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Chelation-Assisted Intramolecular Hydroacylation Catalyzed by Rhodium(I): Synthesis of Medium Rings

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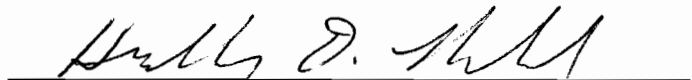
Approved by:



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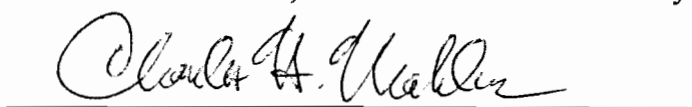

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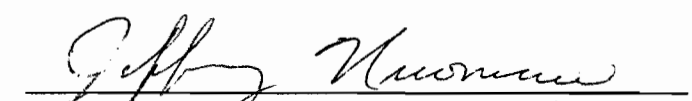

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Chelation-Assisted Intramolecular Hydroacylation Catalyzed by Rhodium(I): Synthesis of Medium Rings

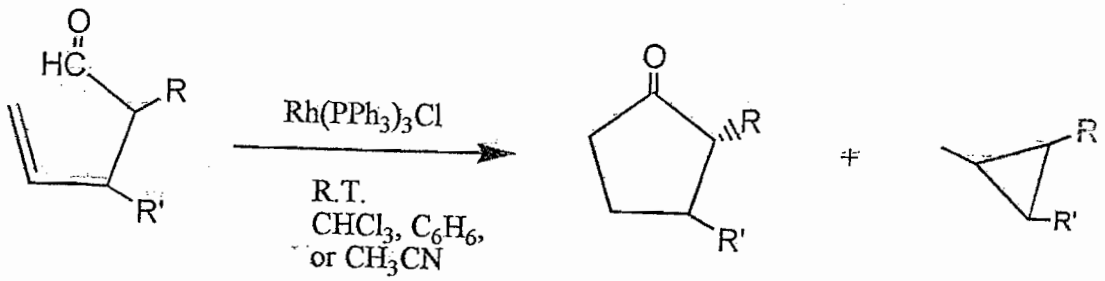
Abstract

The unsaturated aldehyde 4-pentenal can be converted to a cyclic ketone by the catalytic process of intramolecular hydroacylation. Hydroacylation involves oxidative addition of an aldehyde to rhodium (enhanced by proximal assistance), olefin insertion into the Rh-H bond, and reductive elimination of a cyclopentanone from rhodium. The goal of this project was to prepare medium ring heterocyclic ketones by a rhodium catalyzed hydroacylation using chelating, tridentate substrates. To ensure that medium rings were obtained, a tethering atom was incorporated into the substrate. This would further aid in proximal assistance so oxidative addition of the aldehyde could occur. Different substrates were prepared and tested with rhodium catalysts. Intitial work involved substrates containing a nitrogen tethering atom and mainly decarbonylation was observed. An NMR experiment showed that the nitrogen was complexing to the metal but may have been displaced by phosphine ligands. A substrate containing a sulfur tethering atom was tested and upon treatment with Wilkinson's catalyst a 7-membered ring was obtained and verified by ^{1}H NMR spectrum and GC-MS (CI).

I. Introduction/ Background

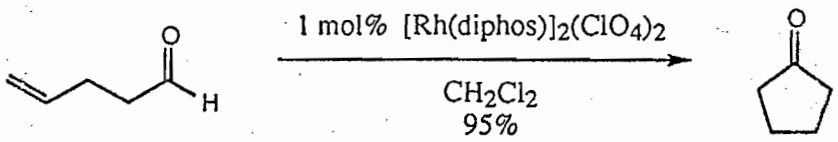
A. Intramolecular Hydroacylation

The exploration of intramolecular hydroacylation has been done by chemists such as Sakai and Larock. Sakai saw that stoichiometric amounts of Wilkinson's catalyst converted 4-pentenal systems into cyclopentanones. Cyclopropane derivatives were also obtained, presumably by a decarbonylation pathway.[1]



Eqn. 1

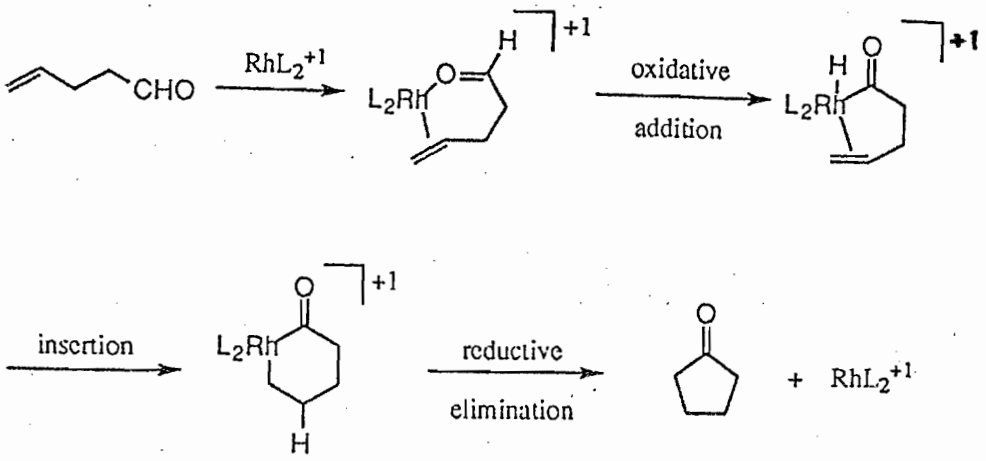
Other work showed that a 4-pentenal could be converted to a cyclic ketone by the catalytic process of intramolecular hydroacylation. The use of rhodium based catalysts almost always produced 5-membered rings.[2] A different rhodium catalyst was used in **Eqn 2** which was seen to have a fast rate of one turnover.



Eqn. 2

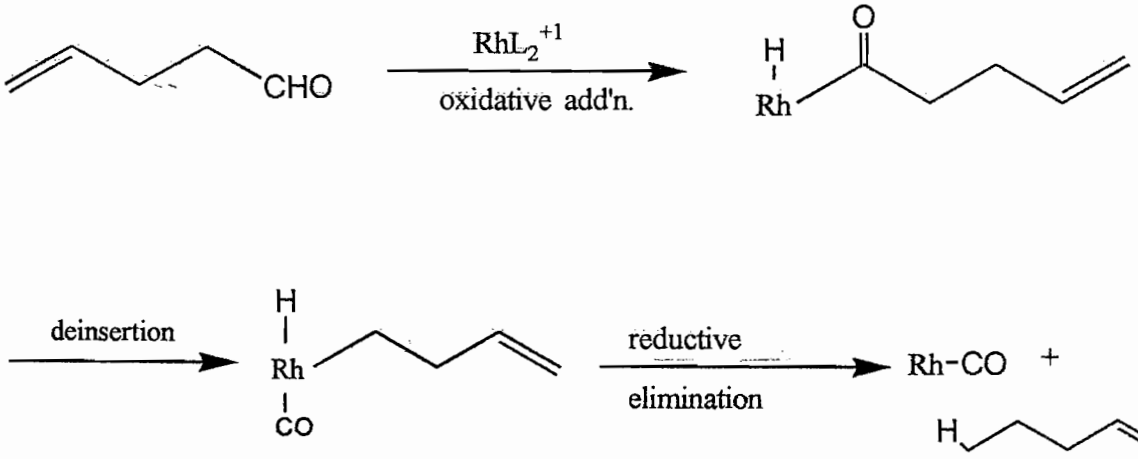
The proposed mechanism for this transformation involves oxidative addition of an aldehyde to rhodium (enhanced by proximal assistance), olefin insertion into the Rh-H bond, and reductive elimination of a cyclopentanone from rhodium.[3]

Scheme 1



As seen earlier, a competing reaction with hydroacylation is decarbonylation of the acyl-metal intermediate (shown in Scheme 2).

Scheme 2



Previous work has shown that decarbonylation can happen at room temperature or at higher temperatures. The use of catalytic amounts of Wilkinson's catalyst along with stoichiometric amounts of diphenyl phosphoryl azide(DPPA)[4] in solvents such as benzene, dichloromethane, and toluene showed decarbonylation upon refluxing (up to 160°) and also at room temperature. Bosnich saw that more basic phosphines bind CO to Rh more tightly because a more basic ligand increases the electron density on the

rhodium. Increased electron density will lead to tighter binding. If the hydroacylation rate is increased, the decarbonylation rate will in turn increase as well.[2] It was also found that aldehydes which were sterically hindered could experience decarbonylation if run in acetonitrile or benzonitrile.

Miller found that in the case of $Rh(PPh_3)_3Cl$, decarbonylation may be inhibited if the reaction is run under an atmosphere of ethylene.[2] Decarbonylation was experienced with the use of $[Rh(dppe)_2]Cl$ and $[Rh(dppp)_2]Cl$ in either xylene or toluene.[5] The reactions were run at room temperature or heated to reflux under N_2. The most active decarbonylation agent known is $Rh_2(PMe_3)_4Cl_2$.[6] Reactions were run with this catalyst at room temperature and at reflux.

B. Limitations to Hydroacylation

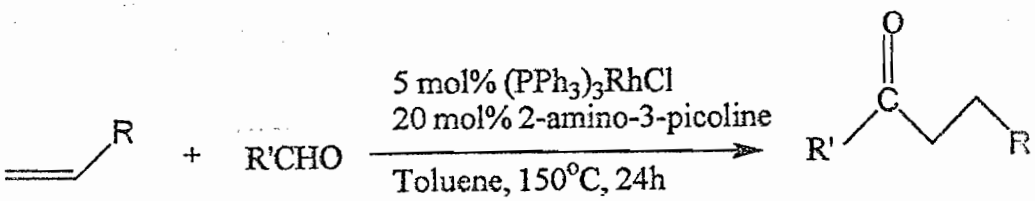
Intramolecular hydroacylation is limited in most cases to the preparation of cyclopentanones. Attempts to prepare larger rings using substrates with larger alkyl chains have proven unsuccessful. The hydroacylation mechanism (shown in Scheme 1) illustrates the limits of hydroacylation. This mechanism suggests that metallacycle intermediates larger than 6 members will not be formed because they are not kinetically and thermodynamically favorable. Another example that shows the limitations is the case of 6-octenals.[7] With 6-octenals it appears that no hydroacylation occurs and the lack of proximal assistance causes oxidative addition of the aldehyde to occur slowly or possibly not at all.

In order for larger size rings to be formed in the hydroacylation reaction two factors will have to be taken into consideration. Large metallacycle intermediates will

have to be avoided and oxidative addition of the aldehyde must be enhanced by proximal assistance.

C. Intermolecular Hydroacylation

The most successful catalyst for the intermolecular hydroacylation is Wilkinson's catalyst.[8] It is interesting to note that $Rh(CO)(PPh_3)_3Cl$ showed catalytic hydroacylation activity even though it is formed by the decarbonylation of the aldehyde.[8]

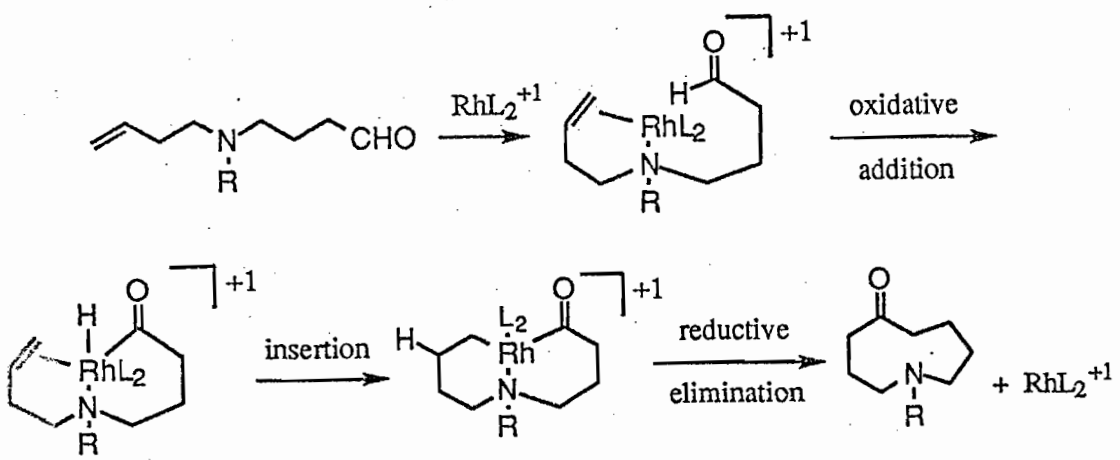


Eqn. 3

II. Project Design

The goal of this project is to prepare medium ring heterocyclic ketones by a rhodium catalyzed hydroacylation using chelating, tridentate substrates. The overall scheme of this project is shown in Scheme 3.

Scheme 3

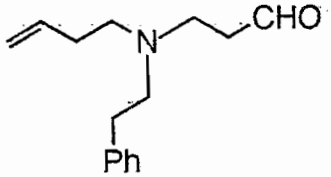


If rings larger than 5 atoms are to be formed, the substrate will have to be designed so that oxidative addition of the aldehyde is encouraged by proximal assistance and large unfavorable metallacycle intermediates will be avoided. The incorporation of a tethering atom should aid in this proximal assistance because it provides another binding site to which the rhodium can attach. The tethering atom (N, S, or O) must be sufficiently basic or the substrate may not complex to the metal and hydroacylation may not occur. If it is too basic, a stable, unreactive complex may form because the tridentate substrate may bind to the metal tightly.

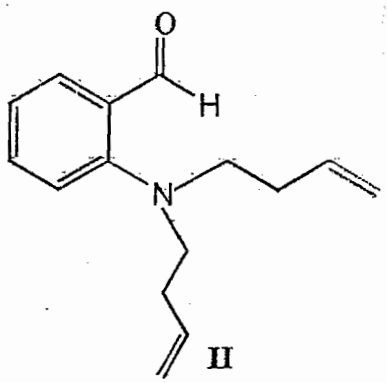
An appropriate rhodium (I) catalyst will need to be found. Wilkinson's catalyst, $Rh(PPh_3)_3Cl$ catalyzes both intramolecular and chelation assisted intermolecular hydroacylation. However, decarbonylation may interfere with the reaction. Complexes analogous to Wilkinson's will be used to screen the effects of various phosphine and phosphite ligands. The decarbonylation products that result could be minimized by ligands that are poorer σ -donors and better π -acceptors (less basic) than triphenylphosphine. The best catalyst will be the one that could supply the four coordination sites required by the reaction and does not promote decarbonylation which can compete with hydroacylation.

.III. Results

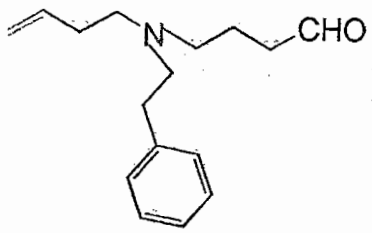
Syntheses of four substrates were attempted. Substrates III and IV were successfully synthesized and tested with rhodium catalysts.



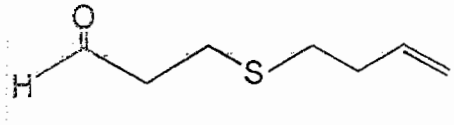
I



II

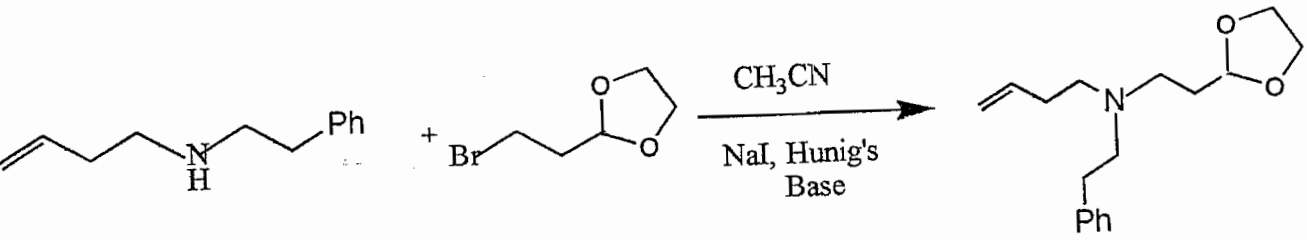


III



IV

Preparation of N-(3-butenyl)-N-(2-phenylethyl)-3-aminopropanal



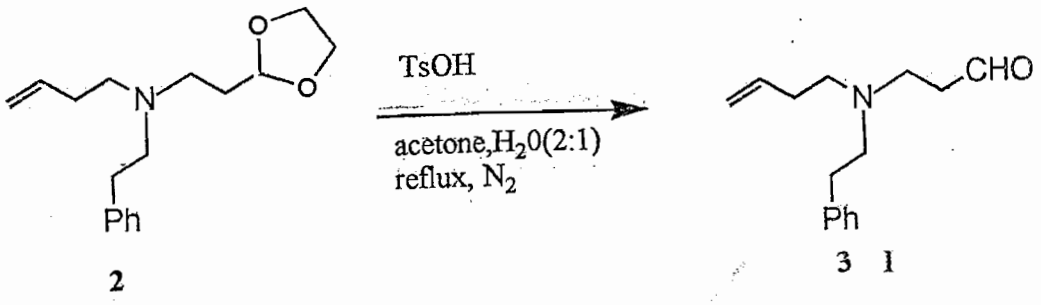
1

37.4%

2

Compound **1** (1eq.) was reacted with the primary alkyl bromide (1.5eq.), NaI (2eq.), and Hunig's base (2eq.) in dry acetonitrile. Compound **1** can be prepared from $PhCH_2CH_2NH_2$ and 4-bromo-1-butene.[9] The reaction was run under N_2 and the resultant reaction mixture was peach in color. It was monitored by GC and was purified by column chromatography. The final product was the tertiary amine obtained as a yellow/brown oil in 37% yield.

The compound was characterized by ^1H NMR. The presence of a multiplet at 3.7-3.9ppm, due to the methylenes of the dioxolane ring, confirmed the presence of the dioxolane fragment.



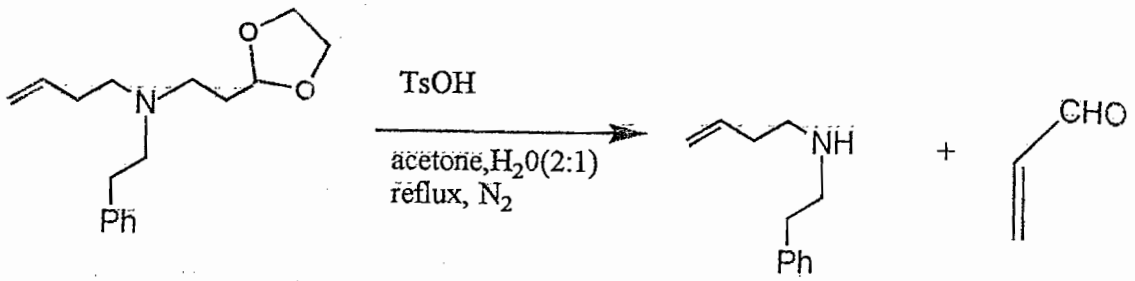
2 3 I

Compound **3(I)** was prepared in 43% yield by deprotecting the aldehyde using p-toluenesulfonic acid (1.5eq.), water, and acetone. The yellow reaction mixture was refluxed overnight and was monitored by GC. The resultant product was a yellow/brown oil that was characterized by ^{1}H NMR. The disappearance of the multiplet between 3.7-3.9 ppm and the presence of an aldehyde peak at 9.7 ppm confirmed that it was the desired product. A variety of conditions were used to prepare compound **3** and are summarized in Table 1.

Table 1

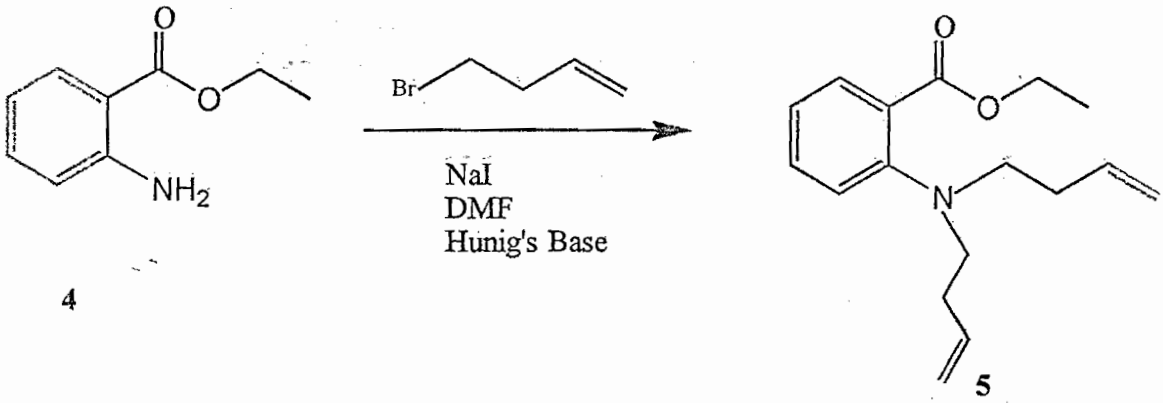
Entry	Reagents	Conditions/ Observations	Yield	Characterization
1	TsOH acetone water	Reflux overnight yellow oil	----	^{1}H NMR, compound underwent elim.
2	THF 5% HCl	r.t. overnight refluxed clear sol'n lt. yellow oil	----	crude ^{1}H NMR could not identify

Both reactions in Table 1 were attempts at a scale-up. However, in one case the compound underwent elimination:



In the second reaction no positive identification could be made on the product. Due to these difficulties encountered, this substrate was abandoned.

Preparation of 2-(bis(3-butenyl)amino)benzaldehyde (Method 1)



4 5

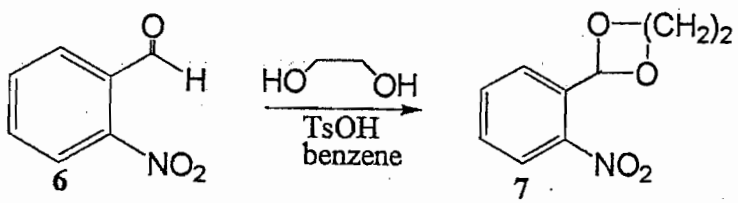
Compound **4,** ethyl 2-aminobenzoate (1eq.), was combined with 4-bromo-1-butene (3eq.), NaI, and Hunig's base (3eq.) in DMF, refluxed under N and monitored by GC. Purification by column chromatography gave amonoalkylated product in a 13% yield. The oil was characterized by IR and ^{1}H NMR. Varied conditions were tried and a summary of these reactions are shown in Table 2. Ideally the nitrogen would have been di-alkylated, however our characterization showed that only monoalkylation occurred. This was probably because the lone pair of electrons on the N were tied up in conjugation with the ring and the ester.

The IR spectrum showed a peak at 3367cm^{-1} indicating the presence of a primary amine. The ^{1}H NMR spectrum showed a peak between 5.1-5.2 ppm indicating the presence of alkene protons. Also the presence of a quartet at 2.4 ppm and a triplet at 3.2 ppm indicated the presence of the methylenes of the butenyl moiety. This confirmed the presence of our mono-alkylated product.

Table 2

Entry	Reagents	Conditions/ Observations	Yield	Characterization
1	R-Br (7eq.) NaI (7eq.) Hunig's base (3 eq.) DMF	refluxed under N_2 oil	0.0407g 37.0%	IR: 3367 cm^{-1} ^{1}H NMR: 1.3 ppm 5.1-5.2 ppm
2	R-Br (7eq.) NaI (7eq.) Hunig's base (3eq.) CH_3CN	refluxed under N_2	0.0511g 46.0%	^{1}H NMR: 1.3 ppm 5.1-5.2ppm
3	R-Br(7eq.) NaI (7eq.) Hunig's base (3eq.) CH_3CN	refluxed under N_2 oil	0.7766g 72.0%	^{1}H NMR: 1.3 ppm, 5.1-5.2 ppm

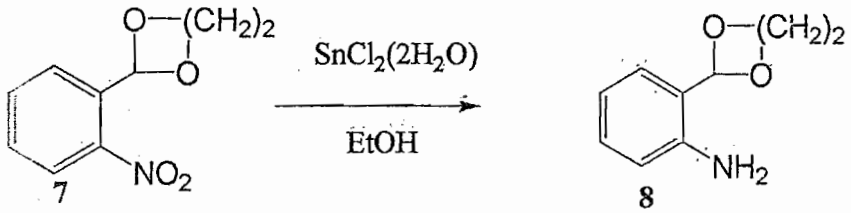
Preparation of of 2-(bis(3-butenyl)amino)benzaldehyde (Method 2)



6 7

Ortho-nitro-benzaldehyde (1eq.), **6**, was treated with ethylene glycol (1.1eq.) and p-toluenesulfonic acid in benzene to obtain the protected aldehyde**7**, in 97% yield as a

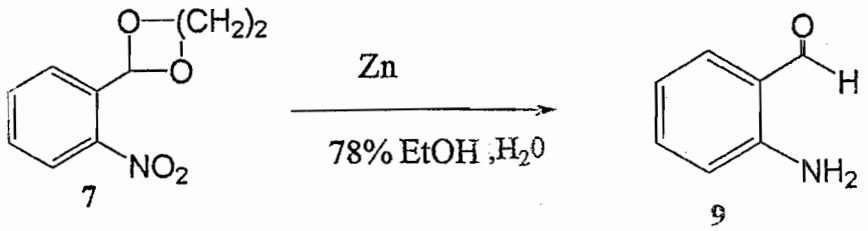
colorless oil. The reaction was refluxed overnight and was used without further purification. The product was characterized by ^{1}H NMR spectrum. The appearance of the multiplet at 4.1 ppm indicated the presence of the methylenes of the dioxolane ring.



7 8

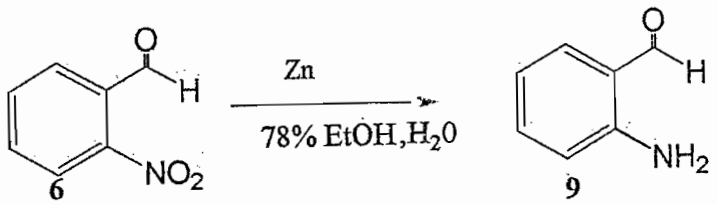
The protected aldehyde (1eq.), 7, was treated with tin(II) chloride dihydrate (5eq.) in ethanol in an attempt to reduce the nitro group to an amine. The reaction was run under N_2 and refluxed. It was monitored by GC. After work-up, a ^{1}H NMR spectrum was taken and it did not appear that the desired product was obtained. The peaks at 4.1 ppm which indicated the methylenes of the protecting group did not have the same coupling pattern as seen before and there was no appearance of an NH peak. An IR spectrum was also taken and a peak at 3368 cm^{-1} was indicative of an NH however it was a weak signal.

The reaction was tried again, only this time starting with 2-nitrobenzaldehyde, 6, instead of compound 7. Again the reaction was refluxed under N_2. A ^{1}H NMR spectrum was acquired but a positive identification could not be made on the product. Since the synthesis using the tin(II) chloride dihydrate proved unsuccessful an alternate method was found using Zn dust.[12]



7 9

The reaction was initially tried on the protectedaldehyde. The reaction was run under N_2 and refluxed for 6 hours. The resulting oil was a pale yellow color obtained in 38% yield. An IR spectrum was obtained and 2 peaks were seen around 3500 cm^{-1} which were indicative of an NH_2. Also a ^1H NMR spectrum was taken and an aldehyde peak was seen at 9.85ppm. The aldehyde had been deprotected and the nitro had been reduced to an amine. So, the reaction was done again using 2-nitrobenzaldehyde instead of the protected amine as starting material.

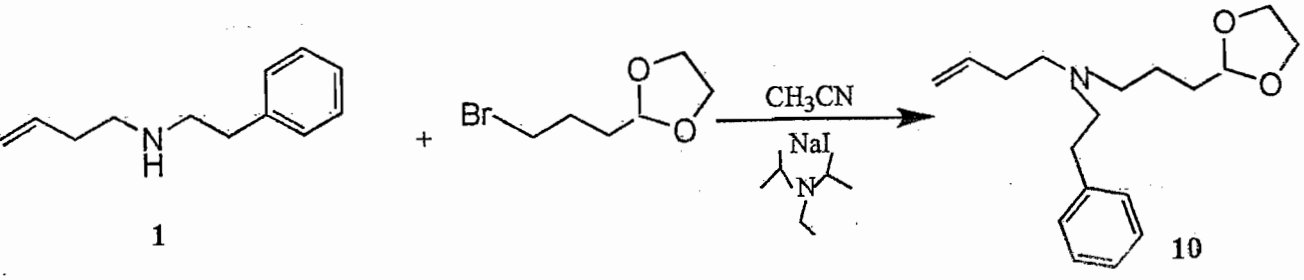


6 9

The reaction was refluxed under N_2 for 6 hours. The resulting oil was pale yellow and obtained in 25% yield. An IR spectrum was taken again and 2 peaks were seen at 3500 cm^{-1} indicating NH_2. A ^1H NMR spectrum was obtained also taken and a peak at 9.85ppm indicated an aldehyde.

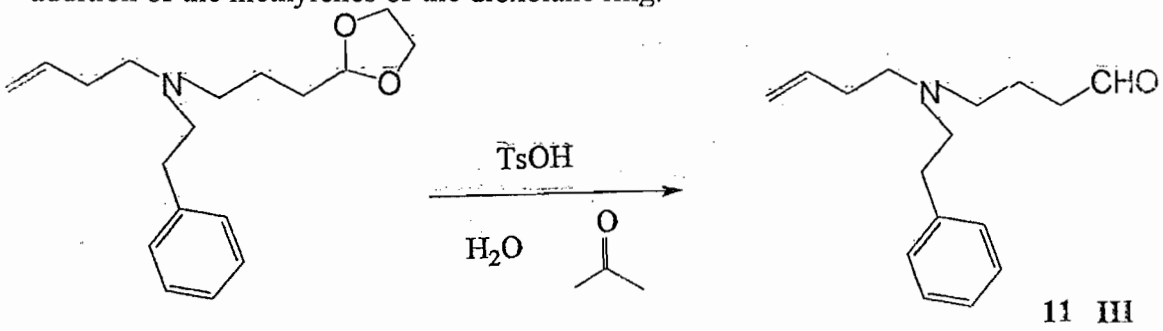
The synthesis of this substrate did not proceed any further due to time constraints on the project. It was thought that this substrate would be a potential candidate for hydroacylation because if decarbonylations were to occur it would produce a four membered metallacycle intermediate which would be unfavorable.

Preparation of N-(3-butenyl)-N-(2-phenylethyl)-3-aminobutanal



1 10

Secondary amine (1eq.), **1**, was combined with a primary alkyl bromide(1.5eq.), NaI (3eq.), and Hunig's Base (2eq.) in dry acetonitrile to give the tertiary amine, **10**. The reaction was refluxed under N_2 and was monitored by GC. Purification by column chromatography produced a yellow oil in a 65% yield. The product was characterized by ^{1}H NMR spectrum. The ^{1}H NMR showed a multiplet between 3.7-4.0 ppm indicating the addition of the methylenes of the dioxolane ring.

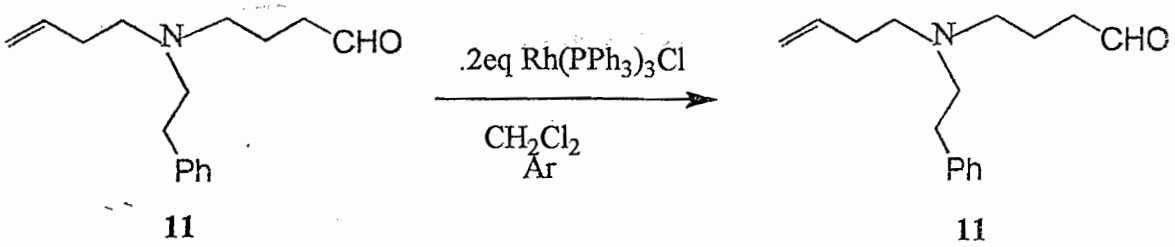


10 11 III

The aldehyde, **11(III)**, was prepared by treating compound **10** with p-toluenesulfonic acid in acetone and water. The reaction was refluxed and monitored by GC. No further purification was done and the result was a brown-yellow oil in 76% yield. The product was characterized by ^{1}H NMR spectrum. The presence of an aldehyde peak, a triplet, at

9.6 ppm and the disappearance of the multiplet between 3.7-4.0 ppm verified the presence of compound **11(III)**.

Compound **11(III)** was then tested with different rhodium catalysts. Both Wilkinson's catalyst and chlorobis(ethylene)rhodium(I)dimer were tested as potential catalysts. The advantage to using the dimer is it allows for different phosphine ligands to be tested. Tris(pentafluorophenyl)phosphine and trimethyl phosphite were tested. These are less basic ligands than triphenylphosphine and should reduce the electron density on the Rh and discourage decarbonylation.



11 **11**

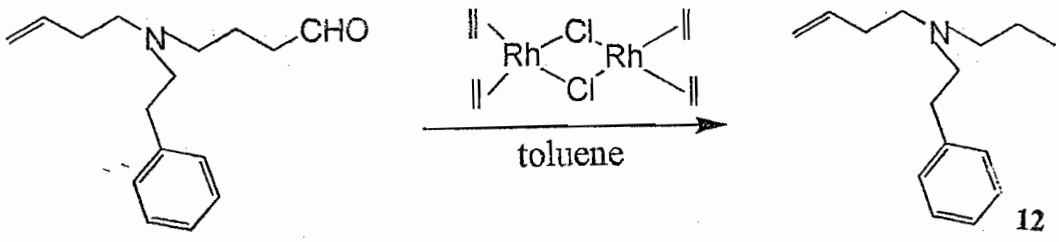
Reaction of **11(III)** with Wilkinson's catalyst did not yield any products. The yellow/orange solution was monitored by GC and only starting material was present. Other reactions were run using Wilkinson's catalyst under varying conditions and they are summarized in Table 3.

Table 3

Entry	Reagents	Conditions/ Observations	Yield	Characterization
1	fresh Wilk. Catalyst(.2eq) CH_2Cl_2	Reflux(Ar) Reaction scorched brown tar	----	no identification was made

2	fresh Wilk Catalyst(.2eq) CH_2Cl_2	Heated in oil bath. (90°C) sealed tube under Ar	----	GC: decarbonylation
3	fresh Wilk. Catalyst, toluene (stoichiometric amounts)	Open to air reflux overnight	---	GC: decarbonylation
4	fresh Wilk. Catalyst CH_2Cl_2 (stoichiometric amounts)	Freeze/thaw degas under Ar Heated in oil bath 95°C, sealed tube, orange sol'n	---	GC: peak at 16 no identification made

Upon heating the reaction mixtures decarbonylation was mainly seen



12

Compound **11(III)** was also reacted with chlorobis(ethylene)rhodium(I)dimer in toluene. It was refluxed under Ar and run at room temperature. The result was a brown mixture which showed decarbonylation (Compound**12**) by GC. The other reactions run with this catalyst are summarized in Table 4.

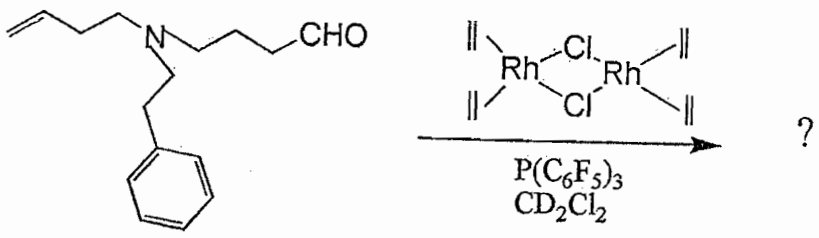
Table 4

Entry	**Reagents**	**Conditions/ Observations**	**Yield**	**Characterization**
1	substrate, Rh catalyst, toluene $P(C_6F_5)_3$ (stoichiometric amounts)	Oil bath, 70°-105°C(reflux), under Ar brown mixture	---	GC: starting material

2	Rh catalyst, dist. P(OMe)3, substrate toluene (stoichiometric amounts)	Freeze/thaw degas 30°C Under Ar, oil bath	---	GC: decarbonylation

Overall no positive results were seen from the reactions performed with the catalyst. It is possible that the amine may not be complexing to the rhodium. To investigate this further an NMR experiment was performed.

NMR Experiment



11

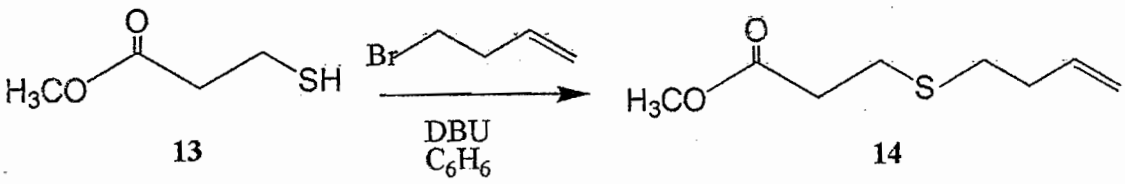
The spectra for this experiment can be found in Appendix A. A ^{1}H NMR spectrum (spectrum #1) was taken of the catalyst and a peak at 3.2 ppm was observed. The peak was a broad and indicating an averaged signal of the ethylenes on the dimer. A ^{31}P NMR spectrum (spectrum #2) was acquired on the tris(pentafluorophenyl)phosphine and a pentet was observed at –74 ppm. A septet would be expected because the phosphine should couple to the six ortho fluorine atoms. However, because the coupling pattern for a septet is 1:6:15:20:15:6:1 the outermost peaks were probably lost in noise.

The catalyst and phosphine were combined and ^{1}H NMR (spectrum #3) and ^{31}P NMR (spectrum #4) spectra were obtained. In the ^{1}H NMR spectrum the same peak

appeared slightly shifted upfield. In the ^{31}P NMR spectrum a pentet was seen again at -74 ppm and a doublet was observed at 1.8 ppm. This showed that some of the phosphine had complexed to the rhodium.

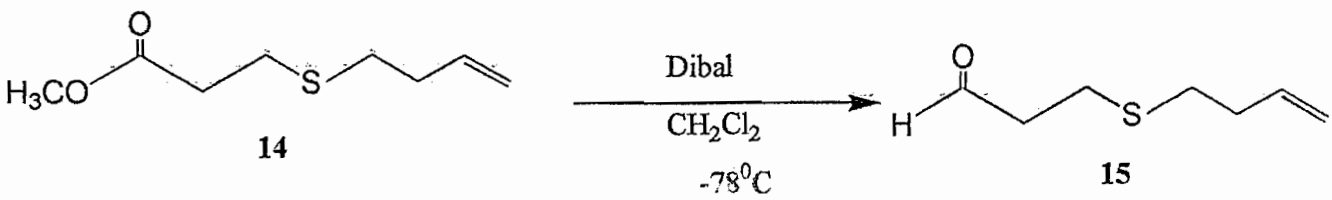
Finally the substrate was added to the mixture and NMR spectra was obtained again. The ^{1}H NMR (spectrum #5) showed an aldehyde peak at 9.7 ppm, alkene peaks at 5.0 ppm and 5.85 ppm. A peak for free ethylene was observed at about 5.3 ppm. There were also some peaks in the range of 3.0-4.0 ppm which indicated that there may have been some complexation of the alkene. The ^{31}P NMR spectrum (spectrum #6) showed both complexed and uncomplexed phosphine to rhodium. Throughout the remainder of the experiment the results seemed ambiguous. After the substrate was added the ratio of complexed phosphine to uncomplexed phosphine increased with time. This showed that the substrate was initially complexing to the metal and displaced the phosphine but over time the phosphine recomplexed to the metal.

Preparation of 3-(3-butenylthio)propanal



13 14

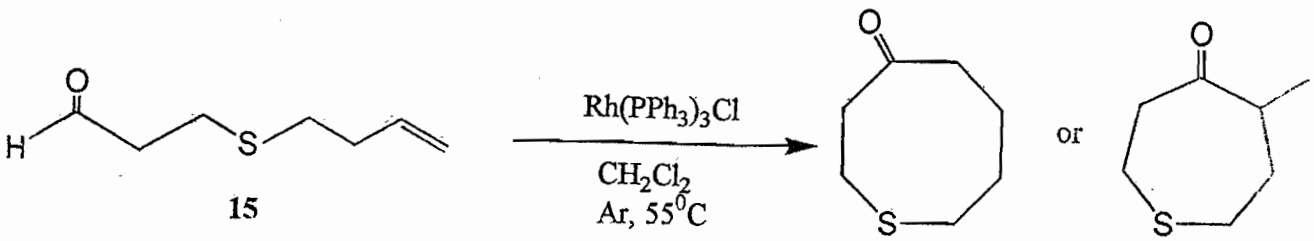
Methyl 3-mercaptopropionate (1eq.), **13**, was treated with 4-bromo-1-butene (1eq.) and diazabicyclo[5,4,0]undec-7-ene (1eq., DBU) in benzene. The reaction was run under N_2 at room temperature and monitored by GC. Purification by column chromatography gave a colorless, foul-smelling oil in 82% yield. The ^{1}H NMR spectrum indicated the presence of an alkene (multiplets at 5.0 ppm and 5.8 ppm).



14 15

Compound **14** was treated with Dibal in CH_2Cl_2 at -78°C under N_2. Purification by column chromatography produced the product in 53% yield. The ^1H NMR spectrum contained a triplet at 9.75 ppm indicating the presence of analdehyde.

Two reactions were run with the sulfur substrate and rhodium catalysts. One reaction used Wilkinson's catalyst and the other usedchlorobis(ethylene)rhodium(I) dimer with added perfluorophenylphosphine. The reactions were run in sealed tubes under Ar. They were both heated in oil baths to 55°C - 60°C for three days and monitored by GC. The reaction using using the dimer showed the disappearance of starting material but nothing else significant. No further work-up was done on this reaction.



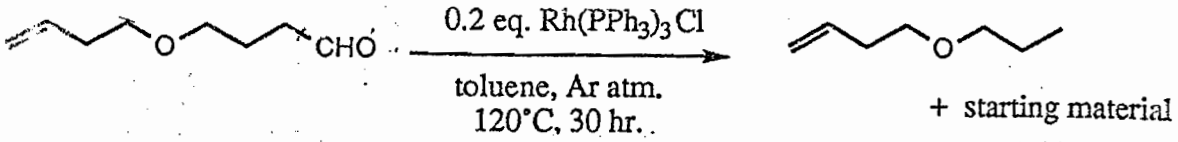
15 16 17

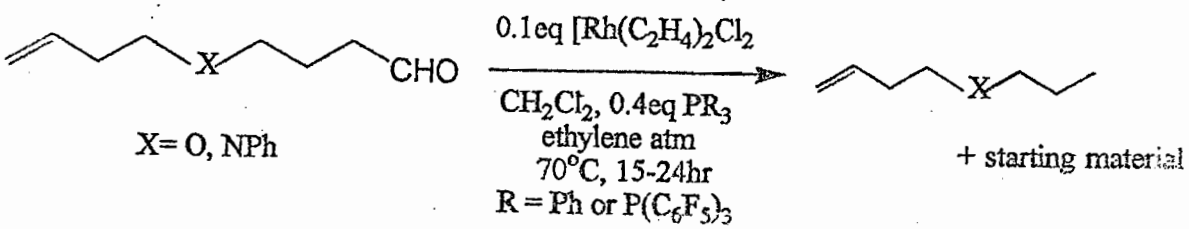
The reaction run with Wilkinson's catalyst showed a new peak in the GC and disappearance of starting material. The compound was isolated by column chromatography. The GC-MS(CI) showed a peak at 145 which suggests that either **16** or **17** was obtained. The ^1H NMR indicated the absence of an aldehyde peak and alkene

peaks. Also peaks were seen in the region near 3.0ppm which may be indicative of protons attached to the carbons that are directly attached to the sulfur. In the ^{1}H NMR spectrum there is a doublet at 1.05 ppm which would be characteristic of the methyl substituent off of the ring and consistent with17.

IV. Discussion

The work presented here is just part of the work that has been done on this project. Other work has been done using both nitrogen and oxygen as tethering atoms. There have been some reactions run with different Rhodium catalysts under varying conditions. Wilkinson's catalyst,chlorobis(ethylene)rhodium(I)dimer, and $[Rh(diphos)_2](ClO_4)_2$ have all been screened. In some casesdecarbonylation occurred. These reactions are shown and summarized below:





At room temperature with Wilkinson's catalyst, no reaction occurred. The phenethyl imine of the ether was prepared and treated with Wilkinson's catalyst but no reaction occurred.

Although promising results were seen from the use of sulfur as a tethering atom nitrogen should not be counted out. In the rhodium reactions performed with the nitrogen

containing substrates decarbonylation was mostly seen. However, in the NMR experiment some complexation of the substrate to the catalyst was in fact seen. It may be possible that the substrate is initially complexing, but then decarbonylates. Future work with the aryl substituted nitrogen substrate should be focused on. In the case of these should decarbonylation occur a four-membered metallacycle intermediate would be formed which would be unfavorable. It is important to realize that the size of the nitrogen test substrate was one carbon larger than the sulfur substrate and if the nitrogen substrate were smaller a cyclized product may be produced.

Continuing work should also focus on the sulfur containing substrate since promising results have been seen. It was only seen that a seven-membered ring was obtained when it was expected that an eight-membered ring should be formed. The reasons sulfur may have worked is that it is a softer atom and may bind to rhodium more tightly than nitrogen.

Since promising results have been seen with the sulfur substrate, an NMR experiment could be done to see how it differed from the NMR experiment done with the nitrogen containing substrate. Once the sulfur substrate was added to the catalyst the sulfur would probably complex to the rhodium, displacing a lot of the phosphine and not give the phosphine an opportunity to complex back to the metal.

Other things to concentrate on would be to optimize reaction conditions and try to obtain the best possible yields with this reaction.

V. Experimental

Reactions were monitored using Hewlett Packard GC (5890). Characterization of compounds was done using an IR spectrometer (Mattson, Polaris) and NMR (Bruker, 300 MHz). Purification of solvents was done by distillation.

A. Preparation of Substrates

Compound **2**, N-(3-butenyl)-N-(2-phenylethyl)-3-amino-propanal, 1,3-dioxolane

The amine, **1**, (0.599g, 3.42mmol) was weighed into a 100mL round bottom flask (rbf). A septum was placed on the flask and the flask was flushed with N_2. Dry CH_3CN (50mL) was then added to the flask via syringe. While still under N_2, NaI (1.54g, 10.26mmol) was added followed by the addition of bromoethyl-1,3,dioxolane (1.40mL, 5.13mmol) via syringe, and finally Hunig's base (1.20mL, 6.84mmol) added via syringed. A condenser was attached and the reaction was ran under N_2, heated to reflux and run overnight. The reaction mixture was peachish in color. It was monitored by GC and upon disappearance of starting material it was worked up.

The reaction was cooled under N_2 and the CH_3CN was rotovapped off. The residue was dissolved in 10% NaOH (75mL) and ether (75mL). The organic layer was washed with $Na_2S_2O_3$ (aq., 3x50mL), saturated NaCl (50mL), and dried over $MgSO_4$. It was concentrated and purified by column chromatography beginning with a 90/10 hexane/ethyl acetate mixture and slowly moving to 70/30 mix. The resulting product was a yellow oil (0.3552g, 37.4%). Characterization was done by ^1H NMR.

Spectral Data:

^1H NMR: (300MHz, $CDCl_3$) 1.9ppm(2H, m)
2.3ppm(2H, quart., J=7.0Hz)

2.75 ppm(8H,m)
3.8-4.0ppm(4H,m)
4.9ppm(1H, t, J=4.8Hz)
5.1ppm(2H, m)
5.7ppm(1H, m)
7.2-7.3ppm(5H,m)

Compound **3(I)**, N-(3-butenyl)-N-(2-phenylethyl)-3-aminopropanal

The protected amine, **2**, (0.06g, 0.2163mmol) was weighed into a 25mL rbf. Acetone(7mL) and water(3mL) were then added in approximately a 2:1 ratio. P-toluenesulfonic acid was then added (0.056g, 0.302mmol). The reaction was refluxed overnight and monitored by GC. Upon the disappearance of starting material the reaction was worked up.

The reaction was cooled to room temperature and the excess acetone was rotovapped off. The reaction mixture was diluted with ether (30mL) and saturated $NaHCO_3$(50mL) was added. The aqueous layer was extracted with ether (3x25mL) and the ether layers were washed with saturated NaCl (50mL) and dried over MgSO4. This was concentrated and the resulting oil was yellowish in color.

Spectral Data:

^{1}HNMR (300MHz, CDCl3) 1.9ppm(2H,m)
2.3ppm(2H,m)
2.75ppm(8H,m)
5.1ppm(2H,m)
5.6ppm(1H,m)
7.3ppm(5H,m)
9.7ppm(1H,s)

Compound **5**, Ethyl N, butenylamino benzoate

Compound **4** (0.081g, 0.4903mmol) was weighed into a 50mL rbf. A septum was placed on the flask and was flushed with N_2. Dried DMF(15mL) was then added. NaI

(0.3307g, 2.206mmol) was added followed by 4-bromobutene (0.1984g, 0.1492mL) via syringe. Hunig's base (0.2562mL, 1.47mmol) was also added by syringe. The reaction was refluxed under N_2 and was monitored by GC.

It was cooled to room temperature under N_2 and was worked up. Saturated $NaHCO_3$ (100mL) was added and a white solid formed. Ether (50mL) was then added. The white solid was discarded with the aqueous layer. The aqueous layer was extracted with ether (3x50mL). The organic layer was washed with saturated NaCl and dried over $MgSO_4$. It was concentrated and purified by column chromatography using a 95/5 mixture of hexane and ethyl acetate. The result was a yellowish oil (0.0169g, 12.6%). It was characterized by ^1H NMR and IR.

Spectral Data:

^1H NMR (300MHz, $CDCl_3$) 1.2ppm(1H,s(br.))
1.3ppm(3H,m)
2.4ppm(2H,qt, J=6.7Hz, J=1.3Hz)
3.3ppm(2H, t, J=7.0Hz)
4.3ppm(2H,q, J=7.1Hz)
5.1ppm(2H,m)
5.7ppm(1H,m)
6.7ppm(1H, m))
6.9ppm(1H, d, J=8.3Hz)
7.3ppm(1H, td, J=6.8Hz, J=1.6Hz)
7.9ppm(1H, dd, J=6.4Hz, J= 1.5Hz)

IR: cm^{-1}
1254
1400-1500
1677
3100
3367

Compound **7**, o-nitrobenzyaldehyde, 1,3 dioxolane[10]

To a 25mL rbf was added nitro-benzaldehyde (0.05g, 0.3308mmol), benzene (7.0mL), ethylene glycol (0.203mL, 0.3639mmol), and TsOH (0.01g). A water separator, condenser and drying tube were attached to the rbf and the reaction was refluxed overnight. The reaction was monitored by GC and upon completion was worked up. The clear solution was cooled to room temperature and was extracted with saturated $NaHCO_3$ (3x40mL). It was then extracted with saturated NaCl (3x20mL) and dried over $MgSO_4$. The product was characterized by ^1H NMR (6.23g, 97%).

Spectral Data:

^1H NMR ($CDCl_3$, 300MHz): 4.05ppm (4H, m)
7.35ppm (1H, s, J=2214.5Hz)
7.50ppm (2H, td, J=6.3Hz, J=1.4Hz)
7.65ppm (2H, td, J=6.4Hz, J=1.3Hz)
7.80ppm (1H, m)
7.90ppm (1H, dd, J=6.6Hz, J=1.3Hz)

Compound **8**, Method 1[11] ,o-benzylamine, 1,3 dioxolane

The protected aldehyde, **7**, (0.1g, 0.513mmol) was weighed into a 25mL rbf. It was flushed and filled with N_2. Tin(II) chloride dihydrate (0.58g, 2.56mmol) was added and absolute ethanol (10mL) was syringed into the flask.[11] The reaction was run under N_2 and heated to reflux. The mixture turned yellow and was monitored by GC. It ran for six hours. Upon completion, the mixture was cooled to room temperature and poured over ice. The pH was adjusted to 7 using saturated $NaHCO_3$. The mixture was extracted with ethyl acetate (3x15mL). It was washed with saturated NaCl (2x15mL) and dried over $MgSO_4$. It was passed through a plug of silica gel with ether and upon concentrating

turned to a white solid. An ^{1}H NMR was taken and it appeared to be a mixture of products. The multiplet that had been at 4.05ppm which was indicative of the protons on the dioxolane ring were no longer present and there really was no sign of protons attached to nitrogen.

Compound 9, 2-aminobenzaldehyde

A new method was found to reduce a nitro to an amine using Zn dust[12] and this was tried on the compound containing the protected aldehyde. However, while an amine was formed, the aldehyde was deprotected as well.

To a 25mL rbf was added 2-nitrobenzaldehyde (0.1g) and 78% ethanol (20mL). This was flushed with nitrogen and to that was added $CaCl_2$(0.05g) and Zn dust (1.43g).[12] The reaction was refluxed and stirred under N_2 for six hours. Monitoring was done by GC and upon completion the ethanol was rovotapped off. Saturated NaCl was added to adjust the pH to slightly basic. The mixture was extracted with ether (3x10mL) and concentrated.

Characterization was done using 1H NMR and IR. Since the reaction was performed on such a small scale the NMR showed a mix of products. Based on integration there were four significant peaks in the aromatic region with other smaller peaks present. An aldehydic peak, a singlet, was also present at 9.1ppm and a peak was seen at 5.6ppm, a singlet, representative of the protons attached to the nitrogen.

IR: cm-1
3450
3400
2650
1600

Compound **10**, N-(3-butenyl)-N-(2-phenylethyl)-3-aminobutanal, 1,3-dioxolane

Compound **10** was prepared by taking the amine, compound**1**,(1.61g, 9.18mmol) and weighing it into a 250mL rbf. The flask was flushed with N_2. Distilled CH_3CN (100mL) was syringed into the flask followed by the addition of NaI (4.12g, 27.54mmol). Hunig's base (3.2mL, 18.36mmol) and bromopropyl-1,3 dioxolane (2.69g, 13.77mmol) were both added via syringe successively. The reaction was refluxed under N_2 and monitored by GC.

Upon completion it was cooled to room temperature under N_2 and worked up. The CH_3CN was rotovapped off and the residue was taken up in 10% NaOH (150mL) and ether (150mL). The aqueous layer was extracted with ether (3x50mL). The ether layer was washed with water (2x50mL), Na_2SO_3 (aq., 2x50mL), and saturated NaCl(50mL). It was dried over $MgSO_4$ and concentrated. Purification was done using column chromatography beginning with an 85/15 mix of hexane/ethyl acetate and moving to a 70/30 mix. The product was a yellow oil (1.6302g, 65%). It was characterized by ^1H NMR.

Spectral Data:

^1H NMR ($CDCl_3$, 300MHz): 1.9ppm(2H, m)
2.3ppm(2H,m)
2.5-2.7ppm(10H, m)
3.8-4.0ppm(4H, m)
4.9ppm(1H, t, J=4.2Hz)
5.1ppm(2H, m)
5.7ppm(1H, m)
7.3ppm(5H, m)

Compound **11(III)**, N-(3-butenyl)-N-(2-phenylethyl)-3-aminobutanal

The aldehyde (compound **11, III**) was prepared from compound **10**. Compound**10** (1.63g, 5.63mmol) was weighted into a 100mL rbf. Acetone (30mL) and water(15mL) were added followed by TsOH(1.6g, 8.41mmol). The reaction was refluxed overnight and monitored by GC.

Upon completion, the reaction was rotovapped to remove the acetone and was diluted with ether (75mL). Saturated $NaHCO_3$ (50mL) was added. The ether layers were washed with saturated NaCl (3x50mL) and dried over $MgSO_4$. The resultant oil (1.05g, 76%) was characterized by ^1H NMR.

Spectral Data:

^1H NMR ($CDCl_3$, 300MHz): 1.9ppm(2H, quart.m)
2.3ppm(2H, m)
2.6-2.8ppm(10H, m)
5.0ppm(2H, m)
5.6ppm(1H, m)
7.2ppm (5H, m)
9.7ppm(1H, t, J=1.2H)

Test reactions of 11 with Wilkinson's Catalyst:

Trial 1:

Pre-purchased Wilkinson's catalyst (0.0176g, 0.08mmol) was weighed into a flask with a sidearm. A septum was placed over the sidearm and the catalyst was put under Ar. The aldehyde (**11(III)**, 0.0233g, 0.0949mmol) was weighed into a 25mL rbf and put under Ar. Distilled CH_2Cl_2 (2mL) was added to the rbf to dissolve the aldehyde. This solution was syringed intot the flask with the catalyst. CH_2Cl_2(6mL) was then added to the mixture. A condenser was attached onto the sidearm and the flask was flushed and

backfilled with Ar. The reaction ran at room temperature, producing a yellow/orange solution. The reaction was GC and all starting material was seen.

Upon this, the reaction was heated to reflux in an oil bath and ran for 9 days. As a work up the mixture was pushed through a plug of silica gel using ether and the resultant TLC showed starting material.

Trial 2:

The aldehyde (**11(III)**, 0.0105g, 0.0428mmol) and prepared Wilkinson's catalyst (0.0079g, 0.0086mmol) were added to a tube that had the ability to be sealed off from the air. The tube was pumped on and backfilled with Ar. Distilled CH_2Cl_2(3mL) was added via syringe. This mixture underwent a freeze/thaw degas, three times. It was backfilled with Ar and then sealed. It was put in an oil bath and heated behind a blast shield just in case a pressure build-up would occur resulting in the tube exploding. The reaction was heated to 90°C. It ran for three days, turned brown in color. The mixture was put through a plug of silica gel and the GC showed decarbonylation.

Test reactions of 11 with chlorobis(ethylene)rhodium(I)dimer:

Chlorobis(ethylene)rhodium(I)dimer (0.0293g, 0.0754mmol) was added to a 25mL flask containing the amine (7,0.0185g, 0.0754g). The reaction was run under Ar and was heated to reflux (70°C) in an oil bath. The mixture turned brown and the temperature was dropped down to 30°C. GC showed decarbonylation and purification by column chromatography was attempted but the product could not be isolated.

NMR Experiment:

In the NMR experiment, dimer (0.065g, 0.0407mmol) was added to an Ar flushed NMR tube. CD2Cl2 (1.5mL) was added and a freeze/thaw degas was done two times.

After a spectrum had been taken, the dimer (0.016g, 0.1222mmol) was added and a freeze/thaw degas cycle was done again. Again a spectrum was taken and the substrate was added (0.02g, 0.0815mmol). (Refer to Appendix A for spectral data.)

Compound **14**, 3-(3-butenylthio)propionate

To a 25mL rbf was added methyl 3-mercaptopropionate (0.092mL), diazabicyclo[5,4,0]undec-7-ene (0.1245mL) and benzene(15mL).[13] This mixtured was flushed with N_2 and 1-bromo butene (0.085mL, 0.832mmol) was added via syringe. The reaction was stirred at room temperature overnight. A DBU-HBr salt formed within the flask and this was filtered off. The filtrate was washed with water (2x15mL) and dried over $MgSO_4$. The benzene was rotovapped off and the mixture was concentrated. The product, a clear oil was purified by column chromatography using a 95/5 hexane, ethyl acetate mix. Characterization was done using ^1H NMR.

Spectral Data:

^1H NMR ($CDCl_3$, 300 MHz): 2.35ppm(2H, m)
2.60ppm(2H,t, J=7.5Hz)
2.65ppm(2H, m)
2.85ppm(2H, m)
3.7ppm(3H,s,J=11.25Hz)
5.10ppm(2H, m)
5.80ppm(1H, m)

Compound **14** to **15(IV)**, 3-(3-butenylthio)propanal

To a 100mL flame dried, N_2 flushed flask was added the Compound 14 (0.5g) and dry CH_2Cl_2(30mL). This was cooled to –78°C in a dry ice/acetone bath. Upon cooling diisobutyl aluminum hydride (DIBAL) was added slowly via syringe (2.50mL). The reaction was stirred and ran for six hours. It was monitored by GC and upon completion the mixture was quenched at –78°Cwith saturated NH_4Cl(10mL) and 4% HCl(20mL).

The mixture was brought to room temperature and CH_2Cl_2 (30mL) was added. The organic layer (bottom layer) was collected and the aqueous layer was extracted with CH_2Cl_2 (3x10mL) and the organic layer was washed with saturated NaCl(1x 25mL) and dried over $MgSO_4$. Purification was done by column chromatography in a 90/10 hexane, ethyl acetate mix. Characterization was done by ^{1}H NMR.

Spectral Data:
^{1}H NMR ($CDCl_3$, 300MHz): 2.35ppm(2H, m)
2.60ppm(2H,t, J=7.52Hz)
2.65ppm(2H, m)
2.85ppm(2H, m)
5.10ppm(2H, m)
5.80ppm(1H, m)
9.75ppm(1H, t, J=2.3Hz)

Test reactions of 15(IV) with rhodium catalysts:

Compound **15(IV)** (0.0213g) was added to a 10mL rbf and the flask was flushed and backfilled with Ar. Wilkinson's catalyst (0.1377g) was added to a sealable tube and that was flushed and backfilled with Ar. CH_2Cl_2 (2mL) was added to the rbf containing the substrate and this was then transferred via syringe to the tube containing the catalyst. Additional solvent was added and a freeze/thaw degas was performed three times on the mixture and the tube was filled with Ar. The mixture was a deep red color. It was sealed and heated to a temperature of 55°C. The reaction ran for about one week, and upon GC a new peak was seen. Purification was done by column chromatography using a mixture of 80/20 hexane and ethyl acetate. No yield was recorded.

Characterization was done by ^{1}H NMR. It was observed that both the aldehyde peak and the alkene peaks disappeared. Other NMR data is below.

^{1}HNMR (300 MHz, $CDCl_3$): 1.05ppm (3H, 6.2Hz), 2.7ppm (9H, m)

Compound 15(0.0213g) was added to a 10mL rbf and the flask was flushed and backfilled withAr. To a sealable tube the dimer(0.0572g) was added along with perfluorophenyl phosphine(0.2378g) and that was flushed andbackfilled withAr. CH_2Cl_2 (2mL) was added to the rbf containing the substrate and this was then transferred via syringe to the tube containing the catalyst. Additional solvent was added and a freeze/thaw degas cycle was performed three times on the mixture and the tube was filled with Ar. The mixture was very dark brown in color. It was sealed and heated to a temperature of 40°C. The reaction ran for about one week and upon GC starting material had disappeared. No further work-up was done.

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Appendix A
Spectral Data

Appendix A
NMR Experiment
Spectral Data:

^{1}H NMR (300MHz, CD_2Cl_2)

Spectrum # 1
3.2ppm (16H, s, J=956.453Hz)
5.3ppm (1H, t, J= 2.1Hz)

Spectrum #3
3.1ppm (16H, s, J= 913.03Hz)
5.3ppm (1H, t, J=2.1Hz)

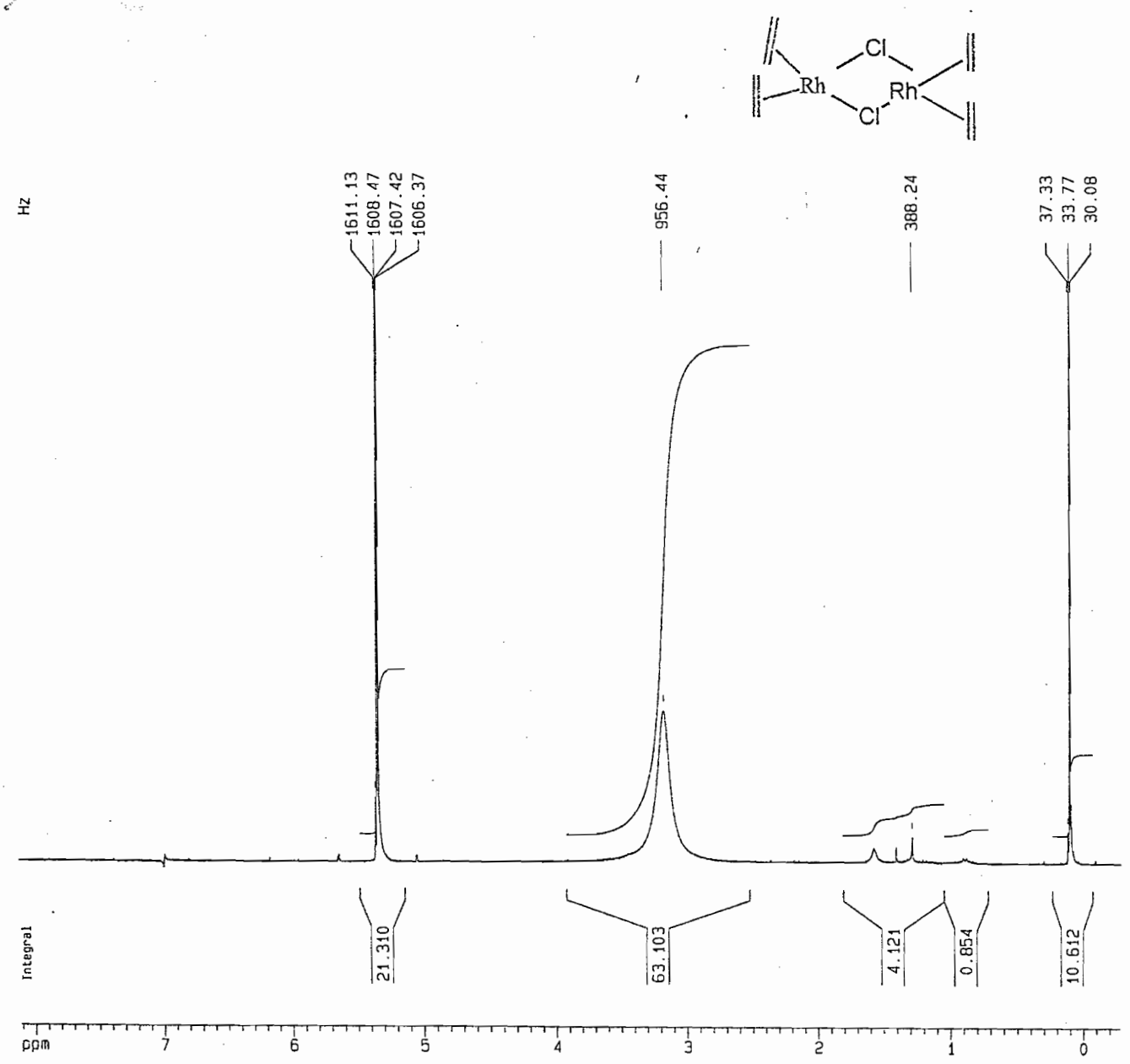
Spectrum #5
1.75 ppm(2H, t, J=13.83Hz)
2.25 ppm (2H, quart. J=7.0Hz)
2.6-2.8ppm (10H, m)
5.05 ppm (2H, m)
5.3ppm (1H, t, J=2.1Hz)
5.45 ppm (4H, s, 1631.75Hz)
5.85 ppm (1H, m)
7.3 ppm (mult.)
9.7 ppm (1H, t, J=3.34Hz)

^{31}P NMR (121.48MHz, CD_2Cl_2)

Spectrum #2
-73.5ppm(1P, pent, J=.589ppm)

Spectrum #4
-73.5ppm (1P, pent, J=.59Hz)
1.8ppm (1P, d, J=.646Hz)

Spectrum #6
-73.5ppm (1P, sept., J=.591Hz)
1.8ppm (1P, s)
3.3ppm (1P, s, J=3.34Hz)



Spectrum #1

Current Data Parameters

NAME	mmdimer
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000118
Time	9.56
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	362
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

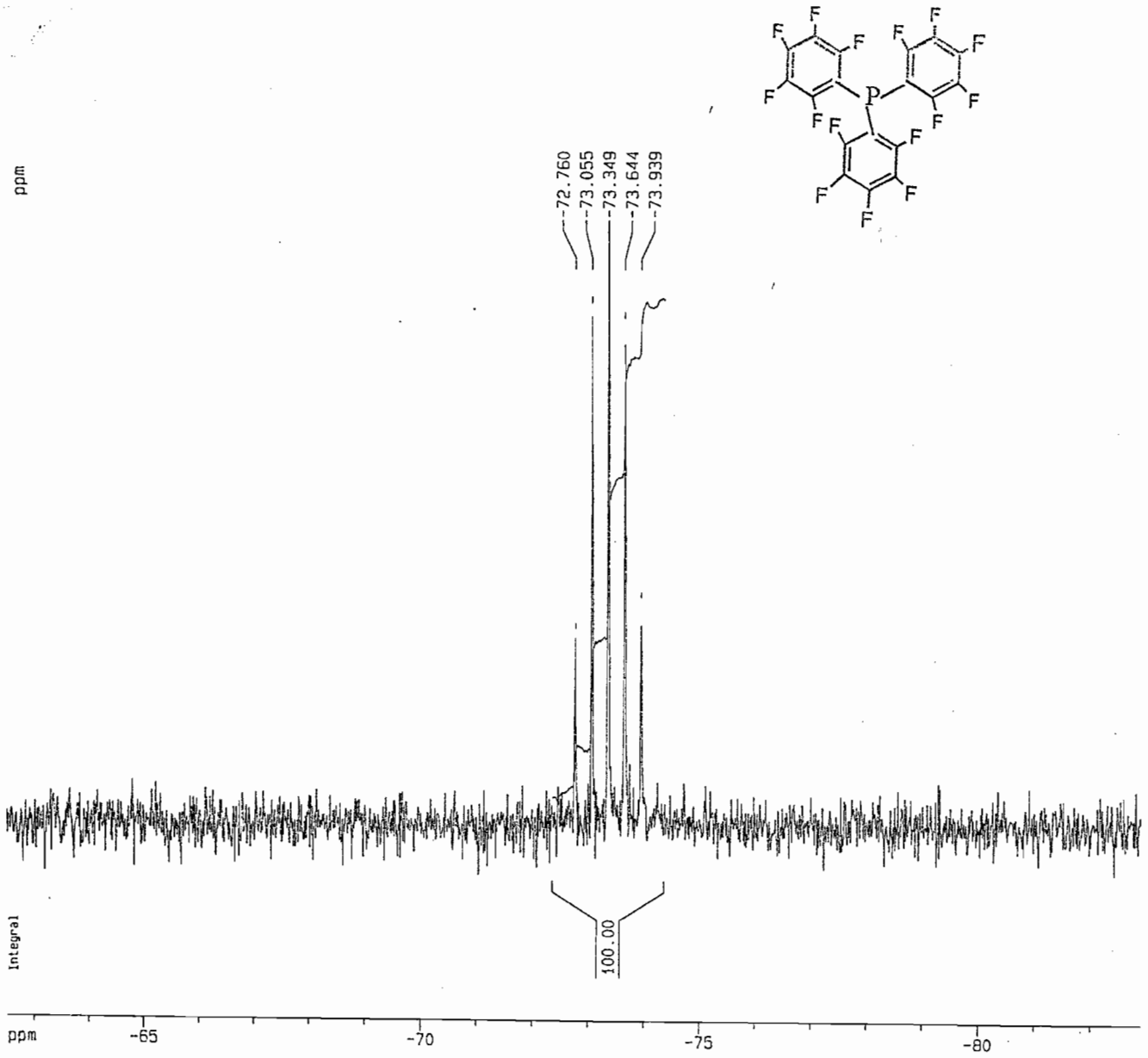
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	8.118 ppm
F1	2436.46 Hz
F2P	-0.277 ppm
F2	-83.23 Hz
PPMCM	0.41977 ppm/cm
HZCM	125.98464 Hz/cm



Spectrum #2

Current Data Parameters

NAME	mm5
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000118
Time	12.13
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zgpg30
TD	116782
SOLVENT	CDCl3
NS	16
DS	4
SWH	48661.801 Hz
FIDRES	0.416689 Hz
AQ	1.1999850 sec
RG	20642.5
DW	10.275 usec
DE	6.00 usec
TE	300.0 K
D1	5.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

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

NUC1	31P
P1	7.50 usec
PL1	-1.50 dB
SFO1	121.4886262 MHz

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

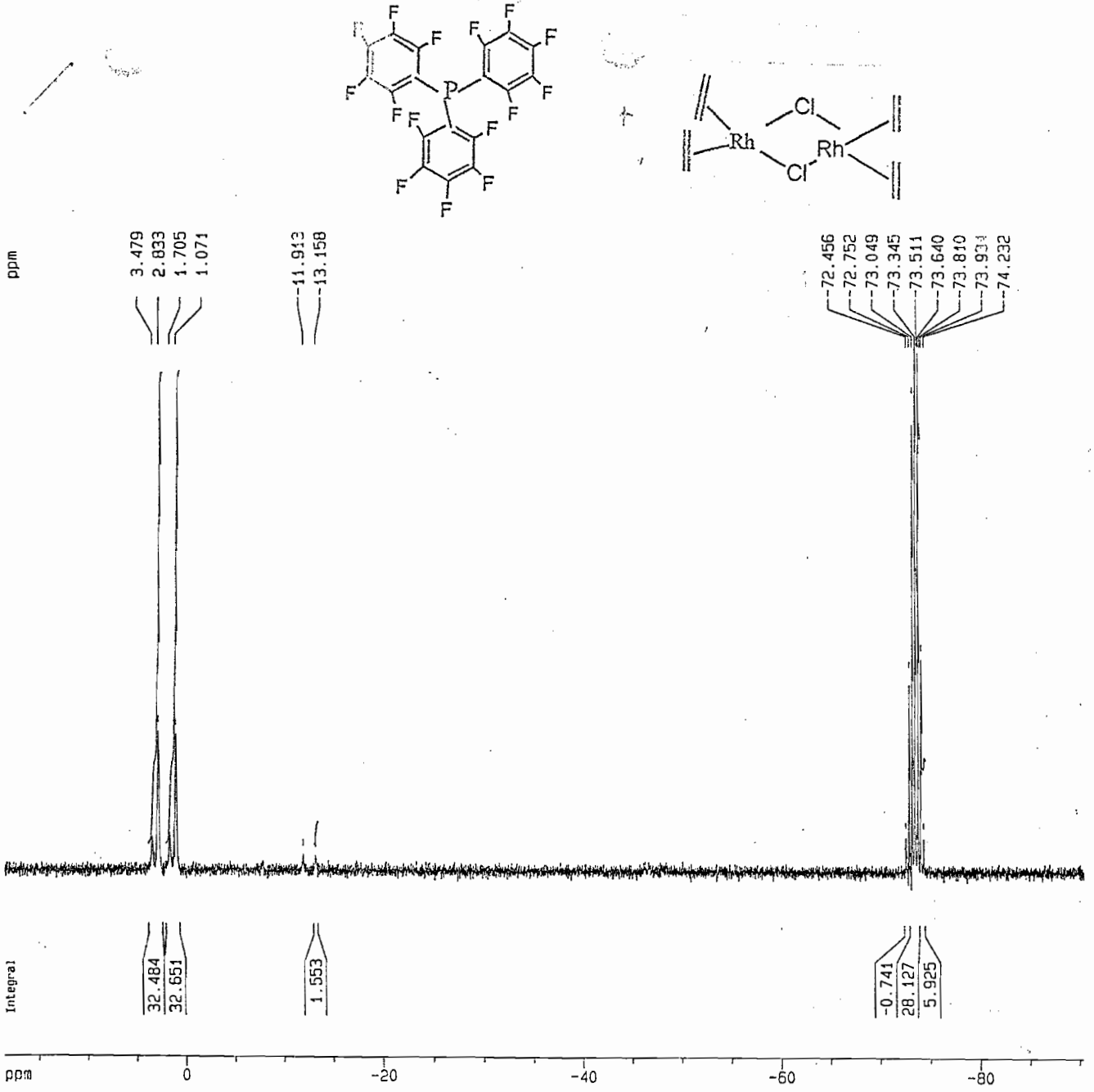
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	18.00 dB
PL13	18.00 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	121.4947010 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	-62.517 ppm
F1	-7595.52 Hz
F2P	-82.914 ppm
F2	-10073.67 Hz
PPMCM	1.01966 ppm/cm
HZCM	123.90733 Hz/cm



Spectrum #3

Current Data Parameters

NAME	[illegible]
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000118
Time	11.23
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zgpg30
TD	116780
SOLVENT	CD2Cl2
NS	128
DS	4
SWH	48661.801 Hz
FIDRES	0.416696 Hz
AQ	1.1999645 sec
RG	20642.5
DW	10.275 usec
DE	6.00 usec
TE	300.0 K
D1	5.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

CHANNEL f1

NUC1	31P
P1	7.50 usec
PL1	-1.50 dB
SFO1	121.4886262 MHz

CHANNEL f2

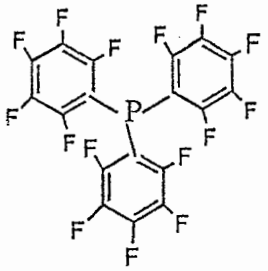
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	18.00 dB
PL13	18.00 dB
SFO2	300.1312005 MHz

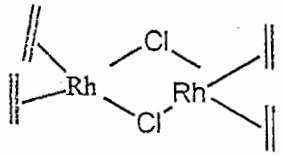
F2 - Processing parameters

SI	32768
SF	121.4947010 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

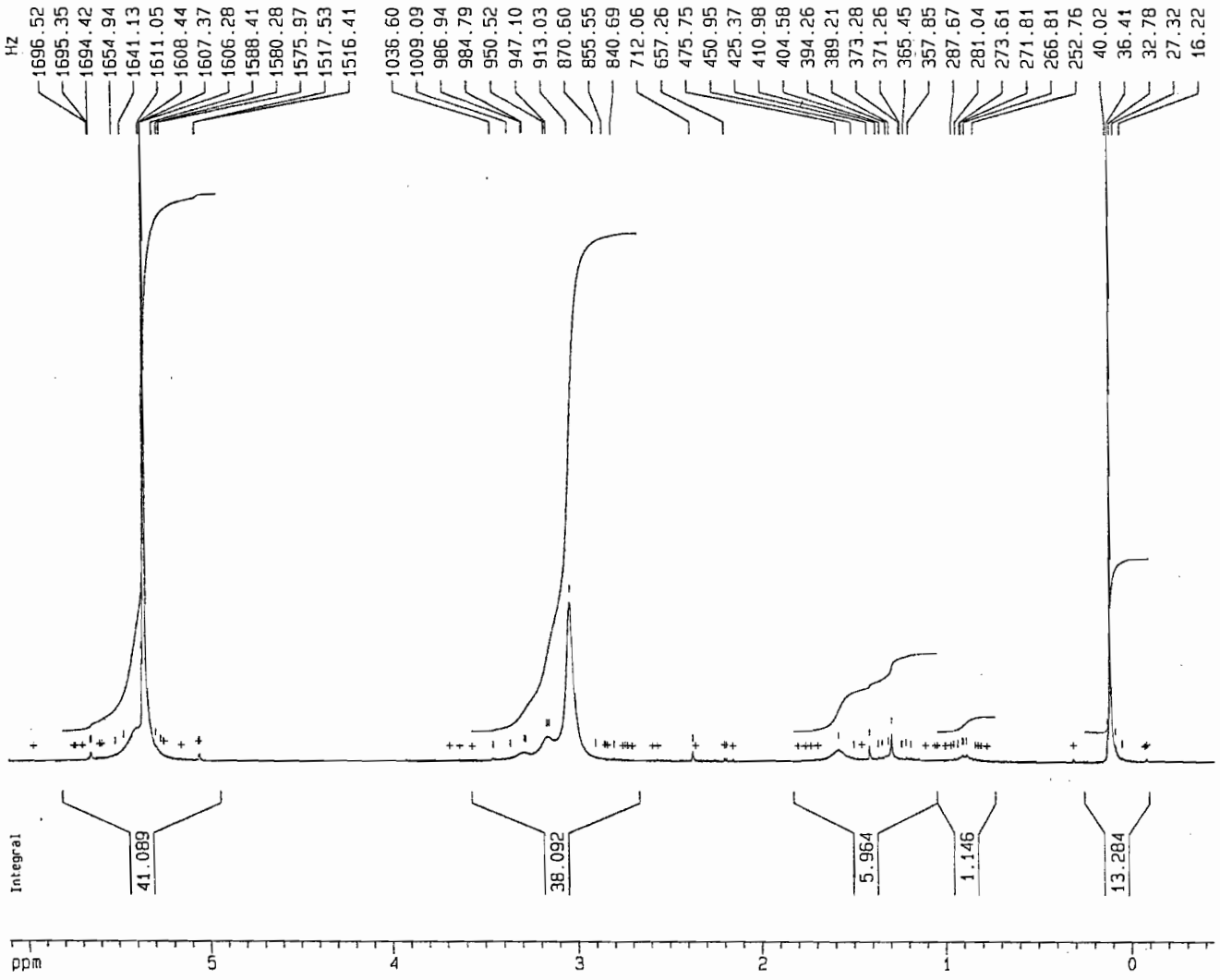
1D NMR plot parameters

CX	20.00 cm
F1P	18.608 ppm
F1	2260.75 Hz
F2P	-90.332 ppm
F2	-10974.81 Hz
PPMCM	5.44697 ppm/cm
HZCM	661.77795 Hz/cm





Spectrum #4



Current Data Parameters

NAME	mmRh+P
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000118
Time	10.48
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	5172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	456.1
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

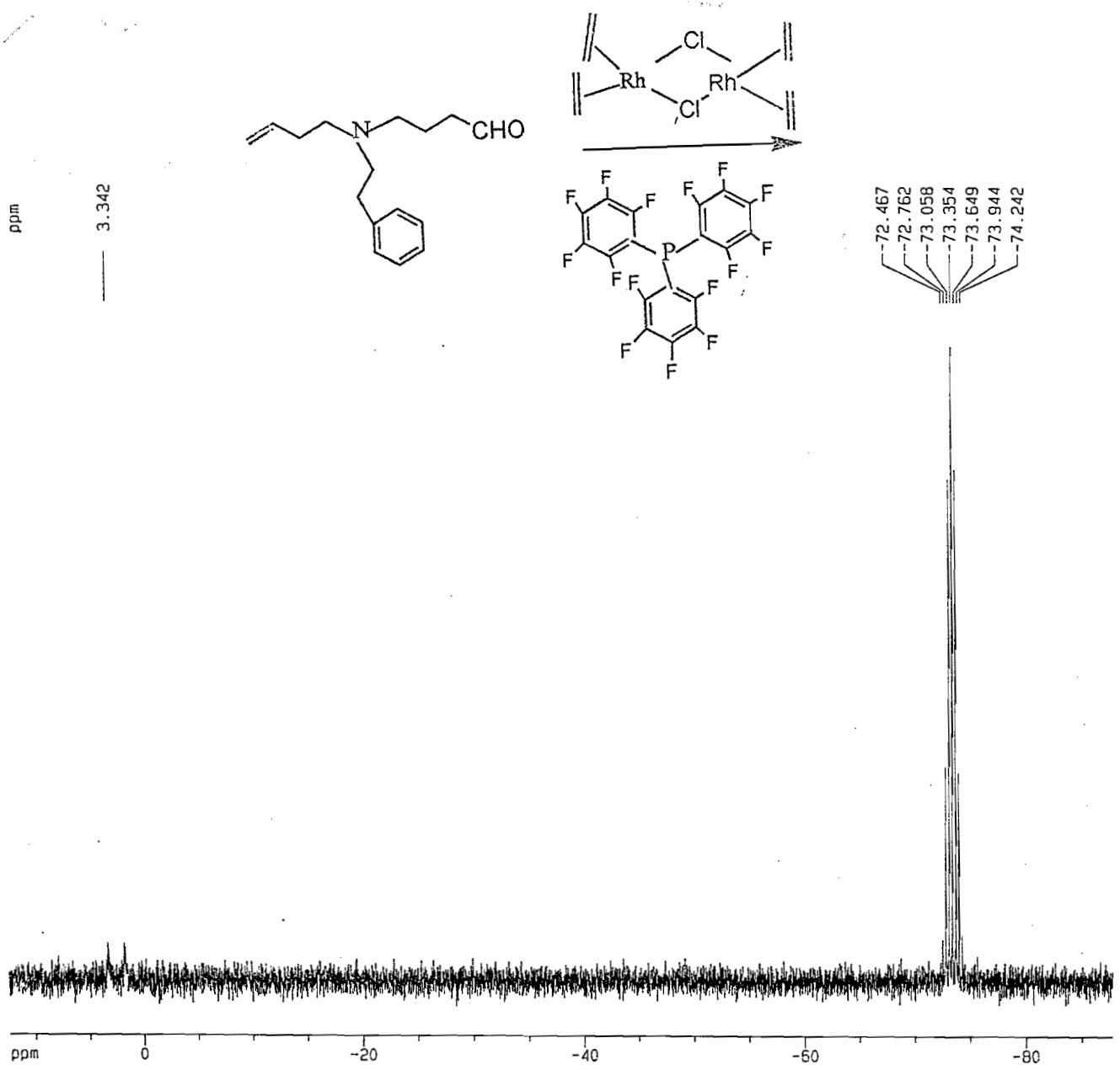
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

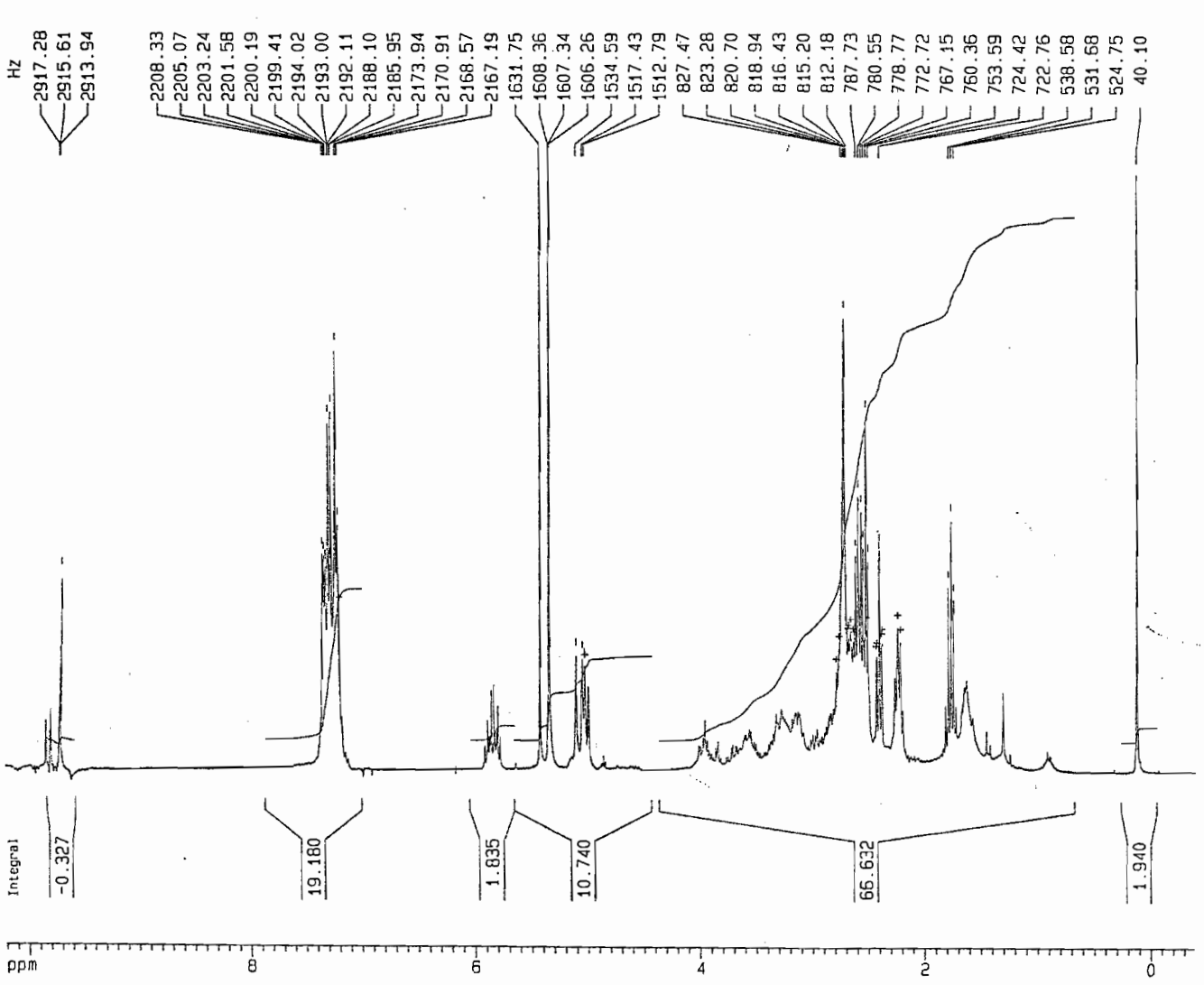
CX	20.00 cm
F1P	6.107 ppm
F1	1833.04 Hz
F2P	-0.440 ppm
F2	-132.16 Hz
PPMCM	0.32739 ppm/cm
HZCM	98.25987 Hz/cm



Spectrum #5

Current Data ...	rs
NAME	mm7
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20000118
Time	13.24
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zgpg30
TD	116780
SOLVENT	CDCl3
NS	128
DS	4
SWH	48661.801 Hz
FIDRES	0.416696 Hz
AQ	1.1999645 sec
RG	20642.5
DW	10.275 usec
DE	6.00 usec
TE	300.0 K
D1	5.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
========== CHANNEL f1 ==========	
NUC1	31P
P1	7.50 usec
PL1	-1.50 dB
SFO1	121.4886262 MHz
========== CHANNEL f2 ==========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	18.00 dB
PL13	18.00 dB
SFO2	300.1312005 MHz
F2 - Processing parameters	
SI	32768
SF	121.4947010 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
1D NMR plot parameters	
CX	20.00 cm
F1P	12.407 ppm
F1	1507.35 Hz
F2P	-87.725 ppm
F2	-10658.10 Hz
PPMCM	5.00658 ppm/cm
HZCM	608.27252 Hz/cm

Spectrum #6



Current Data Parameters

NAME	mm6
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000118
Time	13.00
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CD2Cl2
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	300.0 K
D1	1.00000000 sec

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

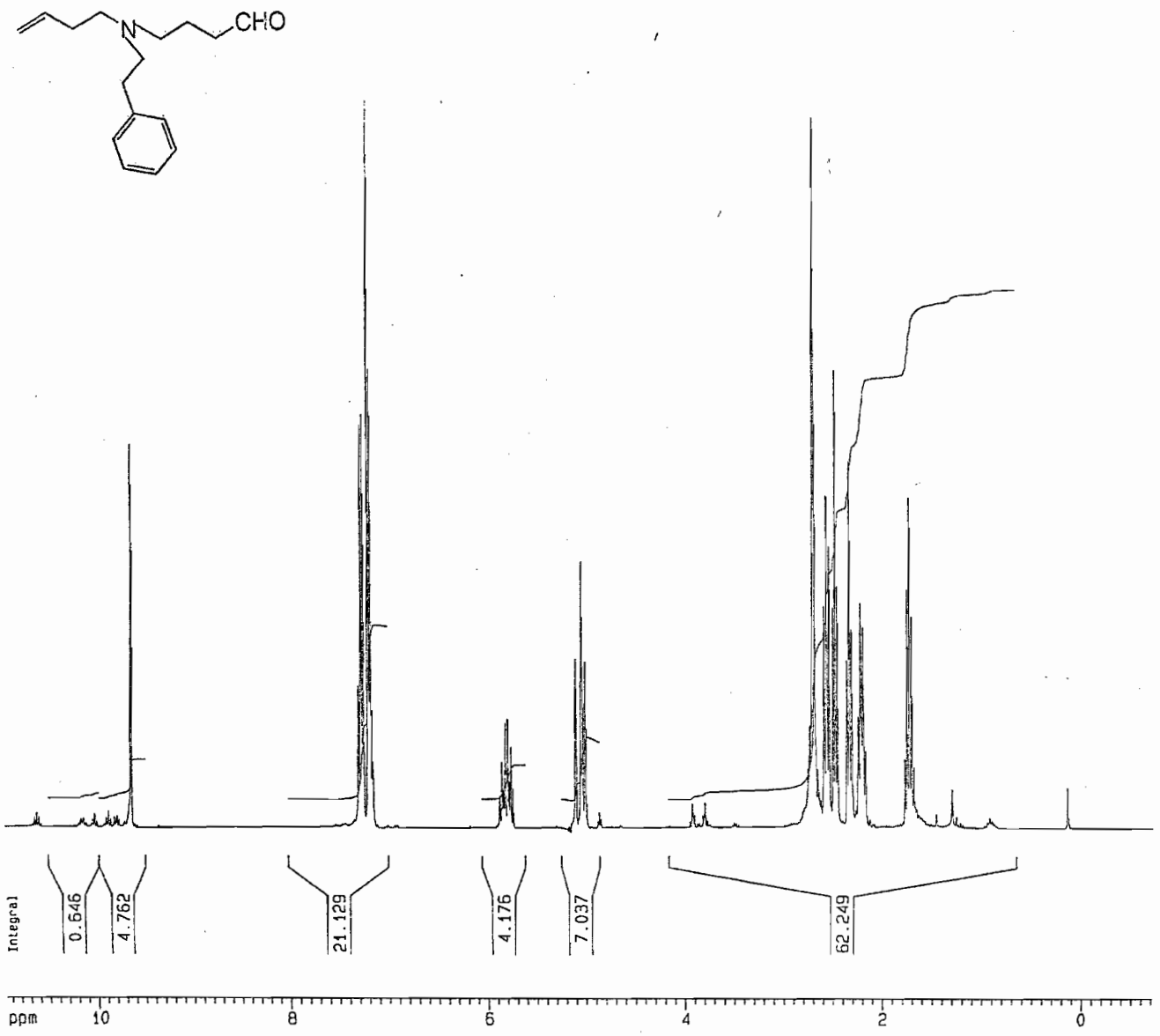
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.210 ppm
F1	3064.35 Hz
F2P	-0.386 ppm
F2	-115.85 Hz
PPMCM	0.52980 ppm/cm
HZCM	159.00975 Hz/cm



Specirum #7

Current Data Parameters

NAME	MM34b
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	991117
Time	12.08
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	14.3
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

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

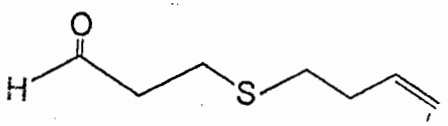
NUC1	1H
P1	11.00 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

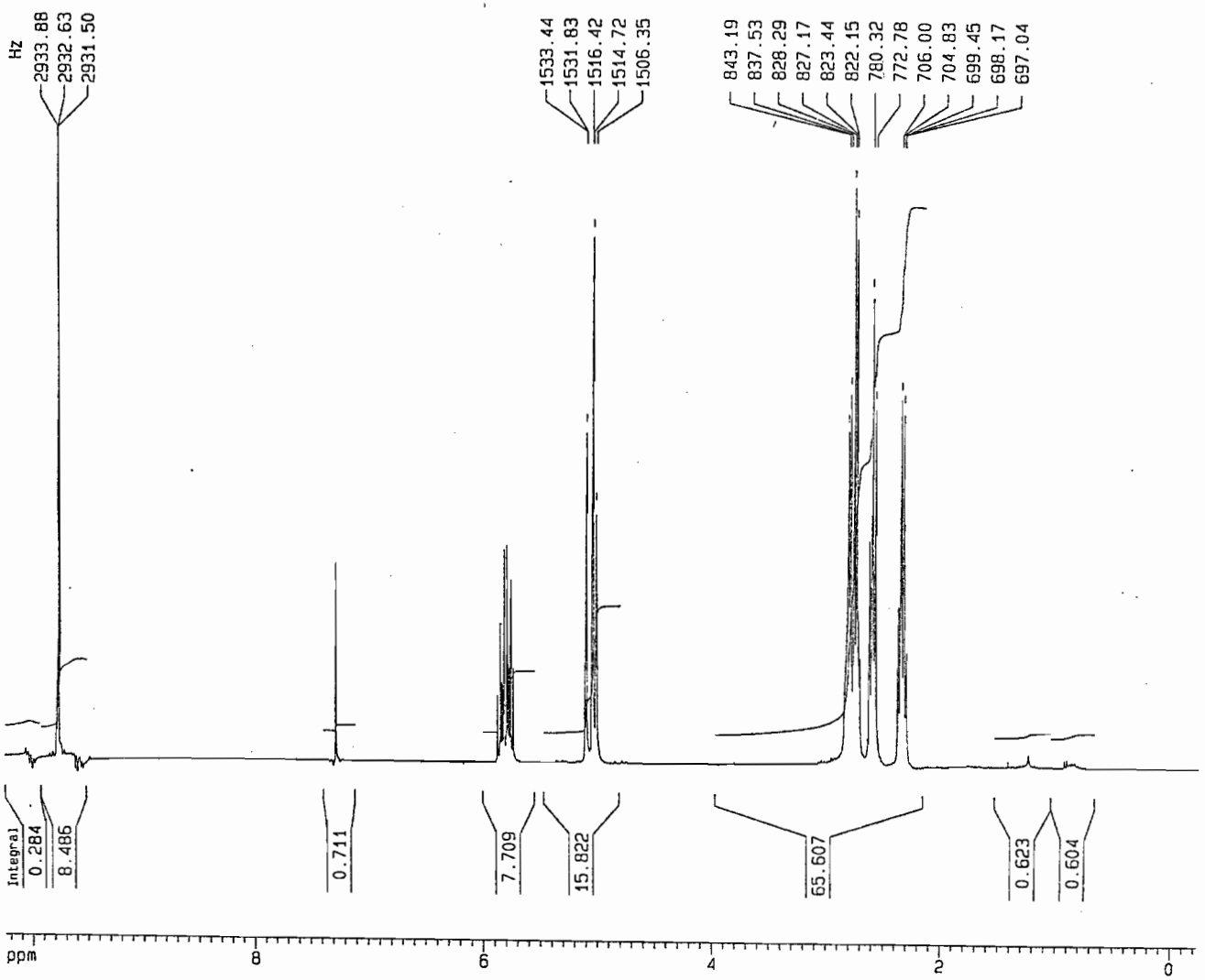
SI	32768
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.957 ppm
F1	3288.56 Hz
F2P	-0.708 ppm
F2	-212.46 Hz
PPMCM	0.58325 ppm/cm
HZCM	175.05067 Hz/cm



Spectrum #8



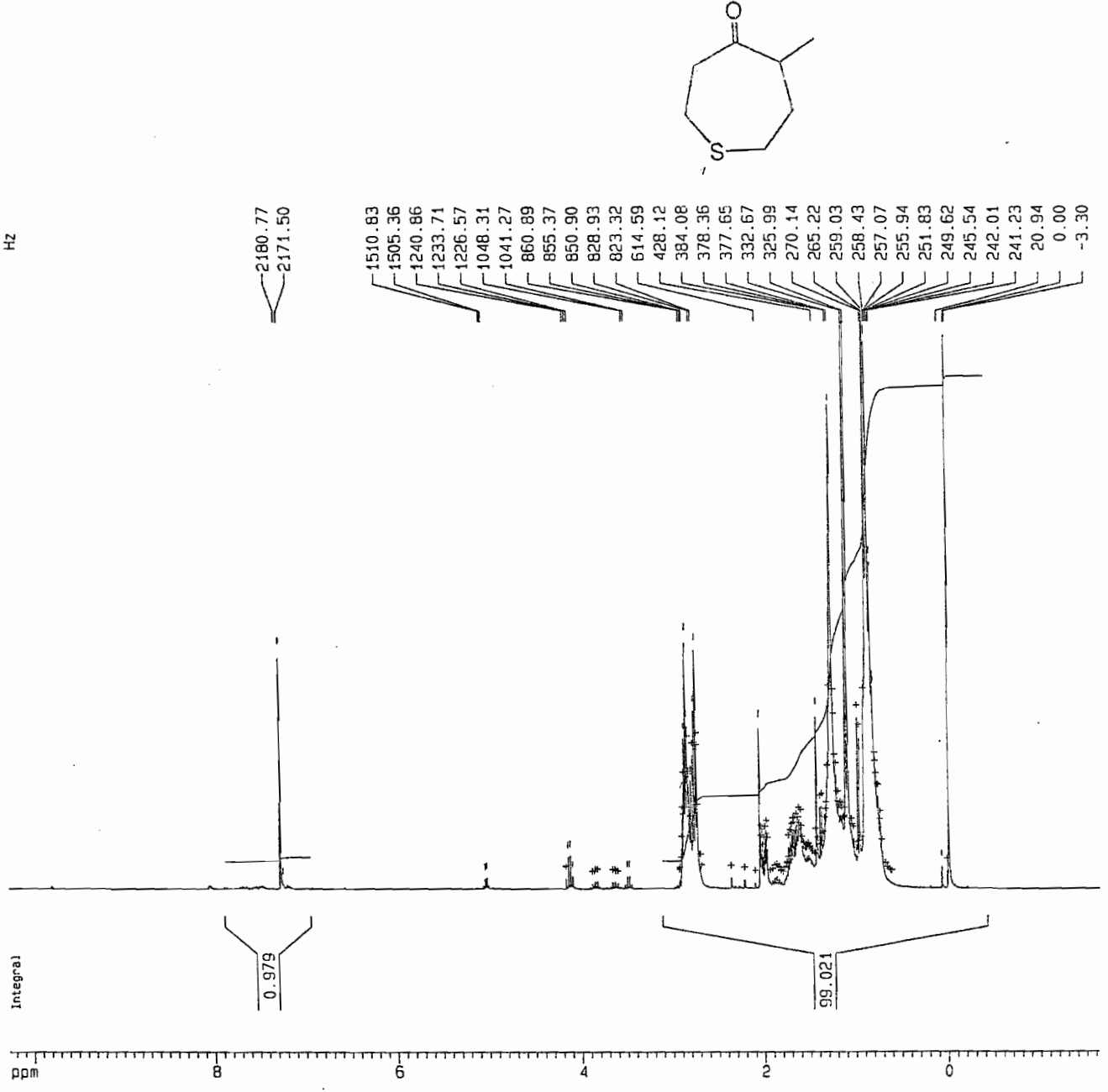
Current Data Parameters
NAME mm448
EXPNO 9999
PROCNO 1

F2 - Acquisition Parameters
Date_ 20000330
Time 14.03
INSTRUM spect
PROBHD 5 mm BBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 80.6
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

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

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

1D NMR plot parameters
CX 20.00 cm
F1P 10.246 ppm
F1 3075.13 Hz
F2P -0.228 ppm
F2 -68.44 Hz
PPMCM 0.52370 ppm/cm
HZCM 157.17880 Hz/cm



Spectrum #9

Current Data Parameters

NAME	mm00
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20000417
Time	20.23
INSTRUM	spect
PROBHD	5 mm BBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	1500
DS	2
SWH	6172.839 Hz
FIDRES	0.094190 Hz
AQ	5.3084660 sec
RG	181
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

---------- CHANNEL f1 ---------

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

F2 - Processing parameters

SI	32768
SF	300.1300046 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.278 ppm
F1	3084.79 Hz
F2P	-1.624 ppm
F2	-487.46 Hz
PPMCM	0.59512 ppm/cm
HZCM	178.61226 Hz/cm

Spectrum # 491 Filename: 190400C Acquired: Jan-04-1980 16:16:34 + 8:12
Comment: NH CI OF SULFUR EXPT
Base Pk: 145 Int: 10637 Range: 77-146 RIC: 72579 100.00% = 10637
AGC time: 40