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Synthesis and characterization of novel 1-substituted meta-terphenyls for platinum complexes

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SYNTHESIS AND CHARACTERIZATION OF NOVEL 1-SUBSTITUTED META-TERPHENYLS FOR PLATINUM COMPLEXES

By

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Abstract

SPARKS, SARAH M. Synthesis and characterization of novel 1-substituted meta-terphenyls for platinum complexes. Department of Chemistry, June 2006.

The unique luminescent properties of aryl, tridentate platinum complexes has led to an increased interest and investigation of various binding modes, with an emphasis on ligand design. These complexes are anticipated to be useful in chemical sensing, organic light emitting diodes, and solar energy converters. We have designed and synthesized novel compounds with N^C^C binding modes. These N^C^C complexes have yet to be investigated and once coordinated to a platinum metal center are anticipated to have unique photoluminescent properties as well. Here we report the novel complexes and an innovative synthetic route towards various substituted meta-terphenyl compounds. The generalized synthetic scheme can be used to generate a wide variety of compounds with the meta-terphenyl Grignard as an ideal starting point. This Grignard can be obtained from the corresponding halide. The halide is a known compound that can be generated using Hart chemistry starting from tribromoiodobenzene which is readily accessible from the corresponding amine via Sandmeyer chemistry. The synthesis and characterization of several new compounds generated using this approach, will be presented.

Acknowledgements

I would like to begin by thanking the person without whom I might not be a chemistry major, Professor Joanne Kehlbeck. She has been an amazing advisor and a great friend. Despite people saying it may be better to work for someone who is not on sabbatical, it forced me to become more confident in my laboratory skills, to become more independent, and a greater problem solver. Plus, I have her digits, so I called her all the time! There are no words that can express how grateful I am for everything she has done.

Next, I would like to thank Professor G. Reid for adopting Dave and I. Without some of his amazing ideas and super shortcuts on my lazy days I probably would not have gotten so much done!

I would like to thank my roommates, Michelle Glaser, Amanda Stella, and Rachel Valade, and my boyfriend, Evan Read, for being loving and understanding of my moodiness due to late nights in lab.

What kind of person would I be if I didn't thank Eric Dimise '05 for designing all the syntheses last year and working out most of the kinks. To Aaron Almeida for making me starting materials without which I would have never gotten as far as I did. To Kristina Gehring for allowing us to use pretty much everything in her lab and for helping me with all the outreach. We're a great duo, pres & vice-pres, maybe I should have chose Pittsburgh (wink, wink)!

Of course, my deepest and most sincere thanks go to my lab partner, David E. Olson. When no one else is in the lab, you can find us there (even when our boss is on sabbatical)! I don't know what I would have done without you this year. You've been a great colleague and an amazing friend. I will miss you so much, even though you drive me nuts when you say how long

everything is going to take! Oh, and don't forget to call me when you start your own company, I'll be your CEO and we can make Tigremycin A.

Finally, I would like to dedicate this thesis to my family. To my sisters for always being there to make me smile and my brother for keeping my life interesting. To my parents for putting me through college, their constant support, and their undying love. I'll always do my best to make you proud!

Sarah Sparks
June, 2006

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Introduction

Tridentate aryl Pt complexes possess unique luminescent properties that are projected to be useful in solar energy storage and conversion, chemical sensing, and organic light emitting diodes. To date four distinct binding modes that coordinate the platinum have been studied; N^C^N, C^N^C, C^N^N, and N^N^N[1-6]. Figure 1 shows the general structure of the ligand coordinated to platinum where X, Y, Z are nitrogen or carbon depending upon the binding mode.

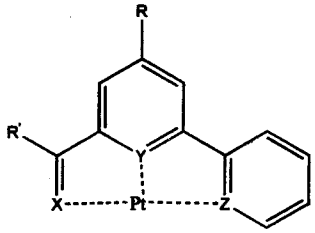


Figure 1. X^Y^Z bound to Pt metal.

By changing the binding mode, the excited state lifetimes and quantum yields can be fine tuned. Earlier research has also looked into the effects on absorption and emission spectra by changing R in Figure 1 to an electron donating or withdrawing group. The lifetimes of the complexes are mainly a product of one of two emission states, those with primarily π-π^* character or from metal to ligand charge transfer (MLCT) states, depending on the nature of the HOMO. The effect of R depends on the emission state of the complex. Complexes with π-π^* emission states experience only slightly smaller lifetimes and quantum yields when R is an electron donating group[1]. For those with MLCT emission states, increasing the electron donating effect of R causes a more significant decrease in the lifetime and quantum yield[2].

We propose a synthesis of ligands with an N^C^C binding mode, using a m-terphenyl backbone structure. This m-terphenyl structure is fundamental as it will ensure a tridentate binding mode is always achieved when the ligand is coordinated to the platinum. Without this unique structure there is the

possibility of bidentate ligand coordination to the Pt. Free rotation along single bonds gives X the ability to rotate. This bidentate product, pictured in Figure 2, is kinetically favored and will predominate.

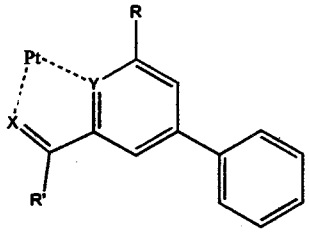


Figure 2. Bidentate coordination of the ligand to Pt.

However, when X rotates in the m-terphenyl ligands we have designed there is still a degenerate, tridentate N^C^C binding mode, as pictured in Figure 3.

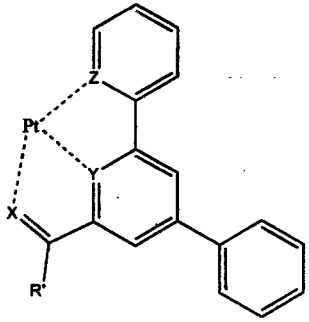


Figure 3. Tridentate coordination of the ligand to Pt with X having rotated.

An ideal starting point for these N^C^C ligands is a m-terphenyl Grignard. This Grignard can be made from the corresponding halide, a known compound made using Hart chemistry starting from tribromoiodobenzene[7] which is readily accessible from the corresponding amine via Sandmeyer chemistry[8].

The ligands are synthesized by functionalizing the center ring at positions 1, 3, and 5, adding the two peripheral rings to positions 3 and 5, and finally using the final functional position in various coupling reactions to afford the desired ligands (Scheme 1). To do this we start with 2,4,6-tribromoaniline and functionalize position 1 using Sandmeyer chemistry. This yields product (1), 2,4,6-tribromoiodobenzene. By adding a phenyl Grignard we produce a functional m-terphenyl bromide, product (2), to which we can add a wide variety of reagents in order to produce various desired compounds. Scheme 1 is outlined in Figure 4.

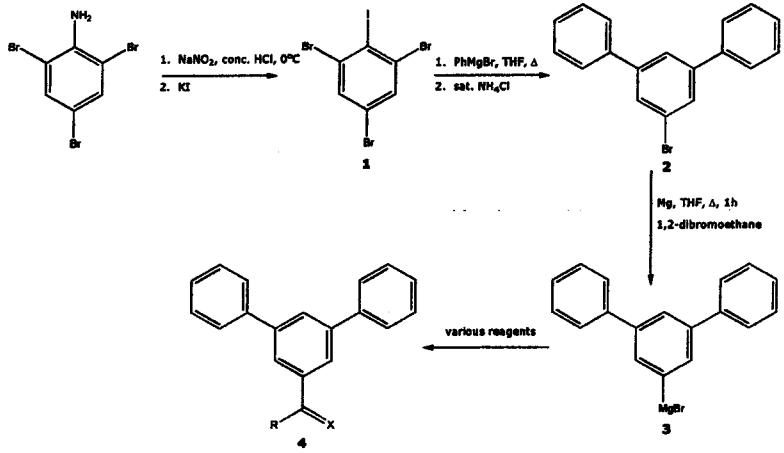


Figure 4. Scheme 1

The proposed ligands include 3,5-diphenylbenzaldehyde (5), 3,5-diphenylacetophenone (6), m-terphenylpyridine (7), and m-terphenylpyrimidine (8), all of which are new compounds except for the 3,5-diphenylbenzaldehyde which has been made but insufficiently characterized. The aldehyde was previously generated by the reduction of the corresponding acid in 43% yield[9]. However, we propose a formylation reaction using N-formylmorpholine to synthesize the aldehyde, outlined by Olah[10].

Synthesis and Characterization of Novel 1-Substituted Meta-Terphenyls

Synthetic Plan

The novel terphenyl compounds can readily be accessed through straightforward reactions starting from 2,4,6-tribromoaniline, which undergoes a variety of interesting chemistry. Beginning with the Sandmeyer reaction[8], the amine is essentially replaced with iodine of potassium iodide through a diazonium salt intermediate, as shown in Figure 5.

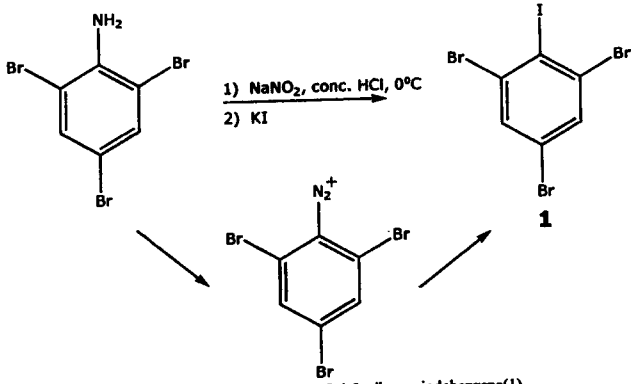


Figure 5. Sandmeyer reaction of 2,4,6-tribromoaniline to form 2,4,6-tribromoiodobenzene(1)

This fully functional intermediate, 2,4,6-tribromoiodobenzene (**1**), can now be used to build the crucial meta-terphenyl backbone using benzyne chemistry outlined by Hart[7]. By adding **1** to phenylmagnesium bromide we construct the backbone of the desired ligands while leaving the position meta to the rings functional. This is a result of the mechanism with which this chemistry occurs, as rings can only add in positions ortho to the iodine, as shown in Figure 6.

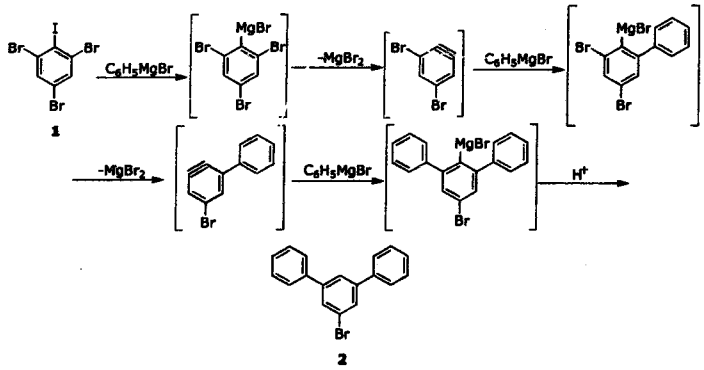
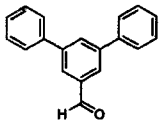


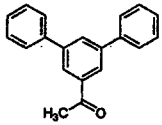
Figure 6. Hart chemistry on 1 to yield 2.

This meta-terphenyl bromide (1-bromo-3,5-diphenylbenzaldehyde (2)) intermediate allows single step reactions to be employed to access each of the target compounds, show in Figure 7.



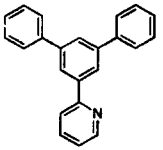
3, 5-diphenylbenzaldehyde

5



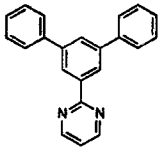
3, 5-diphenylacetophenone

6



m-terphenylpyridine

7



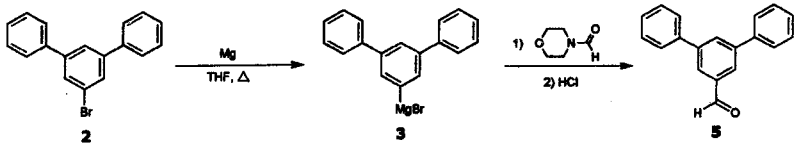
m-terphenylpyrimidine

8

Figure 7. Novel, target compounds

3,5-diphenylbenzaldehyde

The first compound made was 3, 5-diphenylbenzaldehyde (**5**), which was formed in 53% yield through a formylation reaction of **2** and N-formylmorpholine[10], as shown in Figure 8. The Grignard was generated in situ by the addition of magnesium turnings initiated by a small amount of dibromoethane.



2 **3** **5**

Figure 8. Scheme for the preparation of **5** from **2**.

CHARACTERIZATION

Final product **5** was fully characterized by ^{1}H and ^{13}C NMR, GC-MS, EA, MP, and UV/VIS, all of which are available in Appendix I.

^{1}H NMR

As seen in the ^{1}H NMR in Appendix I, I (AI-ii), the diagnostic peak of the 3, 5-diphenylbenzaldehyde is the singlet at 10.15 ppm, characteristic of an aldehyde. It is important to note the positions and multiplicities of the aromatic peaks, 7-8.2 ppm, as they are different than what would have been predicted, shown more clearly in AI-ii.

Hydrogens of **5** are referred to by their assigned letter as shown in Figure 9. Note that hydrogens in magnetically equivalent environments were assigned the same letter.

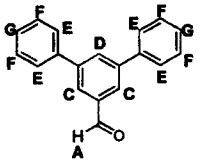


Figure 9. Letters A-G assigned to the hydrogens of **5**.

Table 1 shows the chemical shifts of the peaks assigned to each of the hydrogens of **5**.

^{1}H NMR Chemical Shifts	
Hydrogen	3,5-diphenylbenzaldehyde 5
A	10.152
B	———
C	8.073
D	8.073
E	7.663-7.710
F, G	7.417-7.547

Table 1. Chemical Shifts of hydrogens A-G of **5**.

It was predicted that the hydrogens on the two rings meta to the varying substituent (hydrogens E, F, and G) would result in overlapping peaks in the aromatic region, 7-8 ppm. Hydrogen D was predicted to be a singlet while hydrogens C were expected to result in one peak, a singlet, integrating for 2 H's. We do indeed see the overlapping of peaks for hydrogens F and G, while hydrogens E are shifted slightly downfield. The three hydrogens of the central ring (C and D) result in one peak, a singlet. This is unexpected because a singlet would imply that each hydrogen on the central ring is magnetically equivalent, which is not the case. Thus, coincidentally the peaks overlap to form a singlet.

^{13}C NMR

The carbons of **5** were each assigned a letter, with carbons in identical magnetic environments being assigned the same letter as shown in Figure 10.

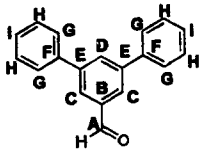


Figure 10. Letters A-I assigned to the carbons of **5**.

The tentative chemical shift assignments, from the spectra found in AI-v, for each carbon are shown in Table 2.

^{13}C NMR Chemical Shifts	
Hydrogen	3,5-diphenylbenzaldehyde δ
A	192.521
B	142.968
C	129.257
D	132.042
E	139.933
F	137.649
G	127.459
H	128.347
I	127.376

Table 2. Chemical shifts of carbons A-I for **5**.

UV/Vis

Absorbance data was collected over the UV region in methanol. The resulting peak absorbances are shown in Table 3 from the spectra in AI-vii.

UV/VIS Data			
M (mol/L)	$6.968*10^{-6}$	$6.968*10^{-6}$	$6.968*10^{-6}$
λ (nm)	202	205	249
Absorbance (A.U.)	0.27283	0.28988	0.25954
ε (M-1cm-1)	$3.92*10^{4}$	$4.16*10^{4}$	$3.72*10^{4}$

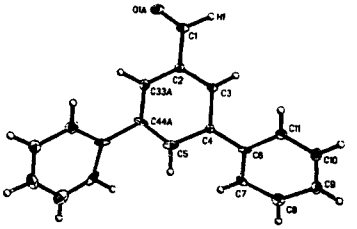
Table 3. UV/Vis Data for **5**.

GC-MS

For all compounds, gas chromatography-mass spectrometry was performed using a 39 minute method including a 2 minute solvent delay. The temperature was increased from 70 to 250°C at 10°C/min, holding at 70°C for one minute and at 250°C for 20 minutes. The GC retention time for **5** was 21.38 min with a e/m of 258. The spectrum is located in AI-viii

Crystal Structure

The most conclusive data in confirming the assignment of the compound synthesized as 3,5-diphenylbenzaldehyde is the crystal structure shown in Figure 11.



Orthorhombic
Cmc2(1)
a = 23.647 (3)
b = 6.9588 (8)
c = 8.3389 (9)
V = 1372.2 (3)
Final R1 = 0.0240
Interring angle = 36

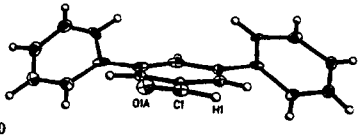


Figure 11. Crystal structure of **5**.

3, 5-diphenylacetophenone

Next, we synthesized 3, 5-diphenylacetophenone (**6**), which was prepared in 51% yield by inverse addition of the meta-terphenyl Grignard to acetic anhydride[11], as shown in Figure 12.

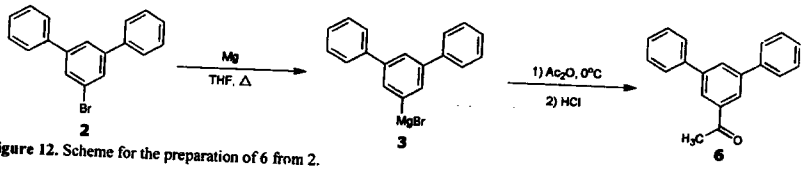


Figure 12. Scheme for the preparation of 6 from 2.

The reaction is performed by inverse addition of the m-terphenyl Grignard to the acetic anhydride so that there is never an excess of Grignard, thus we avoid duplicate addition of the Grignard to the acetic anhydride.

CHARACTERIZATION

This compound was also fully characterized by ^{1}H and ^{13}C NMR, GC-MS, EA, and UV/VIS, all of which are available in Appendix II.

^{1}H NMR

The ^{1}H NMR spectra for **6** can be found in AII-xi. The hydrogens of **6** were each assigned a letter, shown in Figure 13, with hydrogens in identical magnetic environments having the same letter. Also,

hydrogens analogous to those in **5** were assigned the same letter to allow for direct comparison of the hydrogens in each compound

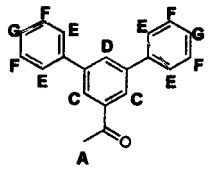


Figure 13. Letters A-G assigned to the hydrogens of **6**.

The chemical shifts assigned to the hydrogens of **5** and **6** are shown in Table 4.

^{1}H NMR Chemical Shifts (ppm)		
Hydrogen	3,5-diphenylbenzaldehyde **5**	3,5-diphenylacetophenone **6**
A	10.152	2.713
B	———	———
C	8.073	8.150-8.157
D	8.073	7.993-8.009
E	7.663-7.710	7.656-7.703
F, G	7.417-7.547	7.410-7.542

Table 4. Chemical shifts for hydrogens A-G of compounds **5** and **6**.

In the spectrum of **6**, the diagnostic peak is that of the methyl group (A) at 2.71 ppm. The interesting aspect of the spectrum of the acetophenone in comparison to that of the aldehyde are the peaks just above 8, those peaks resulting from the hydrogens on the central ring (C and D). Judging by the spectrum of **5**, one would anticipate that the all aromatic peaks of **6** would be almost identical as the two structures differ only by one methyl group. However, this is not the case. Instead, we see what was predicted for **5**; the two hydrogens closest to the oxygen (C) result in a peak, integrating for two hydrogens slightly downfield from another peak, integrating for one hydrogen (D). The interesting aspect of this spectrum is that instead of simply seeing two singlets for hydrogens C and D, because there are no hydrogens on the adjacent carbons, the peaks are split into doublets. This is a result of meta coupling of C and D. It is also worth noting that the peak for C is shifted downfield from the analogous hydrogens of **5**, while the peak for D is shifted slightly upfield.

^{13}C NMR

The carbons of **6** were each assigned a letter, with those in identical magnetic environments having the same letter. As with the ^{1}H NMR, carbons analogous to those in **5** were assigned the same letter to allow for direct comparison of chemical shifts in each compound

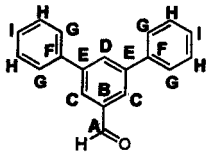


Figure 14. Letters A-J assigned to the carbons of **6**.

The tentative chemical shift assignments from the spectra (AII-v) for each carbon in **5** and **6** are shown in Table 5.

^{13}C NMR Chemical Shifts (ppm)		
Hydrogen	3,5-diphenylbenzaldehyde **5**	3,5-diphenylacetophenone **6**
A	192.521	198.265
B	142.968	142.558
C	129.257	128.165
D	132.042	130.790
E	139.933	140.441
F	137.649	138.408
G	127.459	127.520
H	128.347	129.197
I	127.376	126.146
J	———	29.915

Table 5. Chemical shifts of carbons A-J of compound **5** and **6**.

In general, the analogous carbons are in equivalent magnetic environments, as the chemical shifts vary by only 1 or 2 ppm. This variance of 1-2 ppm is less significant than the same variance in a ^{1}H NMR because it is over a much larger range. However, for carbon A, the peak shifts about 6 ppm in **6** from the position in **5**.

UV/Vis

Absorbance data was collected over the UV region in methanol. The resulting peak absorbances as seen in AII-vii are shown in Table 6.

UV/Vis Data			
M (mol/L)	$6.81*10^{-5}$	$6.81*10^{-5}$	$6.81*10^{-5}$
λ (nm)	204	249	315
Absorbance (A.U.)	$6.9914*10^{-2}$	$8.3323*10^{-2}$	$6.3467*10^{-4}$
ε (M-1cm-1)	$9.46*10^{2}$	$7.94*10^{2}$	7.2

Table 6. UV/Vis data for **6**.

GC-MS

The GC retention time for **6** was 22.42 min with a e/m of 272, as seen in AII-viii.

m-terphenyl pyridine

The synthesis of the *m*-terphenyl pyridine (**7**) was accomplished through a nickel catalyzed Kumada-like ring coupling of the *m*-terphenyl Grignard to 2-chloropyridine[12], as shown in Figure 15.

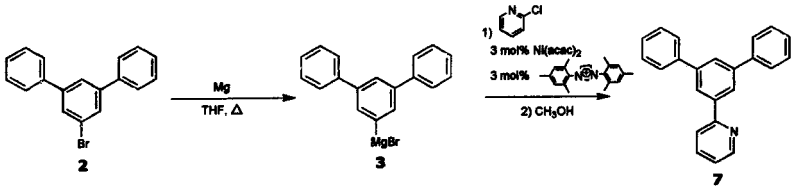


Figure 15. Scheme for the preparation of **7** from **2**.

This coupling takes 19 hours and compound **7** in 40% yield.

CHARACTERIZATION

This compound was also fully characterized by ^{1}H and ^{13}C NMR, GC-MS, EA, and UV/VIS, the spectra of which are available in Appendix III.

^{1}H NMR

The most interesting method of characterization to use for comparison of all the new compounds is ^{1}H NMR, as the environments of the protons change fairly dramatically depending on the identity of X. The ^{1}H NMR spectra for **7** can be found in AIII-xxi. The hydrogens of **7** were each assigned a letter, shown in Figure 16, with hydrogens in identical magnetic environments having the same letter. Also,

hydrogens analogous to those in **5** and **6** were assigned the same letter to allow for direct comparison of the hydrogens in each compound.

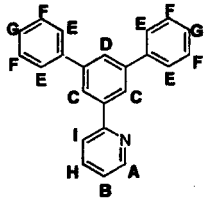


Figure 16. Letters A-I assigned to the hydrogens of compound 7.

The chemical shifts assigned to the hydrogens of **5**, **6**, and **7** are shown in Table 7.

^{1}H NMR Chemical Shifts (ppm)			
Hydrogen	3,5-diphenylbenzaldehyde 5	3,5-diphenylacetophenone 6	m-terphenyl pyridine 7
A	10.152	2.713	8.736-8.760
B	———	———	7.271-7.315
C	8.073	8.150-8.157	8.200-8.207
D	8.073	7.993-8.009	7.824-7.844
E	7.663-7.710	7.656-7.703	[illegible]-7.764
F, G	7.417-7.547	7.410-7.542	[illegible]-7.531
H	———	———	7.745-7.798
I	———	———	7.857-7.874

Table 7. Chemical shifts for hydrogens A-I of compounds **5**, **6**, and **7**.

Assigning the peaks of the **7** was more difficult as the instrument is low resolution and peaks D, H, I, and E overlap in the region of 7.703-7.874 ppm. Therefore, assignments D, H, I, and E are tentative. However, regardless of where in the overlapping region these peaks fall, the peak due to hydrogen D shifts slightly upfield while the peak for E shifts slightly downfield with respect to the analogous peaks in both **5** and **6**. The peaks due to hydrogens F and G and that due to D both shift upfield from their analogous hydrogens in **5** and **6**. Also, meta coupling for C and D similar to that seen in the spectrum of **6** is seen in **7**.

^{13}C NMR

The ^{13}C NMR spectra for **7** can be found in AIII (i-iii). The carbons of **7** were each assigned a letter, with those in identical magnetic environments having the same letter. As with the ^{1}H NMR, carbons analogous to those in **5** and **6** were assigned the same letter to allow for direct comparison of chemical shifts in each compound.

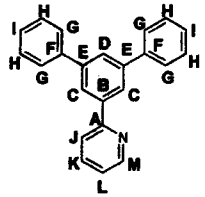


Figure 17. Letters A-M assigned to carbons of compound **7**.

The tentative chemical shift assignments from the spectra (AIII-xxiv) for each carbon in **5**, **6**, and **7** are shown in Table 8.

^{13}C NMR Chemical Shifts (ppm)			
Hydrogen	3,5-diphenylbenzaldehyde 5	3,5-diphenylacetophenone 6	m-terphenyl pyridine 7
A	192.521	198.265	157.574
B	142.968	142.558	141.261,140.692
C	129.257	128.165	126.966
D	132.042	130.790	125.077
E	139.933	140.441	142.558
F	137.649	138.408	137.050
G	127.459	127.520	127.778
H	128.347	129.197	129.030
I	127.376	126.148	127.611
J	———	29.915	122.568
K	———	———	141.261,140.692
L	———	———	121.056
M	———	———	149.994

Table 8. Chemical Shifts of carbons A-M for **5**, **6**, and **7**.

The most significant differences between the ^{13}C NMR spectra of the three compounds is the considerable shift upfield of the peaks for carbons A, C and D in **7**. There is a less significant shift of the peak for carbons E downfield.

UV/Vis

Absorbance data was collected over the UV region in methanol. The resulting peak absorbances as see in AIII-xxvi are shown in Table 9.

UV/VIS Data			
M (mol/L)	$1.952*10^{-5}$	$1.952*10^{-5}$	$1.952*10^{-5}$
λ (nm)	200	202	250
Absorbance (A.U.)	0.79578	0.72927	0.68682
ε (M-1cm-1)	$4.08*10^{4}$	$3.74*10^{4}$	$3.52*10^{4}$

Table 9. UV/Vis data for **7**.

GC-MS

The GC retention time for **7** was 35.11 min with a e/m of 307, as seen in AIII-xxvii.

m-terphenyl pyrimidine

The m-terphenyl pyrimidine (**8**) was synthesized using a similar method to **7**, a Kumada-like nickel catalyzed ring coupling of **3** to 2-chloropyrimidine[12], shown in Figure 15.

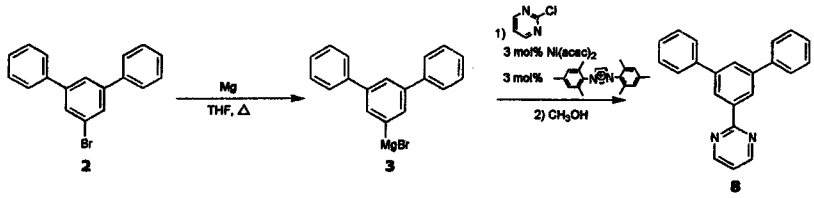


Figure 18. Scheme for the preparation of **8** from **2**.

CHARACTERIZATION

This compound was also fully characterized by ^{1}H and ^{13}C NMR, GC-MS, EA, and UV/VIS, the spectra of which are available in Appendix IV.

^{1}H NMR

The ^{1}H NMR spectra for **8** can be found in AIV-xxix. The hydrogens of **8** were each assigned a letter, shown in Figure 19, with hydrogens in identical magnetic environments having the same letter. Also, hydrogens analogous to those in **5**, **6**, and **7** were assigned the same letter to allow for direct comparison of the hydrogens in each compound.

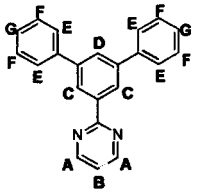


Figure 19. Letters A-G assigned to the hydrogens of **8**.

The chemical shifts assigned to the hydrogens of **5**, **6**, **7**, and **8** are shown in Table 10.

^{1}H NMR Chemical Shifts (ppm)				
Hydrogens	3,5-diphenylbenzaldehyde **5**	3,5-diphenylacetophenone **6**	m-terphenyl pyridine **7**	m-terphenylpyrimidine **8**
A	10.152	2.713	8.736-8.760	8.839-8.870
B	———	———	7.271-7.315	7.207-7.238
C	8.073	8.150-8.157	8.200-8.207	8.696-8.711
D	8.073	7.993-8.009	7.824-7.844	7.941-7.967
E	7.663-7.710	7.656-7.703	7.703-7.764	7.749-7.797
F, G	7.417-7.547	7.410-7.542	7.351-7.531	7.346-7.535
H	———	———	7.745-7.798	———
I	———	———	7.857-7.874	———

Table 10. Chemical shifts for hydrogens A-G of **5**, **6**, **7**, **8**.

In comparison the spectra of **7**, as compound **8** is most similar to **7**, the peak resulting from hydrogens A shifts downfield past 8.8 ppm. Based on the coupling constant, we then find the peak due to the hydrogen between those hydrogens adjacent to the nitrogens, B, just above 7.2 ppm which is shifted slightly upfield from the analogous hydrogen in **7**. Next, the peak at 8.7 ppm is due to the hydrogens of the central ring closest to the nitrogens, hydrogen C. As shown in Table 10, this peak is shifted downfield compared to that caused by the analogous hydrogens in each of the other compounds. It is also split into a doublet, as seen in the spectra of the **6** and **7**. Hydrogen D is shifted downfield with respect to the analogous hydrogens in **7** and upfield with respect to those in **5** and **6**. Again, there is meta coupling present between hydrogens C and D which causes the singlet to split into a doublet and a triplet, respectively. Also worth nothing is hydrogens E are shifted downfield when compared to the analogous hydrogens in all of the other compounds.

^{13}C NMR

The ^{13}C NMR spectra for **8** can be found in AIV (i-iii). The carbons of **8** were each assigned a letter, with those in identical magnetic environments having the same letter. As with the ^{1}H NMR, carbons analogous to those in **5**, **6**, and **7** were assigned the same letter to allow for direct comparison of chemical shifts in each compound

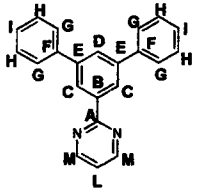


Figure 20. Letters A-H and L-M assigned to the carbons of **8**.

The tentative chemical shift assignments from the spectra (AIV-xxxv) for each carbon in **5, 6, 7, and 8** are shown in Table 11.

^{13}C NMR Chemical Shifts (ppm)				
Hydrogens	3,5-diphenylbenzaldehyde 5	3,5-diphenylacetophenone 6	m-terphenyl pyridine 7	m-terphenylpyrimidine 8
A	192.521	198.265	157.574	164.774
B	142.968	142.558	141.261,140.692	138.764
C	129.257	128.165	126.986	126.139
D	132.042	130.790	125.077	127.580
E	139.933	140.441	142.558	142.391
F	137.649	138.408	137.050	141.078
G	127.459	127.520	127.778	128.590
H	128.347	129.197	129.030	129.014
I	127.376	126.146	127.611	———
J	———	29.915	122.588	———
K	———	———	141.261,140.692	———
L	———	———	121.055	119.563
M	———	———	149.994	157.505

Table 11. Chemical shifts for the carbons of **5**, **6**, **7**, and **8**.

In comparison of the spectra of **8** with **7**, it is clear that the added nitrogen has a large impact on the adjacent hydrogens, M, as the peak shifts far downfield with respect to that of **7**. In looking at the peak due to hydrogen A, which shifted far upfield upon the introduction of the aromatic, nitrogen containing moiety to replace the oxygen containing group, the peak shifts downfield with respect to that in **7** but not

as far downfield as the peak for the analogous hydrogen in **5** and **6**. The peak due to hydrogen B shifts upfield in comparison to all three of the other spectra while the peak for hydrogens F and G shifts downfield compared to the other three spectra. The peak due to hydrogen L, that carbon located two away from both nitrogens of **8**, shifts upfield compared to the analogous carbon 2 away from the one nitrogen in **7**.

UV/Vis

Absorbance data was collected over the UV region in methanol. The resulting peak absorbances, as seen in AIV-xxxvii, are shown in Table 12.

UV/Vis Data			
M (mol/L)	$1.038*10^{-4}$	$1.038*10^{-4}$	$1.038*10^{-4}$
λ (nm)	202	252	310
Absorbance (A.U.)	0.50258	0.60045	$1.5003*10^{-2}$
ε (M-1cm-1)	$4.84*10^{4}$	$5.79*10^{4}$	$1.45*10^{3}$

Table 12. UV/Vis data of **8**.

GC-MS

The GC retention time for **8** was 36.35 min with a e/m of 308, as shown in AIV-xxxviii.

Methods

The synthesis follows Scheme 1 as outlined in Figure 4. The syntheses were all followed by TLC and GC-MS. All products were also characterized by ^{1}H NMR, ^{13}C NMR, MP, EA, and UV/Vis. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini 2020 200MHz spectrometer with $CDCl_3$ solvent using $Si(CH_3)_4$ as an internal standard. Chemical shifts are reported in δ units (ppm). GC-MS analysis was performed on an Agilent 6890N gas chromatograph equipped with an N10149 autosampler coupled to an Agilent 5973 mass spectrometer. UV/Vis absorption data was collected on an HP 8453 Diode Array in methanol. Anhydrous magnesium sulfate was used as the drying reagent in all reactions. All reactions were run under an atmosphere of dry nitrogen except in the preparation of (1) 2,4,6-tribromoiodobenzene. All reagents and solvents were purchased from Sigma-Aldrich and were used without additional purification.

(1) 2,4,6-tribromoiodobenzene[8]

A solution of sodium nitrite (3.28 g, 47.5 mmol) in 15 mL of water was added drop wise to a mechanically stirred slurry of 2,4,6-tribromoaniline (15 g, 45.5 mmol) in 23 mL of concentrated HCl at 0 °C. Stirring was continued for 30 min after complete addition of sodium nitrite. The diazonium salt was slowly transferred through a glass wool filter to a solution of potassium iodide (75.53 g, 0.455 mol) in 114 mL of water. The solution was stirred vigorously with both magnetic and mechanical stirring for 1 h at room temperature. 200 mL of CH_2Cl_2 and 20 mL of 0.5 M Na_2SO_3 were added successively. The aqueous layer was separated and washed with CH_2Cl_2. The combined organic layers were washed with 10% NaOH and saturated NaCl and dried. A red solid was isolated upon solvent removal. Recrystalization in 25% hexane/CH_2Cl_2 gave 11.6 g (26 mmol) of pure product (58%), mp 101-103 °C. ^{1}H NMR δ 7.71 (s, 2H). TLC (10% CH_2Cl_2/hexane) R_f 0.61.

(2) 1-bromo-3,5-diphenylbenzene[7]

A solution of **1** (10.0 g, 22.7 mmol) in 200 mL dry THF was added dropwise over 1 h to a 227 mL stirred, refluxing solution of 1 M phenylmagnesium bromide in THF (Sigma-Aldrich). Reflux was continued for 1 h after complete addition of **1**. Stirring was continued for 12 h at room temperature. Excess phenylmagnesium bromide was quenched with saturated NH_4Cl. The aqueous layer was washed with diethyl ether. The combined organic layers were washed with saturated NaCl and dried. A white solid was isolated after solvent removal. Recrystalization in 40% CH_2Cl_2/hexane gave 4.4 g (14.3 mmol) of pure product (63%), mp 102-104 °C. TLC (30% CH_2Cl_2/hexane) R_f 0.57.

(5) 3,5-diphenylbenzaldehyde[10]

A solution of **2** (3.09 g, 10 mmol) in 10 mL dry THF was added dropwise to a stirred, refluxing mixture of magnesium turnings (0.27 g, 11 mmol) in 10 mL dry THF. Two drops of 1,2-dibromoethane were added to aid in Grignard initiation. Reflux was continued for 1 h after complete addition of **2**. A solution of *N*-formylmorpholine (10 mmol) in 10 mL dry THF was slowly transferred via canula to the stirring *m*-terphenyl Grignard and was stirred at room temperature for 30 min. Excess Grignard was quenched with 3 M HCl to a pH of 2. The aqueous layer was washed with diethyl ether and the combined organic layers were washed with saturated $NaHCO_3$ and NaCl. The product was purified by flash chromatography (30% CH_2Cl_2/hexane, 200-425 mesh silica gel) and recrystalized in 30% CH_2Cl_2/hexane to give 1.37 g (5.29 mmol) of pure product (53%). R_f (50% CH_2Cl_2/hexanes) = 0.36; mp 101-102°C. Spectral Data: ^{13}C NMR($CDCl_3$, 50 MHz) δ 192.521 (s), 142.968 (s), 139.933 (s), 137.649 (s), 132.042 (s), 129.257 (s), 128.347 (s), 127.459 (s), 127.376 (s). ^1H NMR($CDCl_3$, 200 MHz) δ 7.417-7.546 (m, 6H), 7.663-7.710 (m, 4H), 8.003 (s, 3H), 10.152 (s, 1H). Anal calcd for $C_{19}H_{14}O$: C, 88.34;

H, 5.46; O, 6.19. Found: C, 88.05; H, 5.47; O, 5.93. UV/VIS: $\varepsilon_{202} = 3.92*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{205} = 4.16*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{248} = 3.72*10^4\ M^{-1}cm^{-1}$.

(6) **3,5-diphenylacetophenone**[11]

A solution of **2** (1.00 g, 3.24 mmol) in 3.24 mL dry THF was added dropwise to a stirred, refluxing mixture of magnesium turnings (0.128 g, 5.24 mmol) in 3.24 mL dry THF. Two drops of 1,2-dibromoethane were added to aid in Grignard initiation. Reflux was continued for 1 h after complete addition of **2**. The *m*-terphenyl Grignard was then slowly transferred via canula to a stirring solution of acetic anhydride (6 mL 99.5%, 63.5 mmol) at 0 °C. After 2 h of stirring at 0 °C, the reaction was quenched with water. The aqueous layer was washed with diethyl ether and the combined organic layers were washed with 10% NaOH and saturated NaCl and dried (61% by GC-MS). The product was purified by flash chromatography (20% CH_2Cl_2/hexane, 200-425 mesh silica gel) and recrystalized in 20% CH_2Cl_2/hexane to give 0.524 g (5.13 mmol) of pure product (68%). R_f (50% CH_2Cl_2/hexanes) = 0.16; mp 99-101°C. Spectral Data: ^{13}C NMR($CDCl_3$, 50 MHz) δ 27.115 (s), 126.139 (s), 127.520 (s), 128.157 (s), 129.189 (s), 130.782 (s), 138.400 (s), 140.434 (s), 142.550 (s), 198.258 (s). ^1H NMR($CDCl_3$, 200 MHz) δ 2.713 (s, 3H), 7.410-7.542 (m, 6H), 7.656-7.703 (m, 4H), 7.993-8.009 (t, 1H), 8.150-8.157 (d, 2H). Anal calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92; O 5.87. Found: C, 87.97; H, 5.92; O, 5.74. UV/VIS: $\varepsilon_{204} = 9.46*10^2\ M^{-1}cm^{-1}$, $\varepsilon_{249} = 7.94*10^2\ M^{-1}cm^{-1}$, $\varepsilon_{315} = 7.2\ M^{-1}cm^{-1}$.

(7) **m-terphenylpyridine**[12]

A solution of **2** (1.29 g, 4.17 mmol) in 4.17 mL dry THF was added dropwise to a stirred, refluxing mixture of magnesium turnings (0.164 g, 6.74 mmol) in 4.17 mL dry THF. Two drops of 1,2-dibromoethane were added to aid in Grignard initiation. Reflux was continued for 1 h after complete addition of **2**. The *m*-terphenyl Grignard was added dropwise by canula

transfer to a stirred solution of 2.84 mmol 2-chloropyridine, 0.085 mmol (3 mol%) $Ni(acac)_2$, and 0.085 mmol (3 mol%) 1,3-bis-(2,4,6-trimethylphenyl)imidizolium in 2.84 mL dry THF at room temperature and was allowed to stir for 18 h. The reaction was quenched with methanol. The methanol layer was washed with diethyl ether and the combined organic layers were washed with saturated NaCl and dried (56% by GC). The product was purified by flash chromatography (25% CH_2Cl_2/hexane, 200-425 mesh silica gel) and recrystalized in 40% CH_2Cl_2/hexane to give 0.2700g (0.878 mmol) of pure product (21.1%). R_f (100% CH_2Cl_2) = 0.46; mp 137-139°C. Spectral Data: ^{13}C NMR($CDCl_3$, 50 MHz) δ 121.055 (s), 122.588 (s), 125.077 (s), 126.966 (s), 127.611 (s), 127.778 (s), 129.030 (s), 137.050 (s), 140.692 (s), 141.261 (s), 142.558 (s), 149.994 (s), 157.574 (s). ^1H NMR($CDCl_3$, 200 MHz) δ 7.271-7.315 (m, 1H), 7.388-7.531 (m, 6H), 7.703-7.874 (m, 7H), 8.200-8.207 (d, 2H), 8.736-8.766 (d, 1H). Anal calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N 4.56. Found: C, 88.73; H, 5.56; N, 4.51. UV/VIS: $\varepsilon_{200} = 4.08*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{202} = 3.74*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{250} = 3.52*10^4\ M^{-1}cm^{-1}$.

(8) m-terphenylpyrimidine[12]

A solution of **2** (1.29 g, 4.17 mmol) in 4.17 mL dry THF was added dropwise to a stirred, refluxing mixture of magnesium turnings (0.164 g, 6.74 mmol) in 4.17 mL dry THF. Two drops of 1,2-dibromoethane were added to aid in Grignard initiation. Reflux was continued for 1 h after complete addition of **2**. The *m*-terphenyl Grignard was added dropwise by canula transfer to a stirred solution of 2.84 mmol 2-chloropyrimidine, 0.085 mmol (3 mol%) $Ni(acac)_2$, and 0.085 mmol (3 mol%) 1,3-bis-(2,4,6-trimethylphenyl)imidizolium in 2.84 mL dry THF at room temperature and was allowed to stir for 18 h. The reaction was quenched with methanol. The methanol layer was washed with diethyl ether and the combined organic layers were washed with saturated NaCl and dried (32% by GC). The product was purified by flash chromatography

(25% CH_2Cl_2/hexane, 200-425 mesh silica gel) and recrystallized in 40% CH_2Cl_2/hexane to give 0.4291g (1.39 mmol) of pure product (49 %). R_f (80% CH_2Cl_2/hexanes) = 0.34; mp 145-147°C. Spectral Data: ^{13}C NMR($CDCl_3$, 50 MHz) δ 119.553 (s), 126.139 (s), 127.580 (s), 127.778 (s), 128.590 (s), 129.014 (s), 138.764 (s), 141.078 (s), 142.391 (s), 157.505 (s), 164.774 (s). ^1H NMR($CDCl_3$, 200 MHz) δ 7.207-7.238 (m, 1H), 7.346-7.535 (m, 6H), 7.749-7.797 (m, 4H), 7.941-7.967 (m, 1H), 8.696-8.711 (t, 2H), 8.839-8.870 (m, 2H). Anal calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N 9.08. Found: C, 85.39; H, 5.22; N, 8.98. UV/VIS: $\varepsilon_{202} = 4.84*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{252} = 5.79*10^4\ M^{-1}cm^{-1}$, $\varepsilon_{310} = 1.45*10^3\ M^{-1}cm^{-1}$.

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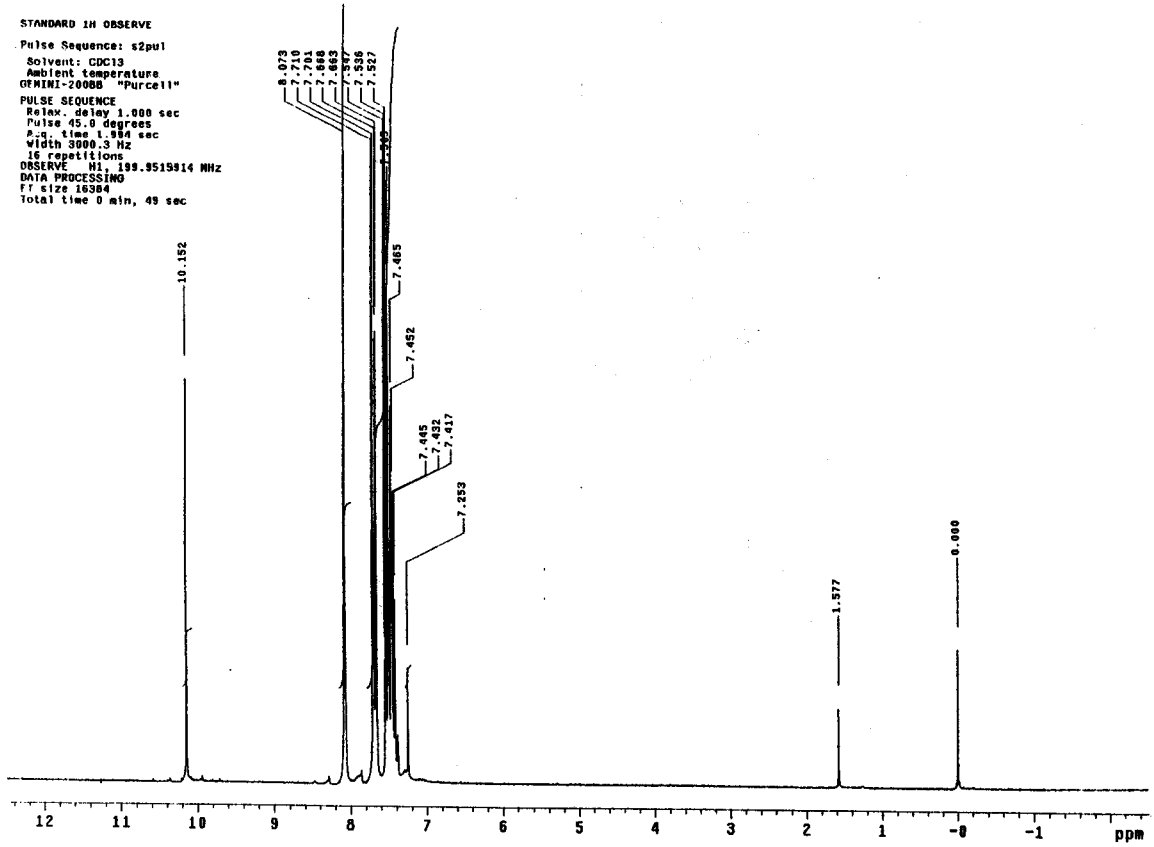
Appendix I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7.253
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9
8
7
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ppm

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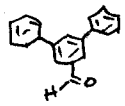

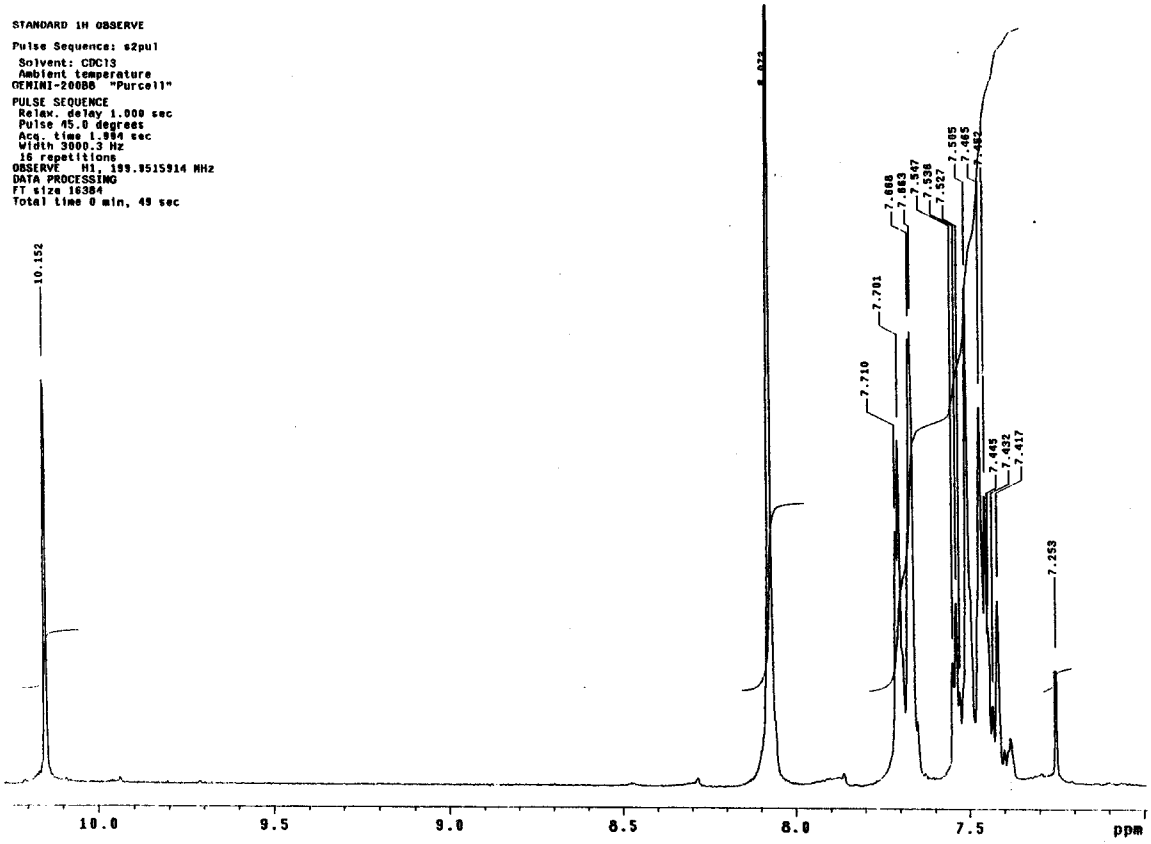
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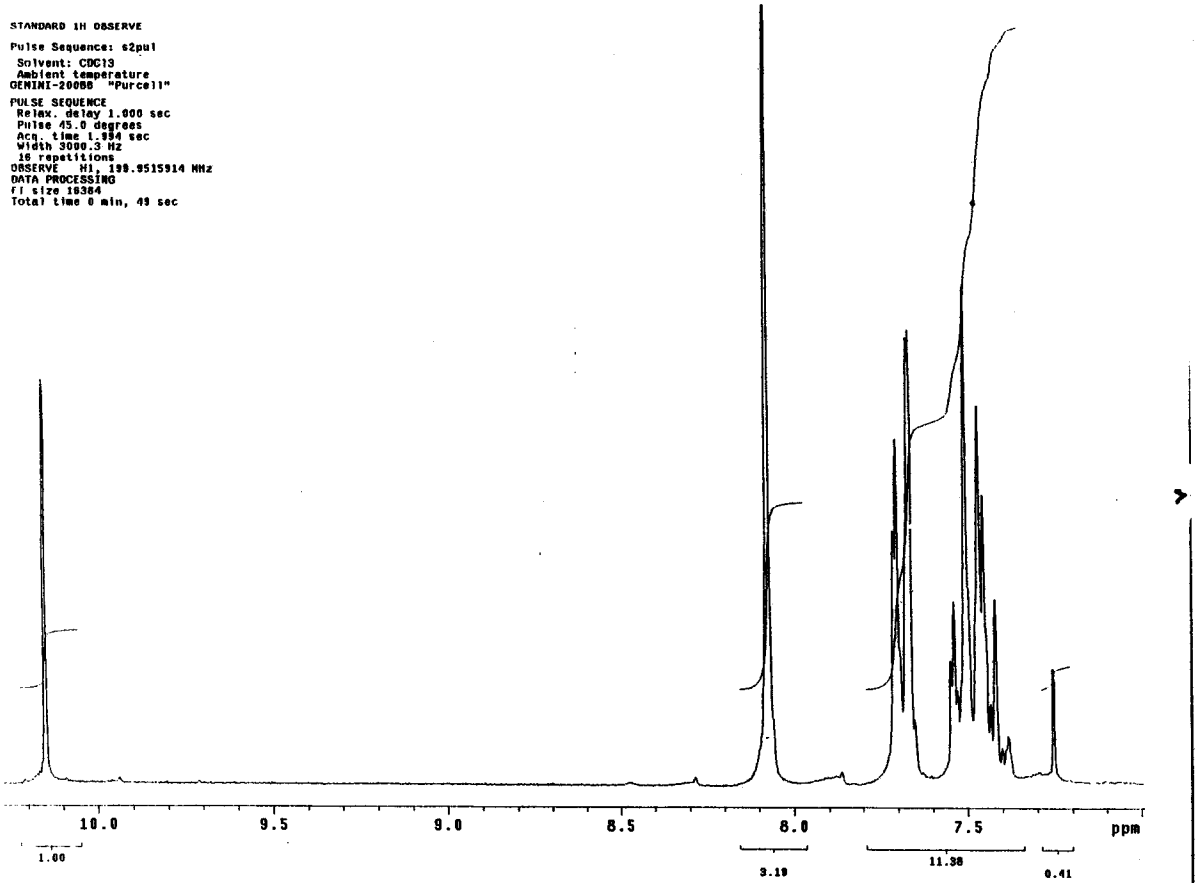
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0.41

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Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"

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Power 37 dB
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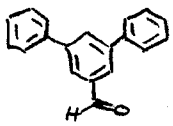
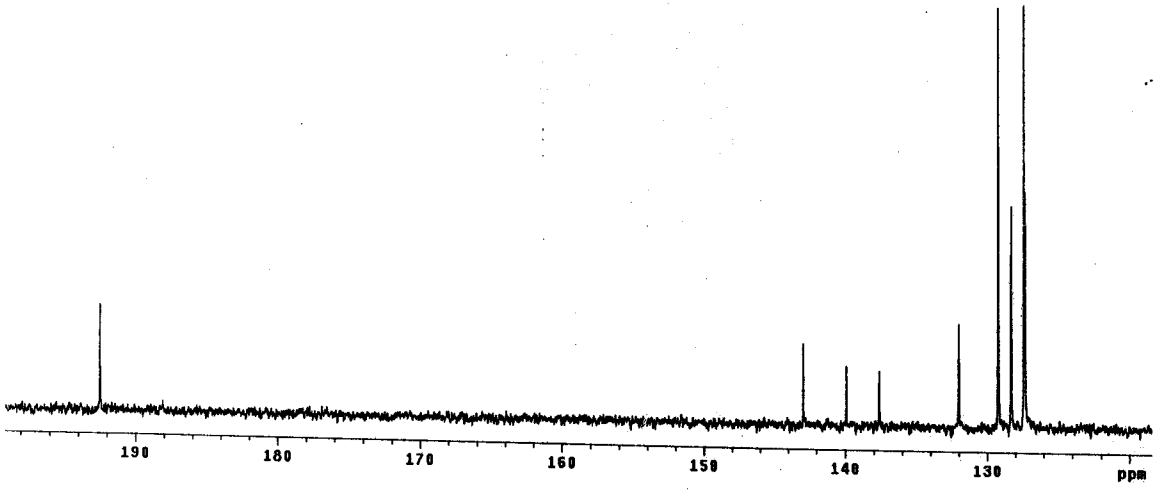
Line broadening 1.0 Hz
FT size 65536
Total time 45 min, 47 sec



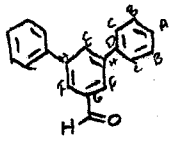


13C OBSERVE

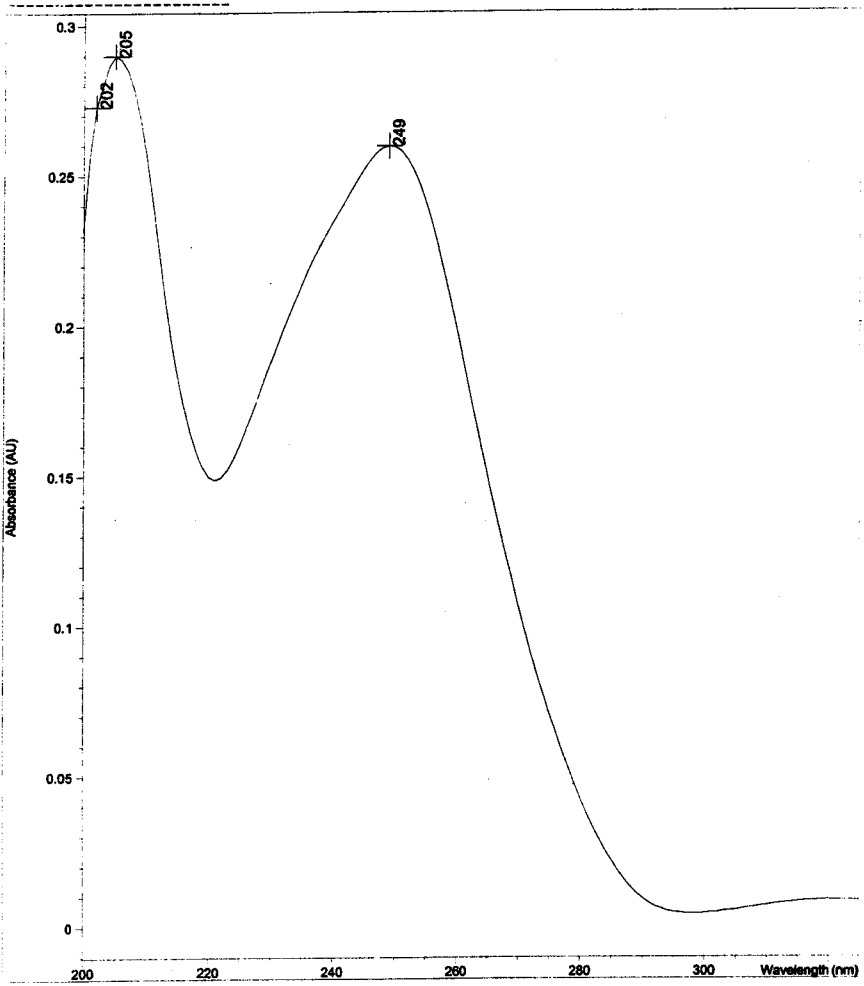
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-2000B "Purcell"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.488 sec
Width 12500.0 Hz
1024 repetitions
OBSERVE C13, 50.2778569 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 45 min, 47 sec

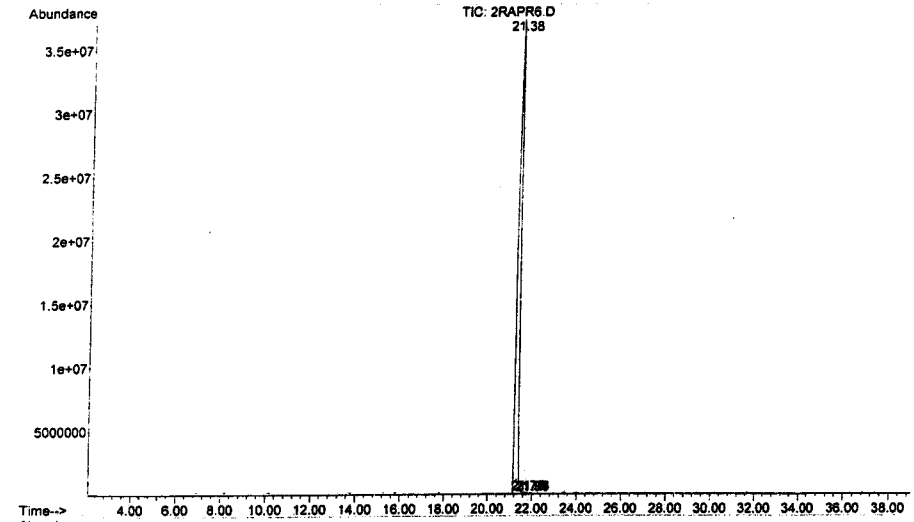


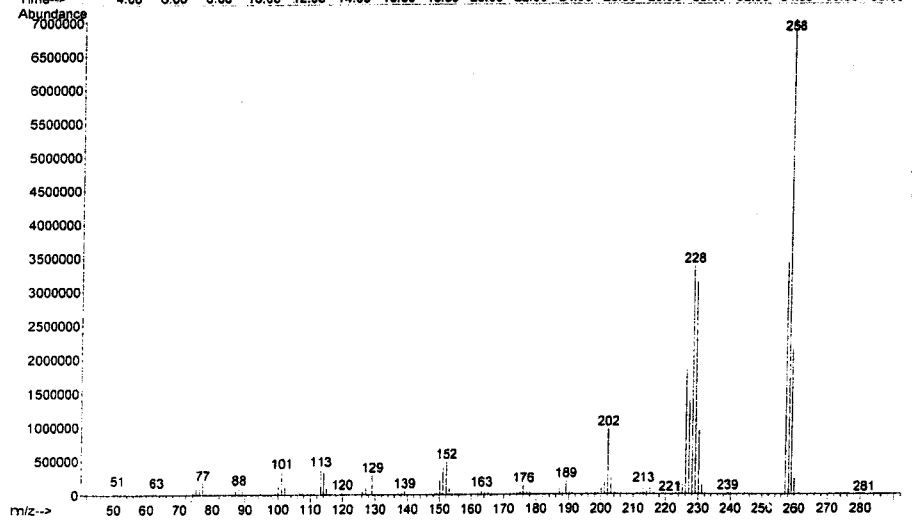
Overlaid Sample Spectra



*** End Hardcopy window ***

File : C:\MSDChem\1\DATA\KehlBeck\Sparks\2RAPR6.D
Operator : Sparks
Acquired : 6 Apr 2006 23:27 using AcqMethod KEHLBECK3
Instrument : Instrumen
Sample Name: aldehyde column fraction 2
Misc Info : purity check
Vial Number: 5

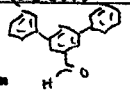




ATLANTIC MICROLAB, INC.

Sample No. $C_{14}H_{14}O$ (258.1) JK080305

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0062
www.atlanticmicrolab.com



PROFESSOR/SUPERVISOR: Professor Joanne Kehlbeck
P.O. #: L40016

SUBMITTER

Company / School: Union College
Address: Chemistry Department
807 Union Street
Schenectady, NY 12308
NAME: Prof. Joanne Kehlbeck DATE: 7/26/05

Element	Theory	Found	
C	88.34	88.05	
H	5.46	5.47	
O	6.19	5.93	

Single ☑ Duplicate ☐
Elements Present: C, H, O
Analyze for: C, H, O
Hygroscopic ☐ Explosive ☐
M.P. 101-102 B.P.
To be dried: Yes ☐ No ☑
Temp. Vac. Time
FAX Service ☑
FAX Phone # 518-388-6795
Rush Service ☐ (SEE CURRENT
Phone Service ☐ PRICE LIST)
Phone No.

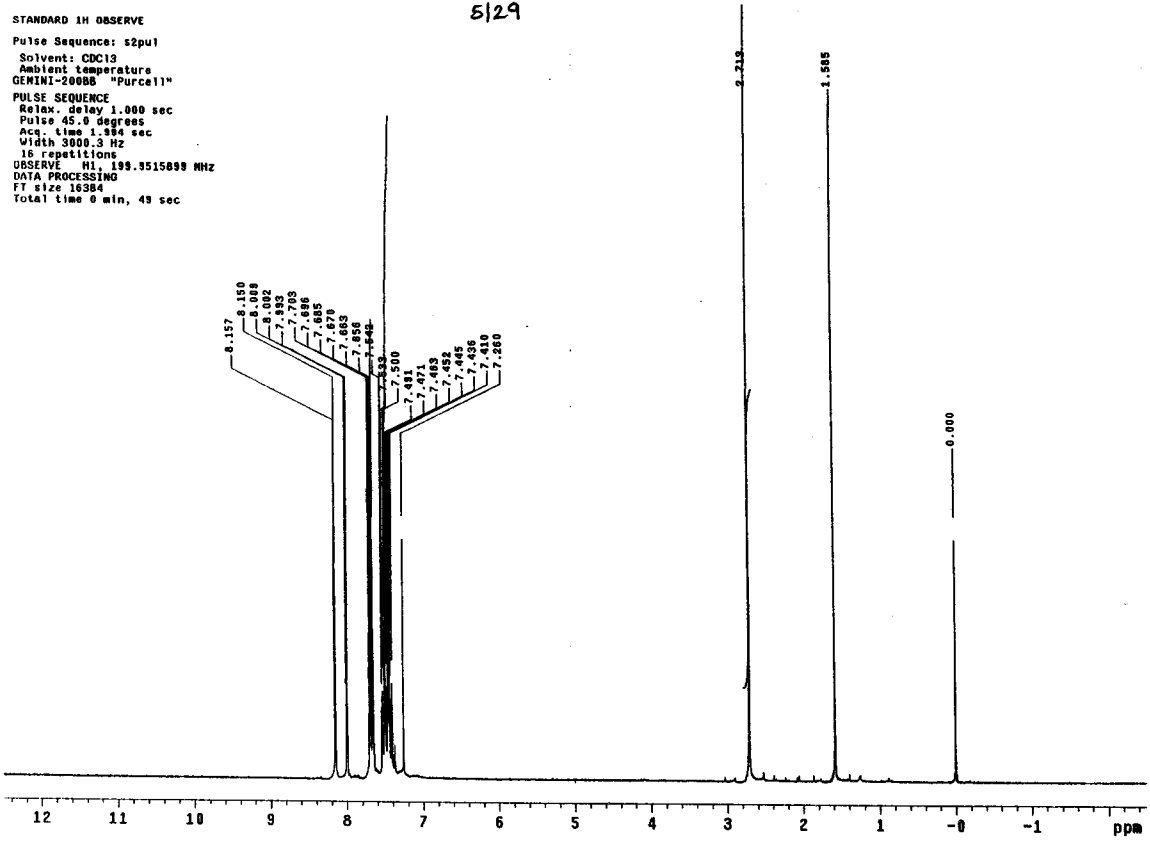
Date Received AUG 0 3 2005 Date Completed AUG 0 4 2005

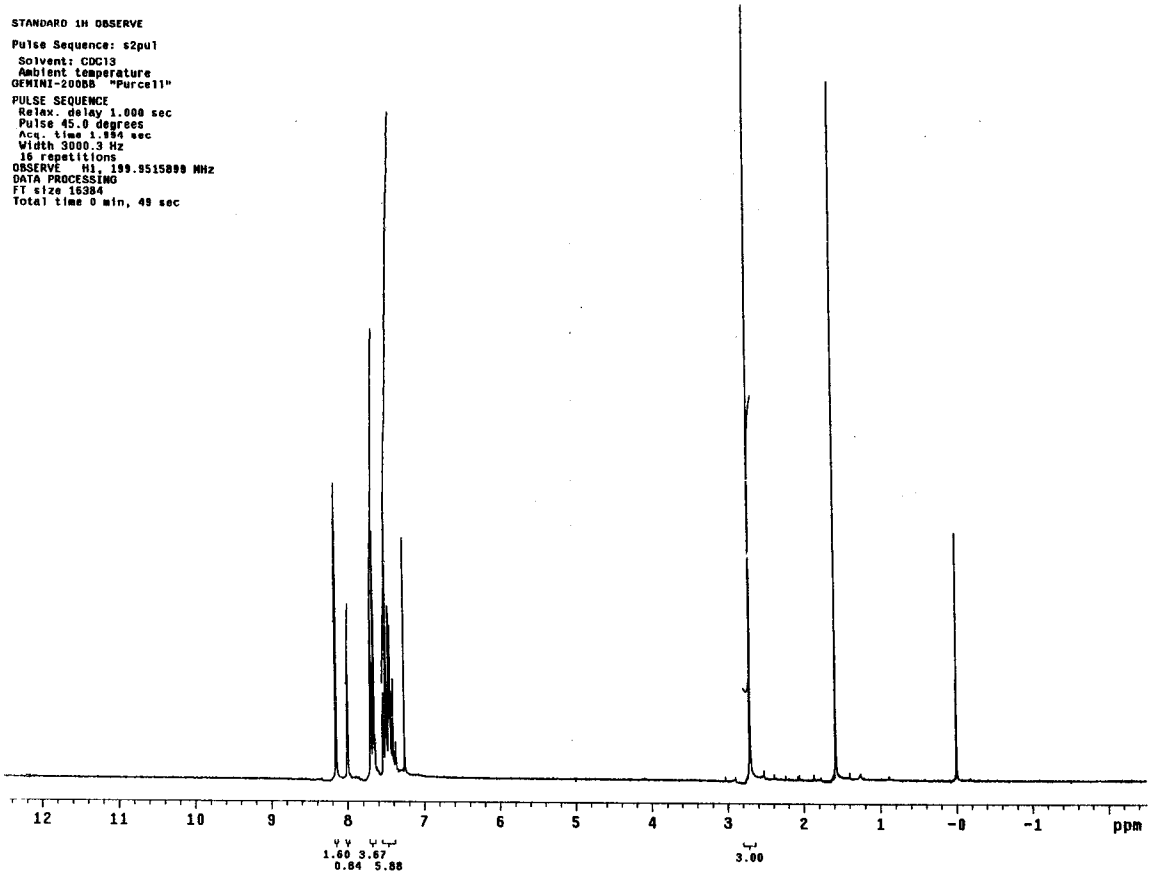
Remarks: Bill to: Union College, Accounts Payable Dept.
PO Box 769
Schenectady, NY 12301-0769

Appendix II

5,5-diphenylidene...

5/29



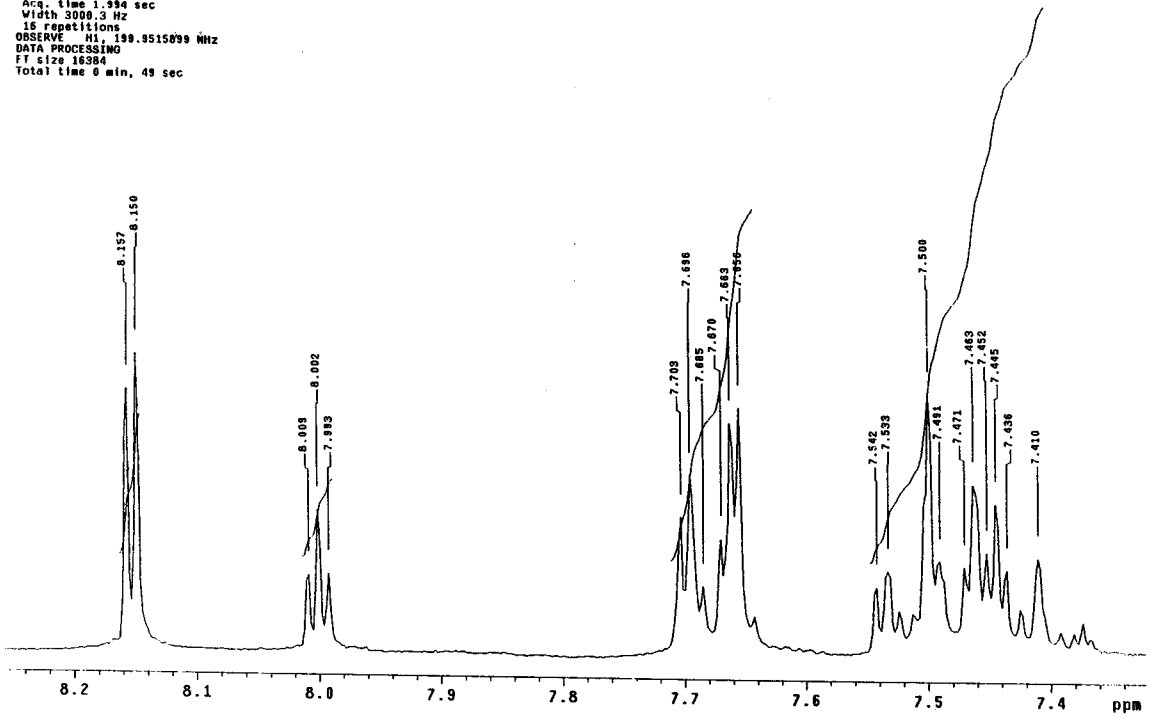

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.884 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515899 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
1.60 3.67
0.84 5.88
3.00

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515099 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec

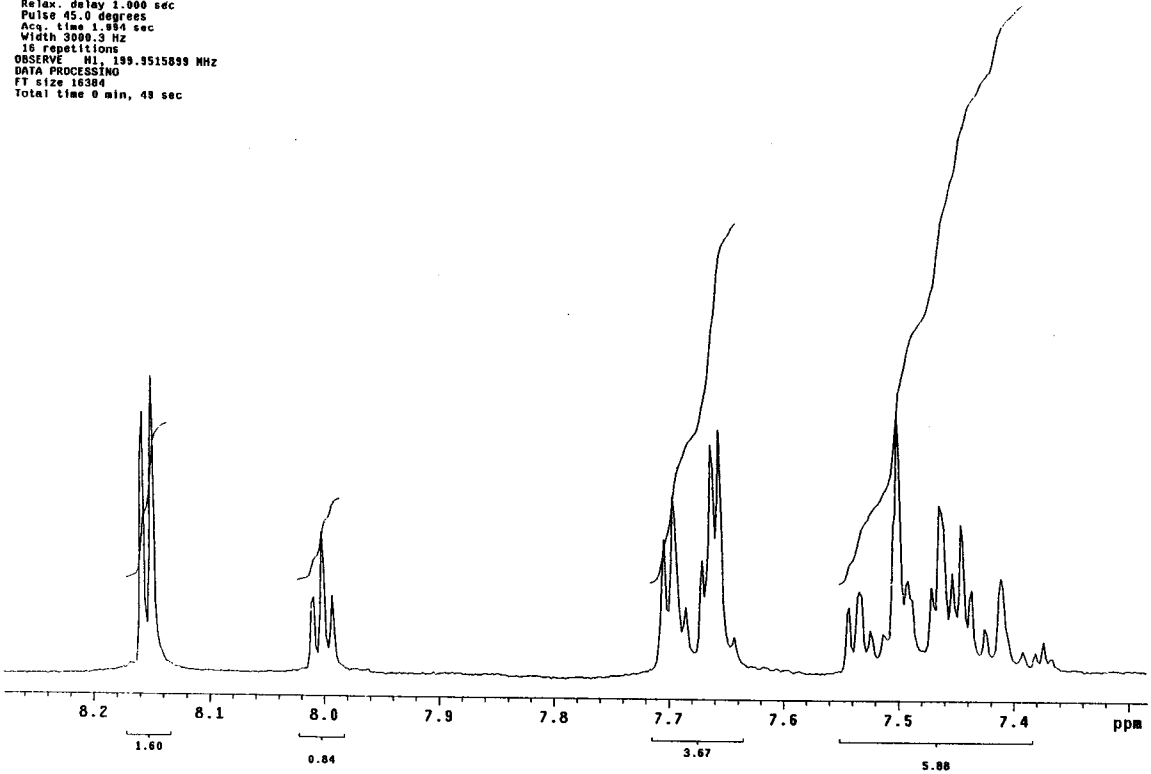


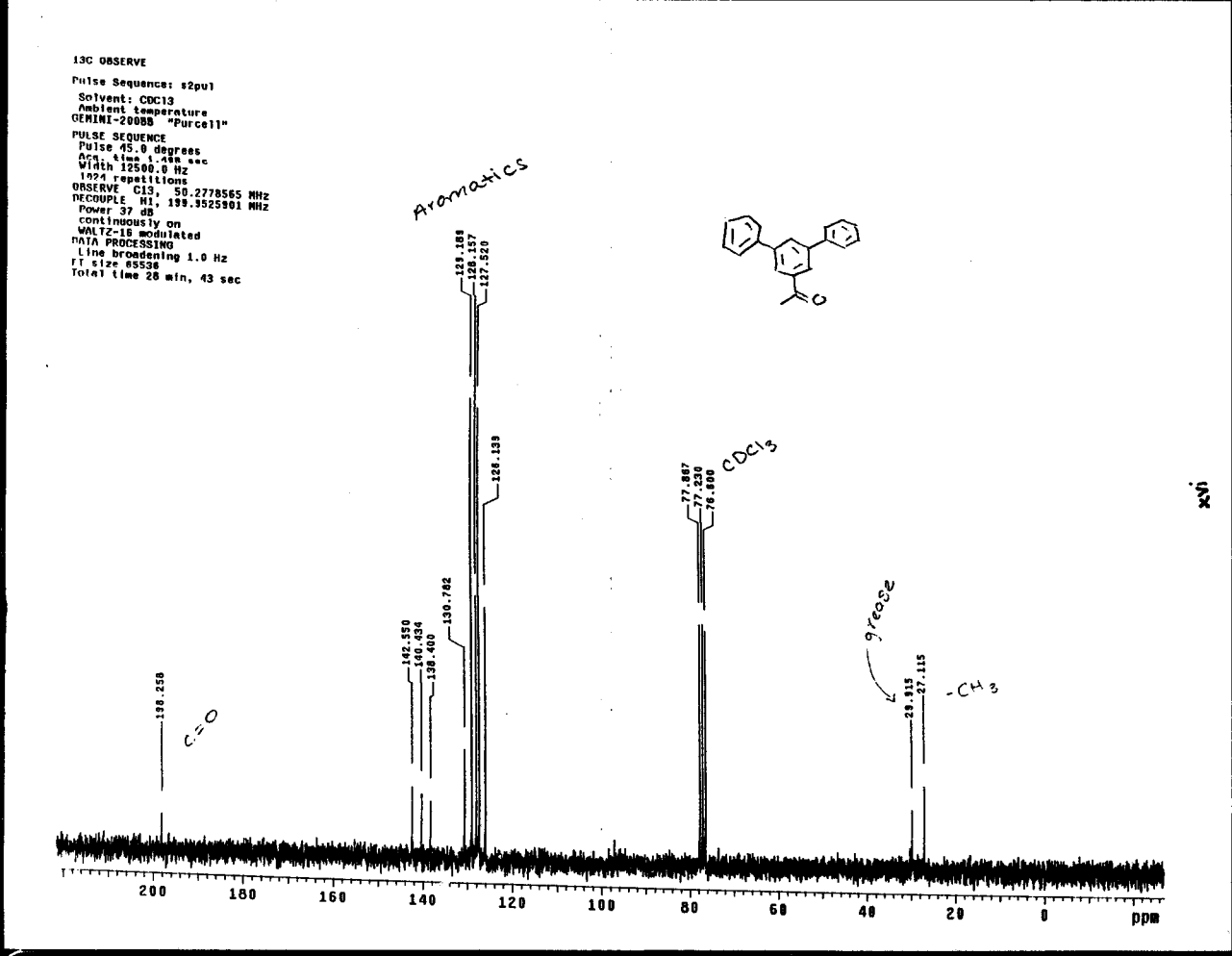
STANDARD 1H OBSERVE

Pulse Sequence: s2pul

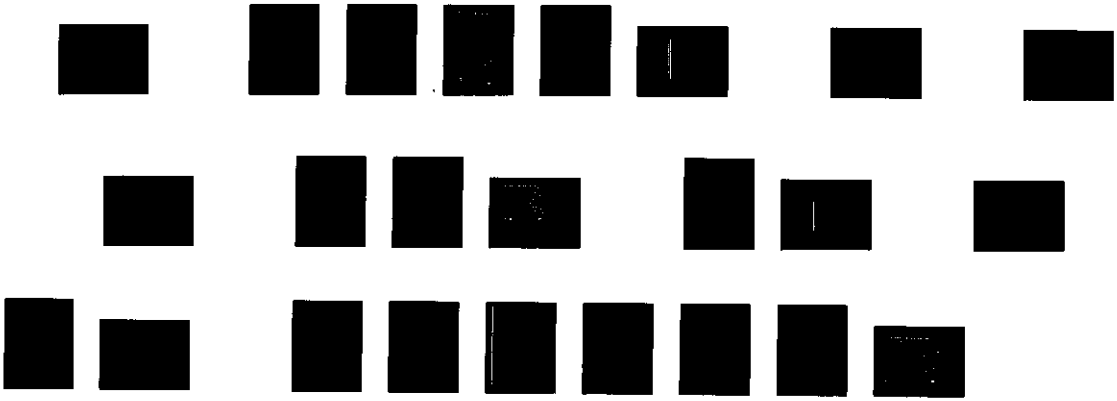
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515899 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec




13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000B "Purcell"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.498 sec
Width 12500.0 Hz
1024 repetitions
OBSERVE C13, 50.2778565 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 28 min, 43 sec
Aromatics
129.188
128.557
127.520
128.139
130.782
142.550
140.434
138.400
198.256
C=O
77.867
77.230
76.600
CDCl3
grease
29.915
27.115
-CH3
O
200
180
160
140
120
100
80
60
40
20
0
ppm

xvi

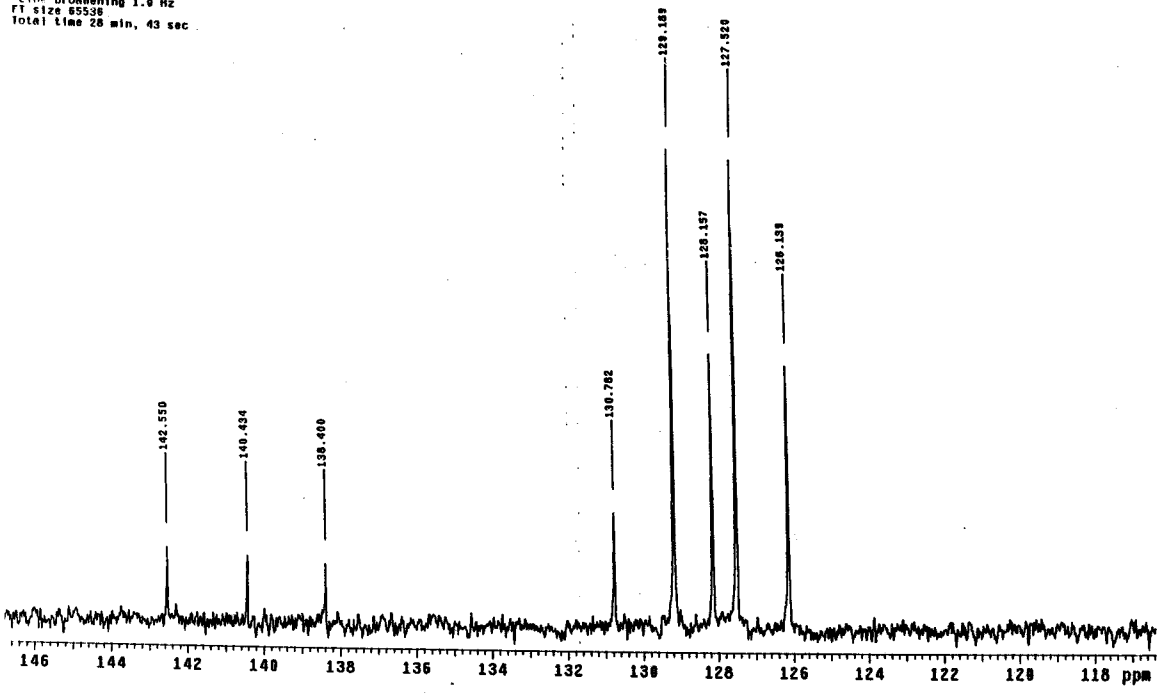


13C OBSERVE

Pulse Sequence: s2pul

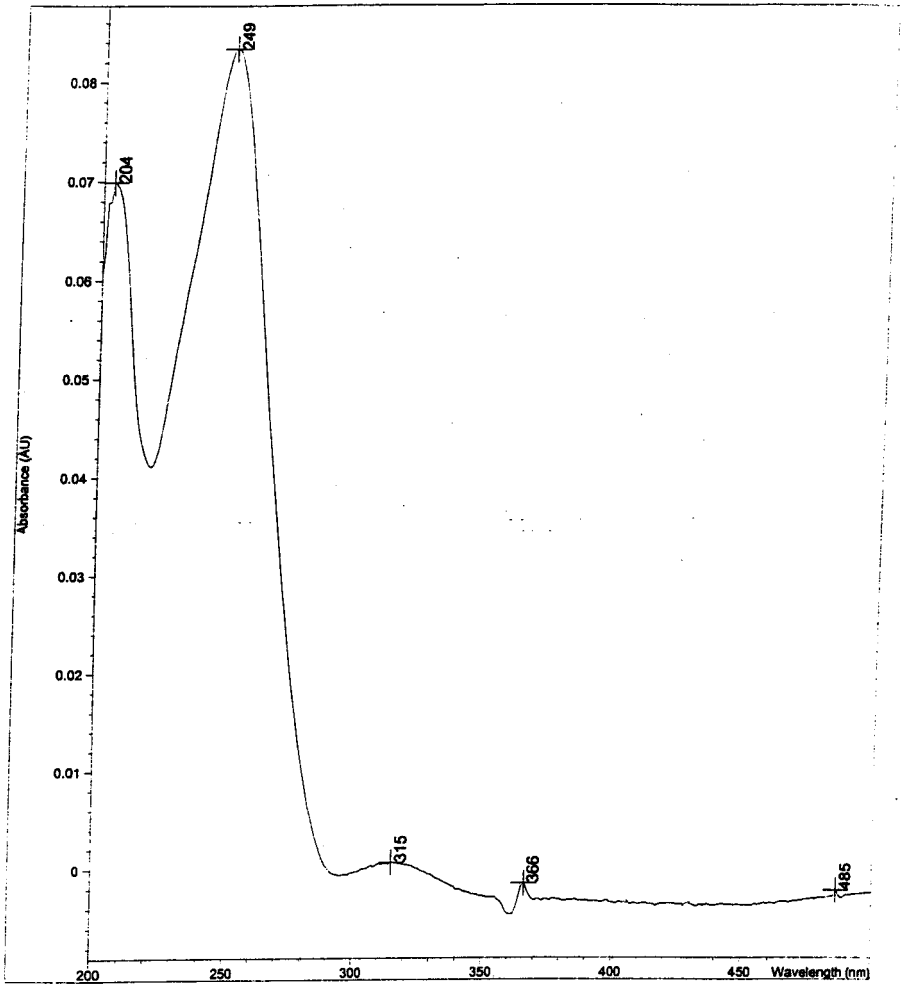
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"

PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.440 sec
Width 12500.0 Hz
1024 repetitions
OBSERVE C13, 50.2778565 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 28 min, 43 sec



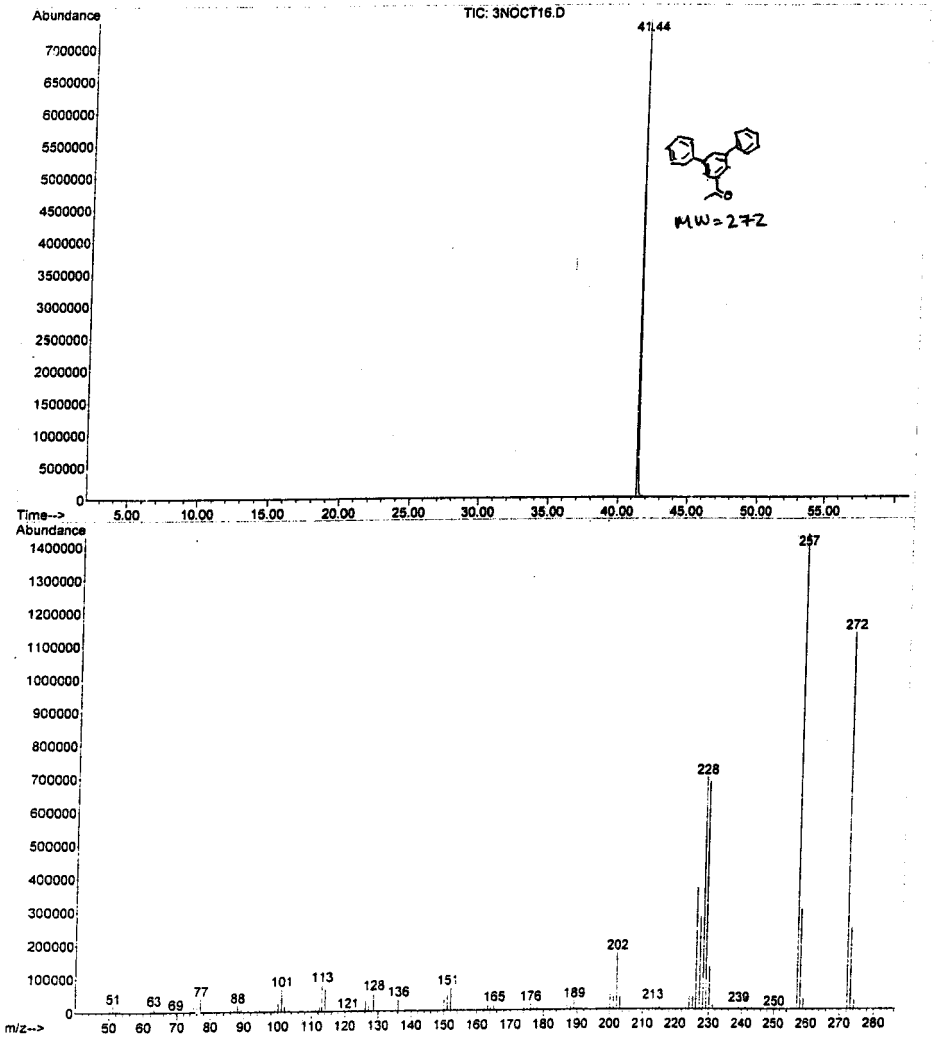
XVII

Overlaid Sample Spectra



*** End Hardcopy window ***

```
Operator  : Sparks
Acquired  : 16 Oct 2005  20:20      using AcqMethod KEHLBECK2
Instrument :
    Instrumen
Sample Name: acetyl recryst.
Misc Info  : purity check
Vial Number: 13
```



ATLANTIC MICROLAB, INC.

Sample No. $C_{20}H_{16}O$ (272.12)

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0082
www.atlanticmicrolab.com

PROFESSOR/SUPERVISOR:
P.O. #: L40238

SUBMITTER
Company / School Union College
Address Chemistry Department
807 Union Street
Schenectady, NY 12308
NAME Prof. Joanne Kenlbeck DATE 9/22/05

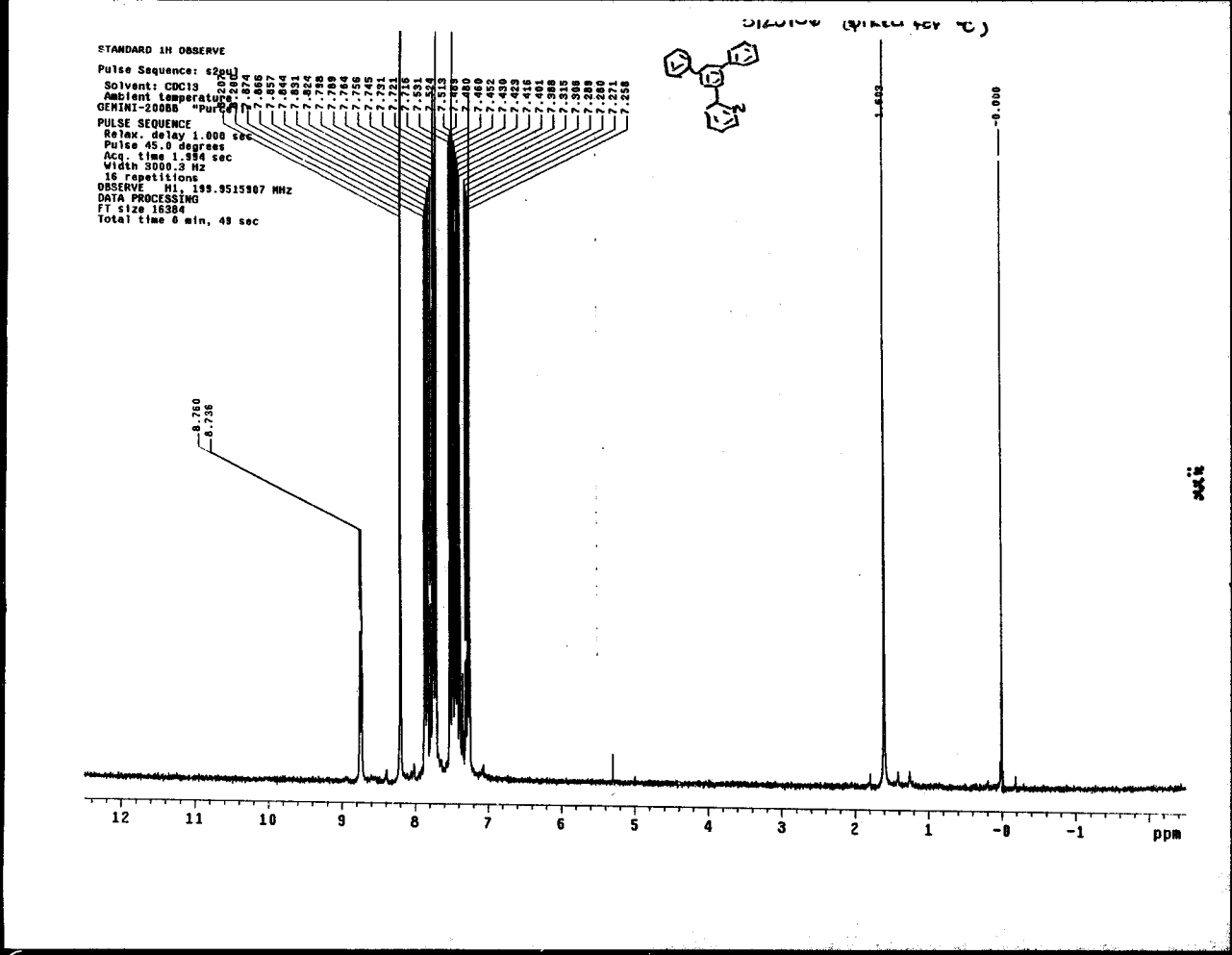
Element	Theory	Found	
C	88.20	87.97	
H	5.92	5.92	
O	5.87	5.74	

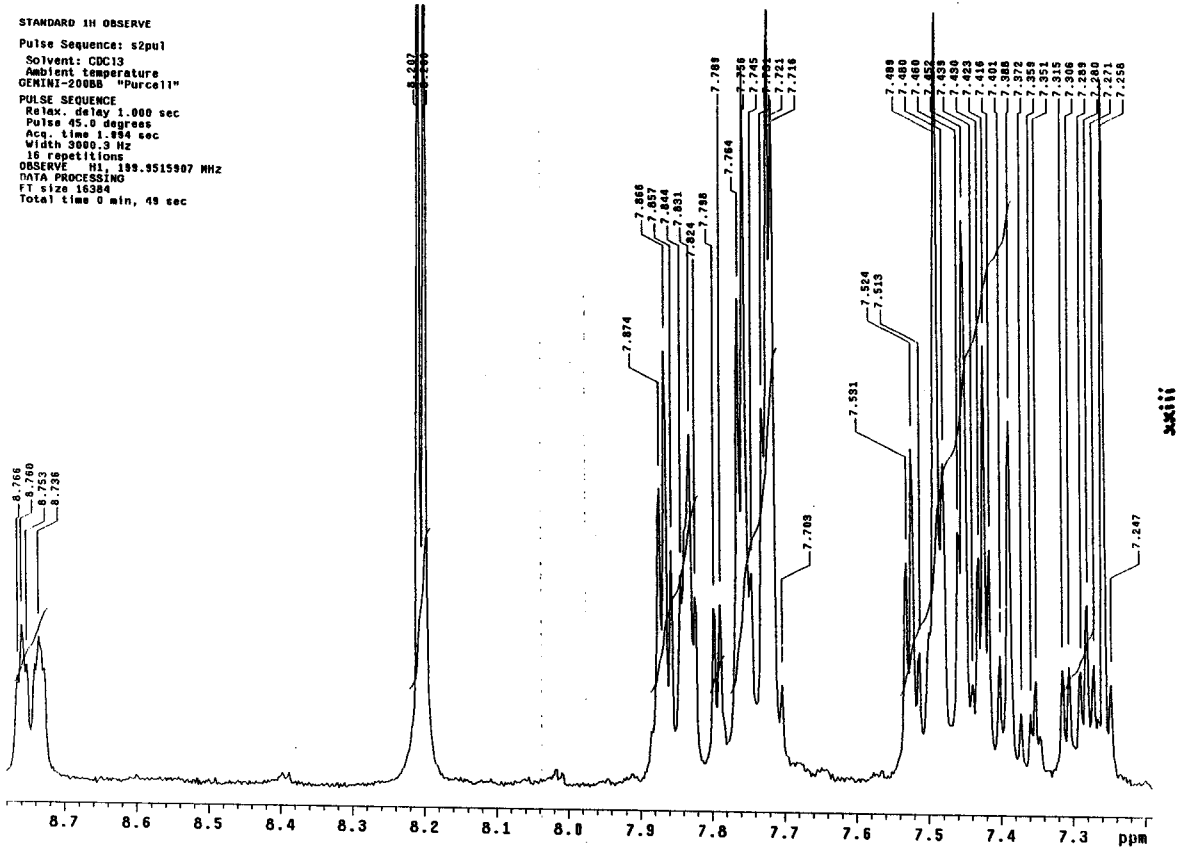
Single ☒ Duplicate ☐
Elements Present:
Analyze for: CHO
Hygroscopic ☐ Explosive ☐
M.P. 96°-98° B.P.
To be dried: Yes ☐ No ☒
Temp. Vac. Time
FAX Service ☒
FAX Phone #
Rush Service ☐ (SEE CURRENT
Phone Service ☐ PRICE LIST)
Phone No.

Date Received OCT 04 2005
Remarks:
Date Completed OCT 05 2005

xx

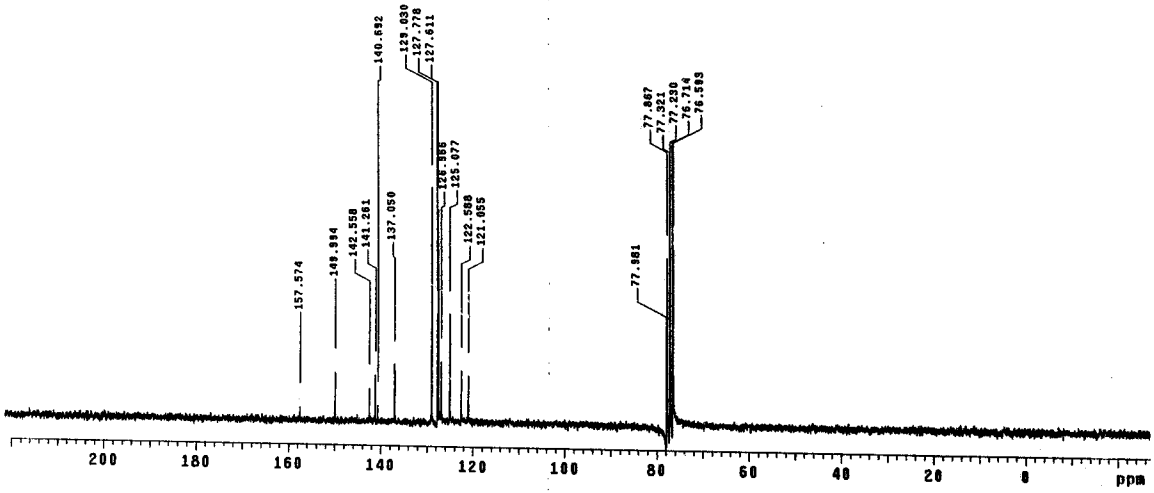
Appendix III


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000B "Purcell"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515907 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec
8.760
8.736
7.716
7.691
7.513
7.489
7.480
7.460
7.452
7.436
7.423
7.416
7.401
7.388
7.315
7.308
7.288
7.280
7.271
7.258
1.603
0.000
N
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.884 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515907 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec
8.766
8.760
8.753
8.736
8.287
8.866
8.857
8.844
8.831
8.824
8.788
7.874
7.788
7.764
7.758
7.745
7.731
7.716
7.708
7.591
7.524
7.515
7.489
7.480
7.460
7.452
7.439
7.430
7.423
7.416
7.401
7.388
7.372
7.351
7.315
7.306
7.289
7.280
7.271
7.258
7.247
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.498 sec
Width 12500.0 Hz
7000 repetitions
OBSERVE C13, 50.2778561 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 16 min, 24 sec



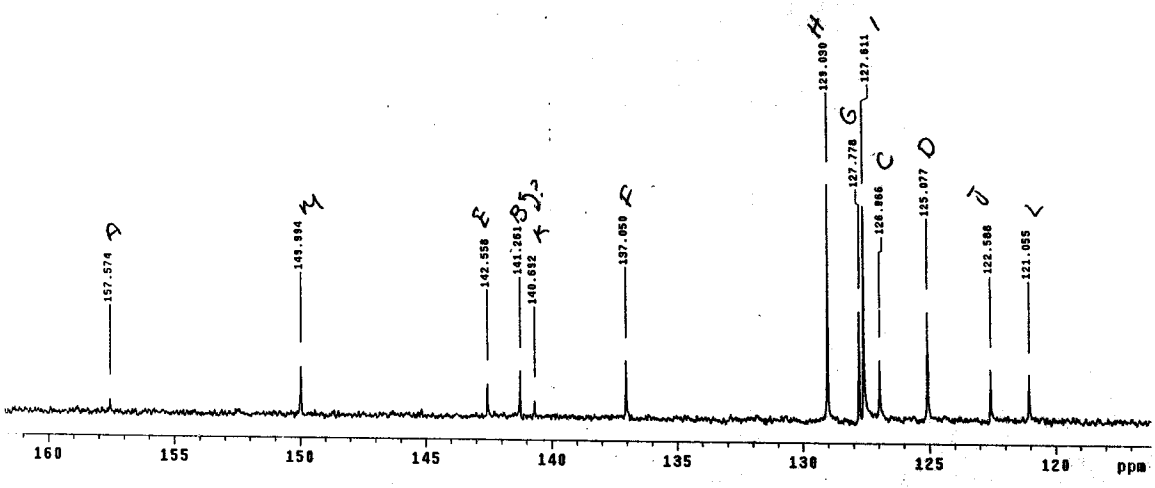
x2IV

13C OBSERVE

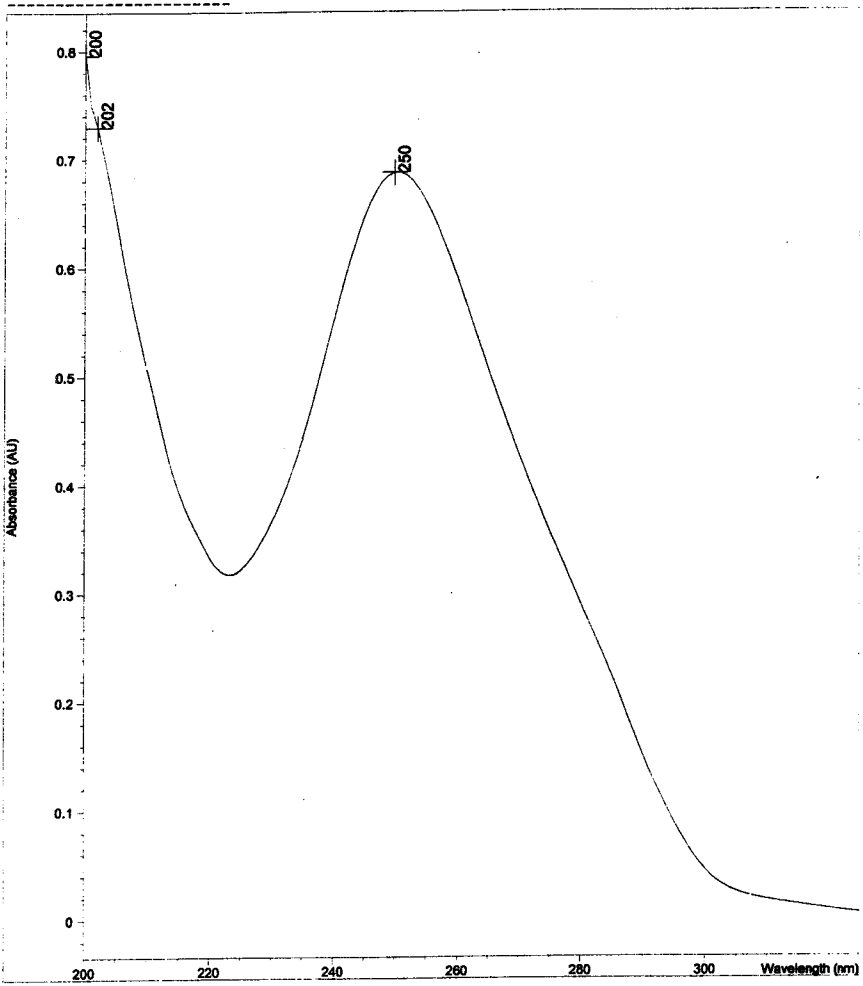
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-2000B "Purcell"

PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.495 sec
Width 12500.0 Hz
7000 repetitions
OBSERVE C13, 50.2778561 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 16 min, 24 sec

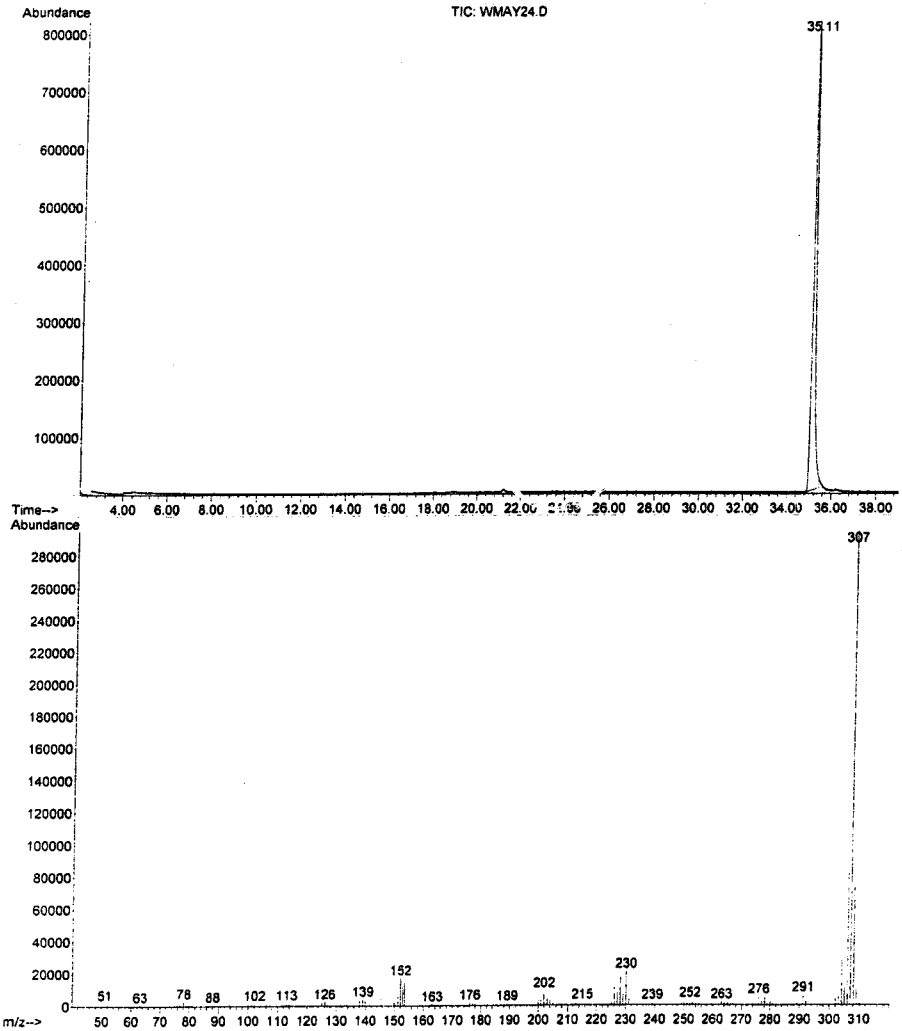


Overlaid Sample Spectra



*** End Hardcopy window ***

[illegible] : [illegible]\Chem\DATA\Kehlbeck\Sparks\WMAY24.D
perator : Sparks
cquired : 24 May 2006 14:49 using AcqMethod KEHLBECK3
nstrument : Instrumen
mple Name: pyridine
sc Info : purity check
ial Number: 20



ATLANTIC MICROLAB, INC.

Sample No. $C_{23}H_{17}N$ (307.39)

P.O. Box 2288
Norcross, Georgia 30091
(770) 242-0062
www.atlanticmicrolab.com

PROFESSOR/SUPERVISOR:
P.O. #:

SUBMITTER

Company / School Union College
Address Chemistry Department
807 Union Street
Schenectady, NY 12308
NAME Prof. Jeanine Mehlrecks DATE 5/26/06

NO CHARGE FOR DUPLICATES

Element	Theory	Found	
C	89.87	89.90	89.73
H	5.57	5.43	5.56
N	4.56	4.63	4.51

Single ☒ Duplicate ☐

Elements Present: C, H, N
Analyze for: C, H, N

Hygroscopic ☐ Explosive ☐
M.P. 183-184°C B.P.

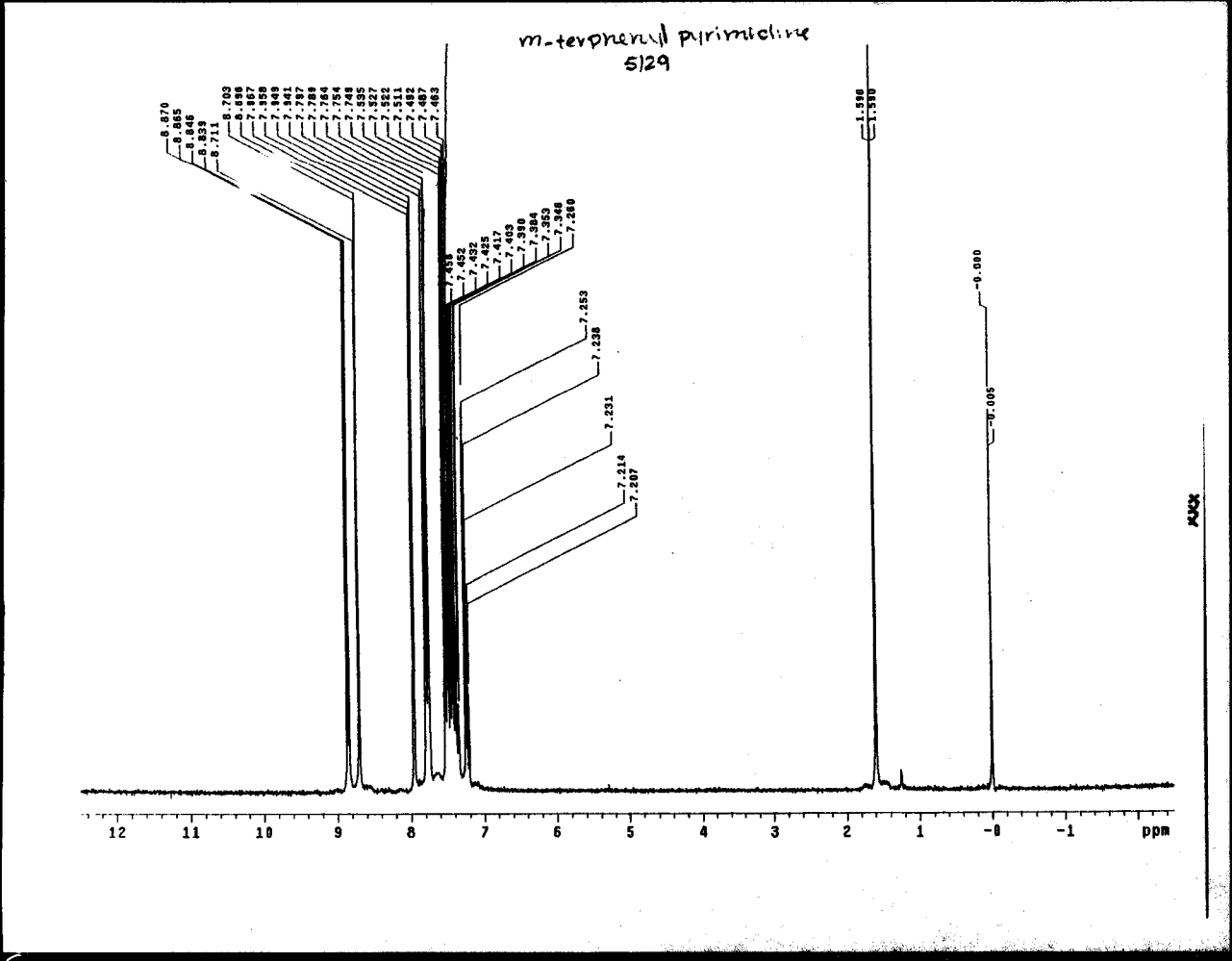
To be dried: Yes ☐ No ☒
Temp. Vac. Time

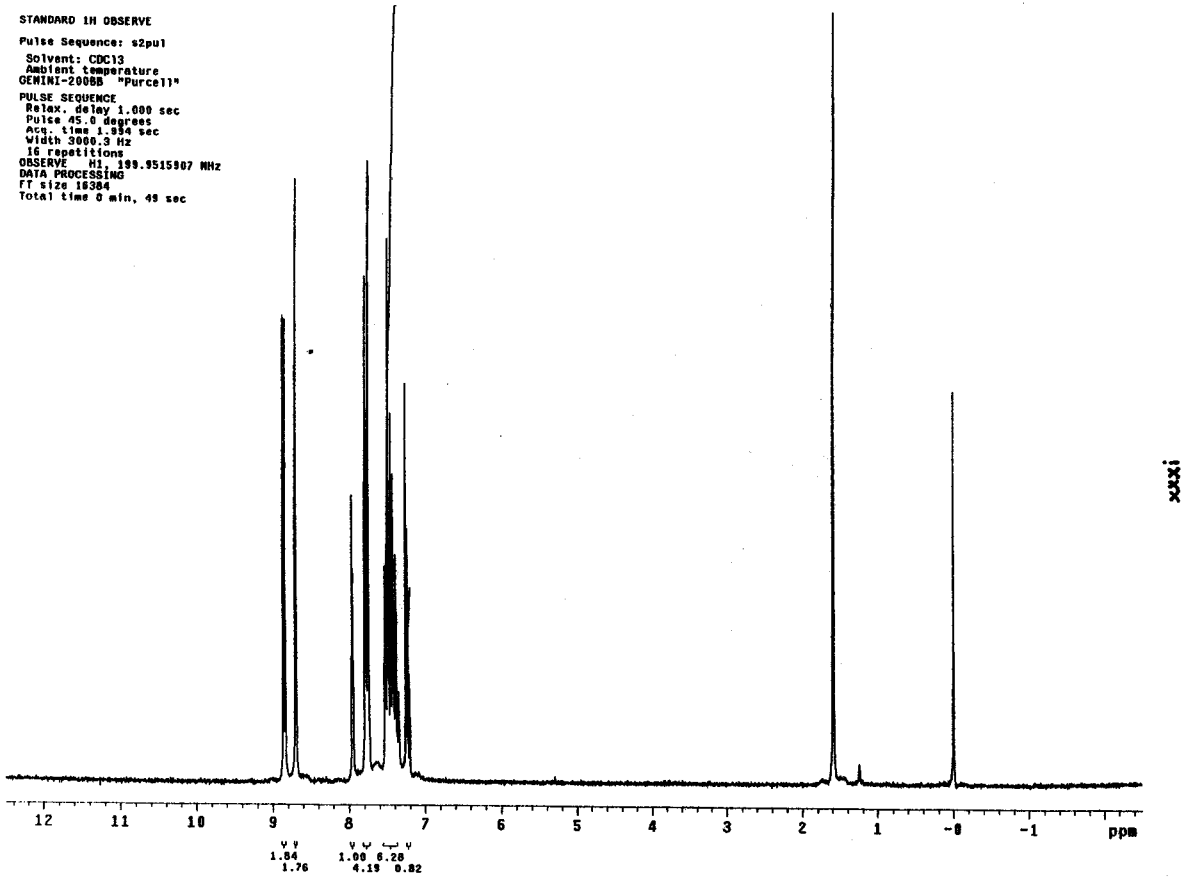
FAX Service ☒
FAX Phone # 518-388-6795

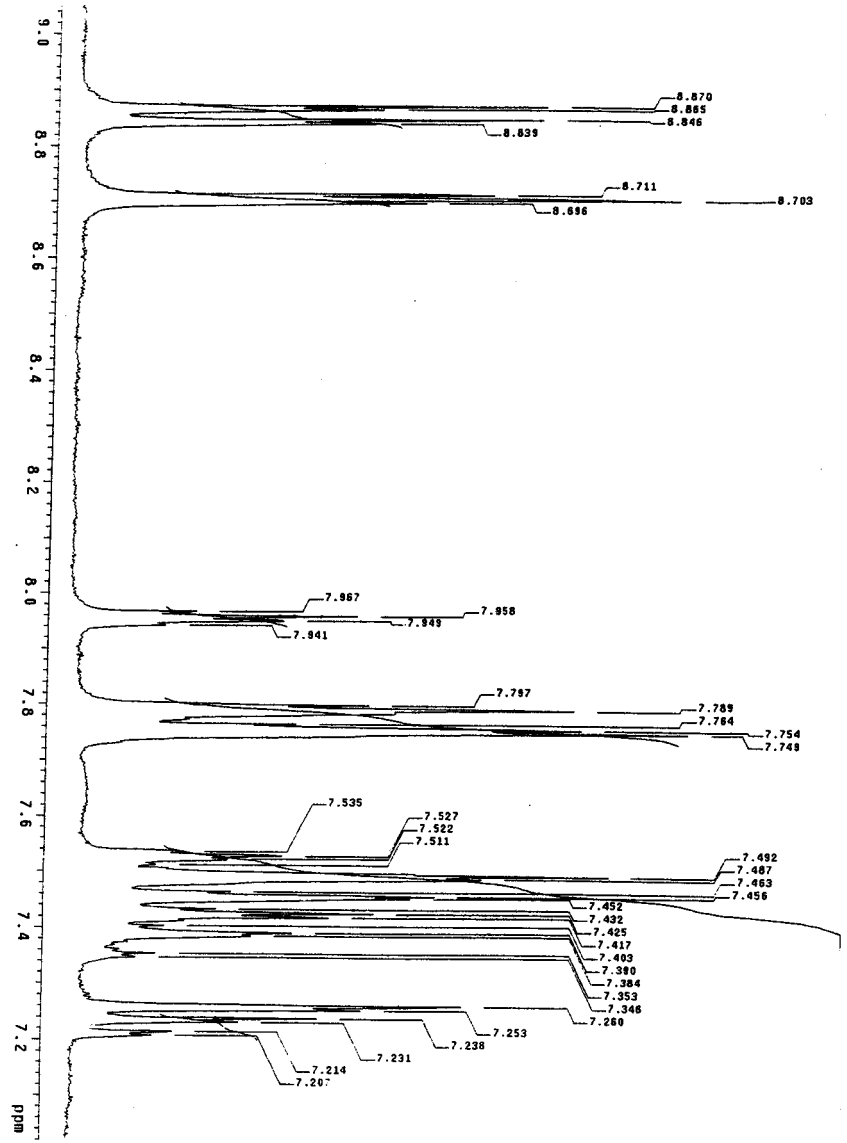
Rush Service ☐ (SEE CURRENT
Phone Service ☐ PRICE LIST)
Phone No.

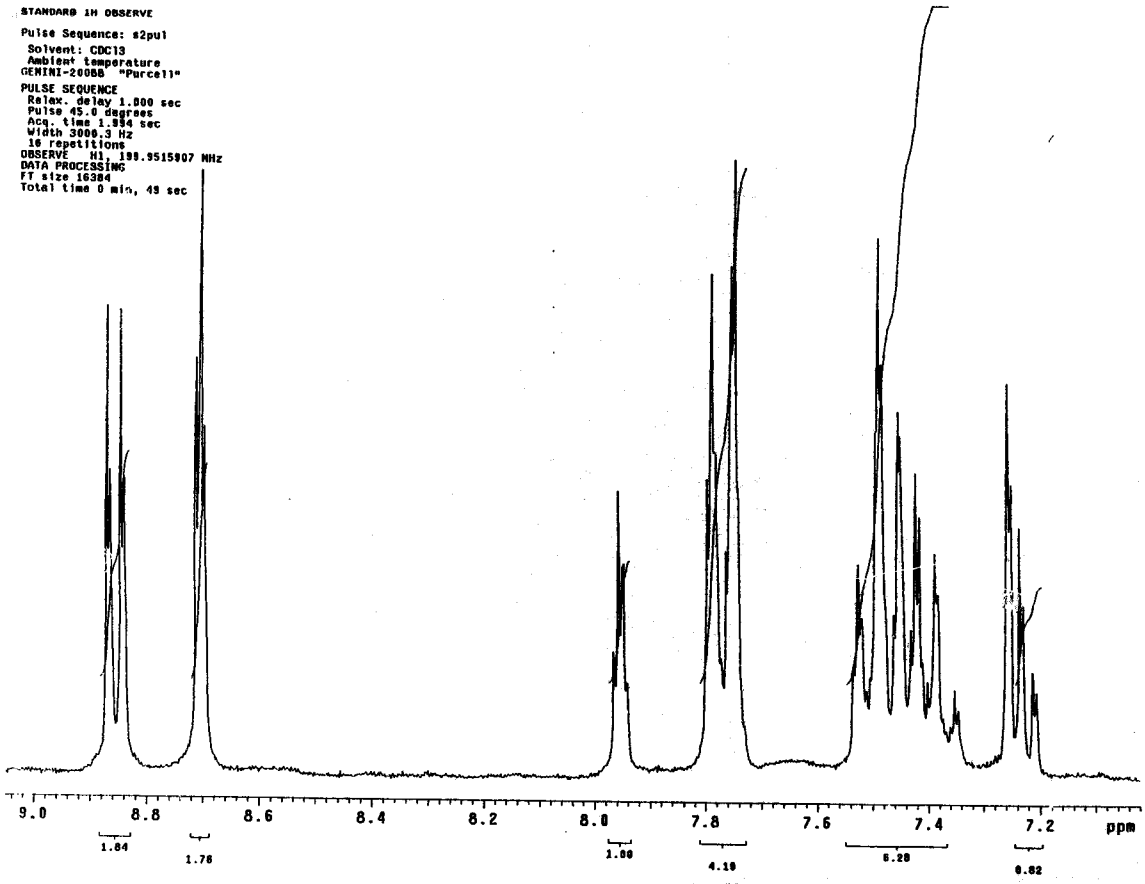
Date Received JUN 01 2006 Date Completed JUN 02 2006
Remarks:

Appendix IV

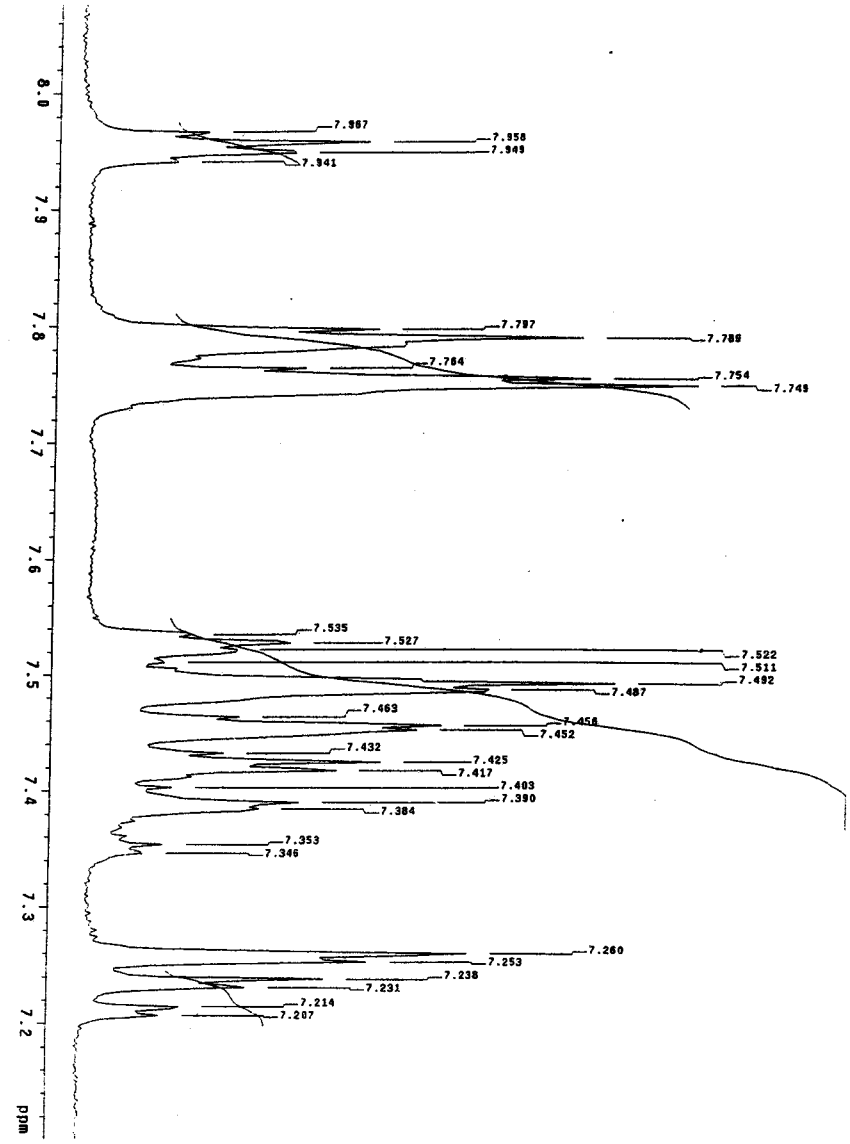

m-terphenyl pyrimidine
5129
8.870
8.865
8.846
8.839
8.711
8.703
8.656
7.867
7.358
7.349
7.341
7.797
7.788
7.784
7.754
7.748
7.535
7.527
7.522
7.511
7.492
7.487
7.463
7.458
7.452
7.432
7.425
7.417
7.403
7.390
7.384
7.353
7.348
7.280
7.253
7.238
7.231
7.214
7.207
1.596
1.590
0.000
0.005
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000B "Purcell"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515907 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
1.84
1.76
1.00
6.28
4.19
0.82

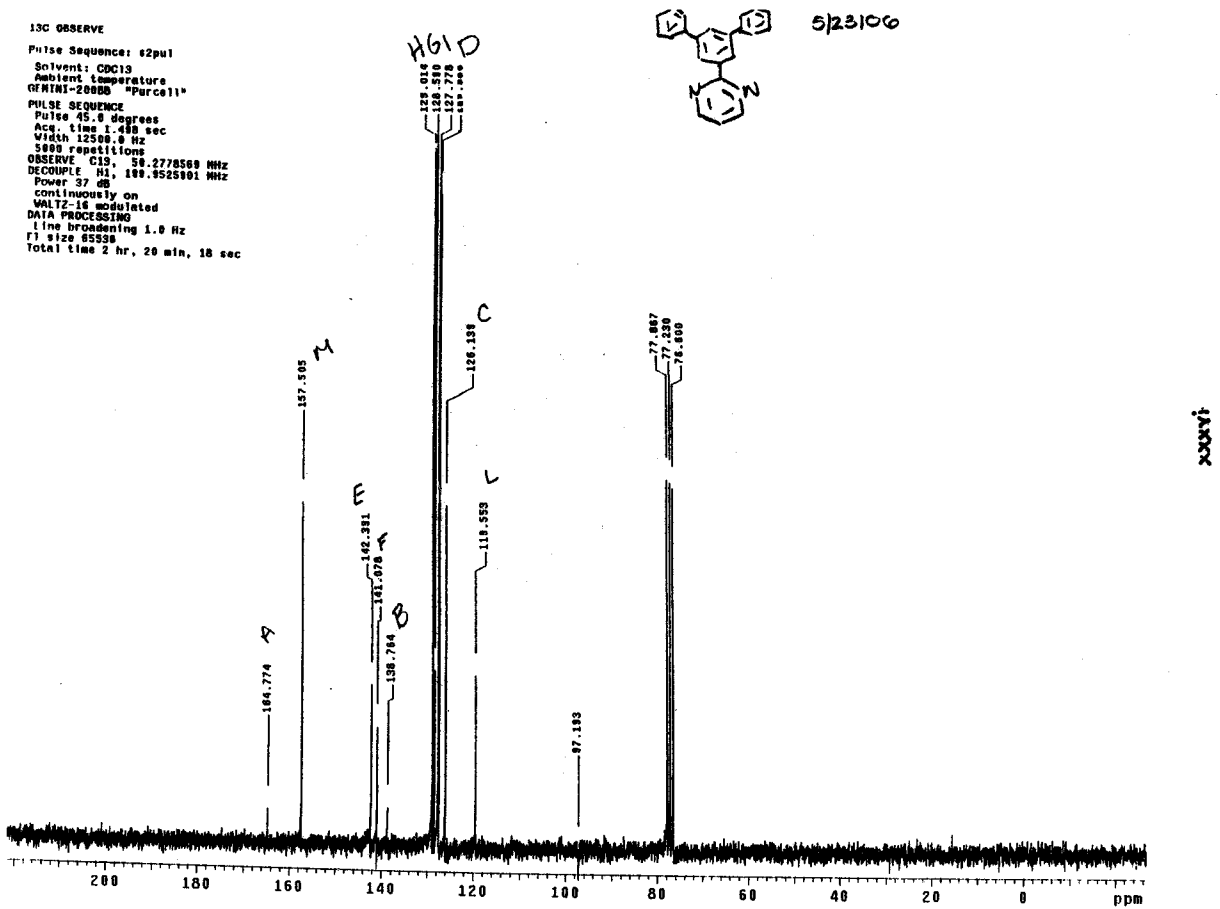

9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
8.870
8.865
8.846
8.839
8.711
8.703
8.696
7.967
7.958
7.949
7.941
7.797
7.789
7.764
7.754
7.749
7.535
7.527
7.522
7.511
7.492
7.487
7.463
7.456
7.452
7.432
7.425
7.417
7.403
7.390
7.384
7.353
7.346
7.260
7.253
7.238
7.231
7.214
7.207

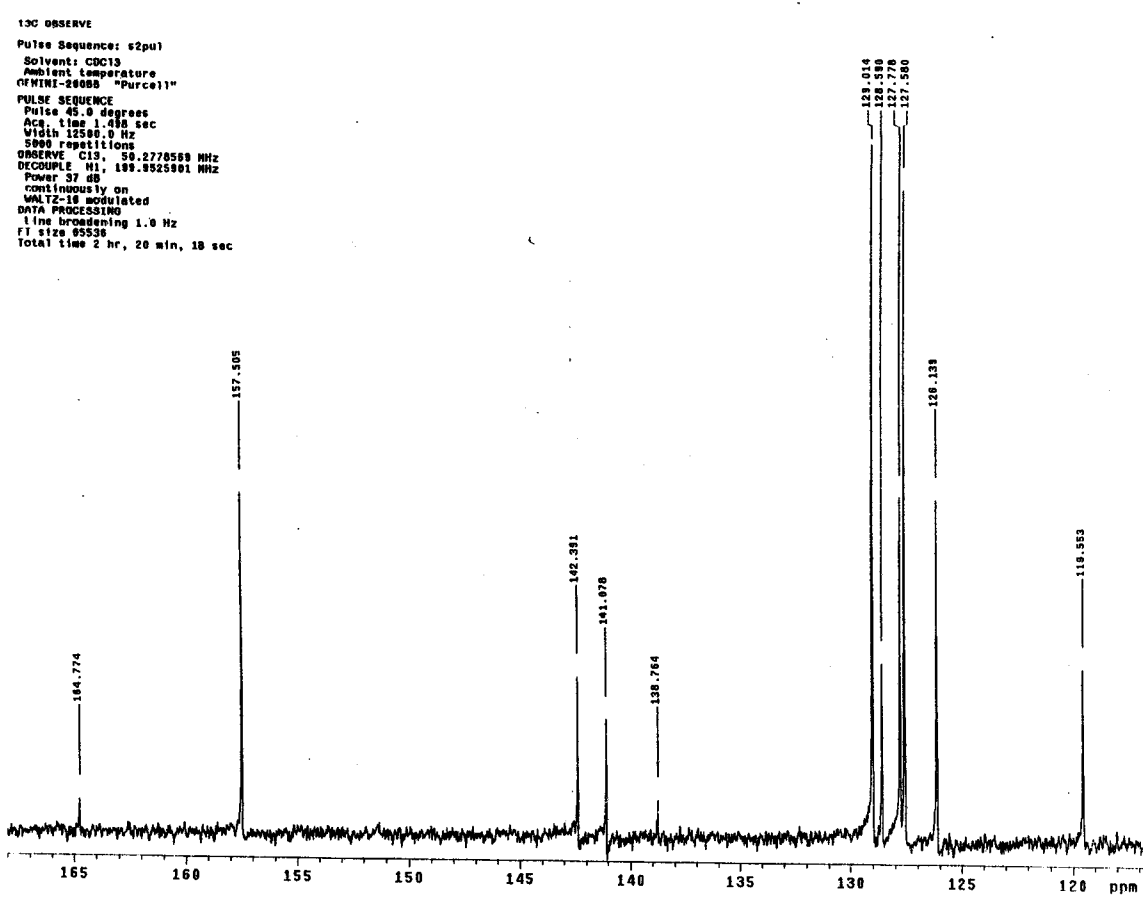

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "Purcell"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.884 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9515907 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.84
1.78
1.00
4.19
5.28
0.82

xxxiii

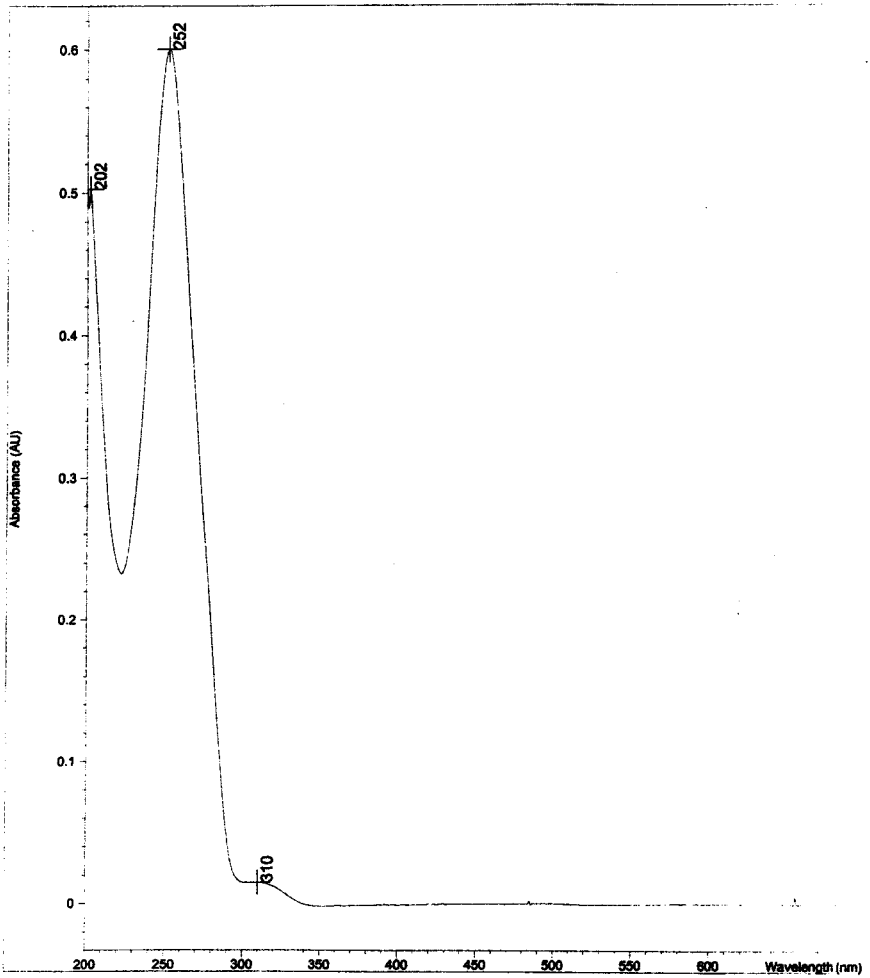

8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
7.967
7.958
7.949
7.941
7.797
7.789
7.764
7.754
7.749
7.535
7.527
7.522
7.511
7.492
7.487
7.463
7.456
7.452
7.432
7.425
7.417
7.403
7.390
7.384
7.353
7.346
7.260
7.253
7.238
7.231
7.214
7.207

9.00
8.95
8.90
8.85
8.80
8.75
8.70
8.65
8.60
ppm
8.876
8.865
8.846
8.839
8.711
8.703
8.696


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000 "Purcell"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.488 sec
Width 12500.0 Hz
5000 repetitions
OBSERVE C13, 50.2778589 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 20 min, 18 sec
H61
D
C
M
E
F
B
A
L
129.014
128.590
127.778
126.188
157.505
142.391
141.678
138.764
164.774
119.559
97.193
77.867
77.230
76.600
200
180
160
140
120
100
80
60
40
20
0
ppm
5/23/06

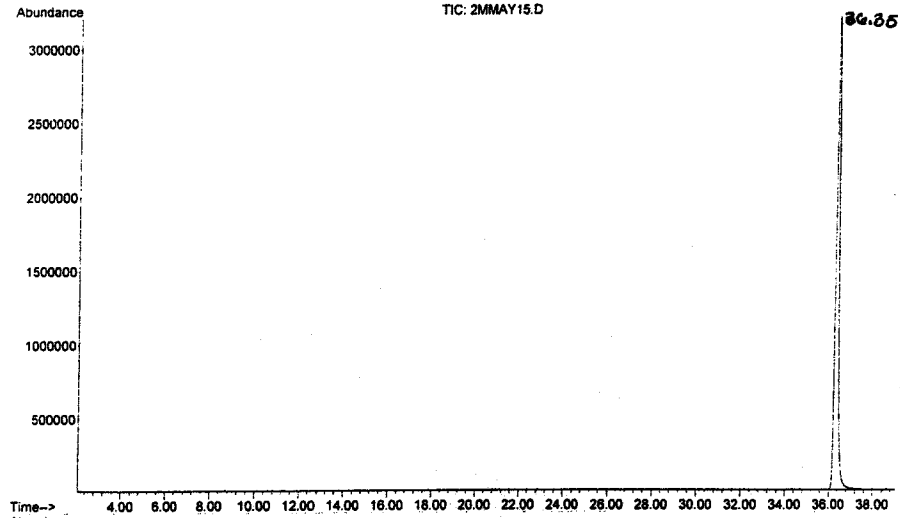

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000S "Purcell"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.408 sec
Width 12580.0 Hz
5000 repetitions
OBSERVE C13, 50.2778569 MHz
DECOUPLE H1, 199.9525901 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.0 Hz
FT size 65536
Total time 2 hr, 20 min, 18 sec
164.774
157.505
142.391
141.078
138.764
128.014
128.580
127.778
127.580
120.139
110.553
165
160
155
150
145
140
135
130
125
120
ppm

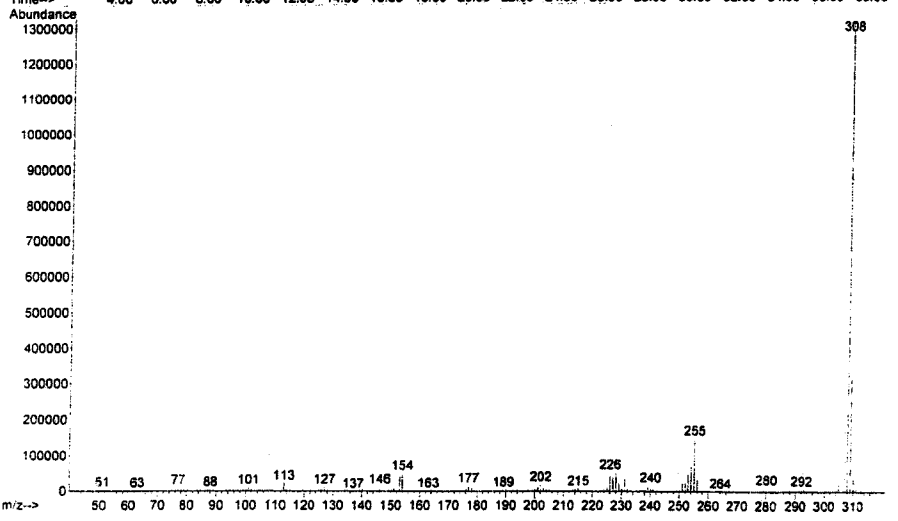
Overlaid Sample Spectra



*** End Hardcopy window ***

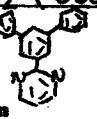
erator : Sparks
quired : 15 May 2006 16:24 using AcqMethod KEHLBECK3
strument : Instrumen
mple Name: pyrimidine
se Info : purity check
al Number: 25





ATLANTIC MICROLAB, INC.

Sample No. $C_{22}H_{16}N_2$ (308.38)



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PROFESSOR/SUPERVISOR:
P.O. #:

SUBMITTER

Company / School Union College
Address Chemistry Department
807 Union Street
Schenectady, NY 12308
NAME Prof. Joanne Kehlbeck DATE 5/22/

Element	Theory	Found	
C	85.69	85.39	
H	5.23	5.22	
N	9.08	8.98	

Single ☒ Duplicate ☐

Elements Present: C, H, N

Analyze for: C, H, N

Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____

To be dried: Yes ☐ No ☒
Temp. _____ Vac. _____ Time _____

FAX Service ☒
FAX Phone # 518-388-6795

Rush Service ☐ (SEE CURRENT PRICE LIST)
Phone Service ☐
Phone No. _____

Date Received MAY 25 2006 Date Completed MAY 26 2006

Remarks: