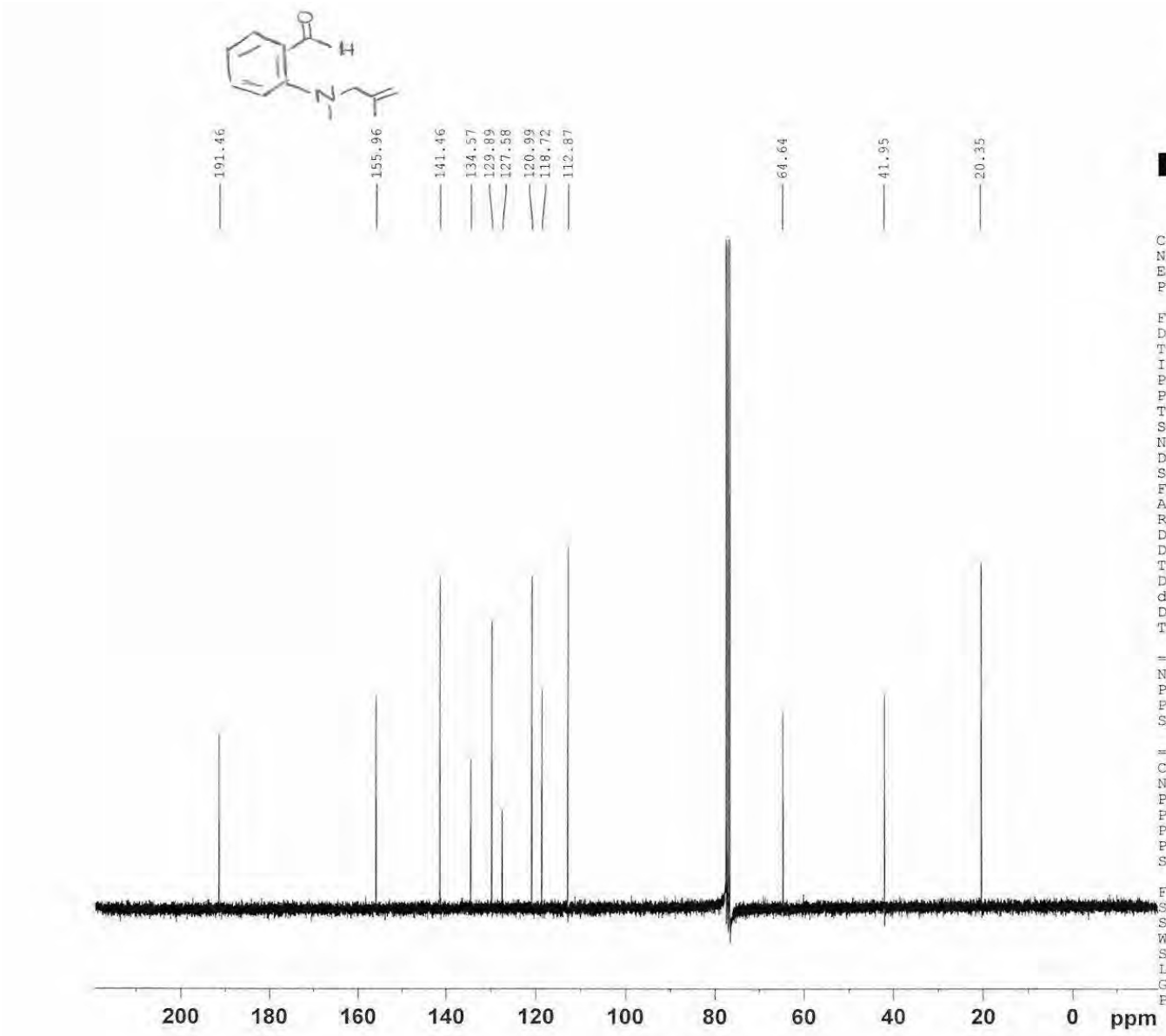
BRUKER

Current Data Parameters
NAME KAW-I-059 & 060
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120716
Time 16.09
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 645.1
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 300.1300055 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



BRUKER

Current Data Parameters
NAME KAW-I059 AND 60
EXPNO 1
PROCNO 1

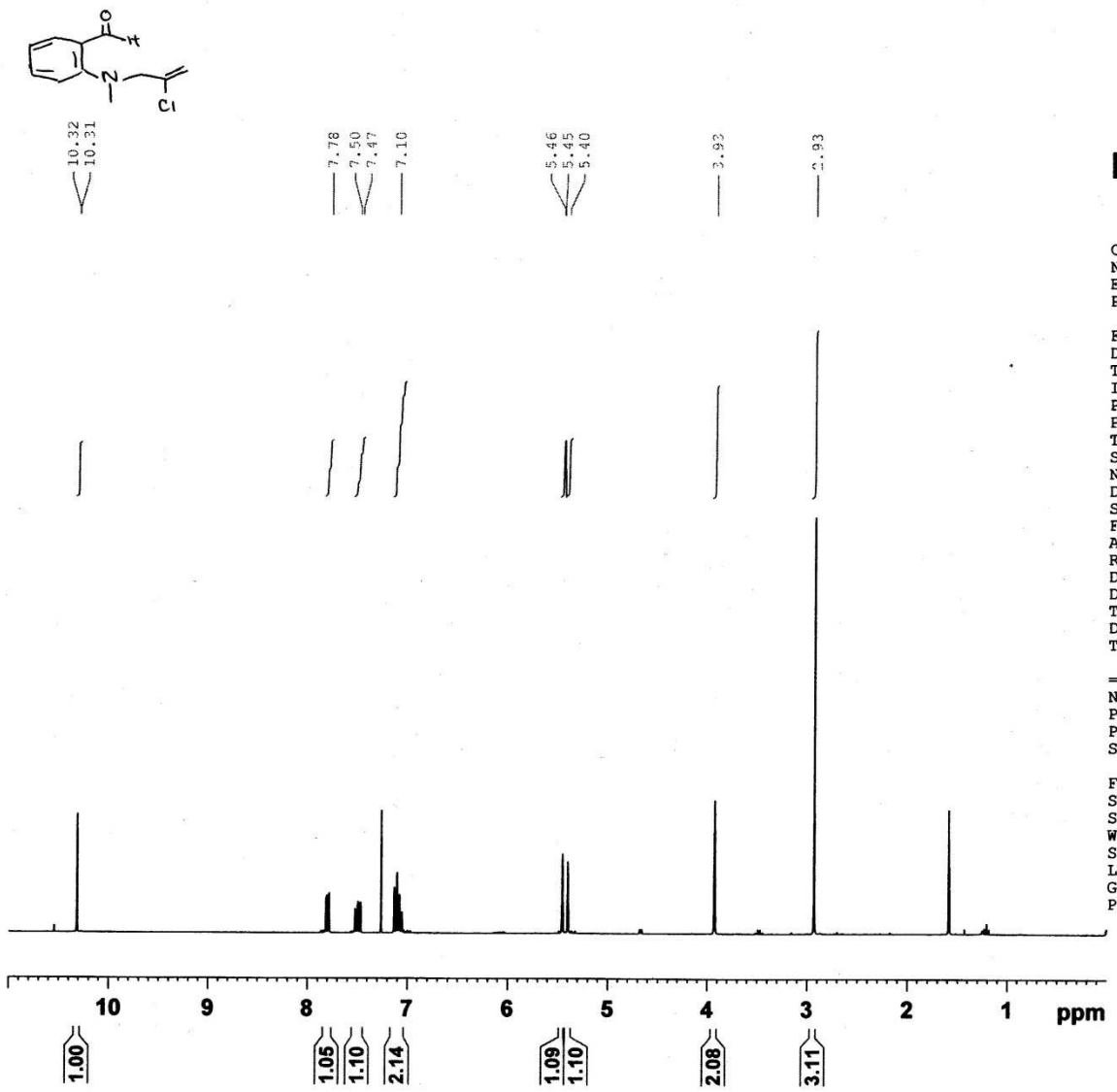
F2 - Acquisition Parameters
Date_ 20130425
Time 21.38
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3251
DW 27.800 usec
DE 6.00 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-1-074



BRUKER

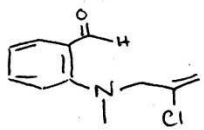
Current Data Parameters
NAME KAW-I-074
EXPNO 1
PROCNO 1

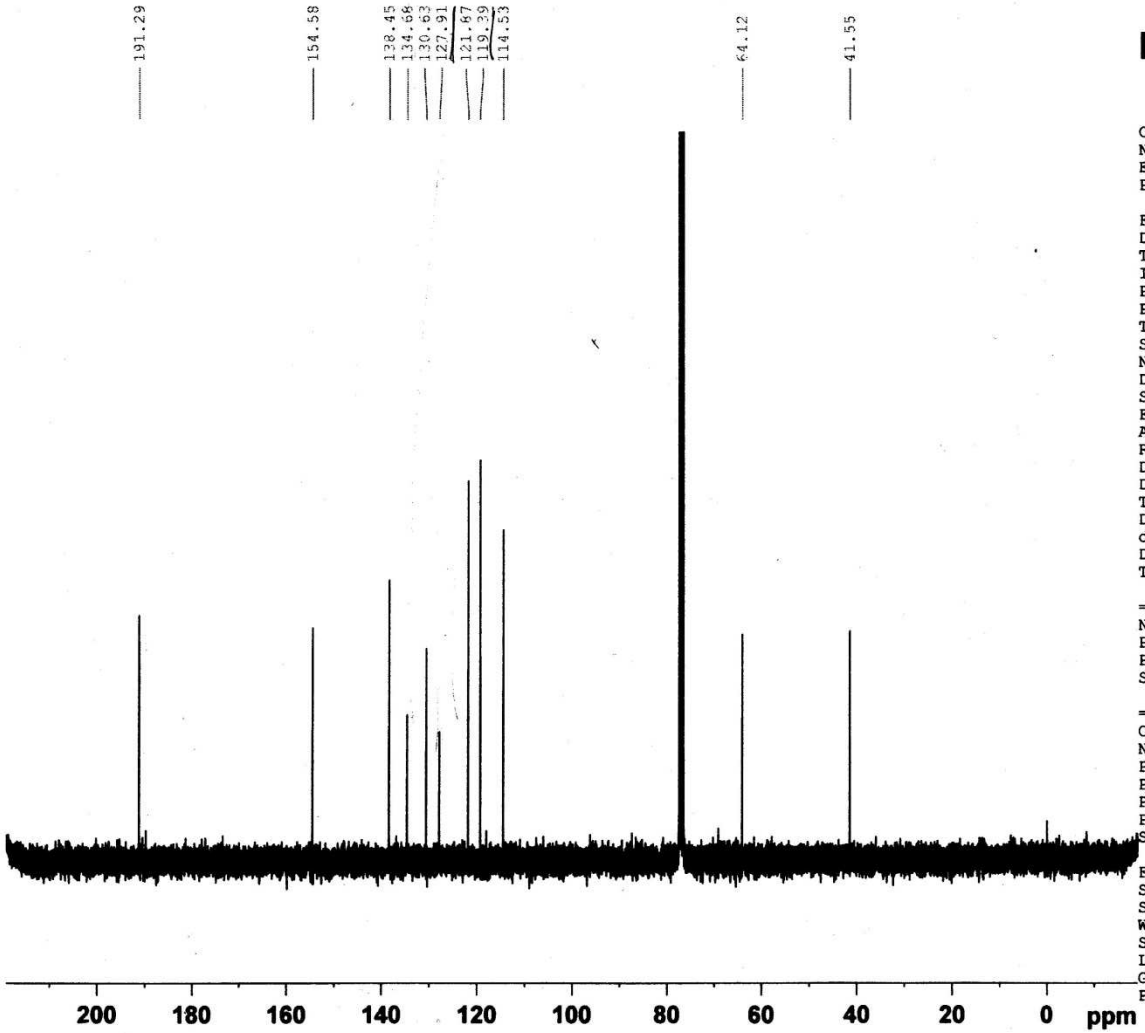
F2 - Acquisition Parameters
Date_ 20120802
Time 17.42
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300053 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-1-074





BRUKER

Current Data Parameters
NAME KAW-I-074 C13
EXPNO 1
PROCNO 1

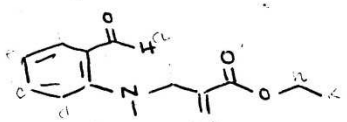
F2 - Acquisition Parameters
Date_ 20120803
Time 2.23
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2580.3
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

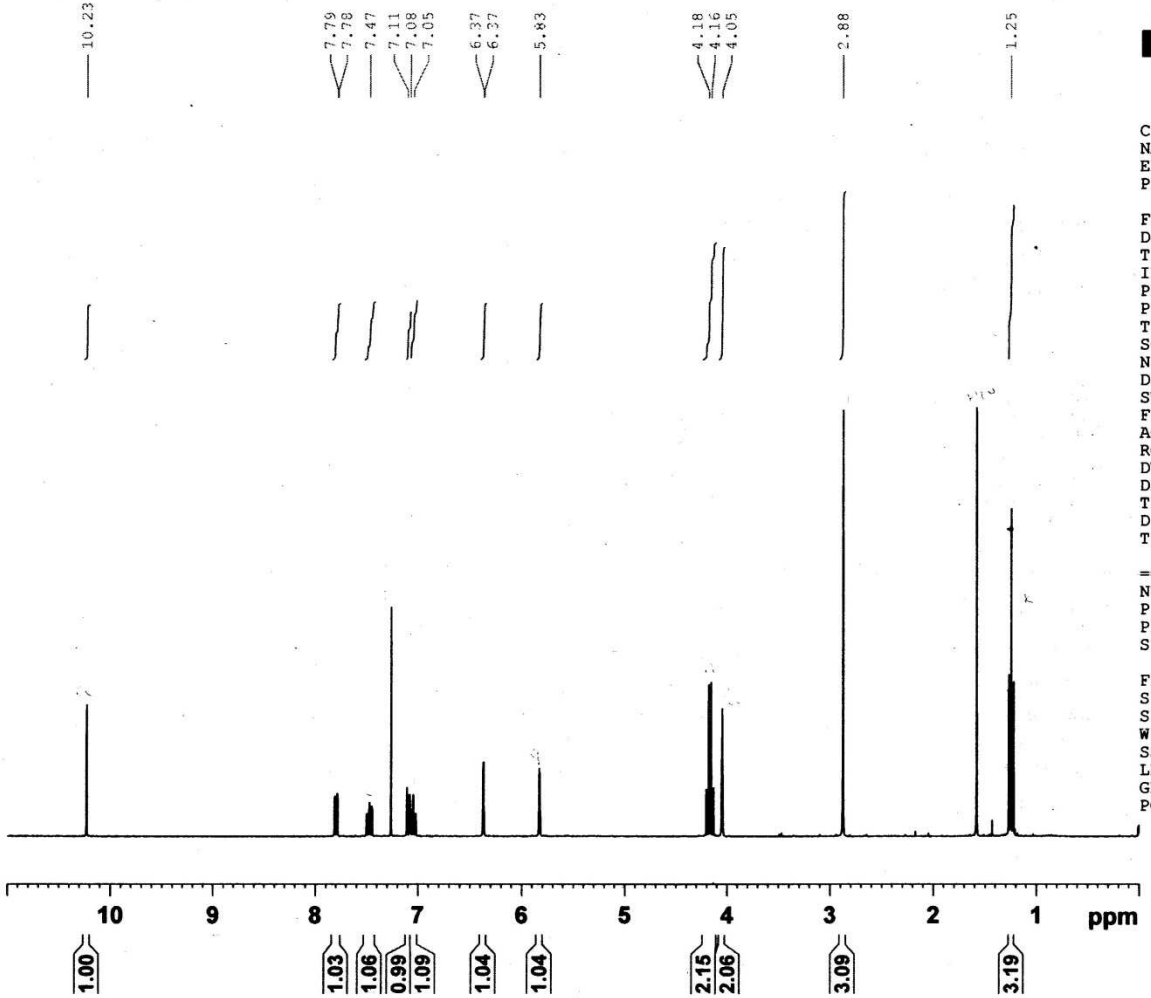
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-067

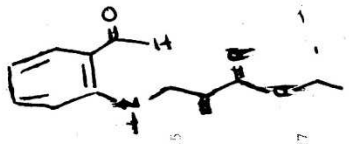


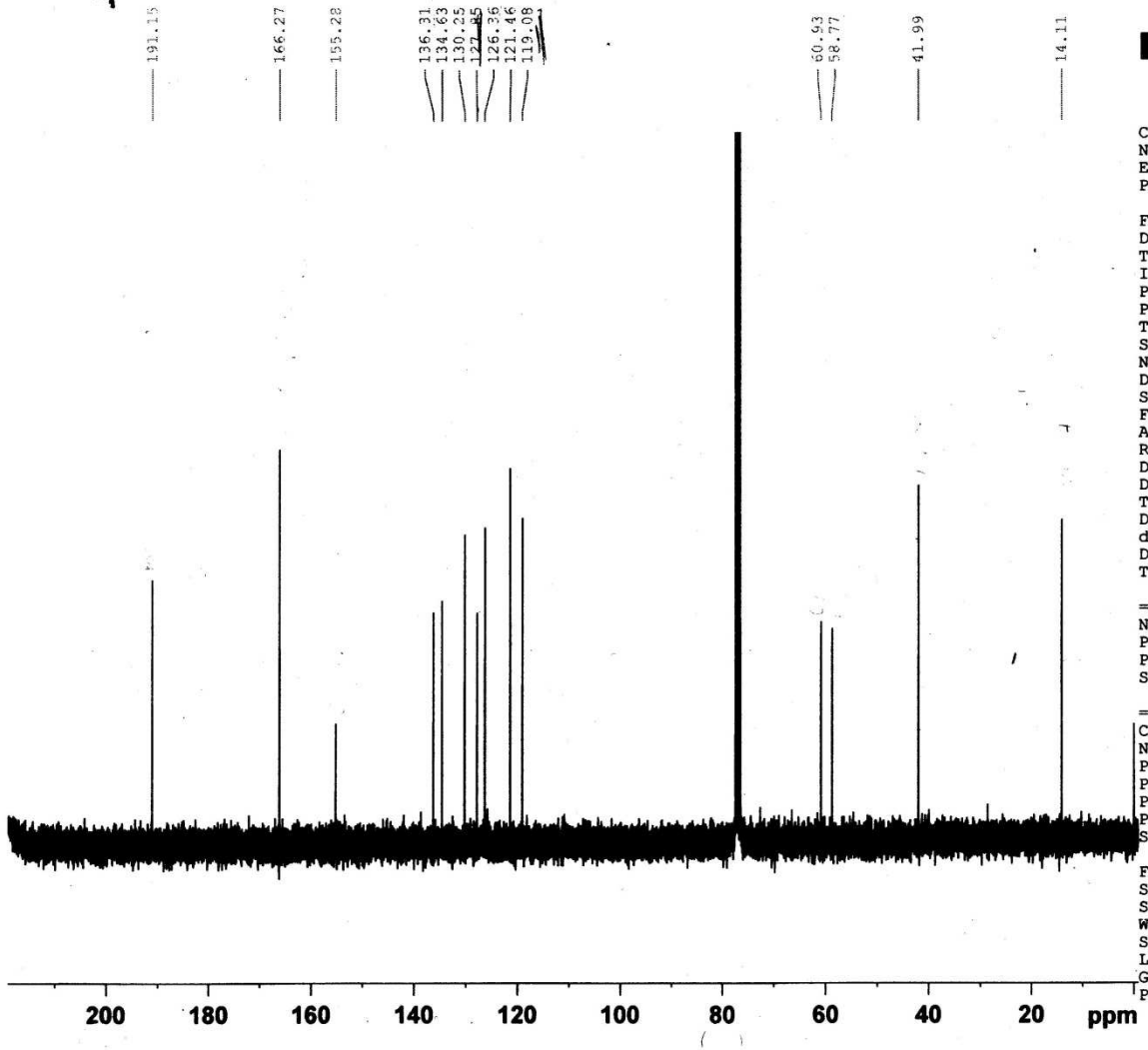


BRUKER

```
Current Data Parameters
NAME                  KAW-i-067
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20120726
Time                       8.55
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                      812.7
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                 300.1300053 MHz
WDW                         no
SSB                          0
LB                      0.00 Hz
GB                           0
PC                        1.00
```

KAW-I-067





BRUKER

Current Data Parameters
NAME KAW-I-067 C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_	20120728
Time	15.51
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8000
DS	4
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	3649.1
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 ========

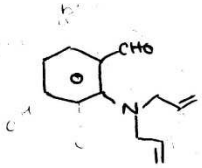
NUC1	13C
P1	7.10 usec
PL1	-1.50 dB
SFO1	75.4752953 MHz

======== 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	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40



KAW-i-003

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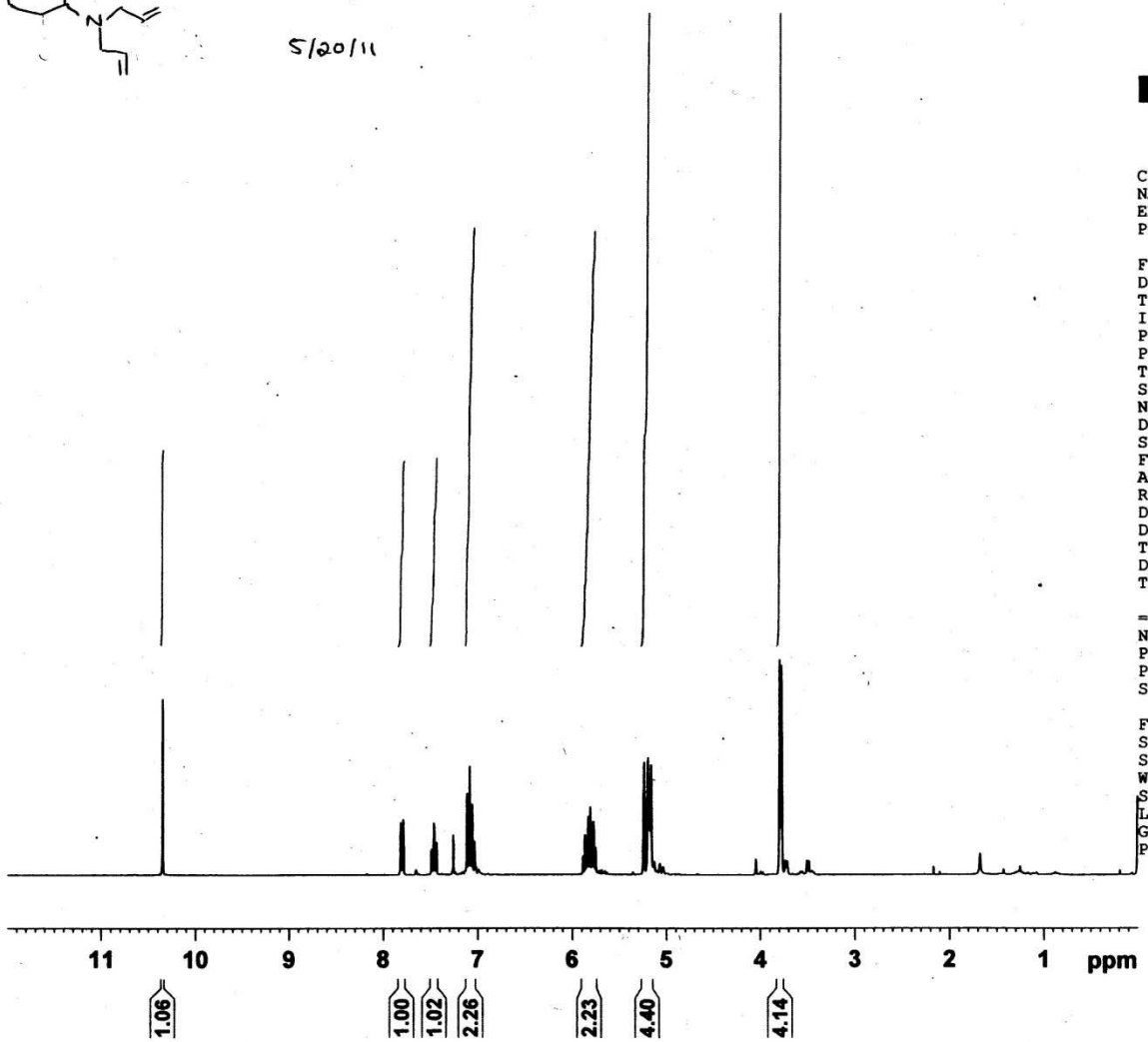
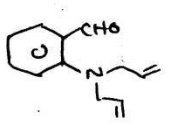


BRUKER

```
Current Data Parameters
NAME                 KAW-i-003
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20110520
Time                   11.59
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                        101.6
DW                       81.000 usec
DE                        6.00 usec
TE                       475.2 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                  300.1300063 MHz
WDW                         no
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.00
```

5/24/11

KAW-i-003 13c



BRUKER

Current Data Parameters

NAME	KAW-i-003 13c
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20110525
Time	2.29
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	32768
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

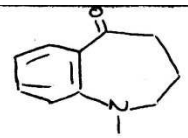
======== CHANNEL f2 ========

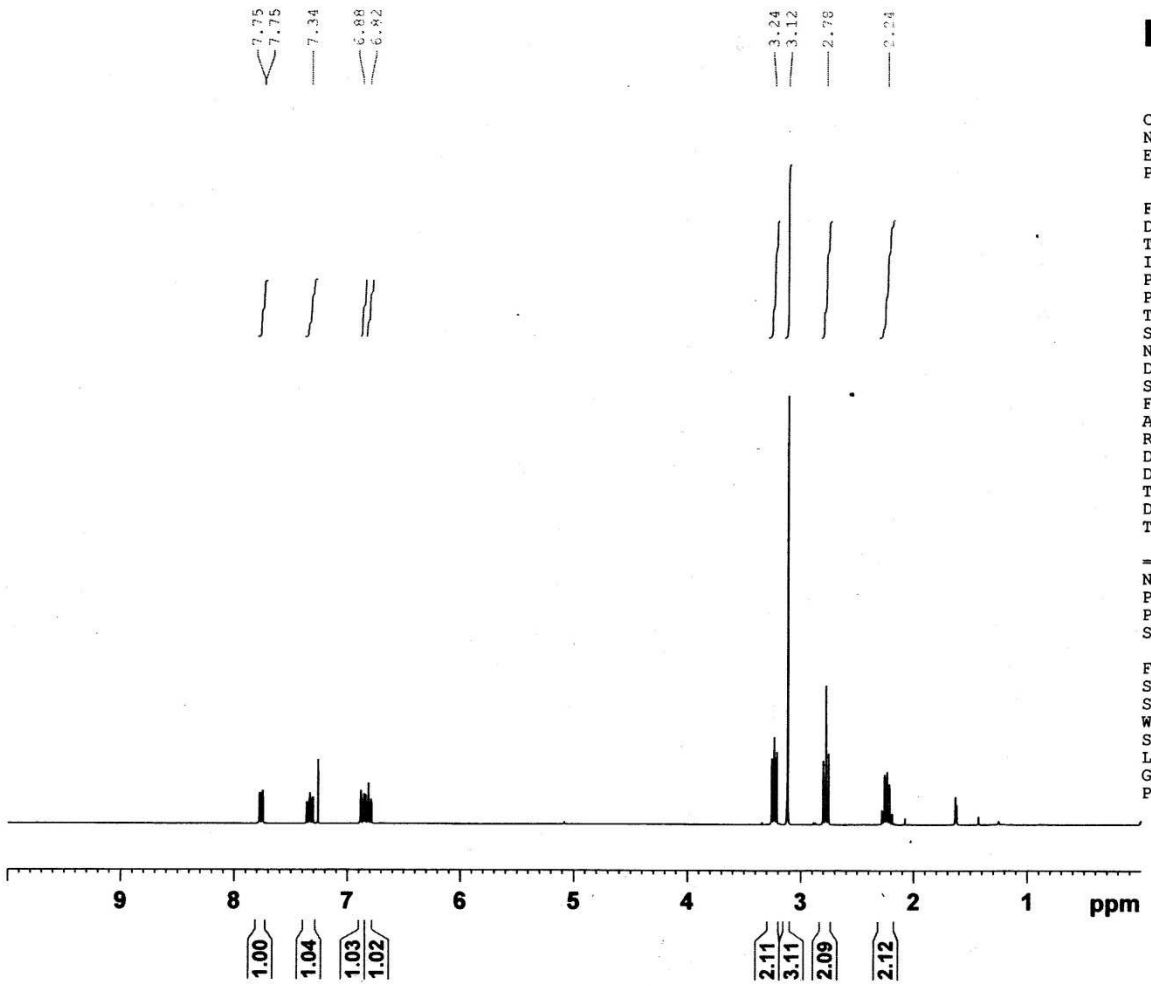
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	17.23 dB
PL13	19.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677490 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

KAW-I-063





BRUKER

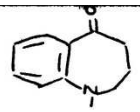
Current Data Parameters
NAME KAW-I-063
EXPNO 1
PROCNO 1

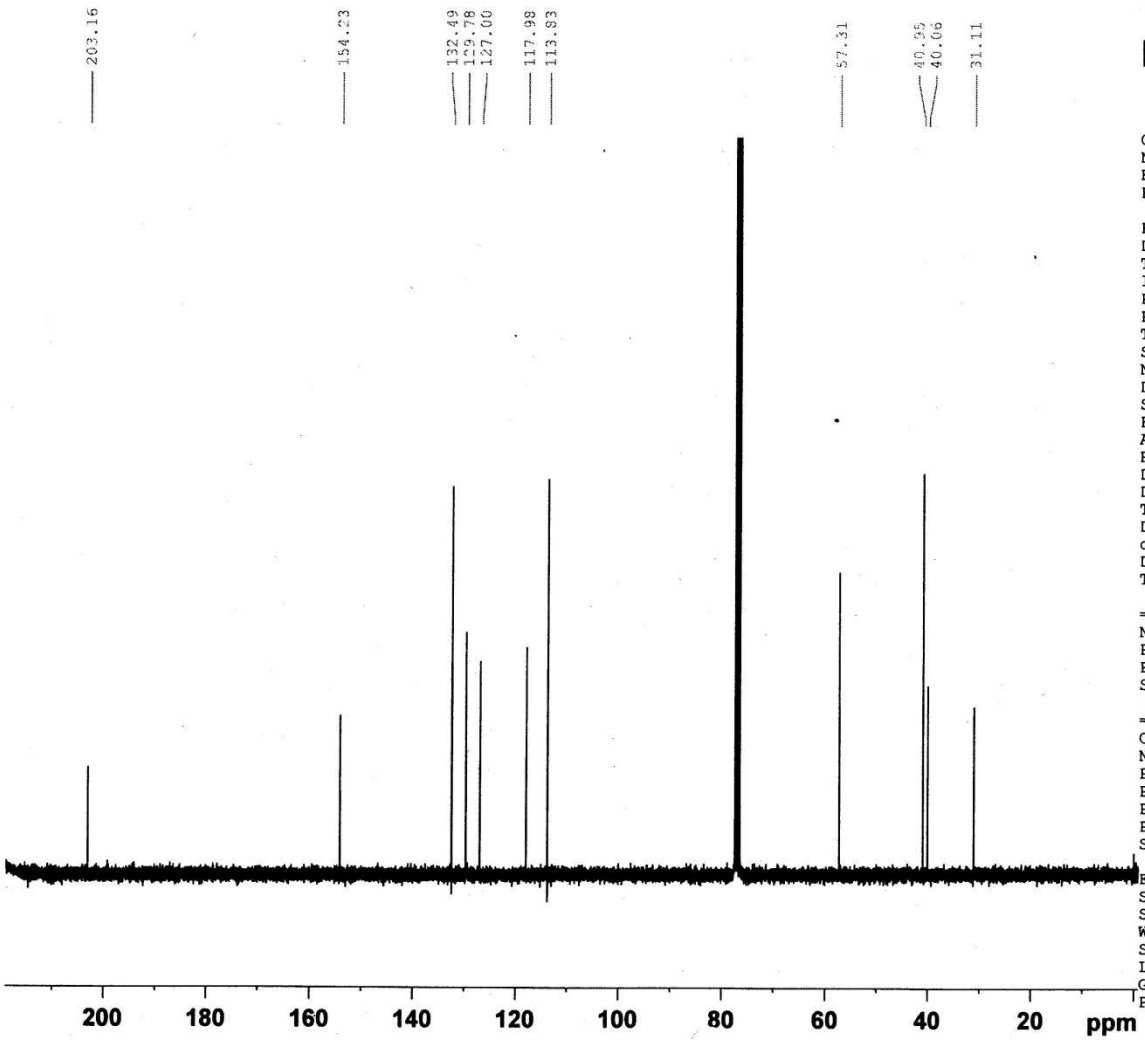
F2 - Acquisition Parameters
Date_ 20120719
Time 13.41
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 512
DW 81.000 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-1-063





BRUKER

Current Data Parameters
NAME KAW-I-063 C13
EXPNO 1
PROCNO 1

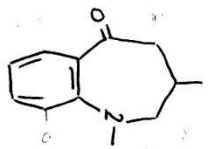
F2 - Acquisition Parameters
Date_ 20120720
Time 0.31
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2896.3
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

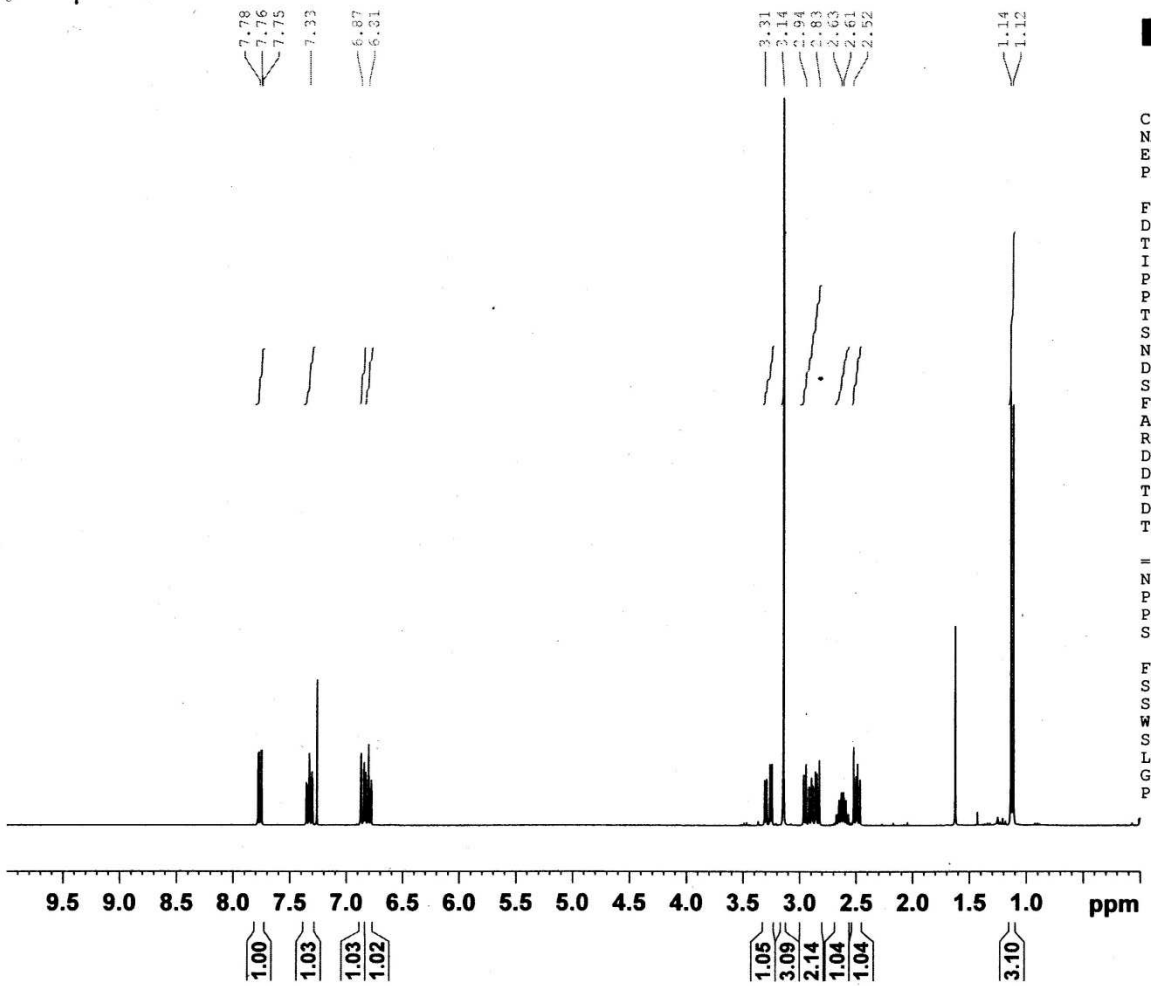
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-061





BRUKER

Current Data Parameters

NAME	KAW-I-061
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

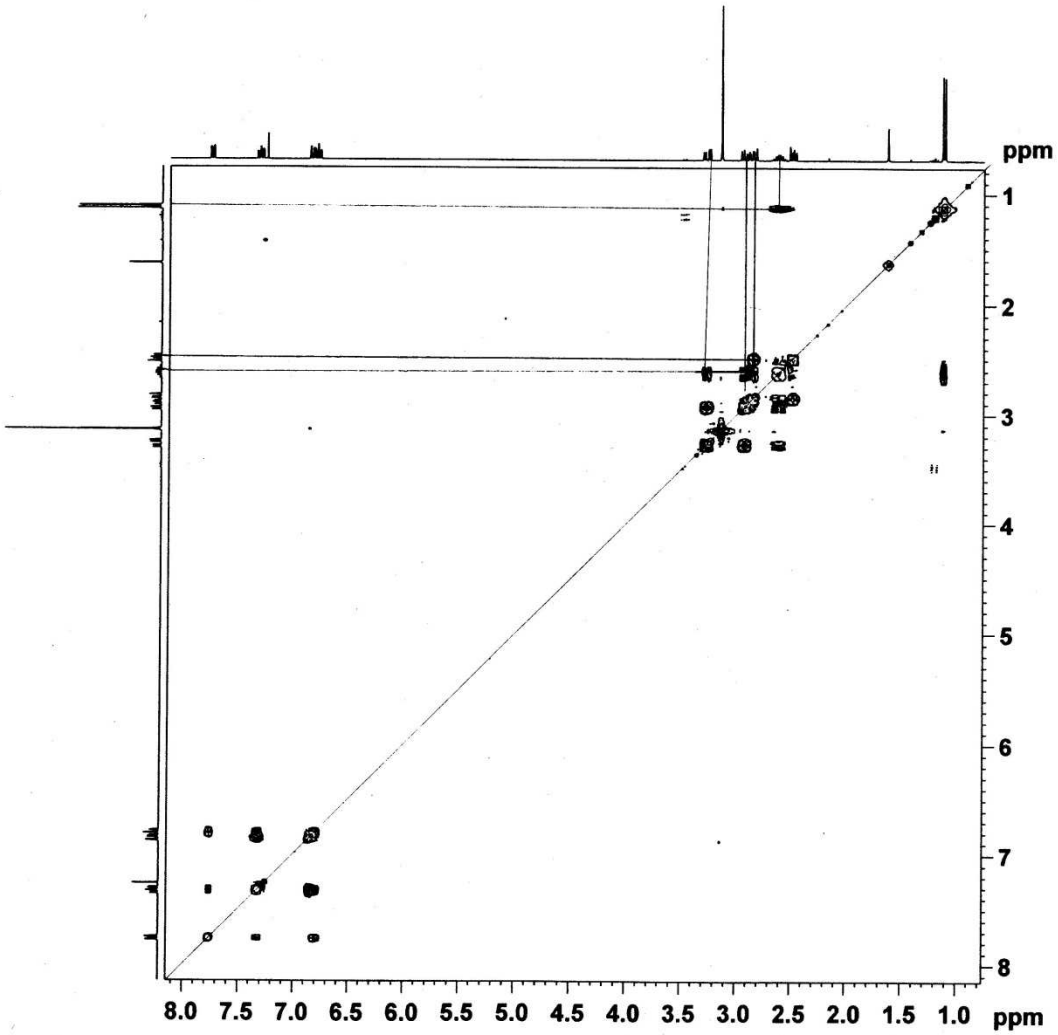
Date_	20120718
Time	11.24
INSTRUM	spect
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	456.1
DW	81.000 usec
DE	6.00 usec
TE	294.2 K
D1	1.00000000 sec
TD0	1

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

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

F2 - Processing parameters

SI	32768
SF	300.1300054 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



BRUKER

Current Data Parameters
NAME KAW-I-061 Cozy Spectra
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120719
Time 14.10
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 1
DS 8
SWH 2216.312 Hz
FIDRES 1.082184 Hz
AQ 0.4620788 sec
RG 228.1
DW 225.600 usec
DE 6.00 usec
TE 294.2 K
d0 0.00000300 sec
D1 1.28168201 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00045120 sec

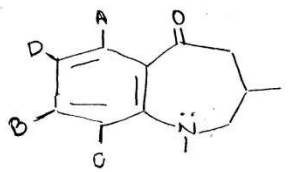
======== CHANNEL f1 ========
NUC1 1H
P0 11.00 usec
P1 11.00 usec
PL1 0.00 dB
SFO1 300.1313426 MHz

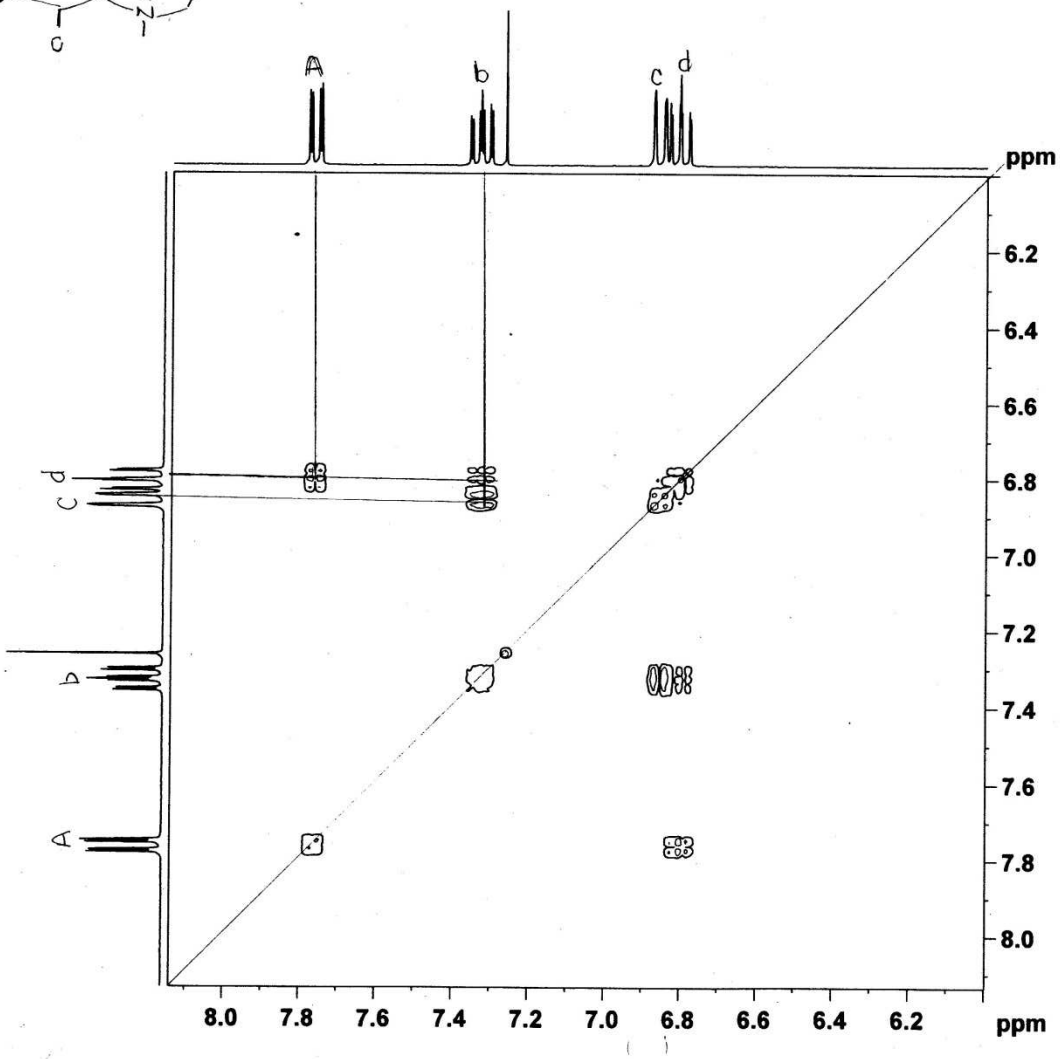
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 1
TD 128
SFO1 300.1313 MHz
FIDRES 17.314938 Hz
SW 7.384 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 300.1300053 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300053 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0





BRUKER

Current Data Parameters
NAME KAW-I-061 Cozy Spectra
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120719
Time 14.10
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 1
DS 8
SWH 2216.312 Hz
FIDRES 1.082184 Hz
AQ 0.4620788 sec
RG 228.1
DW 225.600 usec
DE 6.00 usec
TE 294.2 K
d0 0.00000300 sec
D1 1.28168201 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00045120 sec

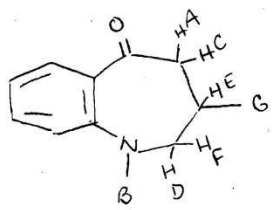
======== CHANNEL f1 ========
NUC1 1H
P0 11.00 usec
P1 11.00 usec
PL1 0.00 dB
SFO1 300.1313426 MHz

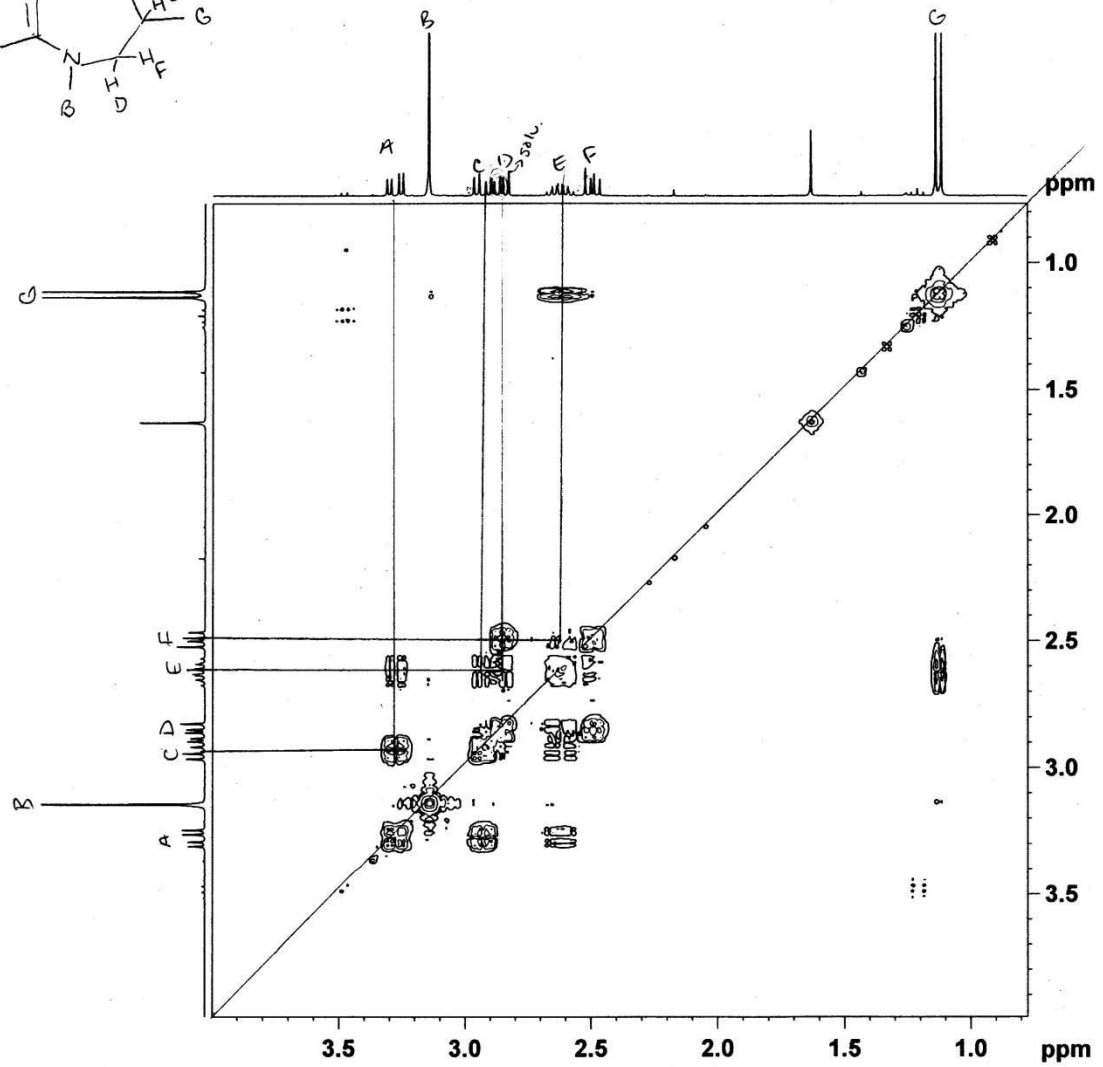
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 1
TD 128
SFO1 300.1313 MHz
FIDRES 17.314938 Hz
SW 7.384 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 300.1300053 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300053 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

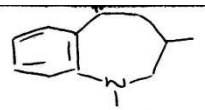


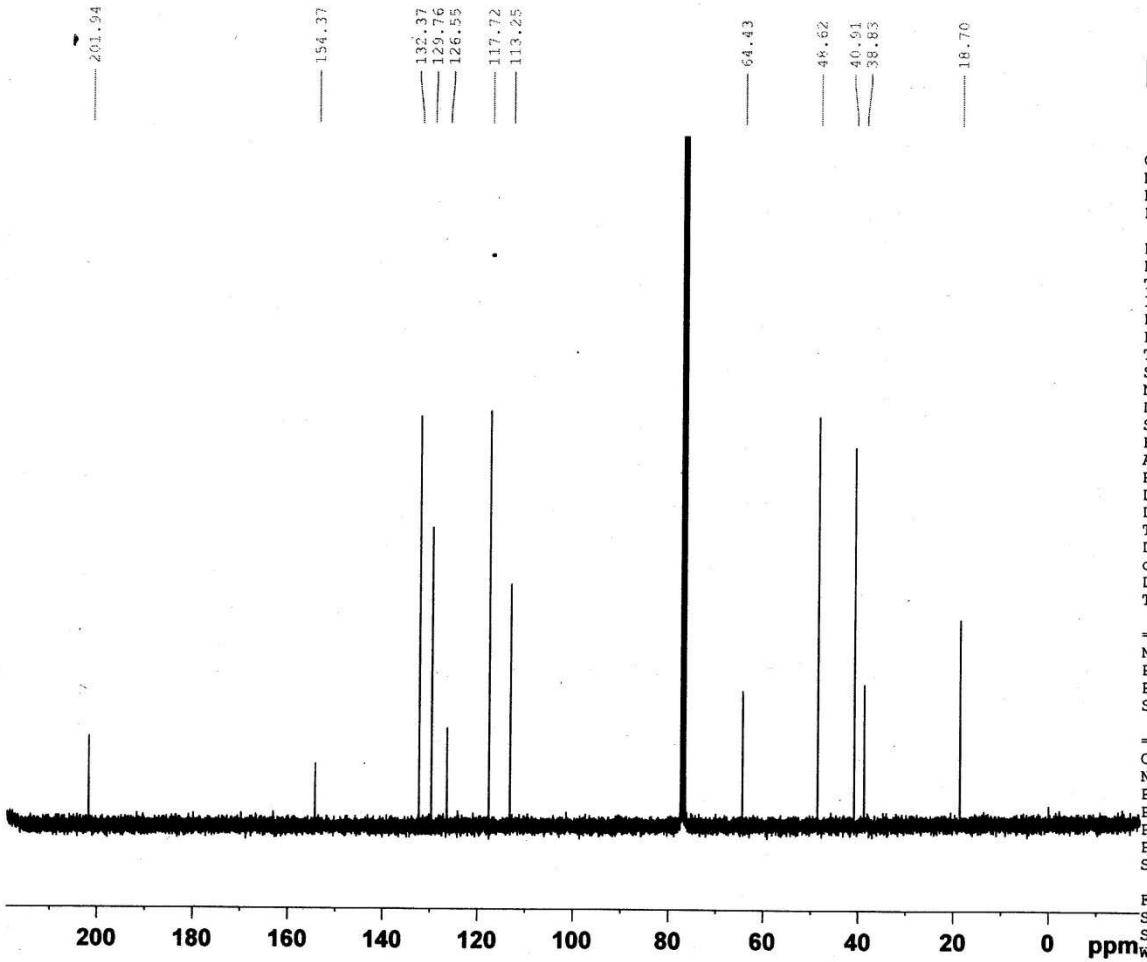


BRUKER

```
Current Data Parameters
NAME      KAW-I-061 Cozy Spectra
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20120719
Time                       14.10
INSTRUM                    spect
PROBHD   5 mm Multinucl
PULPROG                cosygpqf
TD                         2048
SOLVENT                   CDCl3
NS                             1
DS                             8
SWH                   2216.312 Hz
FIDRES                1.082184 Hz
AQ                    0.4620788 sec
RG                         228.1
DW                       225.600 usec
DE                         6.00 usec
TE                        294.2 K
d0                    0.00000300 sec
D1                    1.28168201 sec
d13                   0.00000400 sec
D16                   0.00020000 sec
IN0                   0.00045120 sec

======== CHANNEL f1 ========
NUC1                          1H
P0                         11.00 usec
P1                         11.00 usec
PL1                         0.00 dB
SFO1                300.1313426 MHz

====== GRADIENT CHANNEL =====
GPNAM1                 SINE.100
GPZ1                       10.00 %
P16                      1000.00 usec

F1 - Acquisition parameters
ND0                            1
TD                           128
SFO1                300.1313 MHz
FIDRES               17.314938 Hz
SW                         7.384 ppm
FnMODE                        QF

F2 - Processing parameters
SI                          1024
SF                  300.1300053 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00

F1 - Processing parameters
SI                          1024
MC2                           QF
SF                  300.1300053 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
```

KAW-I-061 C13





BRUKER

Current Data Parameters
NAME KAW-I-061 C13
EXPNO 1
PROCNO 1

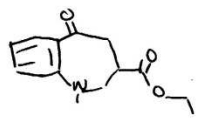
F2 - Acquisition Parameters
Date_ 20120719
Time 1.57
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3251
DW 27.800 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

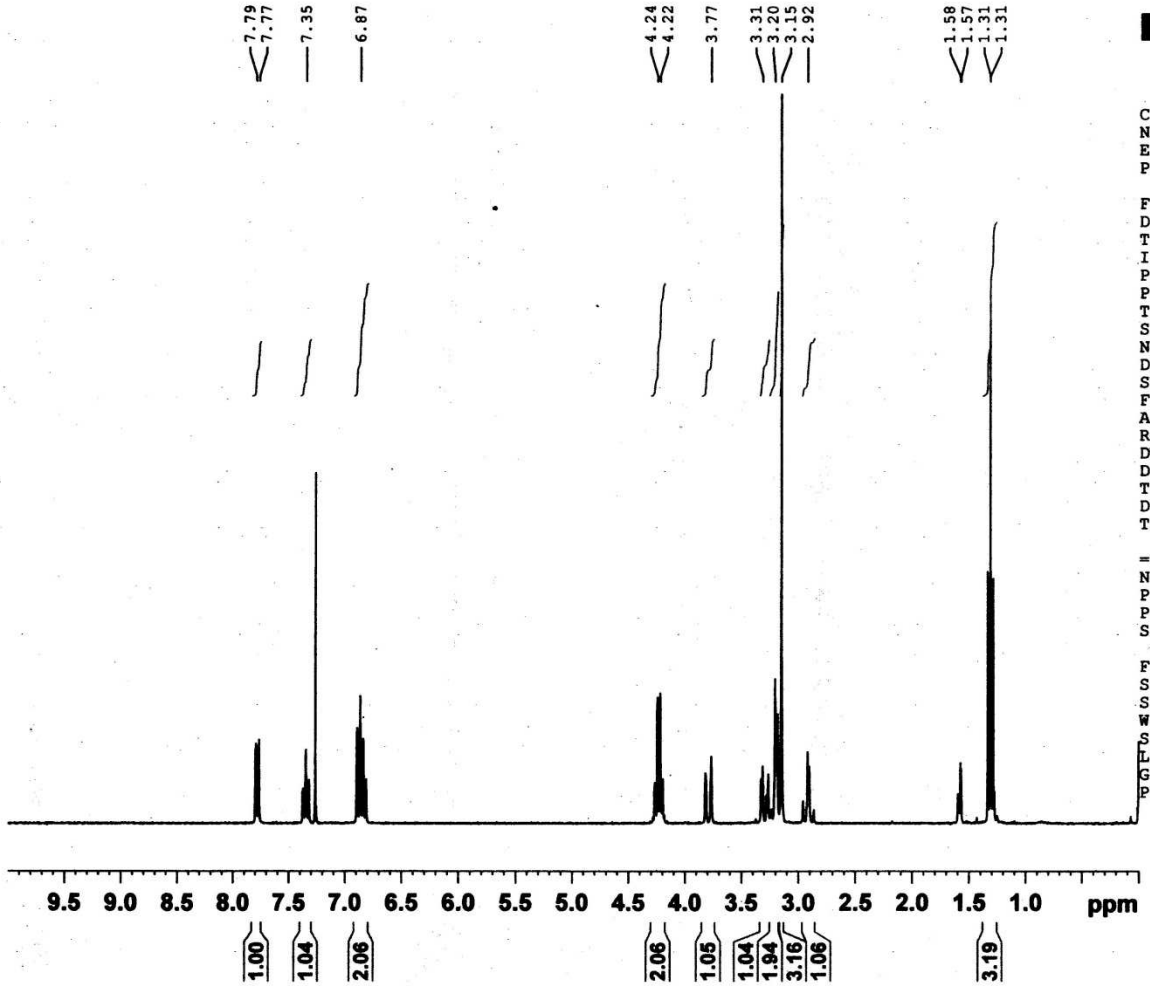
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-II-020





BRUKER

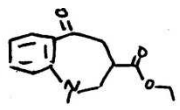
Current Data Parameters
NAME KAW-II-020
EXPNO 1
PROCNO 1

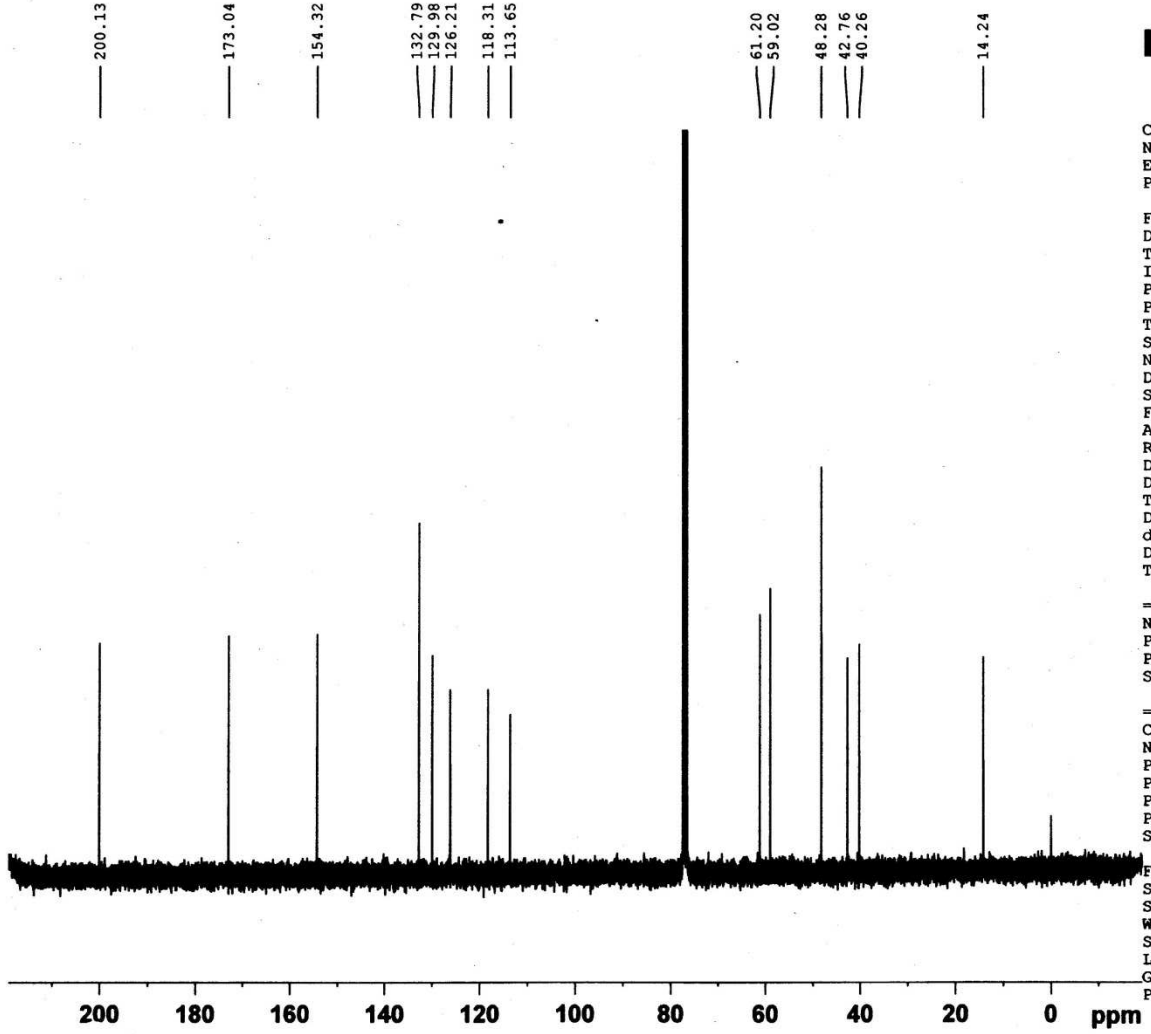
F2 - Acquisition Parameters
Date_ 20130125
Time 11.50
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 724.1
DW 81.000 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

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

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

KAW-II-020





BRUKER

Current Data Parameters
NAME KAW-II-020 C13
EXPNO 1
PROCNO 1

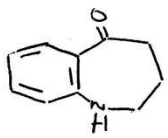
F2 - Acquisition Parameters
Date_ 20130130
Time 0.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

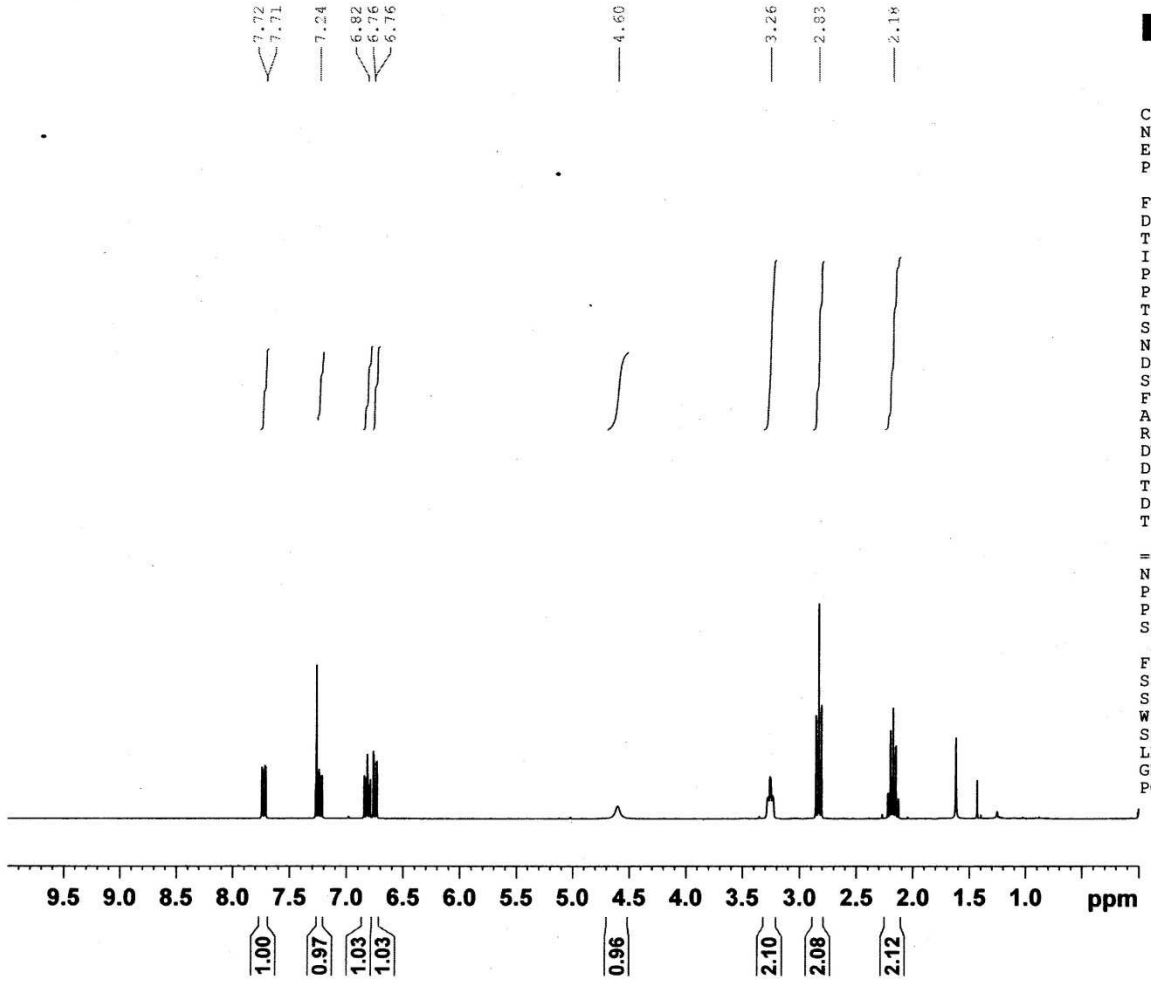
======== CHANNEL f1 ========
NUC1 13C
P1 7.10 usec
PL1 -1.50 dB
SFO1 75.4752953 MHz

======== 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

KAW-I-050 9L

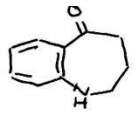


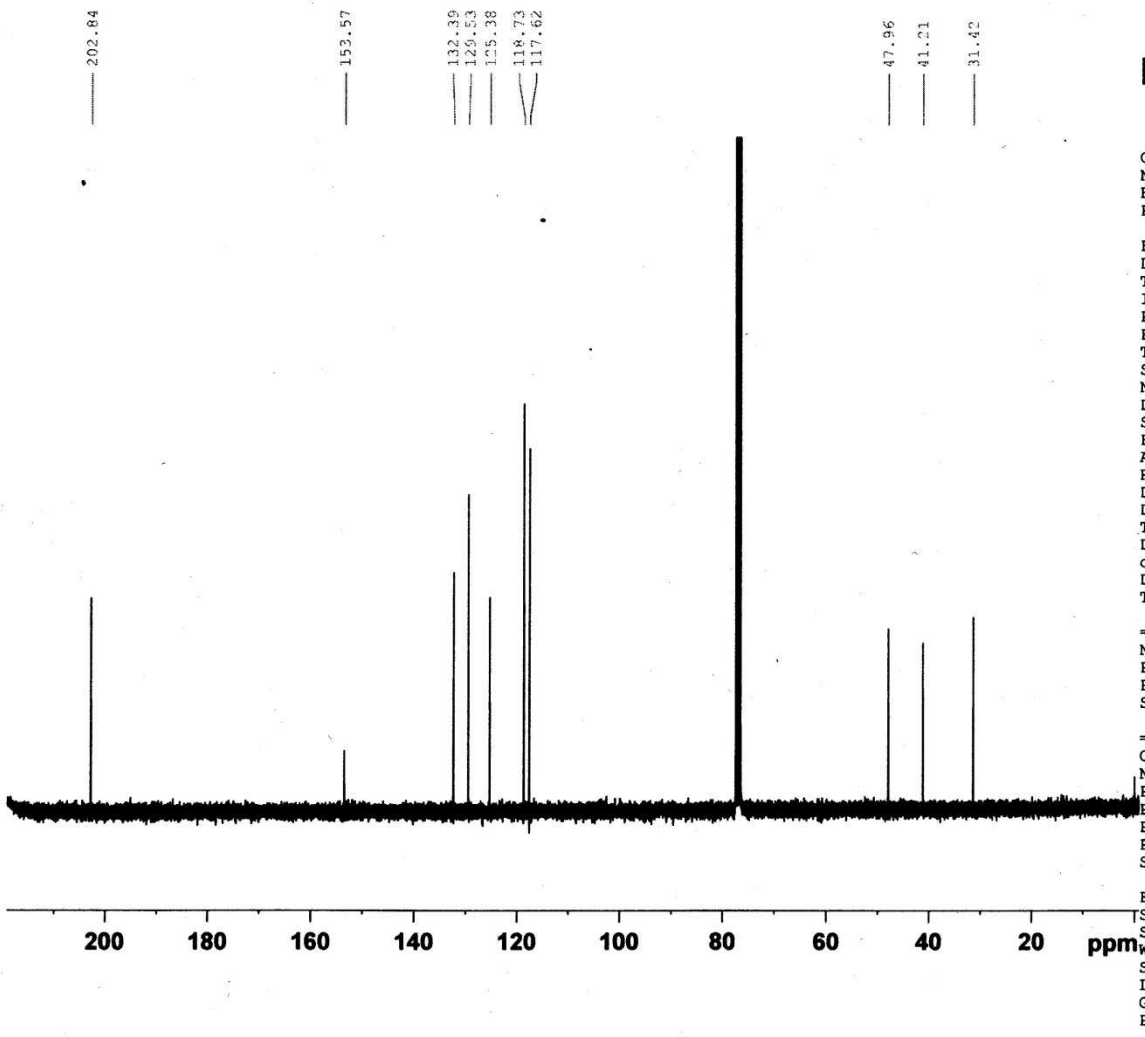


BRUKER

```
Current Data Parameters
NAME      KAW-I-050 Pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120703
Time              17.10
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                574.7
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           300.1300051 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

KAW-1-050





BRUKER

Current Data Parameters
NAME KAW-I-050 C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120706
Time 1.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3649.1
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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40