Direct Synthesis of Pyridine and Pyrimidine Derivatives

by

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B.S.C., Legal Communication
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May 2008

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Department of Chemistry
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Professor Stephen L. Buchwald_____

To my parents, Merrill and Dennis Hill,

to my sister, Mallory Hill

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Preface

Portions of this work have been adapted from the following articles that were co-written by the author and are reproduced in part with permission from:

Movassaghi, M.; Hill, M. D. "Synthesis of Substituted Pyridine Derivatives via the Ruthenium-Catalyzed Cycloisomerization of 3-Azadienynes" *J. Am. Chem. Soc.* **2006**, *128*, 4592–4593. Copyright 2006 American Chemical Society.

Movassaghi, M.; Hill, M. D. "Single-Step Synthesis of Pyrimidine Derivatives" *J. Am. Chem. Soc.* **2006**, *128*, 14254–14255. Copyright 2006 American Chemical Society.

Movassaghi, M.; Hill, M. D.; Ahmad, O. K. "Direct Synthesis of Pyridine Derivatives" *J. Am. Chem. Soc.* **2007**, *129*, 10096–10097. Copyright 2007 American Chemical Society.

Hill, M. D.; Movassaghi, M. "New Strategies for the Synthesis of Pyrimidine Derivatives" *Chem. Eur. J.* **2008**, *in press*. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinhem.

Direct Synthesis of Pyridine and Pyrimidine Derivatives

by

Matthew D. Hill

Submitted to the Department of Chemistry
on May 9, 2008 in partial fulfillment of the
requirements for the Degree of Doctor of Philosophy

ABSTRACT

I. Synthesis of Substituted Pyridine Derivatives via the Ruthenium-Catalyzed Cycloisomerization of 3-Azadienynes

The two-step conversion of various *N*-vinyl and *N*-aryl amides to the corresponding substituted pyridines and quinolines, respectively, is described. The process involves the direct conversion of amides, including sensitive *N*-vinyl amides, to the corresponding trimethylsilyl alkynyl imines followed by a ruthenium-catalyzed protodesilylation and cycloisomerization. A wide range of new alkynyl imines are prepared and readily converted to the corresponding azaheterocycles.

II. Single-Step Synthesis of Pyrimidine Derivatives

The single-step conversion of various *N*-vinyl and *N*-aryl amides to the corresponding pyrimidine and quinazoline derivatives, respectively, is described. The process involves amide activation with 2-chloropyridine and trifluoromethanesulfonic anhydride followed by nitrile addition into the reactive intermediate and cycloisomerization. In situ nitrile generation from primary amides allows for their use as nitrile surrogates. The use of this chemistry with sensitive *N*-vinyl amides and epimerizable substrates in addition to a wide range of functional groups is noteworthy.

III. Direct Synthesis of Pyridine Derivatives

The single-step conversion of various *N*-vinyl and *N*-aryl amides to the corresponding pyridine and quinoline derivatives, respectively, is described. The process involves amide activation with trifluoromethanesulfonic anhydride in the presence of 2-chloropyridine followed by π-nucleophile addition to the activated intermediate and annulation. Compatibility of this chemistry with sensitive *N*-vinyl amides, epimerizable substrates, and a variety of functional groups is noteworthy.

Thesis Supervisor: Assistant Professor Mohammad Movassaghi

Table of Contents

Abbreviations

Ac	acetyl
atm	atmosphere
Bu	butyl
°C	degree Celsius
^{c}Hx	cyclohexyl
CH_2Cl_2	dichloromethane
2-ClPyr	2-chloropyridine
cm	centimeter
COD	cyclooctadiene
Cp	cyclopentadiene
d	deuterium
δ	parts per million
DavePhos	2'-(dicyclohexylphosphino)-*N*,*N*-dimethylbiphenyl-2-amine
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dppf	1,1'-Bis(diphenylphosphino)ferrocene
ee	enantiomeric excess
equiv	equivalent
Et	ethyl
Et_2O	diethyl ether
Et_3N	triethylamine
EtOAc	ethyl acetate
FT	Fourier transform
g	gram
GC-MS	gas chromatography-mass spectroscopy
h	hour
HRMS	high resolution mass spectroscopy
Hz	Hertz
i	iso
IR	infrared
J	coupling constant
L	liter
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilylamide
M	molar
mg	milligram
MHz	megahertz
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
μmol	micromole
mol	mole

n	normal
N	normal (concentration)
N_2	dinitrogen
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
p	*para*
pH	hydrogen ion concentration
Ph	phenyl
Ph_3P	triphenylphosphine
Pr	propyl
ppm	parts per million
R	rectus
R_f	retention factor
s	second
s	secondary
SPhos	dicyclohexyl(2',6'-dimethoxybiphenyl-2-yl)phosphine
t	tertiary
TBAF	tetra-*n*-butylammonium fluoride
TBS	^{t}butyldimethylsilyl
TBSOTf	^{t}butyldimethylsilyl trifluoromethanesulfonate
TBDPS	^{t}butyldiphenylsilyl
TFA	trifluoroacetic acid
Tf_2O	trifluoromethanesulfonic anhydride
TfOH	trifluoromethanesulfonic acid
THF	tetrahydrofuran
TMS	trimethylsilyl
VT	variable temperature
XPhos	dicyclohexyl(2',4',6'-triisopropylbiphenyl-2-yl)phosphine
Z	zusammen

Chapter I

Synthesis of Substituted Pyridine Derivatives via the Ruthenium-Catalyzed Cycloisomerization of 3-Azadienynes

Introduction and Background

Pyridine derivatives are an important class of azaheterocycle found in many natural products, active pharmaceuticals, and functional materials.[1] Diploclidine[2] and nakinadine A[3] are two examples of recently isolated and structurally diverse natural products containing the pyridine core (Figure 1). Significant pyridine derived pharmaceuticals include atazanavir[4] (Reyataz®) and imatinib mesylate[5] (Gleevec®), and are prescribed for human immunodeficiency virus (HIV) and chronic myelogenous leukemia, respectively (Figure 1). Pyridine derivatives are also incorporated into polymers like polyvinyl pyridine (PVP, Figure 1).[6] While invention of synthetic methodologies for pyridines has been an important area of chemical research for well over a century, the importance of the pyridine core in both biological and chemical fields continues to inspire development of new syntheses.

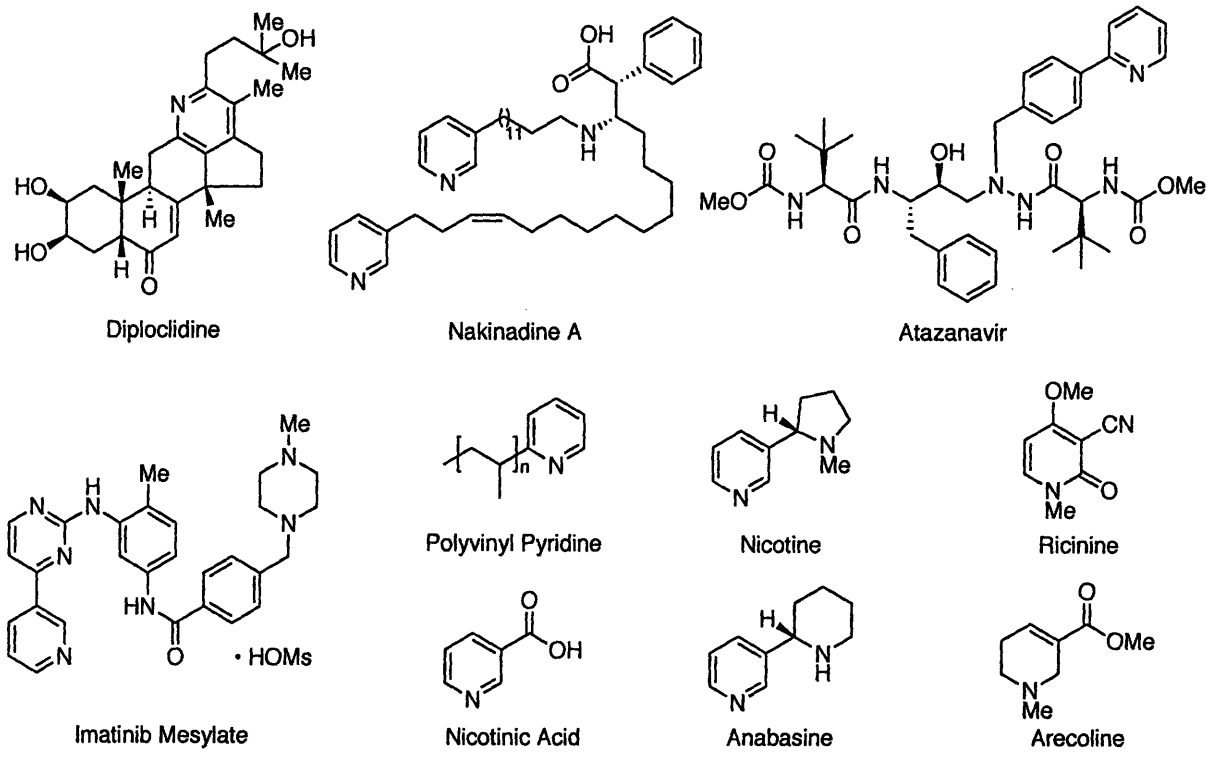
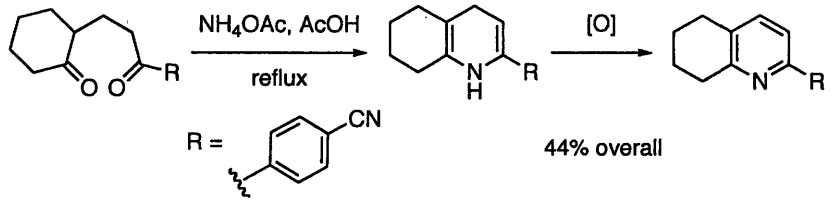


Figure 1. Representative compounds containing a pyridine substructure.

Nicotinic acid (also known as vitamin B_3 and niacin) is an important natural building block for pyridine alkaloids (Figure 1). In nature, this important component of coenzymes NAD^+ and $NADP^+$ is synthesized from L-tryptophan by way of the kynurenine pathway in

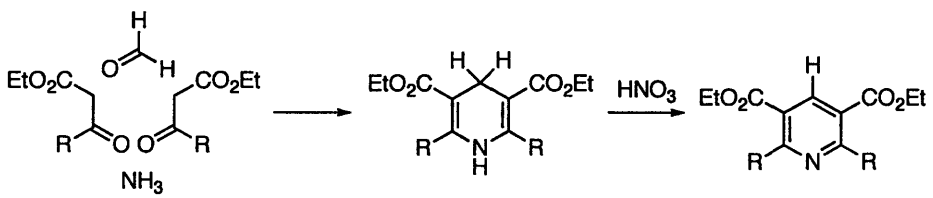
animals or from glyceraldehyde 3-phosphate and L-aspartic acid in many plants.[7] Both pathways rely on decarboxylation of quinolinic acid as a final step, but are otherwise very different. Nicotine, the addictive substance in tobacco, is formed by incorporation of a pyrrolidine moiety derived from L-ornithine onto the molecular framework of nicotinic acid (Figure 1). Like nicotine, similar alkaloids including anabasine, ricinine, and arecoline all originate from nicotinic acid (Figure 1).[7]

While picoline was isolated in 1846,[8] Körner's and Dewar's elucidation of the pyridine structure in 1869 and 1871, respectively, marked the beginning of significant chemical research in the field.[9] Coal tar served as an initial source of pyridine, however recent commercial methods have been developed for its preparation from crotonaldehyde, formaldehyde, and ammonia in the gas phase.[1b]

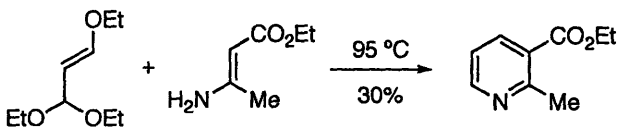


Scheme 1. [5+1] Condensation route to substituted pyridines.[10]

Historically, many pyridine syntheses rely on condensation of amine and carbonyl compounds. The fragments contributing to the six-atom azaheteroaromatic ring often characterize these and other methods for preparation of the pyridine core. Ammonia has served as the nitrogen source in countless protocols including its [5+1] condensation with 1,5-dicarbonyls (Scheme 1).[10] Like many condensation methods a second oxidation step, often autoxidation, is necessary for aromatization. Ammonia is also frequently used in the [2+2+1+1] Hantzsch pyridine synthesis (Scheme 2).[11,12] Other pyridine syntheses rely on alkyl or vinyl amines such as the [3+3] example: 1,3-dicarbonyl derivative condensation with a 3-aminoenone (Scheme 3).[13]

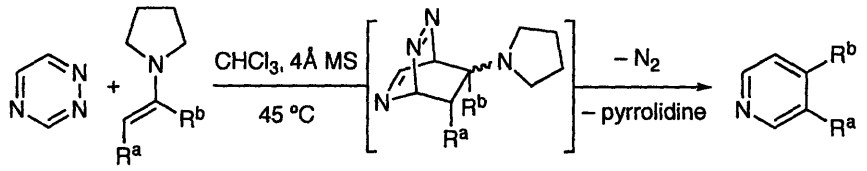


Scheme 2. The [2+2+1+1] Hantzsch pyridine synthesis.[11]

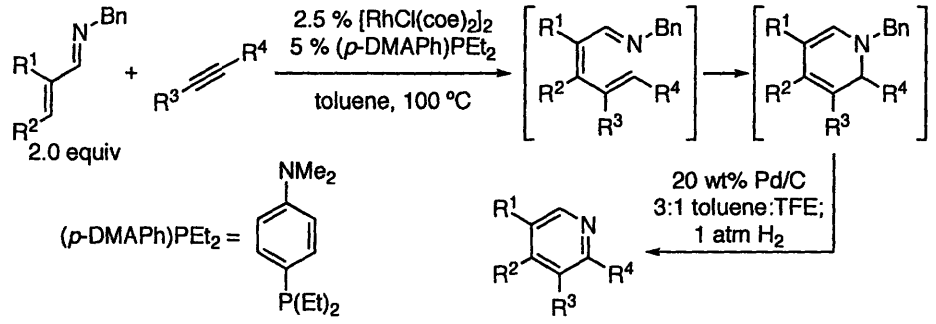


Scheme 3. [3+3] Condensation of a 1,3-dicarbonyl derivative and vinylogous amide.[13]

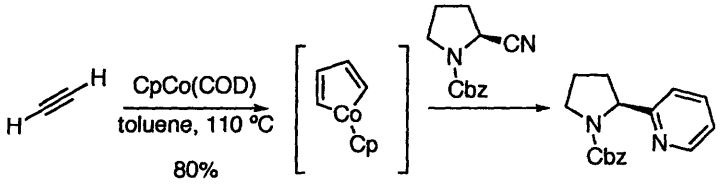
Other methods of pyridine synthesis have become increasingly important. Boger has developed a [4+2] inverse electron demand hetero-Diels-Alder reaction between enamines and 1,2,4-triazine (Scheme 4).[14] 6π-Electrocyclization approaches, including a recent transition-metal mediated [4+2] example by Ellman (Scheme 5), are also of continuing importance.[15] Over the past several decades, many other transition-metal promoted pyridine syntheses have been reported. A well-developed [2+2+2] approach utilizes two alkyne equivalents and a nitrile species (Scheme 6).[16]



Scheme 4. Hetero-Diels-Alder [4+2] approach to pyridine derivatives.[14]

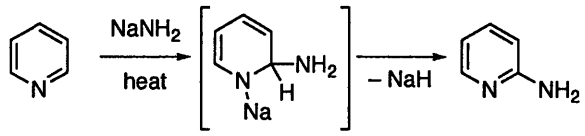


Scheme 5. Rhodium mediated [4+2] synthesis of pyridines.[15]

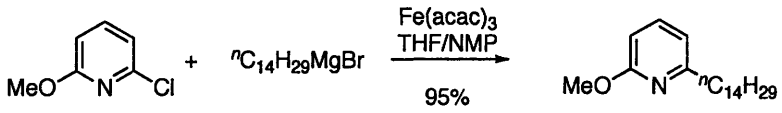


Scheme 6. Cobalt mediated [2+2+2] synthesis of substituted pyridines.[16]

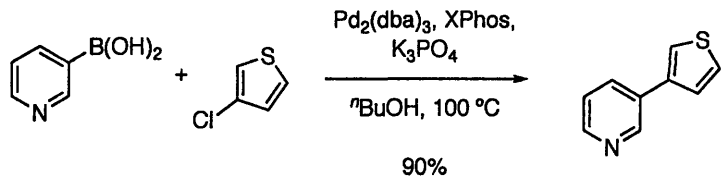
Recent advancements in cross-coupling chemistry have increased the popularity of azaheterocycle substituent modification and have been described in several reviews.[17] Some of these methods, including the Chichibabin reaction (Scheme 7),[18] rely on the electron deficient character of the pyridine ring. Activated pyridines can be used with numerous transition-metal catalysts to afford a structurally diverse set of pyridine derivatives (Schemes 8 and 9).[17,19,20]



Scheme 7. The Chichibabin reaction.[18]

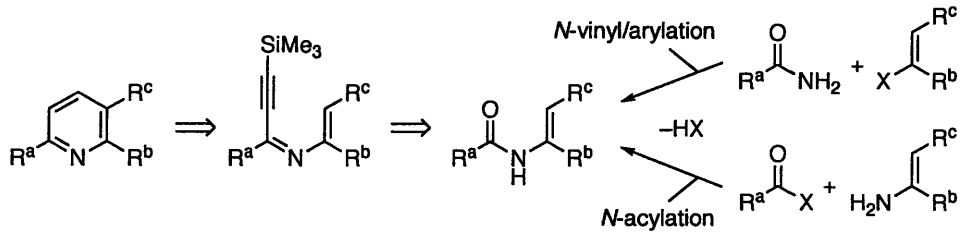


Scheme 8. Iron-catalyzed cross-coupling of activated pyridines.[19]

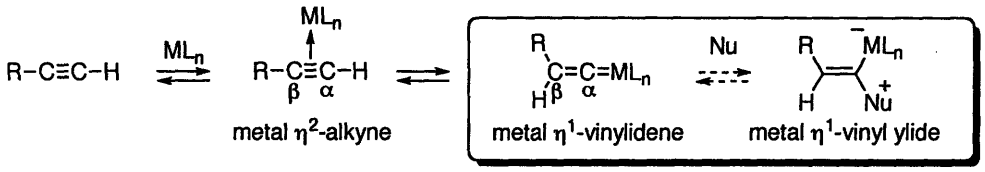


Scheme 9. Suzuki-Miyaura cross-coupling of activated pyridines.[20]

Due to the importance of pyridines, our group is interested in new methodologies for their synthesis. We envisioned readily available *N*-vinyl[21] and *N*-aryl amides could lead to 3-azadienynes that are capable of forming catalytically generated metal vinylidene intermediates. We believed cycloisomerization of these complexes should give pyridine derivatives in two steps from amide precursors (Scheme 10).



Scheme 10. General strategy for two-step synthesis of pyridine derivatives from readily available substrates.



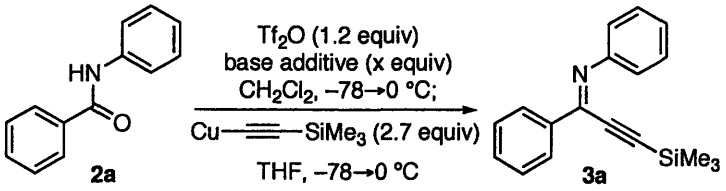
(1)

Metal vinylidene[22] complexes (eq 1) can be directly accessed via the transition metal catalyzed isomerization of terminal alkynes.[23] This isomerization is believed to proceed through the initial formation of a metal η^2-alkyne complex and subsequent formal 1,2-hydride shift of the acetylenic hydrogen to give the thermodynamically favored metal η^1-vinylidene complex.[23] Metal vinylidenes have been employed for a range of transformations that utilize either a catalytic[24] or stoichiometric[25] amount of transition metal complexes. Various neutral and cationic transition metal complexes have demonstrated superb activity for providing metal vinylidene intermediates under mild reaction conditions. Experimental and theoretical studies[23,26] suggest reactivity similar to that of the ketene functional group with an electrophilic C_a-center and nucleophilic C_b-center.[27] Furthermore, the direct nucleophilic addition of carbon nucleophiles to metal vinylidene intermediates offers tremendous potential in development of novel carbon-carbon bond forming reactions (eq 1).

Results and Discussion

The metal catalyzed cycloisomerization of dienynes via catalytically generated metal vinylidene intermediates represents a highly effective method for the synthesis of aromatic compounds.[28] We sought to explore the use of 3-azadienynes as substrates for a metal–catalyzed cycloisomerization reaction, providing a general approach to a broad range of substituted pyridine derivatives **1** (Scheme 10).[29] To take full advantage of the wide range of *N*-vinyl amides available by metal catalyzed *C-N* bond formation,[21] we required a mild and efficient procedure for the direct conversion of amides **2** to the corresponding 3-azadienynes **3**.[30] Inspired by recent reports on the electrophilic activation of amides[31] we developed a single-step process for the conversion of *N*-vinyl/aryl amides **2** to the corresponding alkynyl imines **3**. Under our optimum conditions, a cold solution of the *N*-phenyl benzamide (**2a**, Table 1) in dichloromethane is treated sequentially with 2-chloropyridine (2-ClPyr, 4.0 equiv) and trifluoromethanesulfonic anhydride (Tf_2O, 1.2 equiv), followed by copper trimethylsilylacetylide (2.7 equiv), which affords the desired trimethylsilyl alkynyl imine **3a** in 97% yield (Table 2, entry 1, 2.5-g scale).[32]

Table 1. Base additive screen for alkynyl imine synthesis.

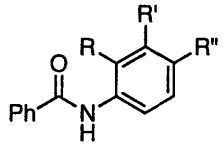
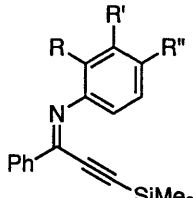
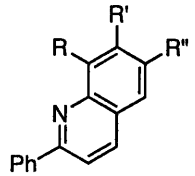
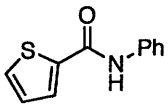
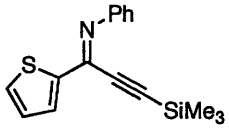
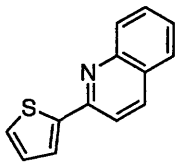


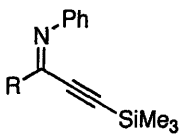
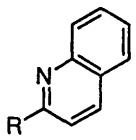
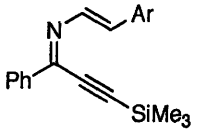
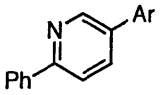
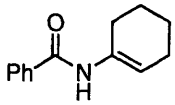
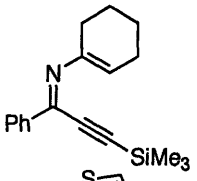
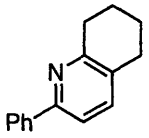
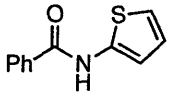
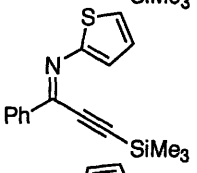
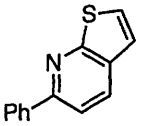
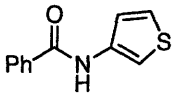
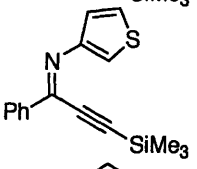
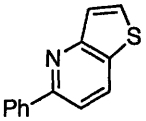
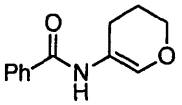
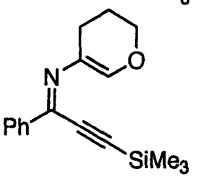
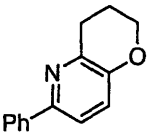
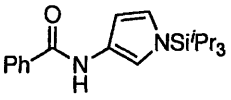
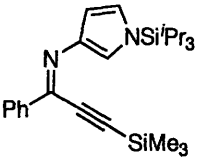
Entry	Base Additive	x	Yield (%)[a]
1	pyridine	4	<10
2	2,6-lutidine	4	27
3	Et_3N	4	<4[b]
4	$^iPr_2NEt$	4	<20
5	***2-chloropyridine***	***4***	***97***
6	2-chloropyridine	3	92
7	2-chloropyridine	2	65

[a] Mass balance is the starting amide. [b] Mixture of products; no recovered SM.

The use of 2-chloropyridine as the base[33] was found to be critical in obtaining the desired alkynyl imines (Table 1).[32] Significantly, this single-step and mild procedure provides access to new alkynyl imines, in particular, those derived from *N*-vinyl amides. For comparison, the use of existing methods[30] for the synthesis of *N*-2-thienyl and *N*-dihydropyranyl alkynyl imines **3** (Table 2, entries 13 and 15) gave none and <10% yield of the desired product, respectively.

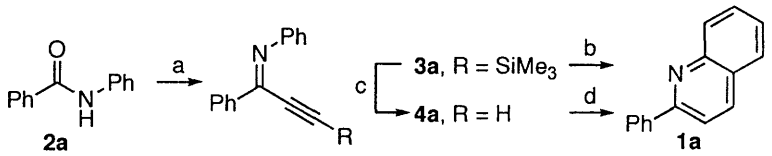
Table 2. Substrate scope for two-step pyridine synthesis.

Entry	Amide Substrate (**2**)	3-Azadienyne (**3**)	Yield (%)[a]	Product (**1**)	Yield (%)[a]
					
1	**2a**, R = H R' = H R" = H	**3a**	97[b]	**1a**	91[b]
2	R = H R' = H R" = OMe		89		92
3	R = OMe R' = H R" = H		96		91
4	R = H R' = CF_3 R" = H		73, <10[c]		89
5			81		75

6	R = ^{c}Hx		85		69
7	R = ^{t}Bu		83, 95[c]		69
8	R = N(CH$_2$CH$_2$)$_2$O		80		62
9	Ar = Ph		78		77
10	Ar = 1-naphthyl		86		83
11	Ar = 3,4-dimethoxyphenyl		92		78
12			75		73
13			63[d]		99
14			98		97
15			99		70
16			82, 91[c]		64[e]

[a] Isolated yields: all entries are average of two experiments. Optimum conditions used uniformly. [b] Gram-scale experiments. [c] Yield of the corresponding desilylated imine.[32] [d] Kept at –78 °C.[32] [e] 5 mol% of catalyst system used.

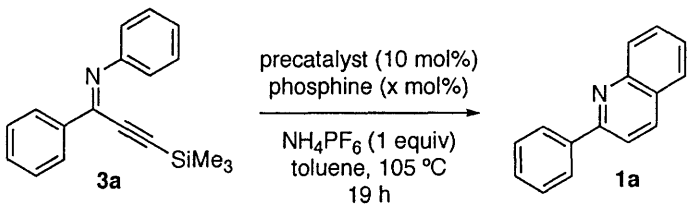
Early in our studies we identified the readily available chlorocyclopentadienyl bis(triphenylphosphine) ruthenium complex (CpRu(PPh$_3$)$_2$Cl, **5**)[34] as an effective catalyst for cycloisomerization of terminal alkynyl imine **4a** to product **1a** (Scheme 11).[35] While imine **4a** could be prepared by protodesilylation of the corresponding trimethylsilyl derivative **3a** (Scheme 11), this required an additional step and resulted in decreased stability of the substrate and yield of the cycloisomerization reaction. These considerations prompted the development of a process for the direct use of trimethylsilyl alkynyl imine **3a** as substrate. The trimethylsilyl alkynyl imine



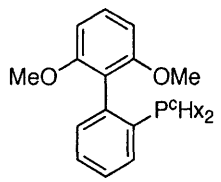
Scheme 11. [a] Tf_2O, 2-ClPyr, CH_2Cl_2; $Me_3SiC{\equiv}CCu$, THF, –78→0 °C. [b] **5**, SPhos, NH_4PF_6, toluene, 105 °C. [c] K_2CO_3, MeOH. [d] **5**, toluene, 105 °C.

3a, was used to survey a series of metal complexes, supporting ligands, additives and solvents (Table 3).[32] The combination of ruthenium complex **5** (10 mol%), 2-dicyclohexyl-phosphino-2′,6′-dimethoxy-1,1′-biphenyl (SPhos[36], 10 mol%), and ammonium hexafluorophosphate (1 equiv) in toluene (0.2 M) at 105 °C was identified as the optimal set of conditions, as illustrated by the clean conversion of imine **3a** to quinoline **1a** in 90% yield (Table 2, entry 1, 1.0-g scale).[32]

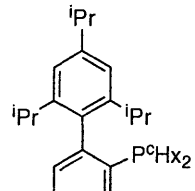
Table 3. Precatalyst and ligand screen.



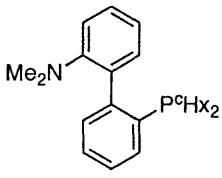
Entry	Precatalyst	Phosphine	x	Yield (%)[a]
1	$InBr_3$	-	-	0
2	$In(OTf)_3$	-	-	0
3	$Sc(OTf)_3$	-	-	0
4	$Pd(OAc)_2$	-	-	<3
5	$Pd(OAc)_2$	-	-	<6[b]
6	$Pd(OAc)_2$	-	-	<4[c]
7	$Pd(OAc)_2$	DavePhos	10	0
8	$Pd(OAc)_2$	XPhos	10	<4
9	$Pd(OAc)_2$	SPhos	10	<3
10	K_2PtCl_4	-	-	0
11	K_2PtCl_4	-	-	0[b]
12	$(RhClCOD)_2$	-	-	0
13	$RhCl(Ph_3P)_2CO$	-	-	0
14	$[Ru(p\text{-cymene})Cl_2]_2$	-	-	<2
15	CpRu(dppf)Cl	-	-	0
16	$CpRu[(EtO)_3P]_2Cl$	-	-	<2
17	$CpRu[(p\text{-}MeOC_6H_4)_3P]_2Cl$	-	-	36
18	$CpRu(Me_3P)_2Cl$	-	-	<1[d]
19	$CpRu(Me_3P)_2Cl$	DavePhos	10	≤10[d]
20	$CpRu(Me_3P)_2Cl$	XPhos	10	19
21	$CpRu(Me_3P)_2Cl$	SPhos	10	19
22	$[Ru(COD)Cl_2]_n$	-	-	0



SPhos



XPhos



DavePhos

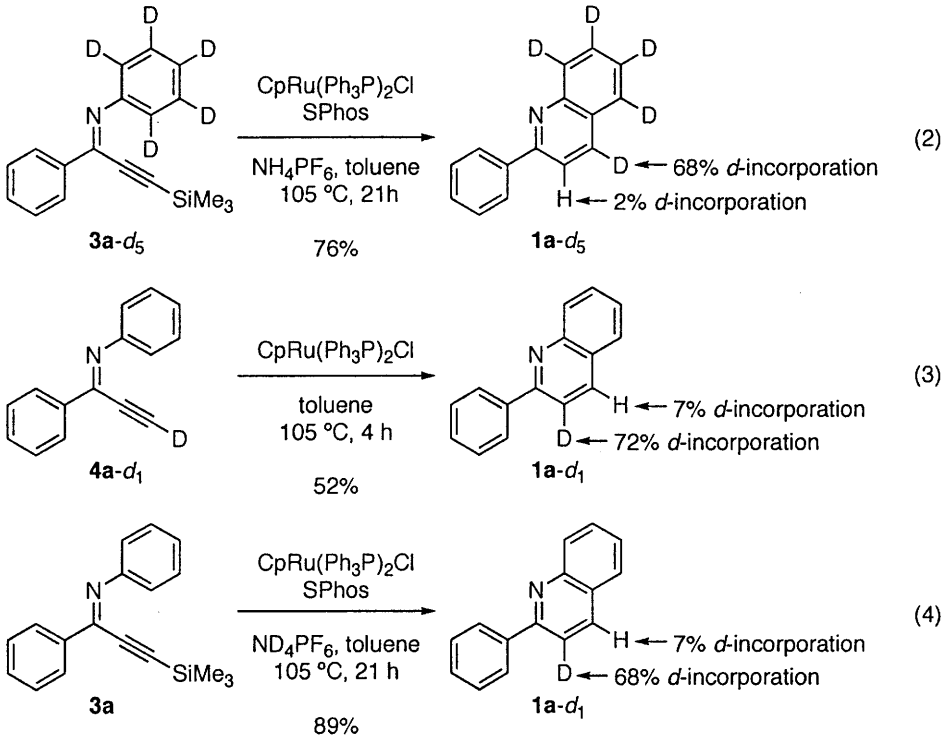
23	$[Ru(COD)Cl_2]_n$	SPhos	10	0
24	CpRu(COD)Cl	-	-	0
25	CpRu(COD)Cl	SPhos	10	<6
26	CpRu(COD)Cl	SPhos	20	<9
27	CpRu(COD)Cl	Ph_3P	10	38
28	CpRu(COD)Cl	Ph_3P	15	62
29	CpRu(COD)Cl	Ph_3P	20	77
30	CpRu(COD)Cl	$(2\text{-furyl})_3P$	15	36
31	CpRu(COD)Cl	$(2\text{-furyl})_3P$, Ph_3P	10, 10	67
32	CpRu(COD)Cl	$(2\text{-furyl})_3P$, SPhos	10, 10	54
33	CpRu(COD)Cl	Ph_3P, SPhos	13, 13	88
34	***CpRu(COD)Cl***	***Ph_3P, SPhos***	***15, 15***	***97***
35	$CpRu(Ph_3P)_2Cl$	-	-	80
36	$CpRu(Ph_3P)_2Cl$	DavePhos	10	30
37	$CpRu(Ph_3P)_2Cl$	XPhos	10	74
38	***$CpRu(Ph_3P)_2Cl$***	***SPhos***	***10***	***95***
39	$CpRu(Ph_3P)_2Cl$	SPhos	5	56
40	$CpRu(Ph_3P)_2Cl$	Ph_3P	10	80
41	$CpRu(Ph_3P)_2Cl$	Ph_3P	20	81
42	$CpRu(Ph_3P)_2Cl$	$(2\text{-furyl})_3P$	10	76

[a] Mass balance is the starting silylated alkynyl imine **3a**. [b] 2.2 mol % TFA additive. [c] 10 mol % AgOAc additive. [d] Same result at 75 °C. [e] 5 mol % Ru-complex.

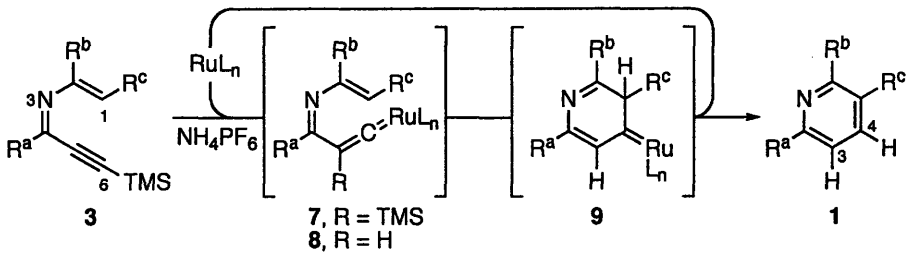
Interestingly, neither SPhos nor PPh_3 alone were ideal ligands when used independently with chlorocyclopentadienyl cycloocta-1,5-diene ruthenium complex (CpRuCODCl, **6**)[37] for cycloisomerization of 3-azadienyne **3a**.[32] However, the combination of these ligands in conjunction with ruthenium complex **6** provided a catalyst system with equal activity to the optimal system.[32] While the exact role of SPhos is unclear at this time,[38] ^{31}P NMR experiments confirm that PPh_3 out competes SPhos in displacement of COD from **6**, providing complex **5** and remaining SPhos, similar to the optimal precatalyst mixture. Also, ^1H NMR monitoring of the cycloisomerization reaction of azadienyne **3a** employing complex **6** and SPhos alone revealed the formation of the inactive $CpRu(\eta^6\text{-PhMe})PF_6$ complex.[39]

The optimal reaction conditions proved to be compatible with a variety of *C*-silyl alkynyl imines (Table 2). In particular, we found even highly sensitive *N*-vinyl/heterocyclic imines to be excellent substrates (Table 2, entries 9-16), providing a convergent and versatile azaheterocycle synthesis. Importantly, the direct conversion of *C*-silyl alkynyl imines **3** to the corresponding azaheterocycles **1** with this Ru-catalyst system avoids the isolation of the more sensitive terminal alkynyl imines (i.e., Table 2, entry 4). In only two cases (entries 7 and 16) in situ desilylation was found to be exceedingly slow, prompting the use of the corresponding terminal alkyne derivatives as the substrates for cycloisomerization. In the synthesis of the acid sensitive *N*-

triisopropylsilylazaindole (entry 16), lowering the catalyst loading (5 mol%) from our standard conditions was beneficial.



Subjecting the alkynyl imine **3a**-d_5 (eq 2) to our standard conditions gave the quinoline **1a**-d_5 (eq 2) with *C*4-deuterium incorporation (68%).[32] The use of terminal alkynyl imine **4a**-d_1 (eq 3, without NH_4PF_6) as substrate provided quinoline **1a**-d_1 (eq 3) with *C*3-deuterium incorporation (72%). Furthermore, employing ammonium hexafluorophospate-d_4 in the cycloisomerization of alkynyl imine **3a** (eq 4) provided the quinoline **1a**-d_1 (eq 4) with *C*3-deuterium incorporation (68%). The protodesilylated imine **4a** (Scheme 11) was not detected as a persistent intermediate by TLC or ^{1}H NMR monitoring experiments (Table 2, entry 1) and the silyl alkynyl imine **3a** was recovered unchanged from the reaction mixture in the absence of Ru-complex **5**. Additionally, only a trace amount of the desired desilylated and cycloisomerized product was detected when the ammonium hexafluorophosphate was omitted, returning the starting material as the mass balance.[40] These observations suggest the direct conversion of the silyl alkynyl imine **3** to the *C*-silyl metal vinylidene[41] **7** (Scheme 12) followed by protodesilylation and cycloisomerization to give **1**.



Scheme 12. Proposed mechanism for synthesis of azaheterocycles **1** from azadienynes **3.**

Conclusion

The chemistry described here provides a two-step process for the synthesis of substituted pyridine derivatives from readily available *N*-vinyl/aryl amides (Scheme 11, steps a and b). Noteworthy features of this chemistry include the single-step conversion of a wide range of readily available amides, including sensitive *N*-vinyl amides, to the corresponding *C*-silyl alkynyl imines and their direct Ru-catalyzed protodesilylation and cycloisomerization to the corresponding azaheterocycles. This Ru-catalyzed conversion of *C*6-trimethylsilyl 3-azadienynes to azaheterocycles, not only reduces a three-step sequence[28c] to a single-step but also does not require the isolation of sensitive and/or inaccessible terminal alkynyl imines as substrates.[42]

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(1) (a) Jones, G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V.; McKillop, A., Eds; Pergamon: Oxford, 1996; Vol. 5; p 167. (b) Henry, G. D. *Tetrahedron* **2004**, *60*, 6043. (c) Joule, J. A.; Mills, K. In *Heterocyclic Chemistry*, 4th ed.; Blackwell Science Ltd.: Cambridge, MA, 2000; p 63. (d) Michael, J. P. *Nat. Prod. Rep.* **2005**, *22*, 627.

(2) Jayasinghe, L.; Jayasooriya, C. P.; Hara, N.; Fujimoto, Y. *Tetrahedron Lett.* **2003**, *44*, 8769.

(3) Kubota, T.; Nishi, T.; Fukushi, E.; Kawabata, J.; Fromont, J.; Kobayashi, J. *Tetrahedron Lett.* **2007**, *48*, 4983.

(4) Harrison, T. S., Scott, L. J. *Drugs* **2005**, *65*, 2309.

(5) Deininger, M. W. N., Druker, B. J. *Pharmacol. Rev.* **2003**, *55*, 401.

(6) Raje, V. P.; Bhat, R. P.; Samant, S. D. *Synlett* **2006**, 2676.

(7) Dewick, P. M. In *Medicinal Natural Products A Biosynthetic Approach*, 2nd ed.; John Wiley & Sons Ltd.: West Sussex, England, 2002; p 311.

(8) Anderson, T. *Edinburgh. New Philos. J.* **1846**, *41*, 146.

(9) Pictet, A. In *The Vegetable Alkaloids With Particular Reference to Their Chemical Constitution*, 2nd ed.; 1904; p 10.

(10) Kelly, T. R.; Lebedev, R. L. *J. Org. Lett.* **2002**, *67*, 2197.

(11) Hantzsch, A. *Liebigs Ann. Chem.* **1882**, *215*, 1.

(12) For a recent example, see: Guillaume, B.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, 130, 18.

(13) Baumgarten, P.; Dornow, A. *Chem. Ber.* **1939**, *72*, 563.

(14) Boger, D. L.; Panek, J. S.; Meier, M. M. *J. Org. Chem.* **1982**, *47*, 895.

(15) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 3645.

(16) Chelucci, G.; Falorni, M.; Giacomelli, G. *Synthesis* **1990**, 1121.

(17) (a) Chinchilla, R.; Nájera, C.; Yus, M. *Chem. Rev.* **2004**, *104*, 2667. (b) Mongin, F.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 4059.

(18) Chichibabin, A. E.; Zeide, O. A. *J. Russ. Phys. Chem. Soc.* **1914**, *46*, 1216.

[19] Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.
[20] Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358.
[21] (a) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (b) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p. 1051. (c) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (d) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.
[22] For reviews, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (d) McDonald, F. E. *Chem. Eur. J.* **1999**, *5*, 3103. (d) Bruneau, C.; Dixneuf, P. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 2176. (e) Varela, J. A.; Saá, C. *Chem. Eur. J.* **2006**, *12*, 6450.
[23] See reference 22. For mechanistic discussions, see: (a) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (b) Sheng, Y.; Musaev, D. G.; Reddy, K. S.; McDonald, F. E.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, 4149. For a review, see: (c) Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092.
[24] For representative examples of transition metal catalyzed processes, see reference 22 and: (a) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739. (b) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (c) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363. (d) McDonald, F. E., Schultz, C. C., Chatterjee A. K. *Organometallics* **1995**, *14*, 3628. (e) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (f) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (g) Manabe, T.; Yanagi, S.-i.; Ohe, K.; Uemura, S. *Organometallics* **1998**, *17*, 2942. (h) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680. (i) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344. (j) McDonald, F. E.; Reddy, K. S.; Díaz, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4304. (k) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990.
[25] For representative examples of transition metal promoted processes, see reference 22 and: (a) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514. (b) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025. (c) Barrett, A. G.; Carpenter, N. E. *Organometallics* **1987**, *6*, 2249. (d) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045. (e) McDonald, F. E.; Bowman, J. L. *Tetrahedron Lett.* **1996**, *37*, 4675. (f) McDonald, F. E.; Olson, T. C. *Tetrahedron Lett.* **1997**, *38*, 7691. (g) McDonald, F. E.; Zhu, H. Y. H. *Tetrahedron* **1997**, *53*, 11061.
[26] Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
[27] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp. 1122. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474.
[28] For related reviews, see: (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (b) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (c) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167. For related representative reports, see: (d) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (e) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045. (f) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (g) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (h) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928.
[29] (a) Boger, D. L. *J. Heterocycl. Chem.* **1998**, *35*, 1003. (b) Jayakumar, S.; Ishar, M. P. S.; Mahajan, M. P. *Tetrahedron* **2002**, *58*, 379.
[30] For reports on the synthesis of alkynyl imines via a two-step procedure involving imidoyl chlorides, see: (a) Ried, W.; Erle, H.-E. *Chem. Ber.* **1979**, *112*, 640. (b) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, 46, 2280. (c) Lin, S.-Y.; Sheng, H.-Y.; Huang, Y.-Z. *Synthesis* **1991**, 235. For related reports, see: (d) Kel'in, A. V.; Sromek, A. W.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 2074. (e) Van den Hoven, B. G.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 10214.
[31] (a) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 3077. (b) Charette, A. B.; Grenon, M. *Can. J. Chem.* **2001**, *79*, 1694.
[32] See the Experimental Section for details.
[33] Myers, A. G.; Tom, N. J.; Fraley, M. E.; Cohen, S. B.; Madar, D. J. *J. Amer. Chem. Soc.* **1997**, *119*, 6072.
[34] (a) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. (A)* **1969**, 1749. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 2376. b) Bruce, M. I.; Windsor, N. J., *Aust. J. Chem.* **1977**, *30*, 1601.
[35] (a) For a related report on metal-catalyzed isomerization of *N*-aryl benzamide derived terminal alkynes (i.e., **4a**) using $W(CO)_5$•THF (20-100 mol%) to afford 2-aryl quinolines after treatment with NMO, see ref. 4c. (b) For a report on Ru-catalyzed C2-vinylation of pyridines, see: Murakami, M.; Hori, S. *J. Am. Chem. Soc.* **2003**, *125*, 4720.
[36] Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 1871.

[37] Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199.
[38] For related discussions on the steric and electronic effects of phosphines used with complex **6** in Ru-vinylidene formation, see: Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680.
[39] McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633.
[40] Incomplete deuterium incorporation at the expected site and leakage to the alternate position (2-7%, eq 1–3) may in part be due to an intermolecular scrambling after cycloisomerization of **8** and prior to release of product **1** (i.e., the intermediate **9** or the metal hydride tautomer in Scheme 12).
[41] Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700.
[42] Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 4592.

Experimental Section

General Procedures. All reactions were performed in oven-dried or flame-dried round bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure.[2] Ammonium hexafluorophosphate was dried at 150 °C under vacuum (~0.5 torr) for 24 h and stored in a glove box under an atmosphere of dinitrogen. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).[3] Hünig's base and 2-chloropyridine were distilled from calcium hydride and stored sealed under an argon atmosphere. The starting amides were prepared by acylation of the corresponding anilines[4] or via previously reported copper–catalyzed C–N bond–forming reactions.[5,6] The ruthenium complex **5** ($CpRu(PPh_3)_2Cl$) is commercially available and was prepared on large scale according to a literature procedure.[7] 2-Dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl (SPhos)[8] is commercially available and we thank the Buchwald group for providing samples for initial studies. Solutions of Copper (I)

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(3) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(4) For a general procedure, see: DeRuiter, J.; Swearingen, B. E.; Wandrekar, V.; Mayfield, C. A. *J. Med. Chem.* **1989**, *32*, 1033.

(5) For the general procedure used for the synthesis of all *N*-vinyl amides, see: Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667.

(6) For related reports, see: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (d) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (e) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (f) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (g) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.

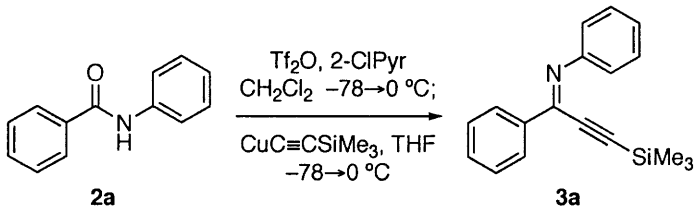
(7) (a) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorganic Syntheses* **1982**, *21*, 78. Also, see: (b) Gilbert, J. D.; Wilkinson, G. *J. Chem. Soc. (A)* **1969**, 1749, (c) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 2376, and (d) Bruce, M. I.; Windsor, N. J., *Aust. J. Chem.* **1977**, *30*, 1601.

(8) (a) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 1871. (b) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334.

trimethylsilylacetylide were prepared immediately prior to use according to literature procedure.[9]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, C_6HD_5: δ7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.2, benzene-d_6: δ 128.0). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Combustion analysis was performed by Atlantic Microlab, Incorporated. We are grateful to Dr. Li Li for obtaining the mass spectroscopic data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology.

(9) Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495.



2a **3a**

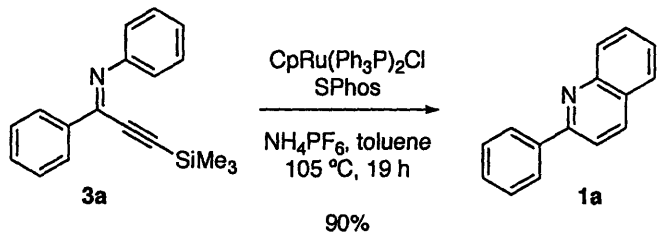
97%

***N*-Phenyl-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3a, Table 2, entry 1):**

Trifluoromethanesulfonic anhydride (2.51 mL, 15.2 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2a** (2.50 g, 12.7 mmol, 1 equiv) and 2-chloropyridine (4.81 mL, 50.7 mmol, 4.00 equiv) in CH_2Cl_2 (25 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (5.50 g, 34.2 mmol, 2.70 equiv) in THF (60 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7% EtOAc in hexanes) to give the alkynyl imine **3a**[10] as a yellow oil (3.42 g, 97%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.21–8.18 (m, 2H, Ar**H** (*o*-C=N)), 7.51–7.45 (m, 3H, Ar**H**), 7.40–7.36 (m, 2H, Ar**H**), 7.17 (tt, 1H, *J* = 7.5, 1.1 Hz, Ar**H**), 7.14–7.11 (m, 2H, Ar**H**), 0.14 (s, 9H, Si($C\mathbf{H}_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	151.7, 150.1, 137.0, 131.4, 128.6, 128.5, 128.3, 125.0, 120.9, 105.4, 97.5, –0.5.
FTIR (neat) cm^{-1}:	3063 (m), 3030 (w), 2960 (m), 1588 (s, C=N), 1565 (s).
HRMS (ESI):	calcd for $C_{18}H_{20}NSi$ $[M+H]^+$: 278.1360, found: 278.1365.
Analysis	calcd for $C_{18}H_{19}NSi$: C, 77.93; H, 6.90; N, 5.05, found: C, 77.97; H, 6.87; N, 5.10.
TLC (20% EtOAc in hexanes), R_f:	0.59 (UV, CAM).

[10] For a prior synthesis, see: Ito, Y.; Inouye, M.; Murakami, M. *Chem. Lett.* **1989**, *7*, 1261.

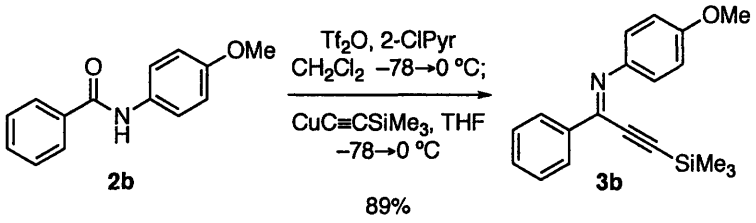


2-Phenylquinoline (1a, Table 2, entry 1):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (587 mg, 3.60 mmol, 1.00 equiv), $CpRuCl(PPh_3)_2$ (262 mg, 0.35 mmol, 0.10 equiv) and SPhos (148 mg, 0.35 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3a** (1.00 g, 3.60 mmol, 1 equiv) and toluene (18 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 20-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (15→50 % EtOAc in hexanes) to afford the quinoline **1a** as a pale yellow solid (668 mg, 90%).[11]

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.25 (d, 1H, J = 8.5 Hz, Ar**H**), 8.21–8.16 (m, 3H, Ar**H**), 7.90 (d, 1H, J = 8.5 Hz, Ar**H**), 7.85 (d, 1H, J = 8.2 Hz, Ar**H**), 7.75 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.57–7.52 (m, 3H, Ar**H**), 7.48 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.5, 148.4, 139.8, 137.0, 129.9, 129.9, 129.5, 129.0, 127.8, 127.7, 127.3, 126.5, 119.2.
FTIR (neat) cm^{-1}:	3189 (s), 3055 (w), 2091 (s), 1617 (w), 1597 (s), 1491 (m), 1447 (s).
HRMS (EI):	calcd for $C_{15}H_{11}N$ $[M]^+$: 205.0886, found: 205.0885.
TLC (20% EtOAc in hexanes), R_f:	0.51 (UV, CAM).

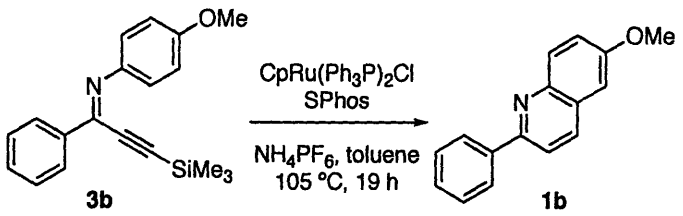
[11] Sangu, K.: Fuchibe, K.: Akiyama, T. *Org. Lett.* **2004**, *6*, 353.



***N*-(4-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3b, Table 2, entry 2):**

Trifluoromethanesulfonic anhydride (174 μL, 1.06 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2b** (200 mg, 0.88 mmol, 1 equiv) and 2-chloropyridine (333 μL, 3.52 mmol, 4.00 equiv) in CH_2Cl_2 (1.8 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (383 mg, 2.38 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→10% EtOAc in hexanes) to afford the alkynyl imine **3b** as a yellow oil (240 mg, 89%).

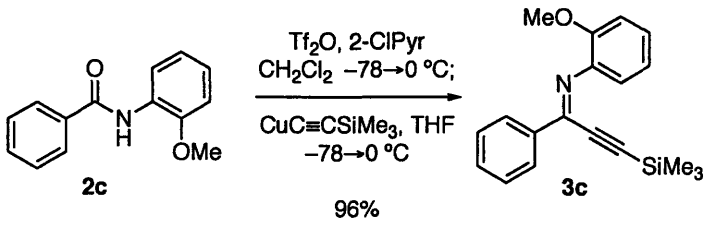
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.21–8.15 (m, 2H, Ar**H** (*o*-C=N)), 7.50–7.42 (m, 3H, Ar**H** (*m*-C=N, *p*-C=N)), 7.31–7.25 (m, 2H, Ar**H**), 6.96–6.90 (m, 2H, Ar**H**), 3.83 (s, 3H, CH_3O), 0.21 (s, 9H, $Si(CH_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.7, 148.1, 144.2, 137.6, 131.0, 128.5, 128.1, 123.3, 113.7, 104.8, 98.1, 55.6, –0.4.
FTIR ($CDCl_3$) cm^{-1}:	3066 (w), 2962 (m), 2838 (w), 1605 (m, C=N), 1559 (m), 1503 (s), 1251 (s).
HRMS (ESI):	calcd for $C_{19}H_{22}NOSi$ $[M+H]^+$: 308.1465, found: 308.1472.
TLC (20% EtOAc in hexanes), R_f:	0.49 (UV, CAM).



6-Methoxy-2-phenylquinoline (1b, Table 2, entry 2):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.24 mmol, 1.0 equiv), $CpRuCl(PPh_3)_2$ (18 mg, 0.024 mmol, 0.10 equiv) and SPhos (10 mg, 0.024 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3b** (75 mg, 0.24 mmol, 1 equiv) and toluene (1.2 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the quinoline **1b** as a pale yellow solid (52 mg, 91%).[11]

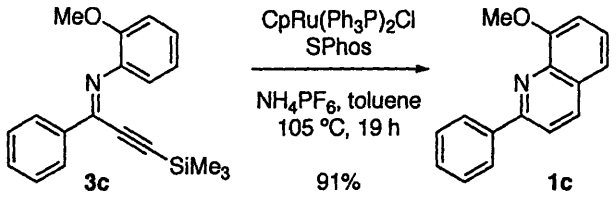
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.16–8.10 (m, 3H, Ar**H**), 8.08 (d, 1H, J = 9.2 Hz, Ar**H**), 7.85 (d, 1H, J = 8.9 Hz, Ar**H**), 7.56–7.50 (m, 2H, Ar**H**), 7.48–7.42 (m, 1H, Ar**H**), 7.40 (dd, 1H, J = 9.2, 2.7 Hz, Ar**H** (CH_3OCCH)), 7.11 (d, 1H, J = 3.1 Hz, Ar**H**(CH_3OCCH)), 3.99 (s, 3H, CH_3O).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.8, 155.2, 144.5, 139.9, 135.7, 131.3, 129.1, 129.0, 128.3, 127.5, 122.5, 119.4, 105.1, 55.7.
FTIR (neat) cm^{-1}:	3057 (w), 2958 (m), 2836 (w), 1621 (m), 1599 (m), 1493 (s).
HRMS (EI):	calcd for $C_{16}H_{13}NO$ $[M]^+$: 235.0992, found: 235.0984.
TLC (20% EtOAc in hexanes), R_f:	0.39 (UV, CAM).



***N*-(2-Methoxyphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3c, Table 2, entry 3):**

Trifluoromethanesulfonic anhydride (218 μL, 1.32 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2c** (250 mg, 1.10 mmol, 1 equiv) and 2-chloropyridine (416 μL, 4.40 mmol, 4.00 equiv) in CH_2Cl_2 (2.2 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (477 mg, 2.97 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→10% EtOAc in hexanes) to afford the alkynyl imine **3c** as a yellow oil (326 mg, 97%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.24–8.20 (m, 2H, Ar**H** (*o*-C=N)), 7.52–7.44 (m, 3H, Ar**H** (*p*-C=N, *m*-C=N)), 7.14 (ddd, 1H, J = 8.3, 7.3, 1.8 Hz, Ar**H**), 7.01 (dd, 1H, J = 7.6, 2.1 Hz, Ar**H**), 6.98–6.94 (m, 2H, Ar**H**), 3.85 (s, 3H, OCH_3), 0.11 (s, 9H, $Si(CH_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	151.6, 150.5, 141.5, 136.8, 131.3, 128.4, 128.4, 125.7, 120.8, 120.5, 111.5, 104.9, 97.7, 55.9, –0.5.
FTIR (neat) cm^{-1}:	3064 (w), 2959 (m), 2900 (w), 2834 (w), 1590 (s), 1567 (s), 1488 (s).
HRMS (ESI):	calcd for $C_{19}H_{22}NOSi$ $[M+H]^+$: 308.1465, found: 308.1477.
TLC (20% EtOAc in hexanes), R_f:	0.49 (UV, $KMnO_4$).

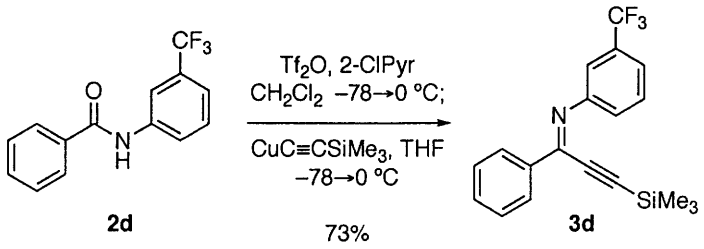


8-Methoxy-2-phenylquinoline (1c, Table 2, entry 3):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (53 mg, 0.33 mmol, 1.0 equiv), $CpRuCl(PPh_3)_2$ (24 mg, 0.033 mmol, 0.10 equiv) and SPhos (13 mg, 0.033 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3c** (100 mg, 0.33 mmol, 1 equiv) and toluene (1.6 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the quinoline **1c** as a pale yellow solid (70 mg, 91%).[12]

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.24–8.18 (m, 3H, Ar**H**), 7.93 (d, 1H, J = 8.5 Hz, Ar**H**), 7.53 (t, 2H, J = 7.5 Hz, Ar**H**), 7.49–7.41 (m, 3H, Ar**H**), 7.10 (dd, 1H, J = 7.6, 1.1 Hz, Ar**H**), 4.13 (s, 3H, O**CH**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	156.5, 155.7, 140.3, 140.0, 137.0, 129.4, 129.0, 128.5, 127.9, 126.7, 119.7, 119.5, 108.2, 56.3.
FTIR (neat) cm^{-1}:	3060 (m), 2934 (m), 2834 (w), 1599 (s), 1556 (s), 1467 (s), 1258 (s).
HRMS (ESI):	calcd for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1066.
TLC (20% EtOAc in hexanes), R_f:	0.23 (UV, $KMnO_4$).

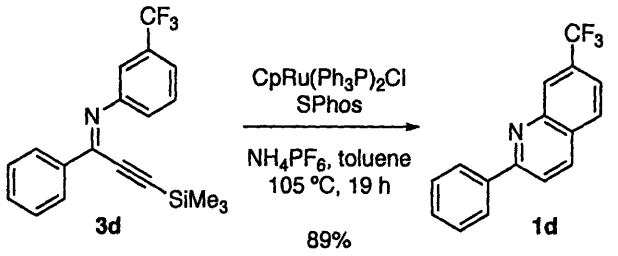
[12] For a prior synthesis, see: Collin, J.; Jaber, N.; Lannou, M. I. *Tetrahedron Lett.* **2001**, *42*, 7405.



***N*-(3-Trifluoromethylphenyl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3d, Table 2, entry 4):**

Trifluoromethanesulfonic anhydride (251 μL, 1.52 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2d** (337 mg, 1.27 mmol, 1 equiv) and 2-chloropyridine (481 μL, 5.08 mmol, 4.00 equiv) in CH_2Cl_2 (2.5 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (552 mg, 3.43 mmol, 2.70 equiv) in THF (7.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3d** as a pale yellow oil (321 mg, 73%). Desilylation of **3d** afforded less than 10% yield of the corresponding terminal alkyne due to rapid nucleophilic addition (i.e., water and methanol) to this terminal alkynyl imine.

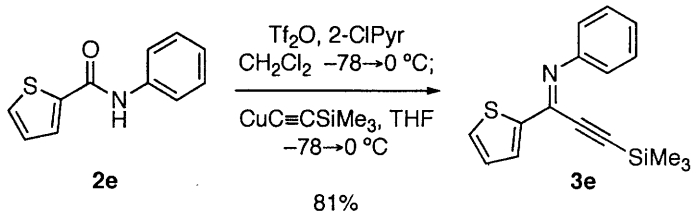
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.20–8.17 (m, 2H, Ar**H** (*o*-C=N)), 7.55–7.47 (m, 4H, Ar**H**), 7.45–7.42 (m, 1H, Ar**H**), 7.40 (s, 1H, Ar**H**), 7.29–7.25 (m, 1H, Ar**H**), 0.06 (s, 9H, $Si(C\mathbf{H}_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	152.3, 151.5, 136.6, 131.8, 131.1 (q, J = 32.0 Hz), 129.2, 128.6, 128.5, 124.6 (q, J = 271.9 Hz), 124.6, 121.5 (q, J = 3.9 Hz), 117.8 (q, J = 3.8 Hz), 106.8, 96.9, –0.7.
FTIR (neat) cm^{-1}:	3067 (m), 2962 (m), 1589 (s, C=N), 1567 (s), 1330 (s).
HRMS (ESI):	calcd for $C_{19}H_{19}F_3NSi$ $[M+H]^+$: 346.1233, found: 346.1236.
TLC (20% EtOAc in hexanes), R_f:	0.57 (UV, CAM).



2-Phenyl-7-trifluoromethyl-quinoline (1d, Table 2, entry 4):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (35 mg, 0.22 mmol, 1.0 equiv), $CpRuCl(PPh_3)_2$ (16 mg, 0.022 mmol, 0.10 equiv) and SPhos (9 mg, 0.022 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3d** (75 mg, 0.22 mmol, 1 equiv) and toluene (1.1 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the quinoline **1d** as a pale yellow solid (53 mg, 89%).

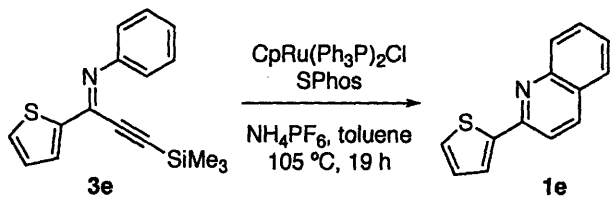
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.46 (s, 1H, Ar**H**), 8.30 (d, 1H, J = 8.2 Hz, Ar**H**), 8.22–8.18 (m, 2H, Ar**H**(*o*-C=N)), 8.03 (d, 1H, J = 8.6 Hz, Ar**H**), 7.97 (d, 1H, J = 8.6 Hz, Ar**H**), 7.72 (dd, 1H, J = 8.5, 1.8 Hz, Ar**H**), 7.59–7.54 (m, 2H, Ar**H**), 7.54–7.50 (m, 1H, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	158.9, 147.5, 139.1, 136.8, 131.7 (q, J = 32.6 Hz), 130.1, 129.2, 128.9, 127.8 (q, J = 4.6 Hz), 127.5, 125.3, 123.2, 122.1 (q, J = 2.9 Hz), 121.0.
FTIR (neat) cm^{-1}:	3067 (w), 3037 (w), 2917 (w), 1603 (s), 1316 (s).
HRMS (EI):	calcd for $C_{16}H_{10}F_3N$ $[M]^+$: 273.0760, found: 273.0750.
TLC (20% EtOAc in hexanes), R_f:	0.46 (UV, CAM).



***N*-Phenyl-2-(thiophen-2-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3e, Table 2, entry 5):**

Trifluoromethanesulfonic anhydride (195 μL, 1.18 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2e** (200 mg, 0.98 mmol, 1 equiv) and 2-chloropyridine (372 μL, 3.94 mmol, 4.00 equiv) in CH_2Cl_2 (2.0 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (428 mg, 2.66 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3e** as a pale yellow oil (227 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.73 (dd, 1H, *J* = 3.7, 1.2 Hz, SC**H**CHCHCC=N), 7.48 (dd, 1H, *J* = 5.0, 0.9 Hz, SCHCHC**H**CC=N), 7.38–7.33 (m, 2H, Ar**H**), 7.20–7.14 (m, 3H, Ar**H**), 7.12 (dd, 1H, *J* = 4.6, 3.7 Hz, SCHC**H**CHCC=N), 0.16 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	150.5, 144.7, 144.0, 131.6, 130.6, 128.5, 127.7, 125.4, 121.6, 103.7, 96.7, –0.5.
FTIR (neat) cm^{-1}:	3078 (m), 2960 (s), 1563 (s, C=N), 1425 (s), 1252 (s).
HRMS (ESI):	calcd for $C_{16}H_{18}NSSi$ $[M+H]^+$: 284.0924, found: 284.0937.
TLC (20% EtOAc in hexanes), R_f:	0.70 (UV, CAM).

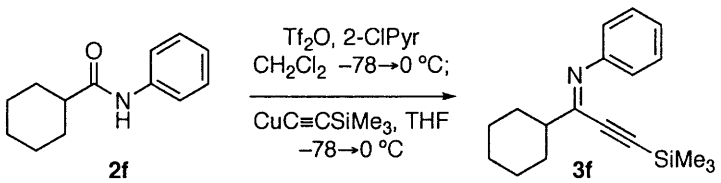


2-Thiophen-2-ylquinoline (1e, Table 2, entry 5):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (58 mg, 0.35 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (26 mg, 0.035 mmol, 0.10 equiv) and SPhos (15 mg, 0.035 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3e** (100 mg, 0.35 mmol, 1 equiv) and toluene (1.8 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the quinoline **1e** as a pale yellow solid (56 mg, 75%).[13]

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.16 (d, 1H, J = 8.9 Hz, Ar**H**), 8.10 (d, 1H, J = 9.2 Hz, Ar**H**), 7.82 (d, 1H, J = 8.6 Hz, Ar**H**), 7.79 (d, 1H, J = 7.9 Hz, Ar**H** (SC**H**CHCHCC=N)), 7.75 (dd, 1H, J = 3.7, 0.9 Hz, Ar**H** (SCHCHC**H**CC=N)), 7.71 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.52–7.47 (m, 2H, Ar**H**), 7.18 (dd, 1H, J = 4.9, 3.7 Hz, Ar**H** (SCHC**H**CHC=N)).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	152.5, 148.3, 145.6, 136.8, 130.0, 129.4, 128.8, 128.3, 127.7, 127.3, 126.3, 126.0, 117.8.
FTIR (neat) cm^{-1}:	3079 (w), 3042 (w), 1962 (w), 1617 (m), 1597 (s), 1561 (m), 1502 (s).
HRMS (ESI):	calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0528, found: 212.0533.
TLC (20% EtOAc in hexanes), R_f:	0.40 (UV, $KMnO_4$).

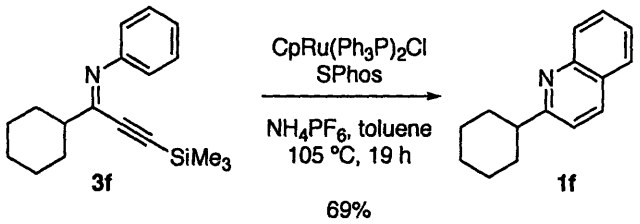
[13] Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.



***N*-Phenyl-2-cyclohexyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3f, Table 2, entry 6):**

Trifluoromethanesulfonic anhydride (98 μL, 0.59 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2f** (100 mg, 0.49 mmol, 1 equiv) and 2-chloropyridine (186 μL, 1.97 mmol, 4.00 equiv) in CH_2Cl_2 (1.0 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (214 mg, 1.33 mmol, 2.70 equiv) in THF (3.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on neutralized silica gel (1% Et_3N/hexanes) to afford the alkynyl imine **3f** as a pale yellow oil (123 mg, 89%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.32–7.28 (m, 2H, Ar**H**), 7.12–7.07 (m, 1H, Ar**H**), 6.96–6.93 (m, 2H, Ar**H**), 2.47 (tt, 1H, J = 23.2, 6.9 Hz, $(CH_2)_2$C**H**C=N), 2.01 (br dd, 2H, J = 12.6, 2.0 Hz, $^cC_6\mathbf{H}_{11}$), 1.86 (dt, 2H, J = 13.1, 3.4 Hz, $^cC_6\mathbf{H}_{11}$), 1.76–1.69 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.52 (qd, 2H, J = 12.5, 3.4 Hz, $^cC_6\mathbf{H}_{11}$), 1.36 (qt, 2H, J = 12.5, 3.2 Hz, $^cC_6\mathbf{H}_{11}$), 1.26 (qt, 1H, J = 12.5, 3.2 Hz, $^cC_6\mathbf{H}_{11}$), 0.06 (s, 9H, Si($C\mathbf{H}_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	159.6, 151.7, 128.4, 124.5, 120.6, 104.0, 98.2, 48.3, 30.3, 26.1, 26.0, –0.5.
FTIR (neat) cm^{-1}:	3049 (w), 2933 (s), 2856 (m), 1660 (w), 1594 (s), 1484 (m).
HRMS (ESI):	calcd for $C_{18}H_{26}NSi$ $[M+H]^+$: 284.1829, found: 284.1836.
TLC (20% EtOAc in hexanes), R_f:	0.67 (UV, $KMnO_4$).

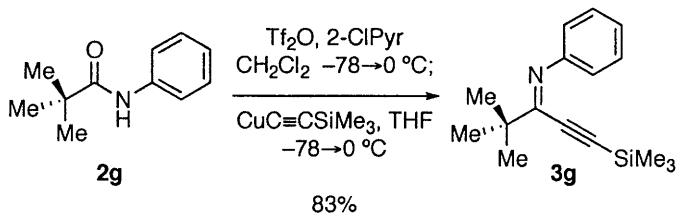


2-Cyclohexyl-quinoline (1f, Table 2, entry 6):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.25 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3f** (70 mg, 0.25 mmol, 1 equiv) and toluene (1.2 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (10 % EtOAc in hexanes) to afford the quinoline **1f** as a pale yellow solid (36 mg, 69%).[14]

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.09 (d, 1H, J = 8.5 Hz, Ar**H**), 8.06 (d, 1H, J = 8.5 Hz, Ar**H**), 7.78 (d, 1H, J = 8.2 Hz, Ar**H**), 7.69 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.49 (ddd, 1H, J = 7.9, 7.0, 1.2 Hz, Ar**H**), 7.35 (d, 1H, J = 8.6 Hz, Ar**H**), 2.94 (tt, 1H, J = 12.1, 3.4 Hz, $(CH_2)_2$C**H**CN), 2.08–2.00 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.98–1.87 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.86–1.76 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.64 (qd, 2H, J = 12.5, 3.1 Hz, $^cC_6\mathbf{H}_{11}$), 1.49 (qt, 2H, J = 13.1, 3.4 Hz, $^cC_6\mathbf{H}_{11}$), 1.35 (qt, 1H, J = 12.8, 3.4 Hz, $^cC_6\mathbf{H}_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	167.0, 148.0, 136.5, 129.4, 129.1, 127.6, 127.2, 125.8, 119.8, 47.9, 33.0, 26.7, 26.3.
FTIR (neat) cm^{-1}:	3058 (w), 2924 (s), 2850 (m), 1720 (w), 1619 (w), 1601 (m), 1502 (m).
HRMS (EI):	calcd for $C_{15}H_{17}N$ $[M]^+$: 211.1356, found: 211.1358.
TLC (20% EtOAc in hexanes), R_f:	0.50 (UV, $KMnO_4$).

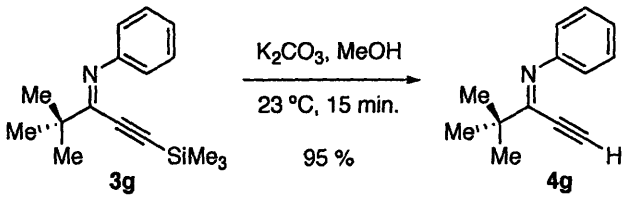
[14] For a prior synthesis, see: Ishikura, M.; Oda, I,; Kamada, M.; Terashima, M. *Synth. Comm.* **1987**, *17*, 959.



N-Phenyl-2-(*tert*-butyl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3g, Table 2, entry 7):

Trifluoromethanesulfonic anhydride (220 μL, 1.33 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2g** (197 mg, 1.11 mmol, 1 equiv) and 2-chloropyridine (420 μL, 4.44 mmol, 4.00 equiv) in CH_2Cl_2 (2.2 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (482 mg, 3.00 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3g** as a pale yellow oil (236 mg, 83%).

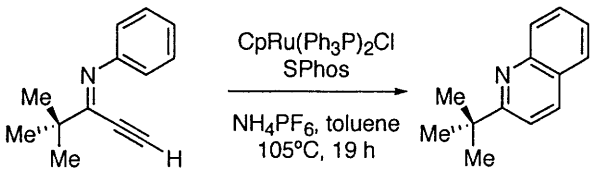
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.32–7.28 (m, 2H, Ar**H**), 7.11–7.06 (m, 1H, Ar**H**), 6.92–6.88 (m, 2H, Ar**H**), 1.31 (s, 9H, $C(CH_3)_3$), 0.50 (s, 9H, $Si(CH_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	162.9, 152.2, 128.5, 124.2, 120.3, 104.7, 97.3, 39.8, 28.0, –0.5.
FTIR (neat) cm^{-1}:	3080 (w), 2967 (s), 2868 (m), 1931 (w), 1593 (s), 1477 (s).
HRMS (ESI):	calcd for $C_{16}H_{24}NSi$ $[M+H]^+$: 258.1673, found: 258.1675.
TLC (20% EtOAc in hexanes), R_f:	0.69 (UV, CAM).



(1-*tert*-Butyl-prop-2-ynylidene)-phenyl-amine (4g, Table 2, entry 7):

Anhydrous potassium carbonate (41 mg, 0.30 mmol, 0.2 equiv) was added to a solution of imine **3g** (380 mg, 1.48 mmol, 1 equiv) in methanol (5.0 mL) and stirred at 23 °C. After 25 min., the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc in hexanes) to afford the alkynyl imine **4g** as a yellow solid (259 mg, 95%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.32–7.28 (m, 2H, Ar**H**), 7.12 (tt, 1H, J = 7.3, 2.3 Hz, Ar**H**), 6.92–6.88 (m, 2H, Ar**H**), 3.14 (s, 1H, C≡C**H**), 1.33 (s, 9H, C(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	161.9, 151.8, 128.7, 124.4, 119.9, 85.4, 76.2, 40.2, 27.8.
FTIR (neat) cm^{-1}:	2962 (s), 2925 (s), 1734 (m), 1717 (m), 1684 (s), 1653 (m).
HRMS (EI):	calcd for $C_{13}H_{15}N$ $[M]^+$: 185.1199, found: 185.1193.
TLC (20% EtOAc in hexanes), R_f:	0.66 (UV, $KMnO_4$).

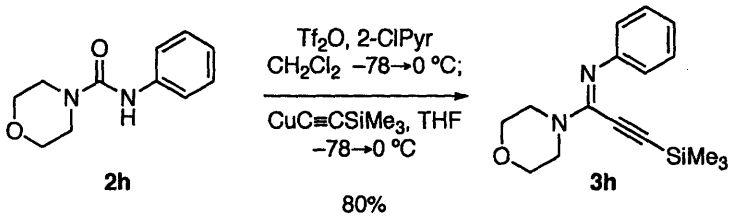


4g 73% **1g**

2-*tert*-Butyl-quinoline (1g, Table 2, entry 7):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (62 mg, 0.38 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (28 mg, 0.038 mmol, 0.10 equiv) and SPhos (16 mg, 0.038 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **4g** (70 mg, 0.38 mmol, 1 equiv) and toluene (1.9 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc in hexanes) to afford the quinoline **1g** as a pale yellow solid (51 mg, 73%).

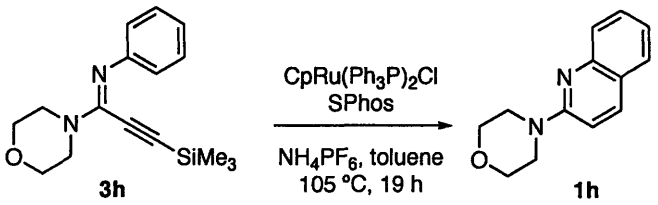
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.09 (d, 1H, J = 8.2 Hz, Ar**H**), 8.07 (d, 1H, J = 8.5 Hz, Ar**H**), 7.78 (dd, 1H, J = 7.9, 1.2 Hz, Ar**H**), 7.65 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.54 (d, 1H, J = 8.9 Hz, Ar**H**), 7.48 (ddd, 1H, J = 8.1, 6.7, 0.9 Hz, Ar**H**), 1.49 (s, 9H, $C(C\mathbf{H}_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	147.6, 136.1, 129.6, 129.2, 127.4, 126.6, 125.8, 118.5, 100.0, 38.3, 30.4.
FTIR (neat) cm^{-1}:	3061 (w), 2960 (s), 2868 (m), 1619 (m), 1601 (s), 1565 (w), 1503 (s).
HRMS (ESI):	calcd for $C_{13}H_{16}N$ $[M+H]^+$: 186.1277, found: 186.1283.
TLC (20% EtOAc in hexanes), R_f:	0.46 (UV, $KMnO_4$)



***N*-Phenyl-2-(morpholin-4-yl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3h, Table 2, entry 8):**

Trifluoromethanesulfonic anhydride (144 μL, 0.87 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2h** (150 mg, 0.73 mmol, 1 equiv) and 2-chloropyridine (275 μL, 2.91 mmol, 4.00 equiv) in CH_2Cl_2 (1.5 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and Hünig's base (190 μL, 1.09 mmol, 1.50 equiv) was added via syringe followed by a freshly prepared solution of copper (I) trimethylysilylacetylide (316 mg, 1.96 mmol, 2.70 equiv) in THF (3.0 mL) at 0 °C via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on neutralized silica gel (50% EtOAc in hexanes) to afford the alkynyl imidate **3h** as a burgandy colored oil (166 mg, 80%).

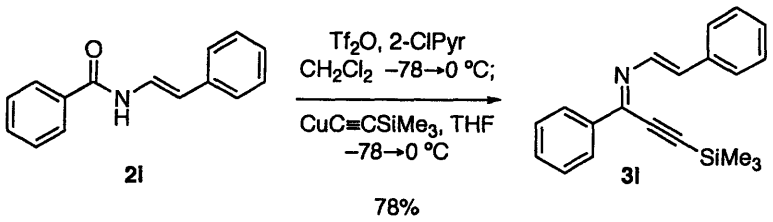
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.27–7.23 (m, 2H, Ar**H**), 7.01 (tt, 1H, J = 7.3, 1.1 Hz, Ar**H**), 6.92–6.88 (m, 2H, Ar**H**), 3.79–3.75 (m, 4H, OCH_2CH_2N), 3.69–3.66 (m, 4H, OCH_2CH_2N), 0.04 (s, 9H, $Si(CH_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	151.2, 144.2, 128.5, 122.9, 122.3, 104.2, 93.2, 66.8, 45.9, –0.7.
FTIR (neat) cm^{-1}:	2967 (m), 2924 (w), 2861 (m), 1577 (s, C=N), 1420 (m) 1247 (s).
HRMS (ESI):	calcd for $C_{16}H_{23}N_2OSi$ $[M+H]^+$: 287.1574, found: 287.1580.
TLC (50% EtOAc in hexanes), R_f:	0.70 (UV, $KMnO_4$).



2-Morpholin-4-yl-quinoline (1h, Table 2, entry 8):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (43 mg, 0.26 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (19 mg, 0.026 mmol, 0.10 equiv) and SPhos (11 mg, 0.026 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3h** (75 mg, 0.26 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the quinoline **1h** as a pale yellow solid (35 mg, 62%).

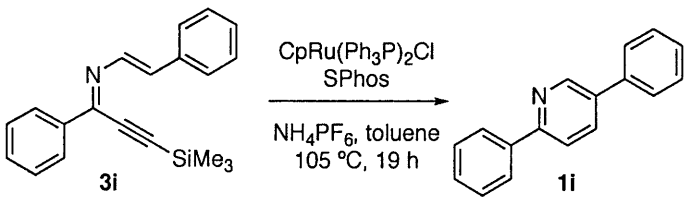
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.95 (d, 1H, J = 8.7 Hz, Ar**H**), 7.74 (d, 1H, J = 7.6 Hz, Ar**H**), 7.65 (dd, 1H, J = 7.9, 1.5 Hz, Ar**H**), 7.56 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.27 (ddd, 1H, J = 8.0, 6.7, 0.9 Hz, Ar**H**), 6.99 (d, 1H, J = 9.2 Hz, Ar**H**), 3.87 (t, 4H, J = 4.9, OCH_2CH_2N), 3.73 (t, 4H, J =4.9 Hz, OCH_2CH_2N).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	157.6, 147.8, 137.7, 129.8, 127.4, 126.9, 123.4, 122.8, 109.4, 67.0, 45.7.
FTIR (neat) cm^{-1}:	3047 (w), 2972 (w), 2917 (w), 2858 (m), 1617 (s), 1605 (m).
HRMS (ESI):	calcd for $C_{13}H_{14}N_2O$ $[M]^+$: 215.1179, found: 215.1178.
TLC (20% EtOAc in hexanes), R_f:	0.21 (UV, $KMnO_4$).



***N*-(*trans*-β-Styryl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3i, Table 2, entry 9):**

Trifluoromethanesulfonic anhydride (133 μL, 0.81 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2i** (150 mg, 0.67 mmol, 1 equiv) and 2-chloropyridine (254 μL, 2.69 mmol, 4.00 equiv) in CH_2Cl_2 (1.3 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (292 mg, 1.81 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3i** as a pale yellow solid (159 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.34 (d, 1H, J = 13.1 Hz, NC**H**CHC), 8.18–8.13 (m, 2H, Ar**H**), 7.56 (d, 2H, J = 7.3 Hz, Ar**H**), 7.48–7.42 (m, 3H, Ar**H**), 7.39 (t, 2H, J = 7.6 Hz, Ar**H**), 7.31 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**), 7.16 (d, 1H, J = 13.4 Hz, NCHC**H**C), 0.39 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	148.0, 139.7, 137.1, 136.7, 133.8, 131.0, 129.0, 128.6, 128.5, 128.0, 127.4, 108.7, 96.8, 0.0.
FTIR ($CDCl_3$) cm^{-1}:	3155 (m), 3062 (m), 3028 (m), 2963 (m), 2902 (m), 1815 (m), 1794 (m), 1643 (w), 1622 (m), 1490 (s).
HRMS (ESI):	calcd for $C_{20}H_{22}NSi$ $[M+H]^+$: 304.1516, found: 304.1526.
TLC (20% EtOAc in hexanes), R_f:	0.59 (UV, CAM).

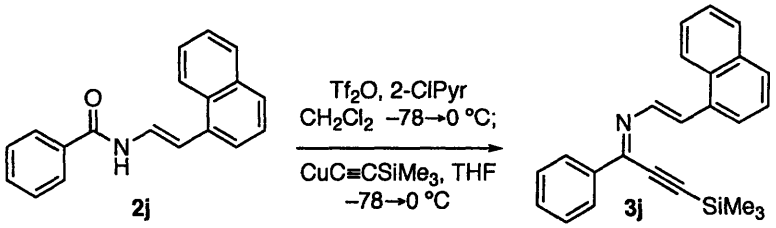


2,5-Diphenyl-pyridine (1i, Table 2, entry 9):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (40 mg, 0.25 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3i** (75 mg, 0.25 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (20 % EtOAc in hexanes) to afford the pyridine **1i** as a pale yellow solid (44 mg, 77%).[15]

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.96 (d, 1H, J = 2.5 Hz, Ar**H**), 8.08–8.05 (m, 2H, Ar**H**), 7.98 (dd, 1H, J = 8.2, 2.5 Hz, Ar**H**), 7.83 (d, 1H, J = 8.2 Hz, Ar**H**), 7.68–7.64 (m, 2H, Ar**H**), 7.54–7.50 (m, 4H, Ar**H**), 7.47–7.42 (m, 2H, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	156.4, 148.3, 139.2, 137.9, 135.3, 135.1, 129.3, 129.2, 129.0, 128.3, 127.2, 127.0, 120.6.
FTIR (CH_2Cl_2) cm^{-1}:	2926 (w), 1735 (s), 1654 (s), 1594 (w), 1472 (s), 1371 (s).
HRMS (ESI):	calcd for $C_{17}H_{14}N$ $[M+H]^+$: 232.1121, found: 232.1126.
TLC (20% EtOAc in hexanes), R_f:	0.43 (UV, CAM).

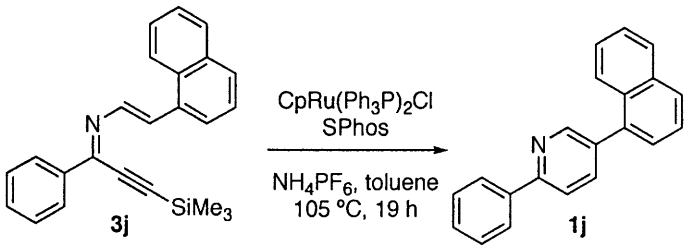
(15) Berthiol, F.; Kondolff, I.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2004**, *689*, 2786.



(2-Naphthalen-1-yl-vinyl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3j, Table 2, entry 10):

Trifluoromethanesulfonic anhydride (127 μL, 0.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2j** (175 mg, 0.64 mmol, 1 equiv) and 2-chloropyridine (242 μL, 2.56 mmol, 4.00 equiv) in CH_2Cl_2 (1.3 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (278 mg, 1.73 mmol, 2.70 equiv) in THF (4.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3j** as a pale yellow oil (197 mg, 87%).

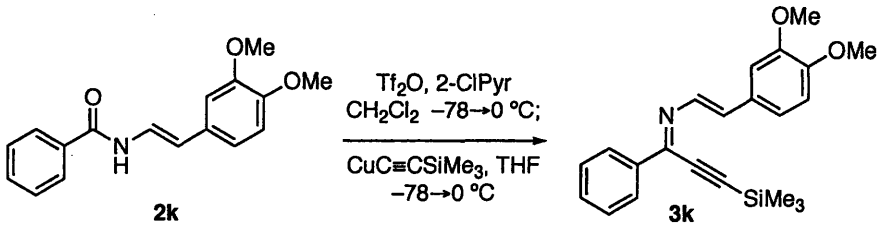
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.39 (dd, 1H, J = 12.8, 0.6 Hz, NC**H**CHC), 8.31 (d, 1H, J = 8.2 Hz, 8.22–8.18 (m, 2H, Ar**H**), 7.94 (d, 1H, J = 13.1 Hz, NCHC**H**C), 7.89 (d, 1H, J = 7.9 Hz, Ar**H**), 7.85 (d, 2H, J = 7.6 Hz, Ar**H**), 7.60–7.47 (m, 6H, Ar**H**), 0.38 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	148.8, 142.4, 137.7, 134.6, 134.3, 132.3, 131.6, 131.2, 129.5, 129.4, 129.2, 128.7, 127.1, 126.8, 126.4, 124.8, 124.6, 109.3, 97.5, 0.6.
FTIR (neat) cm^{-1}:	3059 (m), 2959 (m), 2141 (w), 1810 (w), 1692 (m), 1644 (w), 1590 (w), 1251 (s).
HRMS (ESI):	calcd for $C_{24}H_{24}NSi$ $[M+H]^+$: 354.1673, found: 354.1675.
TLC (20% EtOAc in hexanes), R_f:	0.77 (UV, CAM).



5-Naphthalen-1-yl-2-phenyl-pyridine (1j, Table 2, entry 10):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (28 mg, 0.17 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (12 mg, 0.017 mmol, 0.10 equiv) and SPhos (7 mg, 0.017 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3j** (60 mg, 0.17 mmol, 1 equiv) and toluene (0.9 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (7.5 % EtOAc in hexanes) to afford the pyridine **1j** as a pale brown solid (44 mg, 88%).

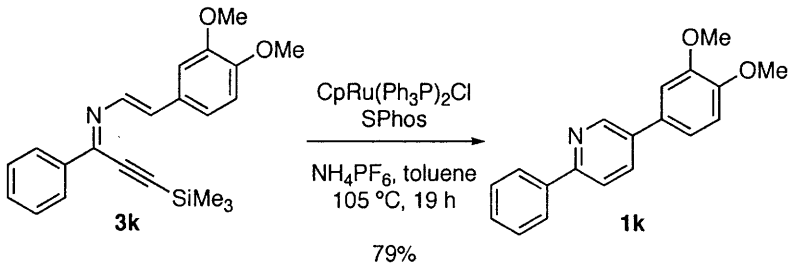
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.87–8.84 (m, 1H, Ar**H**), 8.11 (d, 2H, J = 7.02 Hz, Ar**H**), 7.98–7.87 (m, 5H, Ar**H**), 7.61–7.46 (m, 7H, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	156.4, 150.6, 139.3, 138.4, 136.4, 134.9, 134.0, 131.7, 129.3, 129.0, 128.7, 128.7, 127.6, 127.1, 126.7, 126.3, 125.6, 125.6, 120.1.
FTIR (neat) cm^{-1}:	3058 (m), 2930 (w), 1950 (w), 1595 (m), 1548 (m), 1476 (s), 1396 (m).
HRMS (ESI):	calcd for $C_{21}H_{16}N$ $[M+H]^+$: 282.1277, found: 282.1289.
TLC (15% EtOAc in hexanes), R_f:	0.46 (UV, $KMnO_4$).



[2-(3,4-Dimethoxy-phenyl)-vinyl]-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3k, Table 2, entry 11):

Trifluoromethanesulfonic anhydride (122 μL, 0.74 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2k** (175 mg, 0.62 mmol, 1 equiv) and 2-chloropyridine (234 μL, 2.47 mmol, 4.00 equiv) in CH_2Cl_2 (1.2 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (268 mg, 1.67 mmol, 2.70 equiv) in THF (4.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to afford the alkynyl imine **3k** as a yellow oil (216 mg, 96%).

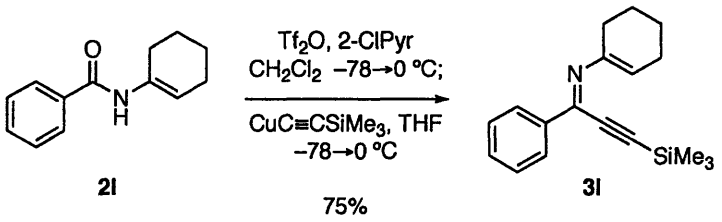
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.26 (d, 1H, J = 13.1 Hz, NC**H**CHC), 8.16–8.12 (m, 2H, NCHC**H**C, Ar**H**), 7.46–7.42 (m, 3H, Ar**H**), 7.14–7.08 (m, 3H, Ar**H**), 6.86 (d, 1H, J = 8.2 Hz, Ar**H**), 3.96 (s, 3H, OC**H**$_3$), 3.94 (s, 3H, OC**H**$_3$), 0.38 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	149.6, 149.2, 146.6, 138.2, 137.1, 133.8, 130.7, 129.6, 128.5, 127.8, 121.4, 111.3, 108.8, 108.1, 96.9, 56.1, 55.8, –0.0.
FTIR (neat) cm^{-1}:	3057 (w), 2958 (m), 2835 (w), 1599 (s), 1578 (m), 1512 (s), 1267 (s).
HRMS (ESI):	calcd for $C_{22}H_{26}NO_2Si$ $[M+H]^+$: 364.1727, found: 364.1733.
TLC (20% EtOAc in hexanes), R_f:	0.52 (UV, CAM).



5-(3,4-Dimethoxy-phenyl)-2-phenyl-pyridine (1k, Table 2, entry 11):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (45 mg, 0.28 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (20 mg, 0.028 mmol, 0.10 equiv) and SPhos (11 mg, 0.028 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3k** (100 mg, 0.28 mmol, 1 equiv) and toluene (1.4 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on neutralized silica gel (30 % EtOAc in hexanes) to afford the pyridine **1k** as a yellow solid (64 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.92 (d, 1H, J = 2.1 Hz, Ar**H**), 8.07–8.03 (m, 2H, Ar**H**), 7.93 (dd, 1H, J = 8.2, 2.5 Hz, Ar**H**), 7.81 (d, 1H, J = 8.2 Hz, Ar**H**), 7.53–7.49 (m, 2H, Ar**H**), 7.44 (tt, 1H, J = 7.3, 1.1 Hz, Ar**H**), 7.22 (dd, 1H, J = 8.2, 2.1 Hz, Ar**H**), 7.15 (d, 1H, J = 1.8 Hz, Ar**H**), 7.02 (d, 1H, J = 8.2 Hz, Ar**H**), 3.99 (s, 3H, O**CH**$_3$), 3.96 (s, 3H, O**CB**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	155.7, 149.5, 149.3, 147.9, 139.1, 134.8, 134.8, 130.5, 129.0, 128.9, 126.8, 120.3, 119.5, 111.8, 110.1, 56.1, 56.1.
FTIR (neat) cm^{-1}:	3055 (w), 3005 (w), 2966 (m), 2837 (m), 1602 (s), 1590 (s), 1522 (s), 1150 (s), 1022 (s).
HRMS (ESI):	calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332, found: 292.1337.
TLC (20% EtOAc in hexanes), R_f:	0.19 (UV, $KMnO_4$).

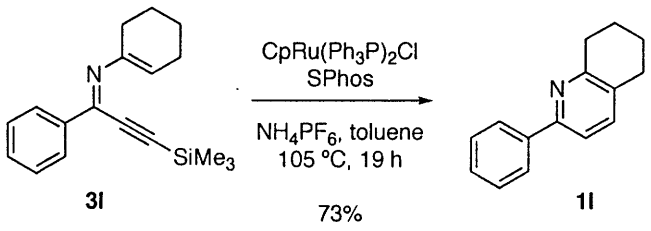


2l **3l**

***N*-(Cyclohexen-1-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3l, Table 2, entry 12):**

Trifluoromethanesulfonic anhydride (148 μL, 0.89 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2l** (150 mg, 0.75 mmol, 1 equiv) and 2-chloropyridine (282 μL, 2.98 mmol, 4.00 equiv) in CH_2Cl_2 (1.5 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (323 mg, 2.01 mmol, 2.70 equiv) in THF (3.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3l** as a yellow oil (157 mg, 75%).

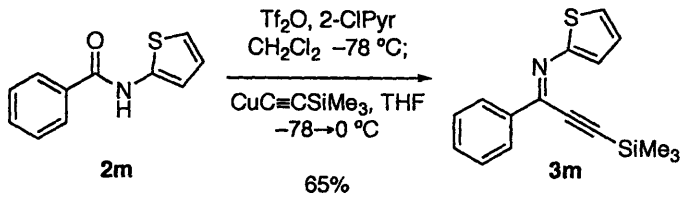
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.09–8.05 (m, 2H, Ar**H**), 7.48–7.39 (m, 3H, Ar**H**), 5.21 (t, 1H, J = 4.0 Hz, NC=C**H**), 2.29–2.23 (m, 2H, C**H**$_2$), 2.22–2.16 (m, 2H, C**H**$_2$), 1.82–1.75 (m, 2H, C**H**$_2$), 1.70–1.64 (m, 2H, C**H**$_2$), 0.28 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	148.7, 147.5, 137.2, 130.8, 128.4, 128.0, 110.3, 103.7, 97.6, 27.9, 24.7, 23.1, 22.5, –0.1.
FTIR (neat) cm^{-1}:	3063 (w), 2927 (s), 2857 (m), 1663 (m), 1562 (m), 1448 (m), 1273 (s), 1251 (s).
HRMS (ESI):	calcd for $C_{18}H_{24}NSi$ $[M+H]^+$: 282.1673, found: 282.1685.
TLC (20% EtOAc in hexanes), R_f:	0.61 (UV, $KMnO_4$).



2-Phenyl-5,6,7,8-tetrahydro-quinoline (1l, Table 2, entry 12):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (43 mg, 0.27 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (19 mg, 0.027 mmol, 0.10 equiv) and SPhos (11 mg, 0.027 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3l** (75 mg, 0.27 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the pyridine **1l** as a pale yellow solid (41 mg, 73%).

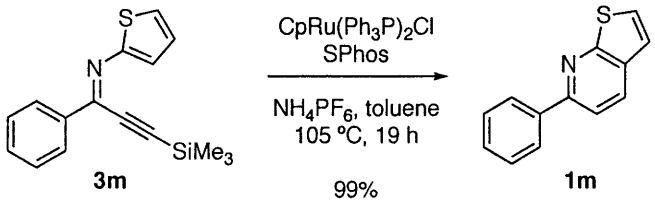
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.97–7.94 (m, 2H, Ar**H**), 7.48–7.36 (m, 5H, Ar**H**), 3.00 (t, 2H, J = 6.4 Hz, C**H**$_2$), 2.82 (t, 2H, J = 6.4 Hz, C**H**$_2$), 1.98–1.92 (m, 2H, C**H**$_2$), 1.89–1.83 (m, 2H, C**H**$_2$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	157.4, 154.9, 140.1, 137.6, 130.9, 128.8, 128.5, 127.0, 118.1, 33.1, 28.8, 23.4, 23.0.
FTIR (neat) cm^{-1}:	3061 (w), 3032 (w), 2935 (s), 2860 (m), 1590 (m), 1566 (m), 1460 (s), 1434 (m), 1253 (m).
HRMS (ESI):	calcd for $C_{15}H_{16}N$ $[M+H]^+$: 210.1277, found: 210.1279.
TLC (20% EtOAc in hexanes), R_f:	0.48 (UV, $KMnO_4$).



N-(Thiophen-2-yl)-2-(phenyl)-4-trimethylsilyl-1-azabut-1-en-3-yne (3m, Table 2, entry 13):

Trifluoromethanesulfonic anhydride (195 μL, 1.18 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2m** (200 mg, 0.98 mmol, 1 equiv) and 2-chloropyridine (372 μL, 3.94 mmol, 4.00 equiv) in CH_2Cl_2 (2.0 mL) at –78 °C. After 10 min., a freshly prepared solution of copper (I) trimethylysilylacetylide (428 mg, 2.66 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 10 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→7.5% EtOAc in hexanes) to afford the alkynyl imine **3m** as a yellow oil (181 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.19–8.13 (m, 2H, Ar**H**), 7.48–7.43 (m, 3H, Ar**H**), 7.42 (dd, 1H, J = 3.8, 1.4 Hz, C**H**S), 7.32 (dd, 1H, J = 5.5, 1.4 Hz, C**H**CHCHS), 7.07 (dd, 1H, J = 5.5, 3.8 Hz, CHC**H**S), 0.40 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	152.2, 140.9, 137.7, 130.6, 129.2, 128.5, 127.9, 125.4, 125.3, 112.0, 99.2, –0.6.
FTIR (neat) cm^{-1}:	3064 (m), 2960 (s), 2144 (m), 2067 (m), 1537 (m), 1412 (s), 1272 (s), 1253 (s).
HRMS (ESI):	calcd for $C_{16}H_{18}NSSi$ $[M+H]^+$: 284.0924, found: 284.0934.
TLC (20% EtOAc in hexanes), R_f:	0.63 (UV, CAM).

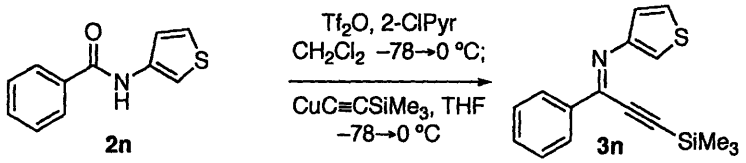


6-Phenyl-thieno[2,3-*b*]pyridine (1m, Table 2, entry 13):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (35 mg, 0.21 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (15 mg, 0.021 mmol, 0.10 equiv) and SPhos (9 mg, 0.021 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **1m** (60 mg, 0.21 mmol, 1 equiv) and toluene (1.1 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (20 % EtOAc in hexanes) to afford the thienopyridine **1m** as a pale yellow solid (44 mg, 99%).[16]

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.15 (d, 1H, J = 8.2 Hz, Ar**H**), 8.11–8.09 (m, 2H, Ar**H**), 7.78 (d, 1H, J = 8.6 Hz, Ar**H**), 7.54–7.49 (m, 3H, Ar**H**, SC**H**), 7.44 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**), 7.30 (d, 1H, J = 5.8 Hz, SCHC**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	162.4, 154.7, 139.4, 131.7, 131.3, 129.1, 129.0, 127.4, 127.2, 121.5, 117.0.
FTIR (neat) cm^{-1}:	3065 (w), 2919 (w), 2850 (w), 1717 (w), 1572 (s), 1557 (s), 1478 (s), 1453 (s), 1425 (s), 1361 (m), 1332 (s), 1260 (m), 1108 (s).
HRMS (ESI):	calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0534, found: 212.0535.
TLC (20% EtOAc in hexanes), R_f:	0.45 (UV, $KMnO_4$).

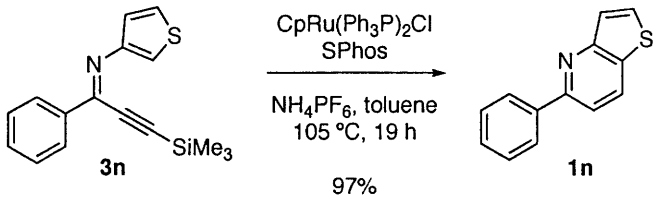
(16) Taylor, E. C.; Macor, J. E. *J. Org. Chem.* **1987**, *52*, 4280.



[1-Phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-thiophen-3-yl-amine (3n, Table 2, entry 14):

Trifluoromethanesulfonic anhydride (294 μL, 1.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2n** (300 mg, 1.48 mmol, 1 equiv) and 2-chloropyridine (559 μL, 5.90 mmol, 4.00 equiv) in CH_2Cl_2 (3.0 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (641 mg, 3.99 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→10% EtOAc in hexanes) to afford the alkynyl imine **3n** as a yellow oil (411 mg, 98%).

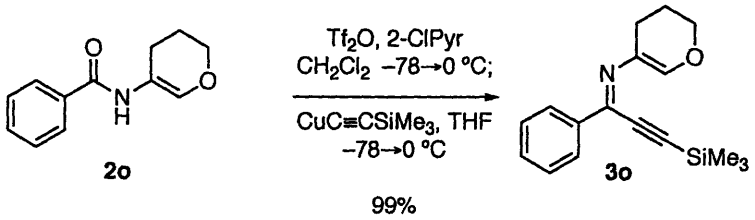
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.17 (dd, 2H, J = 7.6, 1.8 Hz, Ar**H**), 7.50–7.43 (m, 4H, Ar**H**, C**H**S)), 7.38 (d, 1H, J = 5.2 Hz, C**H**S), 7.31 (dd, 1H, J = 5.2, 3.4 Hz, C**H**CHS), 0.29 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	149.9, 147.4, 137.6, 131.0, 128.5, 128.1, 124.9, 124.2, 115.6, 106.1, 98.8, –0.4.
FTIR (neat) cm^{-1}:	3740 (w), 3108 (m), 3063 (m), 2960 (s), 2899 (m), 2147 (m), 1645 (w), 1586 (m), 1556 (s), 1271 (s).
HRMS (ESI):	calcd for $C_{16}H_{18}NSSi$ $[M+H]^+$: 284.0929, found: 284.0933.
TLC (20% EtOAc in hexanes), R_f:	0.74 (UV, $KMnO_4$).



5-Phenyl-thieno[3,2-*b*]pyridine (1n, Table 2, entry 14):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (58 mg, 0.35 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (26 mg, 0.035 mmol, 0.10 equiv) and SPhos (15 mg, 0.035 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3n** (100 mg, 0.35 mmol, 1 equiv) and toluene (1.8 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (15 % EtOAc in hexanes) to afford the thienopyridine **1n** as a pale yellow solid (73 mg, 97%).

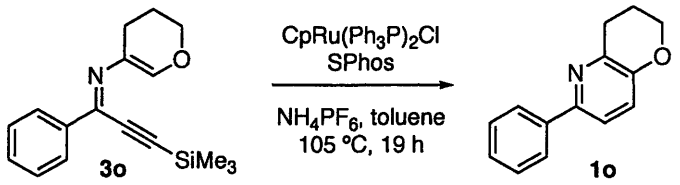
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.26 (d, 1H, J = 8.6 Hz, Ar**H**), 8.08 (d, 1H, J = 7.3 Hz, Ar**H**), 7.78 (d, 1H, J = 5.5 Hz, C**H**S), 7.73 (d, 1H, J = 8.5 Hz, Ar**H**), 7.65 (d, 1H, J = 5.5 Hz, C**H**CHS)), 7.52 (t, 2H, J = 7.0 Hz, Ar**H**), 7.45 (t, 1H, J = 7.3 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	156.4, 155.5, 139.8, 131.7, 131.0, 131.0, 129.0, 128.9, 127.4, 125.5, 116.5.
FTIR (neat) cm^{-1}:	3071 (s), 1906 (w), 1564 (s), 1544 (s), 1397 (s), 1280 (s), 1158 (s).
HRMS (ESI):	calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0534, found: 212.0534.
TLC (20% EtOAc in hexanes), R_f:	0.53 (UV, $KMnO_4$).



(5,6-Dihydro-4*H*-pyran-3-yl)-[1-phenyl-3-(trimethyl-silanyl)-prop-2-ynylidene]-amine (3o, Table 2, entry 15):

Trifluoromethanesulfonic anhydride (292 μL, 1.77 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2o** (300 mg, 1.48 mmol, 1 equiv) and 2-chloropyridine (559 μL, 5.90 mmol, 4.00 equiv) in CH_2Cl_2 (3.0 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (641 mg, 3.99 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to afford the alkynyl imine **3o** as a pale yellow oil (416 mg, 99%).

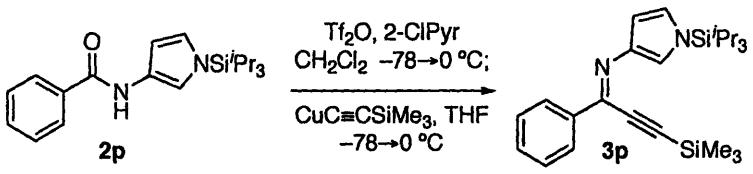
^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ:	8.44–8.40 (m, 2H, Ar**H**), 7.44 (bs, 1H, NC=C**H**O), 7.24–7.20 (m, 2H, Ar**H**), 7.12–7.08 (m, 1H, Ar**H**), 3.58 (t, 2H, J = 5.2 Hz, C**H**$_2$O), 2.80 (t, 2H, J = 6.4 Hz, NCC**H**$_2$), 1.46–1.40 (m, 2H, C**H**$_2$CH$_2$O), 0.14 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, C_6D_6, 20 °C) δ:	149.7, 139.9, 138.2, 134.3, 129.9, 127.9, 103.2, 102.1, 100.5, 66.6, 24.8, 22.5, –0.2.
FTIR (neat) cm^{-1}:	3063 (w), 2960 (m), 2920 (m), 2850 (w), 1783 (w), 1724 (s), 1675 (w), 1251 (s), 1176 (s).
HRMS (ESI):	calcd for $C_{17}H_{22}NOSi$ $[M+H]^+$: 284.1465, found: 284.1471.
TLC (20% EtOAc in hexanes), R_f:	0.67 (UV, $KMnO_4$).



6-Phenyl-3,4-dihydro-2*H*-pyrano[3,2-*b*]pyridine (1o, Table 2, entry 15):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (52 mg, 0.32 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (23 mg, 0.032 mmol, 0.10 equiv) and SPhos (13 mg, 0.032 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3o** (90 mg, 0.32 mmol, 1 equiv) and toluene (1.6 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 19 h, the reaction vessel was allowed to cool to ambient temperature and the mixture was transferred to a recovery flask with a 10-mL portion of dichloromethane. This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (1 % Et_3N/CH_2Cl_2) to afford the dihydropyranopyridine **1o** as a pale yellow solid (47 mg, 70%).

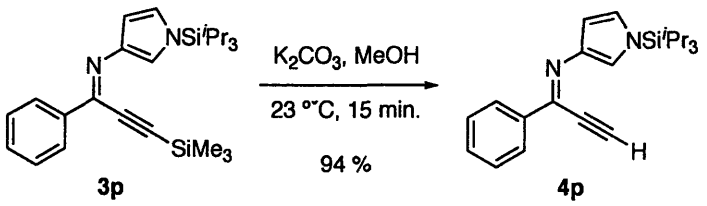
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.92–7.89 (m, 2H, Ar**H**), 7.49–7.47 (m, 1H, Ar**H**), 7.46–7.42 (m, 2H, Ar**H**), 7.35 (tt, 1H, J = 7.3, 1.5 Hz, Ar**H**), 7.16 (d, 1H, J = 8.6, Ar**H**), 4.24 (t, 2H, J = 5.5 Hz, CH_2O), 3.05 (t, 2H, J = 6.6 Hz, $NCCH_2$), 2.19–2.14 (m, 2H, CH_2CH_2O).
^{13}C NMR (125 MHz, C_6D_6, 20°C):	151.5, 149.6, 144.0, 140.3, 129.2, 128.5, 127.1, 124.6, 119.6, 66.6, 29.2, 22.8.
FTIR (neat) cm^{-1}:	3061 (w), 3034 (w), 2949 (m), 2874 (m), 1575 (m), 1471 (s), 1458 (s), 1258 (s).
HRMS (EI):	calcd for $C_{14}H_{13}NO$ $[M]^+$: 211.0992, found: 211.0987.
TLC (20% EtOAc in hexanes), R_f:	0.40 (UV, $KMnO_4$).



N-(N-Triisopropylsilylpyrrol-3-yl)-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne (3p, Table 2, entry 16):

Trifluoromethanesulfonic anhydride (175 μL, 1.05 mmol, 1.20 equiv) was added via syringe over 1 min to a stirred mixture of amide **2p** (300 mg, 0.88 mmol, 1 equiv) and 2-chloropyridine (332 μL, 3.50 mmol, 4.00 equiv) in CH_2Cl_2 (1.8 mL) at –78 °C. After 5 min., the reaction mixture was warmed to 0 °C. After 20 min., the solution was cooled to –78 °C and a freshly prepared solution of copper (I) trimethylysilylacetylide (380 mg, 2.37 mmol, 2.70 equiv) in THF (5.0 mL) at 0 °C was added via cannula. The reaction mixture was kept at –78 °C for 5 min and then warmed to 0 °C. After 10 min., the crude reaction mixture was filtered through celite (2 cm diam. × 3 cm ht.) and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100% hexanes→10% EtOAc in hexanes) to afford the alkynyl imine **3p** as a yellow oil (304 mg, 82%).

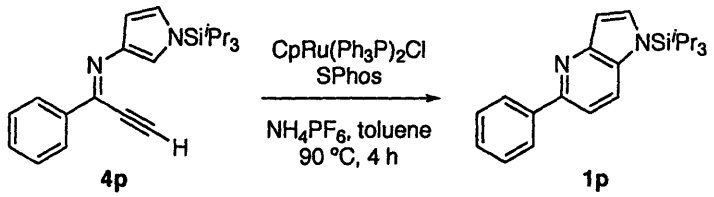
^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ:	8.63–8.60 (m, 2H, Ar**H**), 7.74 (dd, 1H, J = 3.1, 1.2 Hz, C**H**N), 7.50 (dd, 1H, J = 2.4, 1.5 Hz, C**H**N), 7.29–7.24 (m, 2H, Ar**H**), 7.14 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**), 6.73 (dd, 1H, J = 3.1, 2.1 Hz, C**H**CHN), 1.17 (septet, 3H, J = 7.3 Hz, Si(C**H**(CH$_3$)$_2$)$_3$), 0.95 (d, 18, J = 7.3 Hz, Si(CH(C**H**$_3$)$_2$)$_3$), 0.22 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	140.1, 139.2, 138.4, 129.5, 128.3, 127.4, 125.1, 124.4, 105.8, 105.2, 101.0, 18.0, 11.8, –0.2.
FTIR (Neat) cm^{-1}:	2948 (m), 2868 (m), 2141 (w), 1547 (w), 1514 (w), 1488 (m), 1252 (s), 1099 (s).
HRMS (ESI):	calcd for $C_{25}H_{39}N_2Si_2$ $[M+H]^+$: 423.2646, found: 423.2656.
TLC (20% EtOAc in hexanes), R_f:	0.76 (UV, $KMnO_4$).



(1-Phenyl-prop-2-ynylidene)-[1-(triisopropyl-silanyl)-1*H*-pyrrol-3-yl]-amine (4p, Table 2, entry 16):

Anhydrous potassium carbonate (23 mg, 0.17 mmol, 0.2 equiv) was added to a solution of imine **3p** (380 mg, 0.83 mmol, 1 equiv) stirred in methanol (2.8 mL) at 23 °C. After 25 min., the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (7.5 % EtOAc in hexanes) to afford the alkynyl imine **4p** as a yellow solid (274 mg, 94%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.16–8.12 (m, 2H, Ar**H**), 7.44–7.36 (m, 3H, Ar**H**), 7.29 (t, 1H, J = 1.8 Hz, C**H**N), 7.18 (dd, 1H, J = 3.1, 1.2 Hz, CHC**H**N), 6.77 (dd, 1H, J = 2.7, 2.1 Hz, C**H**CHN), 3.69 (s, 1H, C≡C**H**), 1.48 (septet, 3H, J = 7.6 Hz, Si(C**H**$(CH_3)_2)_3$), 1.14 (d, 18H, J = 7.5 Hz, Si(CH(C**H**$_3)_2)_3$).
^{13}C NMR (125 MHz, C_6D_6, 20°C):	139.8, 139.7, 139.4, 130.1, 128.8, 128.0, 125.4, 124.6, 107.2, 86.7, 80.4, 18.1, 12.0.
FTIR (neat) cm^{-1}:	3296 (m, C≡C–H), 2947 (s), 2868 (s), 2088 (w, C≡C), 1547 (w), 1488 (s), 1098 (s).
HRMS (ESI):	calcd for $C_{22}H_{31}N_2Si$ [M+H]: 351.2251, found: 351.2264.
TLC (30% EtOAc in hexanes), R_f:	0.83 (UV, $KMnO_4$).

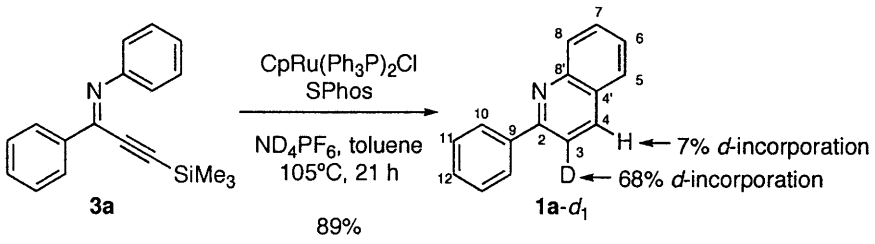


5-Phenyl-1-(triisopropyl-silanyl)-1*H*-pyrrolo[3,2-*b*]pyridine (1p, Table 2, entry 16):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate (33 mg, 0.20 mmol, 1.0 equiv), CpRu(PPh$_3$)$_2$Cl (7.3 mg, 0.01 mmol, 0.05 equiv)[17] and SPhos (4.1 mg, 0.01 mmol, 0.05 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Imine **3p** (70 mg, 0.20 mmol, 1 equiv) and toluene (1.0 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 90 °C. After 4 h, the reaction vessel was allowed to cool to ambient temperature and was diluted with dichloromethane (3 mL). This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on basic alumina (15 % EtOAc in hexanes) to afford the azaindole **1p** as a pale brown solid (46 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.46–8.42 (m, 2H, Ar**H**), 7.58 (dd, 1H, J = 8.7, 0.9 Hz, Ar**H**), 7.53 (d, 1H, J = 8.5 Hz, Ar**H**), 7.39–7.34 (m, 2H, Ar**H**), 7.22 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**), 7.14 (d, 1H, J = 3.4 Hz, NCHC**H**C), 7.11 (dd, 1H, J = 3.4, 0.6 Hz, NC**H**CHC), 1.32 (septet, 3H, J = 7.6 Hz, Si(C**H**(CH$_3$)$_2$)$_3$), 0.93 (d, 18H, J = 7.6 Hz, Si(CH(C**H**$_3$)$_2$)$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	151.9, 151.4, 141.8, 135.5, 133.3, 129.2, 128.5, 127.8, 121.3, 114.5, 107.8, 18.3, 13.0.
FTIR (neat) cm^{-1}:	3062 (w), 2948 (m), 2868 (m), 1561 (w), 1510 (w), 1465 (m), 1407 (s), 1138 (m).
HRMS (ESI):	calcd for $C_{22}H_{31}N_2Si$ [M+H]: 351.2251, found: 351.2245.
TLC (20% EtOAc in hexanes), R_f:	0.58 (UV, $KMnO_4$).

[17] Use of higher catalyst loadings led to more *N*-desilylation of the product without improvement in yield of **1p**.



3-Deutero-2-phenylquinoline (1a-d_1, Equation 4):

An oven-dried pressure vessel containing a magnetic stir bar was charged with ammonium hexafluorophosphate-d_4 (42 mg, 0.25 mmol, 1.0 equiv), $CpRu(PPh_3)_2Cl$ (18 mg, 0.025 mmol, 0.10 equiv) and SPhos (10 mg, 0.025 mmol, 0.10 equiv) under a nitrogen atmosphere in a glovebox and the flask sealed and brought out of the glovebox. Freshly distilled benzene (2 × 3 mL) was added to the pressure vessel and subsequently removed in vacuo. Imine **3a** (70 mg, 0.25 mmol, 1 equiv) and toluene (1.3 mL) were subsequently added via syringe. The flask was flushed with argon, sealed, stirred, and placed in an oil bath at 105 °C. After 21 h, the reaction vessel was allowed to cool to ambient temperature and was diluted with dichloromethane (5 mL). This solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (5 % EtOAc in hexanes) to afford the quinoline **1a**-d_1 as a pale yellow solid (46 mg, 89%). ^1H and ^{13}C NMR analysis indicates the presence of **1a**-C3-H^2, **1a**-C4-H^2, and **1a** in a ratio of 68 : 7 : 25.

^1H NMR (500 MHz, $CDCl_3$, 20 °C; resonances corresponding to the C3-H^2 noted by *) δ:8.25 (d, 1H, J = 8.2 Hz, C4-H*), 8.24 (s, 1H, C4-H), 8.21–8.16 (m, 6H, C8-H, C8-H*, C10-H, C10-H*), 7.91 (d, 1H, J = 8.6 Hz, C3-H), 7.85 (dd, 1H, J = 8.2, 1.2 Hz, C5-H, C5-H*), 7.74 (ddd, 1H, J = 8.2, 6.7, 1.2 Hz, C7-H, C7-H*), 7.57–7.52 (m, 6H, C6-H*, C6-H, C11-H, C11-H*), 7.48 (tt, 1H, J = 7.6, 1.2 Hz, C12-H, C12-H*).

^{13}C NMR (125 MHz, $CDCl_3$, 20 °C; resonances corresponding to the C3-H^2 noted by *) δ:157.5 (C2), 157.4 (C2*), 148.5 (C8'), 148.4 (C8'*), 139.9 (C9), 139.8 (C9*), 136.9 (C4*), 136.8 (C4), 129.9 (C7, C7*), 129.8 (C8, C8*), 129.5 (C12, C12*), 129.0 (C11, C11*), 127.7 (C10, C10*), 127.6 (C5, C5*), 127.3 ((4', 4'*), 126.4 (6, 6*), 119.1 (C3), 119.0 (t, J = 21 Hz, C3*).

FTIR ($CDCl_3$) cm^{-1}: 3056 (m), 2918 (w), 2248 (w, C–D), 1962 (w), 1616 (m), 1589 (s), 1552 (s), 1589 (s), 1490 (s).

HRMS (ESI): calcd for $C_{15}H_{11}DN$ [M+H]: 207.1027, found: 207.1036.

TLC (20% EtOAc in hexanes), R_f: 0.51 (UV, CAM).

Chapter II

Single-Step Synthesis of Pyrimidine Derivatives

Introduction and Background

Azaheterocycles constitute a very important class of compounds. In particular, pyrimidine derivatives include a large number of natural products, pharmaceuticals, and functional materials (Figure 1).[1] Several examples of pharmaceutically important compounds include trimethoprim,[2] sulfadiazine,[3] Gleevec (imatinib mesilate),[4] and Xeloda (capecitabine).[5] Natural and unnatural polymers also contain pyrimidine derivatives.[1,6] While development of important methodologies for the synthesis of pyrimidines enjoys a rich history, the discovery of new strategies for the convergent synthesis of pyrimidines remains a vibrant area of chemical research.

In nature, the pyrimidine ring is synthesized from glutamine, bicarbonate, and aspartate.[1b] These starting materials are converted to orotate (Figure 1), a ribonucleotide biosynthetic precursor, in four enzymatic reactions. In this sequence, carbamoyl phophate synthetase II transforms glutamine, ATP, and bicarbonate to carbamoyl phosphate. Subsequent condensation of carbamoyl phosphate with aspartate is catalyzed by aspartate transcarbamoylase, affording carbamoyl aspartate. Dihydroorotase promoted dehydration followed by oxidation with dihydroorotate dehydrogenase affords the ribonucleotide precursor, orotate.

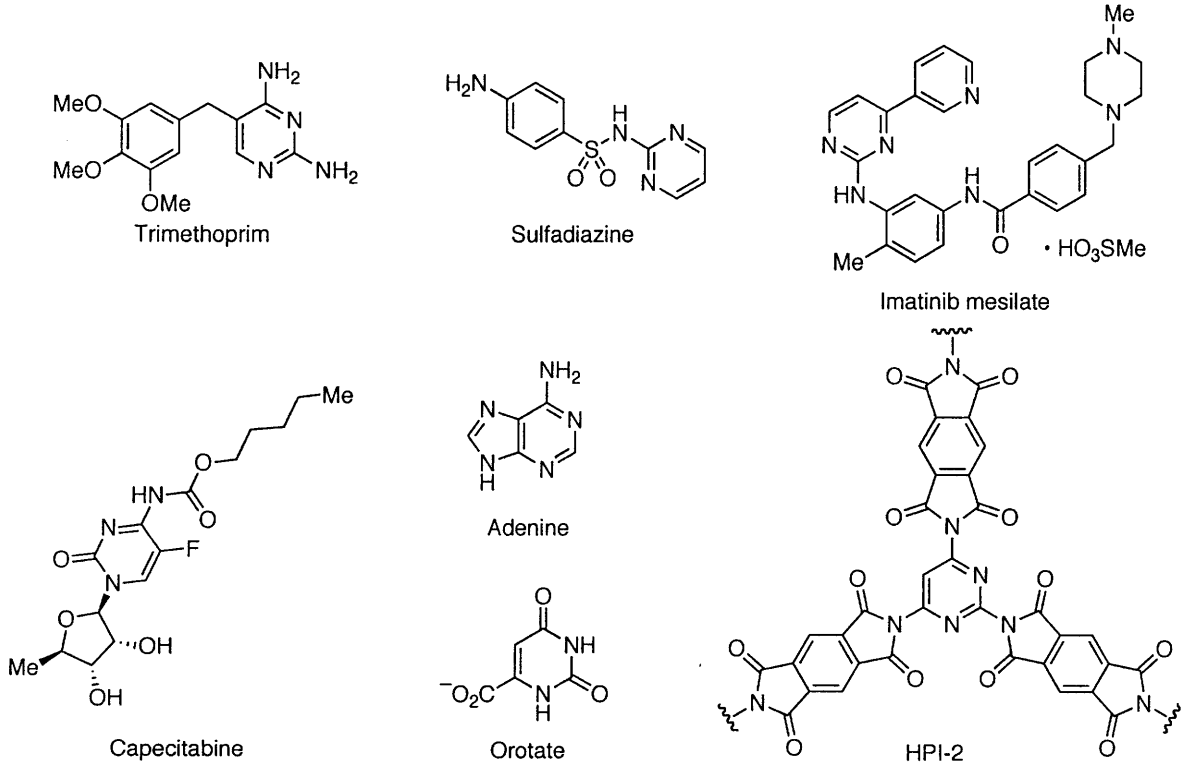
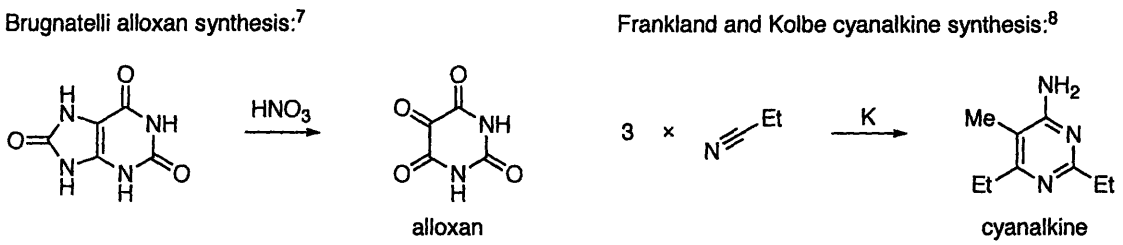


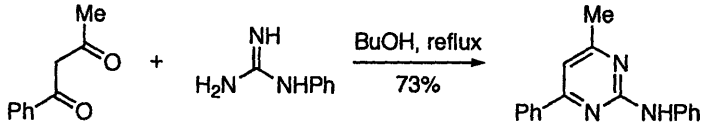
Figure 1. Representative compounds containing a pyrimidine substructure.

In 1818, Brugnatelli synthesized the first pyrimidine derivative, alloxan, by nitric acid oxidative degradation of uric acid (Scheme 1).[7] Another early report, by Frankland and Kolbe in 1848, described the first synthesis of cyanalkine by heating propionitrile with potassium metal (Scheme 1).[8] Gabriel and Colman first isolated pyrimidine in 1899 by decarboxylation of pyrimidine-4-carboxylic acid.[9] Since these early reports many important contributions describing a variety of synthetic strategies for preparation of pyrimidine derivatives have been published.

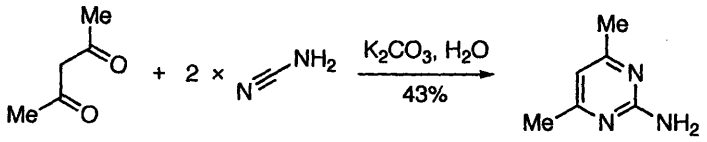
Many of these prevailing strategies rely on condensation of N–C–N fragments, most often amidines or guanidines, with 1,3-dicarbonyl derivatives (Scheme 2).[1,10] Another versatile approach to pyrimidine synthesis utilizes N–C fragments. Nitriles are a common N–C source and have been used to form pyrimidines in many syntheses. Cyanamide is a particularly useful nitrile derivative in the synthesis of pyrimidines as illustrated in Scheme 3.[11]



Scheme 1. Early reports on the synthesis of pyrimidine derivatives.



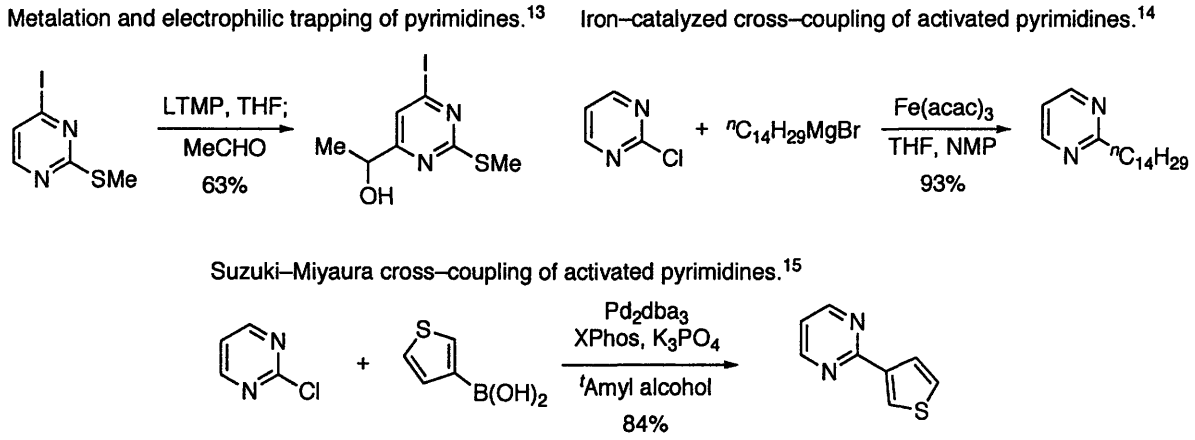
Scheme 2. Representative synthesis of a pyrimidine by condensation of a N–C–N fragment and a diketone.[10]



Scheme 3. Representative use of cyanamide in condensation with acetoacetone for the synthesis of a pyrimidine.[11]

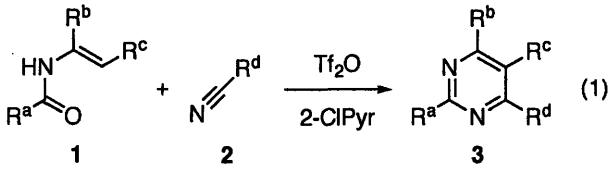
With advances in cross-coupling chemistry, substituent modification of existing pyrimidine derivatives has recently gained considerable attention. Several reviews are available that describe advances in this important synthetic approach to pyrimidine derivatives.[12] Many of these procedures rely on inherent reactivity associated with the pyrimidine core (Scheme 4).[12,13]

Additionally, activated heterocycle cross-coupling has become particularly important with recent advances (Scheme 4).[12,14,15]



Scheme 4. Representative derivatization reactions for synthesis of pyrimidine derivatives.

Due to the importance of pyrimidines, our group is interested in new methodologies for their synthesis. Herein is reported a mild, convergent, and single-step procedure for the conversion of readily available *N*-vinyl and *N*-aryl amides[16] to the corresponding substituted pyrimidines and quinazolines, respectively (eq 1).



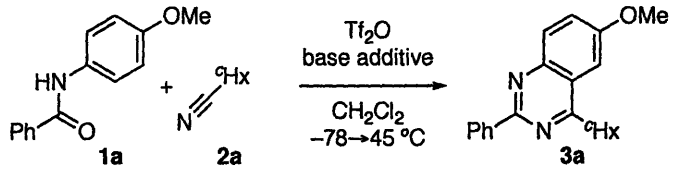
Results and Discussion

We recently reported a mild procedure for electrophilic activation of sensitive amides en route to pyridine derivatives.[17,18] We recognized the unique reactivity associated with electrophilic activation of amides using 2-chloropyridine (2-ClPyr)[19] in combination with trifluoromethanesulfonic anhydride (Tf_2O).[20] The current study concerns trapping of highly activated amide derivatives with weakly nucleophilic nitriles to directly provide the corresponding pyrimidine derivatives (eq 1).

Benzamide **1a** and cyclohexanecarbonitrile (**2a**) were used to identify the optimum reagent combination (Table 1). The use of 2-ClPyr and Tf_2O allowed direct conversion of

benzamide **1a** to the corresponding quinazoline **3a** (Table 1, entry 7).[21] Other base additives largely returned the starting amide **1a** after aqueous work-up. Superstoichiometric quantitites of 2-chloropyridine were found to have an inhibitory effect (Table 1, entry 8), perhaps by competing with the addition of the weakly nucleophilic nitrile **2a** (vide infra). Under optimal conditions, the addition of Tf_2O (1.1 equiv) to a cold solution of amide **1a** (1 equiv), nitrile **2a** (1.1 equiv), and 2-ClPyr (1.2 equiv) in dichloromethane followed by warming afforded the desired quinazoline **3a** in 88-90% isolated yield.

Table 1. Base additive screen.



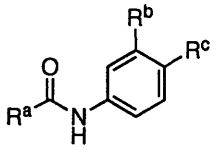
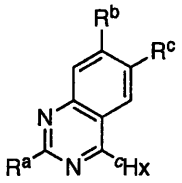
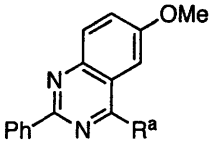
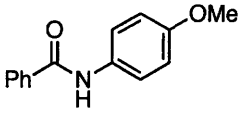
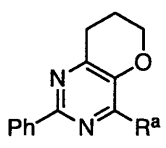
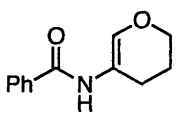
Entry	Base Additive	Equiv	Isolated Yield (%)[a]
1	none	0	29
2	Et_3N	1.2	0
3	$^iPr_2NEt$	1.2	14
4	pyridine	1.2	26
5	2,6-lutidine	1.2	28
6	2,4,6-collidine	1.2	19
7	ethyl nicotinate	1.2	59
8	3-bromopyridine	1.2	54
9	2-bromopyridine	1.2	63
10	2-chloropyridine	1.0	72
11	***2-chloropyridine***	***1.2***	***90***
12	2-chloropyridine	3.0	81

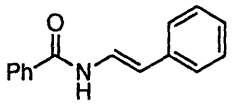
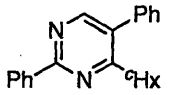
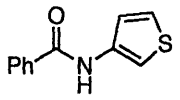
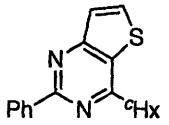
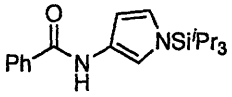
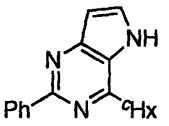
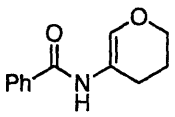
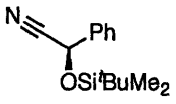
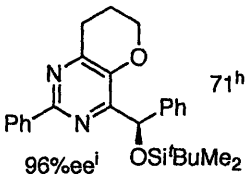
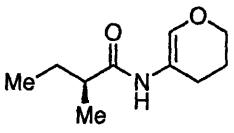
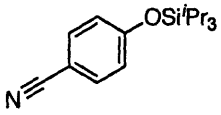
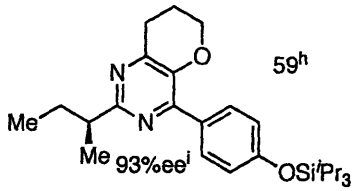
[a] Tf_2O (1.1 equiv), ^{c}HxCN (**2a**, 1.1 equiv), 45 °C, 16 h.

We next explored the substrate scope with a variety of secondary amides and nitriles (Table 2). While electron rich *N*-vinyl and *N*-aryl amides proceeded to afford the corresponding pyrimidine derivatives at ambient temperatures (Table 2, condition A), less reactive electron deficient substrates required heating (Table 2, conditions B and C). Electron donating and electron withdrawing substituents were tolerated in *N*-aryl benzamide derivatives (Table 2, entries 1-9). A wide range of nitriles, including electron rich and electron deficient benzonitriles in addition to saturated and unsaturated nitriles (Table 2, entries 10-16) were compatible with this chemistry. A variety of sensitive *N*-vinyl amides (Table 2, entries 14-21) served as

substrates, giving the corresponding pyrimidine derivatives. Significantly, the use of epimerizable substrates (Table 2, entries 20 and 21) provided the corresponding pyrimidine derivatives without loss in optical activity. For the most reactive substrates, the introduction of the nitrile prior to the low temperature activation of the secondary amide is essential for optimum results (Table 2, entry 18).[22] In the case of highly reactive amides, excess nitrile was found to increase the yield of the desired pyrimidine product (Table 2, entry 17).

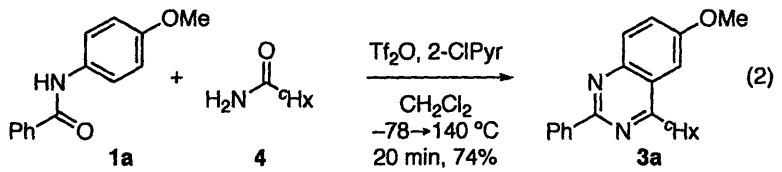
Table 2.[a] Substrate scope for single-step pyrimidine synthesis.

Entry	Amide	Nitrile	Conditions	Product	Yield (%)[b]
					
	R^a R^b R^c				
1	Ph H OMe		B		89
2	Ph H H		B		71
3	Ph CF_3 H		C		61
4	4-MeOPh H OMe		B[c]		87
5	4-NO_2Ph H OMe		C		69
6	^{t}Bu H OMe		C		81
7	^{c}Hx H OMe		C		73
8	$N(CH_2CH_2)_2O$ H H		C		80
9	cyclohex-1-enyl H OMe		B		88[d]
					
10		R^a = 4-NO_2Ph	C		86
11		R^a = 4-MeOPh	C		88
12		R^a = 4-(CO_2Et)Ph	C		74
13		R^a = (*E*)-C_6H_4CH=CH	C		68
					
14		R^a = ^{c}Hx	A		92
15		R^a = ^{t}Bu	A		94 (88)[e]
16		R^a = $(CH_2)_3C{\equiv}CH$	A		77

17			B[f]		70 (89)[d]
18			A		86
19			A		70[g]
20			B[f]		71[h]
21			B[f]		59[h]

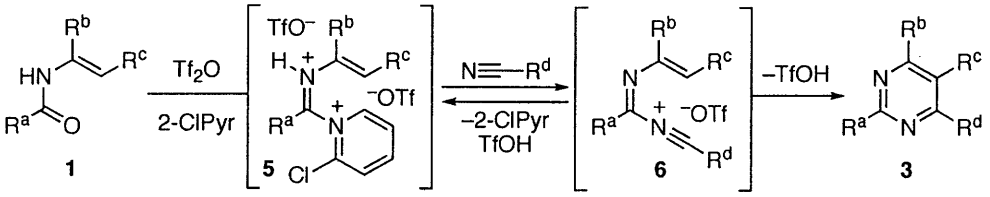
[a] Uniform conditions unless otherwise noted. Tf_2O (1.1 equiv), 2-ClPyr (1.2 equiv), nitrile (1.1 equiv), CH_2Cl_2, heating: A = 23 °C, 1h; B = 45 °C, 16h; C = microwave, 140 °C, 20min. [b] Average of two experiments. [c] 18h. [d] 5 equiv of nitrile. [e] Gram-scale reaction. [f] 1h. [g] TBAF (1 equiv) used to desilylate the product. [h] 3 equiv of nitrile. [i] E.e. determined by chiral HPLC analysis of a derivative.

The dehydration of primary amides to the corresponding nitriles using Tf_2O and triethylamine has been reported.[23] Under optimum conditions, treatment of a solution of secondary amide **1a** (1 equiv), primary amide **4** (1.1 equiv), and 2-ClPyr (2.6 equiv) with Tf_2O (2.3 equiv) at –78 °C followed by microwave heating for 20 min., directly gave quinazoline **3a** in 74% yield (eq 2).[24] The ready availability of primary amides and their use as nitrile surrogates adds to the utility of this chemistry.



(2)

As illustrated in Scheme 5, amide activation and addition of 2-ClPyr to a protonated imidoyl triflate is envisioned to give the highly electrophilic 2-chloropyridinium adduct **5**. In contrast to pyridine, 2-ClPyr was found not to add to Tf_2O.[17,25] Monitoring of the reaction in entry 1 of Table 2 by ^{19}F NMR spectroscopy revealed the presence of trifluoromethanesulfonate (–79.6 ppm, CD_2Cl_2) throughout the reaction, without involvement of a persistent imidoyl triflate. In situ ^{13}C NMR monitoring of the amide activation using **1a**-^{13}C=O (166.0 ppm, CD_2Cl_2) led to observation of a new broad resonance (149.8 ppm, CD_2Cl_2) prior to addition of the nitrile. React-IR monitoring during activation of amide **1a** with Tf_2O in the absence of nitrile **2a** revealed the consumption of 2-ClPyr (1580 cm^{-1}) with concomitant appearance of a new absorption band (1600 cm^{-1}). Introduction of the nitrile **2a** to this mixture led to loss of this absorption band and simultaneous release of 2-chloropyridinium trifluoromethane-sulfonate (1620 cm^{-1}) and the trifluoromethanesulfonate salt of the desired product **3a** (1575 cm^{-1}).[25] The broad ^1H, ^{13}C, and ^{19}F NMR resonances observed for the activated intermediate prior to addition of the nitrile suggests equilibration of **5** with the corresponding triflate adduct.[25] Reversible addition of nitrile[26] and expulsion of 2-ClPyr•HOTf to provide the nitrilium ion **6** is expected to occur en route to pyrimidine derivative **3**.[27] The inhibitory effect of more nucleophilic base additives and excess 2-ClPyr in addition to the benefit of superstoichiometric quantities of nitrile are consistent with the proposed mechanism.



Scheme 5. Proposed mechanism for dehydrative cyclization and formation of pyrimidine derivatives.

Conclusion

We describe a single-step and convergent procedure for the synthesis of pyrimidine derivatives. This chemistry is compatible with a wide range of secondary amides and nitriles, and allows for unique transformations including that in equation 2. This methodology not only alleviates the need for isolation of activated amide derivatives but also does not require the use of stoichiometric Lewis acids.[21] The compatibility of this chemistry with epimerizable substrates is

noteworthy and offers a valuable addendum to methodology for azaheterocycle synthesis.[28] Future work in this area includes synthesis of densely heteroatom-substituted pyrimidine derivatives and more challenging substrates.

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(1) (a) Undheim, K.; Benneche, T. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V.; McKillop, A. Eds; Pergamon: Oxford, 1996; Vol. 6; p 93. b) Lagoja, I. M. *Chem. & Biodiversity* **2005**, *2*, 1. c) Michael, J. P. *Nat. Prod. Rep.* **2005**, *22*, 627. d) Joule, J. A.; Mills, K. In *Heterocyclic Chemistry*, 4th ed.; Blackwell Science Ltd.: Cambridge, MA, 2000; p 194. e) Erian, A. W. *Chem. Rev.* **1993**, *93*, 1991.

(2) Joffe, A. M.; Farley, J. D.; Linden, D.; Goldsand, G. *Am. J. Med.* **1989**, *87*, 332.

(3) Petersen, E.; Schmidt, D. R. *Expert Rev. Anti-infective Ther.* **2003**, *1*, 175.

(4) Nadal, E.; Olavarria, E. *Int. J. Clin. Pract.* **2004**, *58*, 511.

(5) Blum, J. L. *Oncologist* **2001**, *6*, 56.

(6) (a) Köytepe, S.; Pasahan, A.; Ekinci, E.; Seçkin, T. *Eur. Polym. J.* **2005**, *41*, 121. (b) Gompper, R.; Mair, H-J.; Polborn, K. *Synthesis* **1997**, 696. (c) Kanbara, T.; Kushida, T.; Saito, N.; Kuwajima, I.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1992**, 583.

(7) (a) Brugnatelli, G. *Giornale di fisica, chimica, et storia Naturale (Pavia) decada seconda* **1818**, *1*, 117; (b) Brugnatelli, G. *Ann. Chim. Phys.* **1818**, *8*, 201.

(8) Frankland, E.; Kolbe, H. *Justis Liebigs Ann. Chem.* **1848**, *65*, 269.

(9) Gabriel, S.; Colman, J. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 1525.

(10) Wendelin, W.; Schermanz, K.; Schweiger, K.; Fuchsgruber, A. *Monatsh. Chem.* **1983**, *114*, 1371.

(11) Miller, A. *J. Org. Chem.* **1984**, *49*, 4072.

(12) (a) Chinchilla, R.; Nájera, R.; Yus, M. *Chem. Rev.* **2004**, *104*, 2667. (b) Turck, A.; Plé, N.; Mongin, F.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 4489.

(13) Plé, N.; Turck, A.; Heynderickx, A.; Quéguiner, G. *Tetrahedron* **1998**, *54*, 9701.

(14) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.

(15) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358.

(16) (a) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (b) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience; New York, 2002; p. 1051. (c) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (d) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.

(17) Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 4592.

(18) For elegant studies on the activation of amides using Tf_2O and pyridine, see: (a) Charette, A. B.; Grenon, M. *Can. J. Chem.* **2001**, *79*, 1694. (b) Charette, A. B.; Mathieu, S.; Martel, J. *Org. Lett.* **2005**, *7*, 5401.

(19) (a) Myers, A. G.; Tom, N. J.; Fraley, M. E.; Cohen, S. B.; Madar, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 6072. (b) Garcia, B. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2000**, *122*, 4269.

(20) Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 3077.

(21) For quinazoline syntheses requiring stoichiometric activation (with $TiCl_4$, $AlCl_3$ or $SnCl_4$) of imidoyl chloride derivatives, see: (a) Zielinski, W.; Kudelko, A. *Monatsh. Chem.* **2000**, *131*, 895. (b) Kofanov, E. R.; Sosnina, V. V. Danilova, A. S.; Korolev, P. V. *Zh. Prik. Khim.* **1999**, *72*, 813. (c) Madroñero, R.; Vega, S. *Synthesis* **1987**, 628.

(22) Absence of nitrile during activation of the amide substrate in entry 18 of Table 2 gave the desired product in diminished isolated yield (62%).

(23) Bose, D. S.; Jayalakshmi, B. *Synthesis* **1999**, 64.

(24) The complete formation of nitrile **2a** by treatment of amide **4** with Tf_2O and 2-ClPyr under the reaction conditions was confirmed independently.

(25) See Experimental Section for details.

(26) For an example of similar reactivity, the Ritter Reaction, see: (a) Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045. (b) Ritter, J. J.; Kalish, J. *J. Am. Chem. Soc.* **1948**, *70*, 4048. For a review, see: Krimen, L. I.; Cota, D. J. *Org. React.* **1969**, *17*, 213.

(27) The conversion of **6** to **3** may be facilitated by net addition of 2-chloropyridinium triflate across the nitrilium ion.

(28) Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 14254.

Experimental Section

General Procedures. All previously unnumbered compounds are numbered in order of appearance beginning with "S." All reactions were performed in oven-dried or flame-dried round bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure.[2] 2-chloropyridine was distilled from calcium hydride and stored sealed under an argon atmosphere. The starting amides were prepared by acylation of the corresponding anilines[3] or via previously reported copper–catalyzed C–N bond–forming reactions.[4,5]

Instrumentation. All reaction conducted at 140 °C were performed in a CEM Discover Lab Mate microwave reactor. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, C_6HD_5: δ 7.16, $CHDCl_2$: δ 5.32). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

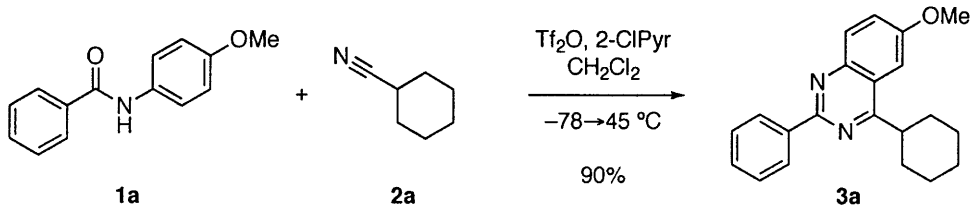
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(3) For a general procedure, see: DeRuiter, J.; Swearingen, B. E.; Wandrekar, V.; Mayfield, C. A. *J. Med. Chem.* **1989**, *32*, 1033.

(4) For the general procedure used for the synthesis of all *N*-vinyl amides, see: Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667.

(5) For related reports, see: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (c) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (d) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (e) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.

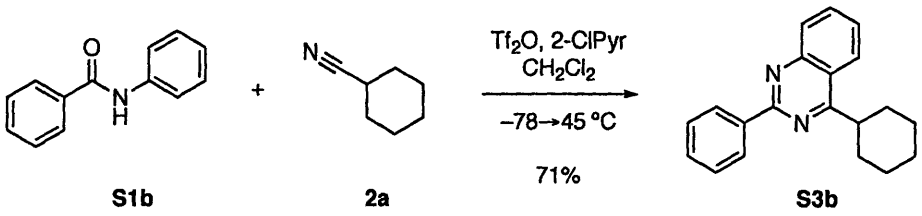
solvent ($CDCl_3$: δ 77.2, benzene-d_6: δ 128.0, DMF-d_7: δ 163.2, CD_2Cl_2: δ 54.0). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Fluorine-19 nuclear magnetic resonance spectra were recorded with a Varian 300 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the fluorine resonances of trifluoroacetic acid (CD_2Cl_2: δ –76.6). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, quint = quintet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. In situ IR reaction monitoring was performed on an ASI ReactIR 1000 spectrometer. Chiral HPLC analysis was performed on an Agilent 1100 Series HPLC with a Chiralpak AD-H column. We thank Dr. Li Li at the Massachusettes Institute of Technology Department of Chemistry instrumentation facility for obtaining mass spectroscopic data.



4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (3a, Table 2, entry 1):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (61 mg, 0.56 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 16 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 7.5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **3a** as a white solid (145 mg, 90%).

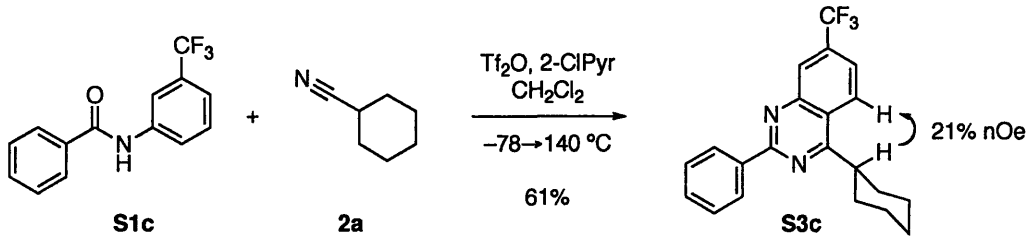
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.67–8.63 (m, 2H, Ar**H**), 8.02 (d, 1H, J = 9.1 Hz, Ar**H**), 7.56–7.46 (m, 4H, Ar**H**), 7.37 (d, 1H, J = 2.6 Hz, Ar**H**), 4.00 (s, 3H, OCH_3), 3.49 (tt, 1H, J = 11.1, 3.3 Hz, $^cC_6H_{11}$), 2.09–1.84 (m, 7H, $^cC_6H_{11}$), 1.64–1.52 (m, 2H, $^cC_6H_{11}$), 1.45 (qt, 1H, J = 12.7, 2.8 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	173.0, 158.6, 157.9, 147.2, 139.0, 131.3, 130.1, 128.6, 128.4, 125.4, 122.6, 102.3, 55.9, 41.7, 32.1, 26.8, 26.4.
FTIR (neat) cm^{-1}:	3064 (w), 2931 (m), 2852 (w), 1622 (w), 1567 (w), 1546 (s), 1222 (s).
HRMS (ESI):	calcd for $C_{21}H_{23}N_2O$ $[M+H]^+$: 319.1810, found: 319.1807.
TLC (15% EtOAc in hexanes), R_f:	0.50 (UV, CAM).



4-Cyclohexyl-2-phenyl-quinazoline (S3b, Table 2, entry 2):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1b** (100 mg, 0.507 mmol, 1 equiv) and 2-chloropyridine (57 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (61 mg, 0.56 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 16 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3b** as a white solid (104 mg, 71%).

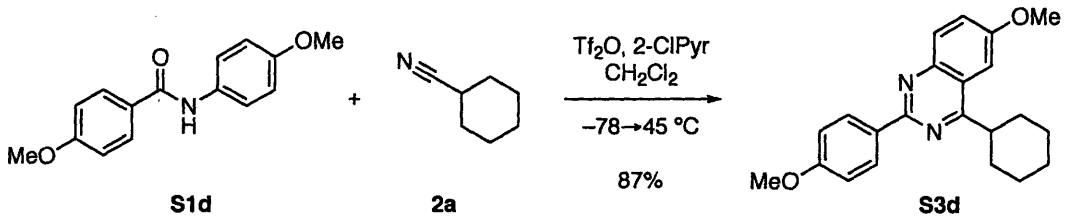
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.72–8.67 (m, 2H, Ar**H**), 8.18 (dd, 1H, J = 8.3, 1.3 Hz, Ar**H**), 8.10 (dd, 1H, J = 8.5, 1.3 Hz, Ar**H**), 7.86 (ddd, 1H, J = 8.3, 6.9, 1.3 Hz, Ar**H**), 7.61–7.48 (m, 4H, Ar**H**), 3.60 (tt, 1H, J = 11.2, 3.4 Hz, ^{c}C$_6$**H**$_{11}$), 2.09–1.84 (m, 7H, ^{c}C$_6$**H**$_{11}$), 1.62–1.52 (m, 2H, ^{c}C$_6$**H**$_{11}$), 1.45 (qt, 1H, J = 12.8, 3.0 Hz, ^{c}C$_6$**H**$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	174.9, 160.2, 151.2, 138.9, 133.3, 130.5, 129.8, 128.8, 128.7, 126.8, 124.3, 121.9, 41.7, 32.3, 26.8, 26.4.
FTIR (neat) cm^{-1}:	3066 (w), 2933 (s), 2852 (s), 1615 (m), 1570 (s), 1546 (s), 1497 (s), 1344 (s), 1027 (m).
HRMS (ESI):	calcd for $C_{20}H_{21}N_2$ $[M+H]^+$: 289.1705, found: 289.1704.
TLC (15% EtOAc in hexanes), R_f:	0.56 (UV, CAM).



4-Cyclohexyl-2-phenyl-7-trifluoromethyl-quinazoline (S3c, Table 2, entry 3):

Trifluoromethanesulfonic anhydride (82 μL, 0.50 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1c** (120 mg, 0.450 mmol, 1 equiv) and 2-chloropyridine (51 μL, 0.54 mmol, 1.2 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (54 mg, 0.50 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3c** as a white solid (97 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.72–8.69 (m, 2H, Ar**H**), 8.40 (s, 1H, Ar**H**), 8.29 (d, 1H, J = 8.7 Hz, Ar**H**), 7.74 (d, 1H, J = 8.7 Hz, Ar**H**), 7.59–7.54 (m, 3H, Ar**H**), 3.60 (tt, 1H, J = 11.4, 3.4 Hz, ^{c}C$_6$**H**$_{11}$), 2.10–1.86 (m, 7H, ^{c}C$_6$**H**$_{11}$), 1.64–1.53 (m, 2H, ^{c}C$_6$**H**$_{11}$), 1.45 (qt, 1H, J = 12.7, 3.0 Hz, ^{c}C$_6$**H**$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	175.4, 161.3, 150.6, 138.1, 134.8 (q, J = 33 Hz), 131.1, 131.0, 128.9, 128.8, 127.7 (q, J = 4.3 Hz), 125.7, 123.8 (q, J = 271 Hz), 123.1, 122.3 (q, J = 4.1 hz), 42.0, 32.3, 26.7, 26.3.
FTIR (neat) cm^{-1}:	2929 (s), 2857 (m), 1575 (s), 1549 (s), 1499 (m), 1344 (s), 1126 (s).
HRMS (ESI):	calcd for $C_{21}H_{20}F_3N_2$ $[M+H]^+$: 357.1579, found: 357.1587.
TLC (20% EtOAc in hexanes), R_f:	0.74 (UV, CAM).

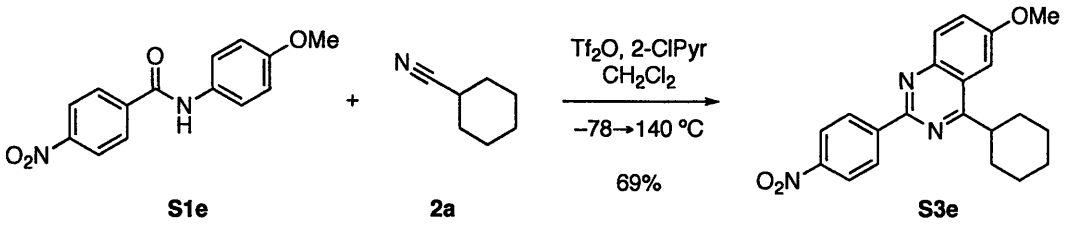


S1d **2a** **S3d**

4-Cyclohexyl-6-methoxy-2-(4-methoxy-phenyl)-quinazoline (S3d, Table 2, entry 4):

Trifluoromethanesulfonic anhydride (71 μL, 0.43 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1d** (100 mg, 0.389 mmol, 1 equiv) and 2-chloropyridine (44 μL, 0.47 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (47 mg, 0.43 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 18 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3d** as a white solid (118 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.62–8.58 (m, 2H, Ar**H**), 7.97 (d, 1H, J = 9.1 Hz, Ar**H**), 7.50 (dd, 1H, J = 9.1, 2.7 Hz, Ar**H**), 7.35 (d, 1H, J = 2.7 Hz, Ar**H**), 7.06–7.03 (m, 2H, Ar**H**), 3.99 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.46 (tt, 1H, J = 11.2, 3.2 Hz, $^cC_6H_{11}$), 2.08–1.84 (m, 7H, $^cC_6H_{11}$), 1.62–1.51 (m, 2H, $^cC_6H_{11}$), 1.45 (qt, 1H, J = 12.7, 3.2 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	172.9, 161.4, 158.4, 157.6, 147.2, 131.7, 131.0, 129.9, 125.3, 122.2, 113.9, 102.4, 55.8, 55.5, 41.7, 32.0, 26.8, 26.4.
FTIR (neat) cm^{-1}:	3001 (w), 2932 (s), 2852 (w), 1623 (m), 1545 (s), 1515 (s), 1250 (s), 1223 (s), 1167(s).
HRMS (ESI):	calcd for $C_{22}H_{25}N_2O_2$ $[M+H]^+$: 349.1916, found: 349.1913.
TLC (20% EtOAc in hexanes), R_f:	0.45 (UV, CAM).

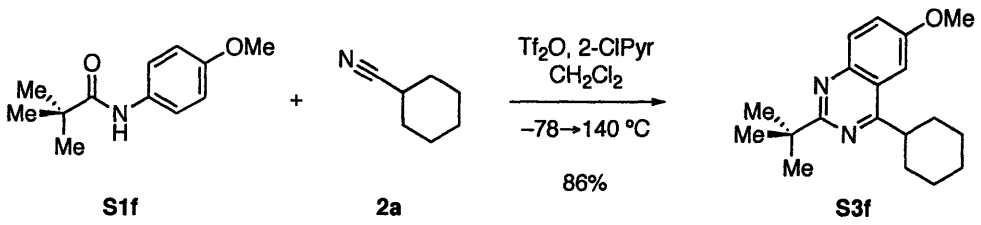


S1e **2a** **S3e**

4-Cyclohexyl-6-methoxy-2-(4-nitro-phenyl)-quinazoline (S3e, Table 2, entry 5):

Trifluoromethanesulfonic anhydride (80 μL, 0.49 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1e** (120 mg, 0.440 mmol, 1 equiv) and 2-chloropyridine (50 μL, 0.53 mmol, 1.2 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (53 mg, 0.49 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3e** as a yellow solid (111 mg, 69%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.84–8.81 (m, 2H, Ar**H**), 8.38–8.35 (m, 2H, Ar**H**), 8.05 (d, 1H, J = 9.1 Hz, Ar**H**), 7.57 (dd, 1H, J = 9.1, 2.6 Hz, Ar**H**), 7.39 (d, 1H, J = 2.7 Hz, Ar**H**), 4.02 (s, 3H, O**CH**$_3$), 3.51 (tt, 1H, J = 11.4, 3.4 Hz, ^{c}C$_6$**H**$_{11}$), 2.09–1.86 (m, 7H, ^{c}C$_6$**H**$_{11}$), 1.64–1.53 (m, 2H, ^{c}C$_6$**H**$_{11}$), 1.46 (qt, 1H, J = 12.5, 3.1 Hz, ^{c}C$_6$**H**$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	173.5, 158.8, 156.2, 148.9, 147.0, 144.9, 131.5, 129.1, 126.1, 123.8, 123.1, 102.3, 56.0, 41.8, 32.1, 26.7, 26.3.
FTIR (neat) cm^{-1}:	2929 (s), 2851 (m), 1621 (w), 1595 (w), 1544 (m), 1512 (s), 1339 (s), 1256 (m), 1223 (m).
HRMS (ESI):	calcd for $C_{21}H_{21}N_3NaO_3$ $[M+Na]^+$: 386.1481, found: 386.1459.
TLC (30% EtOAc in hexanes), R_f:	0.58 (UV, CAM).

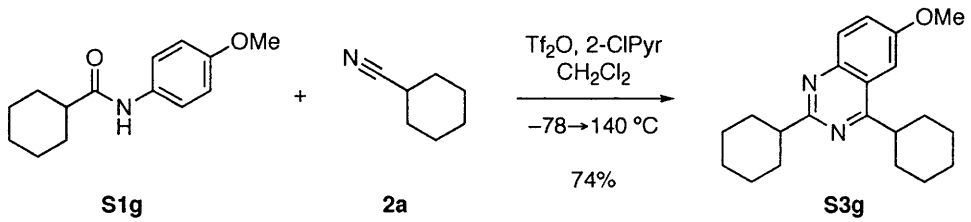


S1f **2a** **S3f**

2-*tert*-Butyl-4-cyclohexyl-6-methoxy-quinazoline (S3f, Table 2, entry 6):

Trifluoromethanesulfonic anhydride (88 μL, 0.53 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1f** (100 mg, 0.480 mmol, 1 equiv) and 2-chloropyridine (55 μL, 0.58 mmol, 1.2 equiv) in dichloromethane (1.6 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (58 mg, 0.53 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3f** as a pale yellow solid (124 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.91 (d, 1H, J = 9.1 Hz, Ar**H**), 7.46 (dd, 1H, J = 9.1, 2.7 Hz, Ar**H**), 7.32 (d, 1H, J = 2.7 Hz, Ar**H**), 3.97 (s, 3H, O**CH**$_3$), 3.40 (tt, 1H, J = 11.4, 3.2 Hz, ^{c}C$_6$**H**$_{11}$), 1.98–1.80 (m, 7H, ^{c}C$_6$**H**$_{11}$), 1.58–1.50 (m, 2H, ^{c}C$_6$**H**$_{11}$), 1.49 (s, 9H, C(**CH**$_3$)$_3$), 1.40 (qt, 1H, J = 12.7, 3.1 Hz, ^{c}C$_6$**H**$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	172.2, 170.9, 157.5, 146.5, 130.9, 124.6, 121.6, 102.1, 55.8, 41.5, 39.6, 32.0, 29.9, 26.7, 26.4.
FTIR (neat) cm^{-1}:	2948 (w), 2912 (m), 2848 (m), 1619 (w), 1556 (m), 1497 (m), 1221 (s).
HRMS (ESI):	calcd for $C_{19}H_{27}N_2O$ $[M+H]^+$: 299.2123, found: 299.2121.
TLC (20% EtOAc in hexanes), R_f:	0.60 (UV, CAM).

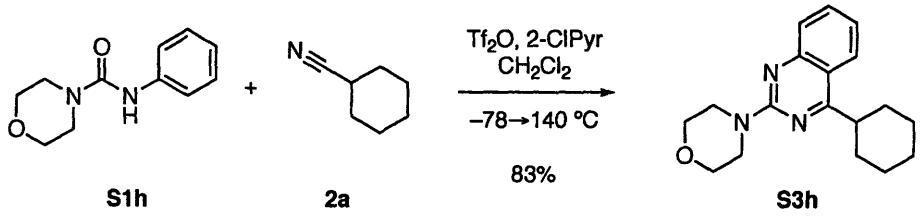


S1g **2a** **S3g**

2,4-Dicyclohexyl-6-methoxy-quinazoline (S3g, Table 2, entry 7):

Trifluoromethanesulfonic anhydride (90 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1g** (115 mg, 0.493 mmol, 1 equiv) and 2-chloropyridine (56 μL, 0.59 mmol, 1.2 equiv) in dichloromethane (1.6 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the nitrile **2a** (59 mg, 0.54 mmol, 1.1 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3g** as a white solid (119 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.89 (d, 1H, J = 9.1 Hz, Ar**H**), 7.47 (dd, 1H, J = 9.1, 2.9 Hz, Ar**H**), 7.32 (d, 1H, J = 2.9 Hz, Ar**H**), 3.97 (s, 3H, OCH_3), 3.44 (tt, 1H, J = 11.5, 3.2 Hz, $^cC_6H_{11}$), 2.95 (tt, 1H, J = 11.7, 3.5 Hz, $^cC_6H_{11}$), 2.08–1.72 (m, 14 H, $^cC_6H_{11}$, $^cC_6H_{11}$), 1.58–1.34 (m, 6H, $^cC_6H_{11}$, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	172.9, 168.4, 157.4, 146.7, 130.5, 125.0, 122.1, 102.2, 55.8, 47.9, 41.5, 32.2, 32.0, 26.7, 26.6, 26.4, 26.3.
FTIR (neat) cm^{-1}:	2927 (s), 2852 (m), 1623 (w), 1556 (m), 1449 (m), 1222 (s).
HRMS (ESI):	calcd for $C_{21}H_{29}N_2O$ $[M+H]^+$: 325.2280, found: 325.2274.
TLC (20% EtOAc in hexanes), R_f:	0.56 (UV, CAM).

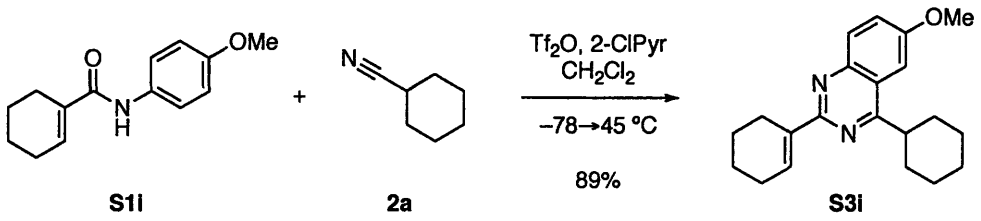


S1h **2a** **S3h**

4-Cyclohexyl-2-morpholin-4-yl-quinazoline (S3h, Table 2, entry 8):

Trifluoromethanesulfonic anhydride (97 μL, 0.59 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1h** (110 mg, 0.530 mmol, 1 equiv), nitrile **2a** (64 mg, 0.59 mmol, 1.1 equiv) and 2-chloropyridine (61 μL, 0.64 mmol, 1.2 equiv) in dichloromethane (1.8 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3h** as a white solid (131 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.92 (d, 1H, J = 8.3 Hz, Ar**H**), 7.65–7.58 (m, 2H, Ar**H**), 7.21 (ddd, 1H, J = 8.2, 6.4, 1.6 Hz, Ar**H**), 3.97 (t, 4H, J = 4.7 Hz, OCH_2CH_2N), 3.83 (t, 4H, J = 4.7 Hz, OCH_2CH_2N), 3.41 (tt, 1H, J = 11.4, 2.9 Hz, $^cC_6H_{11}$), 1.98–1.69 (m, 7H, $^cC_6H_{11}$), 1.51 (tt, 2H, J = 9.6, 4.2 Hz, $^cC_6H_{11}$) 1.35 (tt, 1H, J = 12.8, 3.4 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	175.8, 158.9, 152.6, 133.3, 126.8, 124.6, 122.3, 118.1, 67.2, 44.7, 41.5, 32.1, 26.7, 26.4.
FTIR (neat) cm^{-1}:	3064 (w), 2930 (s), 2852 (s), 1615 (s), 1579 (s), 1554 (s), 1486 (s), 1227 (s).
HRMS (ESI):	calcd for $C_{18}H_{24}N_3O$ $[M+H]^+$: 298.1919, found: 298.1911.
TLC (20% EtOAc in hexanes), R_f:	0.48 (UV, CAM).

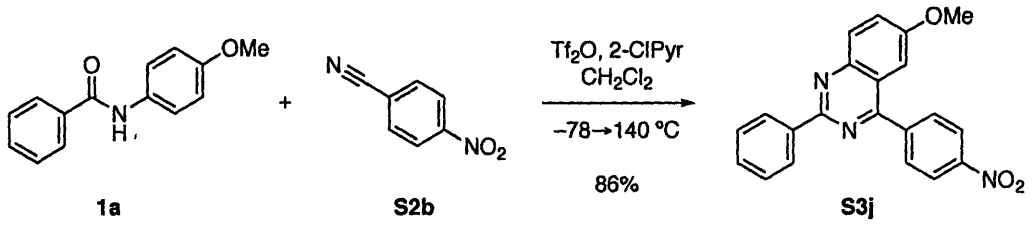


S1i **2a** **S3i**

2-Cyclohex-1-enyl-4-cyclohexyl-6-methoxy-quinazoline (S3i, Table 2, entry 9):

Trifluoromethanesulfonic anhydride (79 μL, 0.48 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1i** (100 mg, 0.432 mmol, 1 equiv), 2-chloropyridine (49 μL, 0.53 mmol, 1.2 equiv), and nitrile **2a** (236 mg, 2.16 mmol, 5.00 equiv) in dichloromethane (1.4 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 16 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced at to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3i** as a white solid (124 mg, 89%).

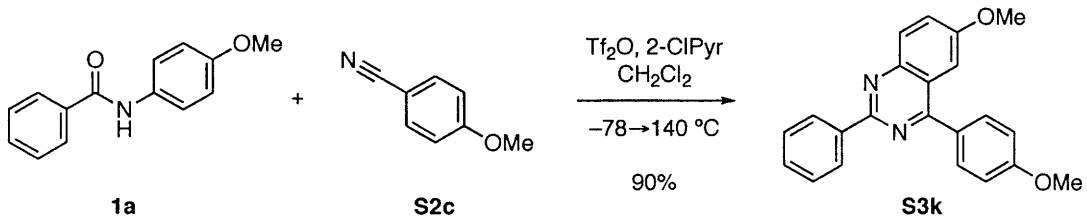
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.90 (d, 1H, J = 9.1 Hz, Ar**H**), 7.47–7.44 (m, 2H, Ar**H**, C=C**H**CH_2), 7.32 (d, 1H, J = 2.7 Hz, Ar**H**), 3.97 (s, 3H, OCH_3), 3.41 (tt, 1H, J = 10.9, 2.7 Hz, $^cC_6H_{11}$), 2.77–2.72 (m, 2H, $^cC_6H_9$), 2.39–2.34 (m, 2H, $^cC_6H_9$), 2.02–1.70 (m, 11H, $^cC_6H_{11}$, $^cC_6H_9$), 1.60–1.49 (m, 2H, $^cC_6H_{11}$), 1.41 (qt, 1H, J = 12.7, 3.4 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	172.0, 160.1, 157.5, 146.7, 137.4, 132.9, 131.0, 124.8, 122.1, 102.5, 55.8, 41.6, 32.0, 26.8, 26.4, 26.4, 25.6, 23.1, 22.5.
FTIR (neat) cm^{-1}:	2929 (s), 2853 (m), 1621 (w), 1547 (s), 1496 (m), 1226 (s).
HRMS (ESI):	calcd for $C_{21}H_{27}N_2O$ $[M+H]^+$: 323.2123, found: 323.2126.
TLC (20% EtOAc in hexanes), R_f:	0.67 (UV, CAM).



6-Methoxy-4-(4-nitro-phenyl)-2-phenyl-quinazoline (S3j, Table 2, entry 10):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv), nitrile **S2b** (83 mg, 0.56 mmol, 1.1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3j** as a pale yellow solid (156 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.66–8.62 (m, 2H, Ar**H**), 8.51–8.47 (m, 2H, Ar**H**), 8.13 (d, 1H, J = 9.3 Hz, Ar**H**), 8.11–8.07 (m, 2H, Ar**H**), 7.64 (dd, 1H, J = 9.3, 2.7 Hz, Ar**H**), 7.57–7.50 (m, 3H, Ar**H**), 7.24 (d, 1H, J = 2.7 Hz, Ar**H**), 3.89 (s, 3H, O**CH**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	164.2, 158.8, 158.7, 148.8, 148.6, 144.4, 138.0, 131.3, 131.0, 130.6, 128.8, 128.4, 127.1, 124.1, 122.3, 103.3, 55.9.
FTIR (neat) cm^{-1}:	3056 (w), 2971 (w), 1996 (w), 1621 (m), 1543 (s), 1513 (s), 1350 (s), 1222 (m).
HRMS (ESI):	calcd for $C_{21}H_{16}N_3O_3$ $[M+H]^+$: 358.1192, found: 358.1183.
TLC (20% EtOAc in hexanes), R_f:	0.36 (UV, CAM).

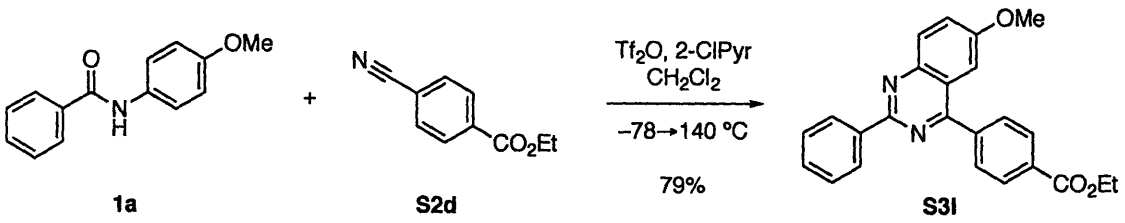


1a **S2c** **S3k**

6-Methoxy-4-(4-methoxy-phenyl)-2-phenyl-quinazoline (S3k, Table 2, entry 11):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv), nitrile **S2c** (74 mg, 0.56 mmol, 1.1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3k** as a pale yellow solid (156 mg, 90%).

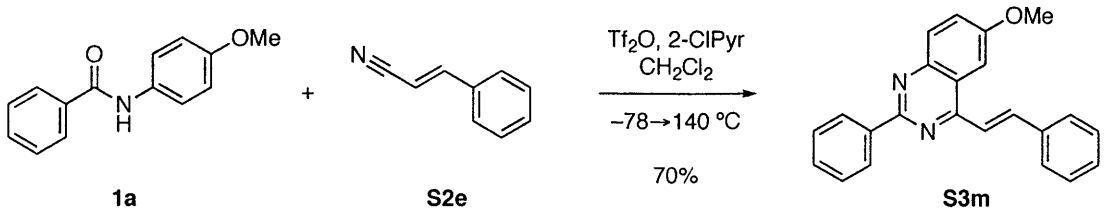
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.67–8.64 (m, 2H, Ar**H**), 8.07 (d, 1H, J = 9.1 Hz, Ar**H**), 7.94–7.90 (m, 2H, Ar**H**), 7.57–7.45 (m, 5H, Ar**H**), 7.16–7.12 (m, 2H, Ar**H**), 3.95 (s, 3H, OC**H**$_3$), 3.89 (s, 3H, OC**H**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	166.1, 161.1, 158.7, 158.1, 148.3, 138.6, 131.6, 130.7, 130.6, 130.2, 128.6, 128.4, 126.1, 122.5, 114.2, 104.6, 55.7, 55.6.
FTIR (neat) cm^{-1}:	3006 (w), 2957 (m), 2839 (w), 1608 (s), 1564 (m), 1534 (s), 1499 (s), 1404 (s), 1259 (s), 1221 (m).
HRMS (ESI):	calcd for $C_{22}H_{19}N_2O_2$ $[M+H]^+$: 343.1447, found: 343.1437.
TLC (20% EtOAc in hexanes), R_f:	0.33 (UV, CAM).



4-(6-Methoxy-2-phenyl-quinazolin-4-yl)-benzoic acid ethyl ester (S3l, Table 2, entry 12):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv), nitrile **S2d** (98 mg, 0.56 mmol, 1.1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3l** as a white solid (154 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.67–8.63 (m, 2H, Ar**H**), 8.30 (d, 2H, J = 8.0 Hz, Ar**H**), 8.10 (d, 1H, J = 9.1 Hz, Ar**H**), 7.98 (d, 2H, J = 7.9 Hz, Ar**H**), 7.58 (dd, 1H, J = 9.1, 2.7 Hz, Ar**H**), 7.56–7.48 (m, 3H, Ar**H**), 7.31 (d, 1H, J = 2.7 Hz, Ar**H**), 4.48 (q, 2H, J = 7.2 Hz, $CO_2C\mathbf{H}_2CH_3$), 3.87 (s, 3H, $OC\mathbf{H}_3$), 1.48 (t, 3H, J = 7.2 Hz, $CO_2CH_2C\mathbf{H}_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	166.4, 165.7, 158.9, 158.4, 148.5, 142.4, 138.3, 131.7, 131.0, 130.4, 130.0, 130.0, 128.8, 128.5, 126.8, 122.5, 103.9, 61.5, 55.8, 14.6.
FTIR (neat) cm^{-1}:	2961 (w), 1717 (s), 1621 (w), 1536 (m), 1407 (m), 1271 (s), 1222 (s).
HRMS (ESI):	calcd for $C_{24}H_{21}N_2O_3$ $[M+H]^+$: 385.1552, found: 385.1544.
TLC (20% EtOAc in hexanes), R_f:	0.39 (UV, CAM).

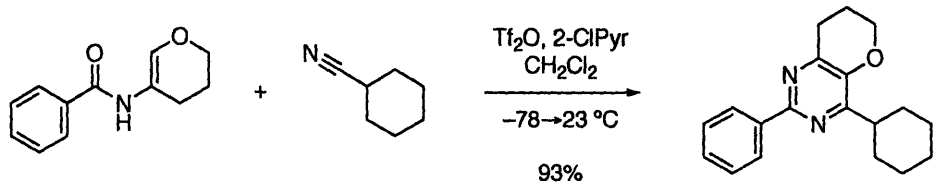


1a **S2e** **S3m**

6-Methoxy-2-phenyl-4-styryl-quinazoline (S3m, Table 2, entry 13):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv), nitrile **S2e** (72 mg, 0.56 mmol, 1.1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **S3m** as a white solid (120 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.71–8.68 (m, 2H, Ar**H**), 8.45 (d, 1H, J = 15.4 Hz, C**H**=CH), 8.03 (d, 1H, J = 9.1 Hz, Ar**H**), 7.89 (d, 1H, J = 15.4 Hz, Ar**H**), 7.80 (d, 2H, J =7.4 Hz, Ar**H**), 7.59–7.55 (m, 3H, Ar**H**), 7.54–7.47 (m, 4H, Ar**H**), 7.45–7.41 (m, 1H, Ar**H**), 4.04 (s, 3H, OC**H**$_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	160.3, 158.5, 158.1, 148.4, 139.1, 138.8, 136.4, 131.0, 130.2, 129.7, 129.1, 128.7, 128.4, 128.2, 126.3, 122.5, 121.3, 101.6, 55.9.
FTIR (neat) cm^{-1}:	3059 (w), 2936 (w), 1621 (m), 1560 (m), 1533 (s), 1499 (m), 1408 (s), 1224 (s).
HRMS (ESI):	calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1497, found: 339.1492.
TLC (20% EtOAc in hexanes), R_f:	0.38 (UV, CAM).

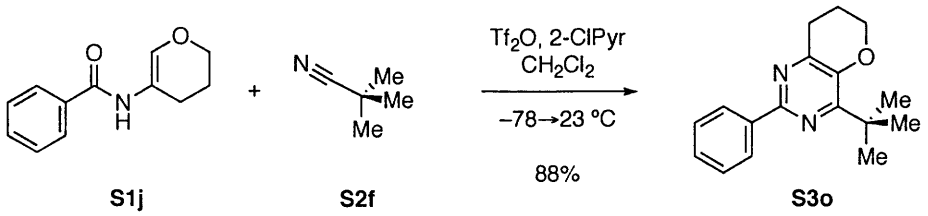


S1j 2a S3n

4-Cyclohexyl-2-phenyl-7,8-dihydro-6*H*-pyrano[3,2-*d*]pyrimidine (S3n, Table 2, entry 14):

Trifluoromethanesulfonic anhydride (63 μL, 0.38 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1j** (70 mg, 0.34 mmol, 1 equiv), nitrile **2a** (41 mg, 0.38 mmol, 1.1 equiv) and 2-chloropyridine (39 μL, 0.41 mmol, 1.2 equiv) in dichloromethane (1.0 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3n** as a white solid (94 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.40–8.36 (m, 2H, Ar**H**), 7.47–7.38 (m, 3H, Ar**H**), 4.27 (t, 2H, J = 5.1 Hz, $CH_2CH_2CH_2O$), 3.06 (tt, 1H, J = 11.9, 3.5 Hz, $^cC_6H_{11}$), 2.98 (t, 2H, J = 6.6 Hz, $CH_2CH_2CH_2O$), 2.18–2.13 (m, 2H, $CH_2CH_2CH_2O$), 1.91–1.69 (m, 7H, $^cC_6H_{11}$), 1.44 (qt, 2H, J = 12.7, 3.2 Hz, $^cC_6H_{11}$), 1.35 (qt, 1H, J = 12.7, 3.2 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	161.7, 155.8, 149.6, 146.0, 138.7, 129.3, 128.5, 127.7, 66.7, 38.8, 30.8, 28.1, 26.6, 26.3, 22.2.
FTIR (neat) cm^{-1}:	3065 (w), 2930 (s), 2852 (m), 1587 (w), 1565 (s), 1430 (s), 1410 (s), 1208 (m).
HRMS (ESI):	calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1810, found: 295.1796.
TLC (20% EtOAc in hexanes), R_f:	0.52 (UV, CAM).

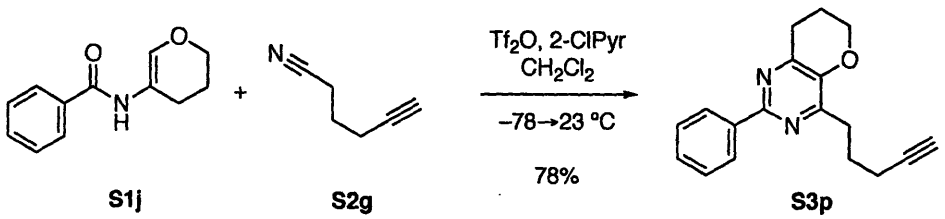


S1j **S2f** **S3o**

4-*tert*-Butyl-2-phenyl-7,8-dihydro-6*H*-pyrano[3,2-*d*]pyrimidine (S3o, Table 2, entry 15):

Trifluoromethanesulfonic anhydride (890 μL, 5.41 mmol, 1.1 equiv) was added via syringe over 3 min to a stirred mixture of amide **S1j** (1.0 g, 4.9 mmol, 1 equiv), nitrile **S2f** (450 mg, 5.41 mmol, 1.1 equiv) and 2-chloropyridine (560 μL, 5.90 mmol, 1.2 equiv) in dichloromethane (16 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature. After 3 h, aqueous sodium hydroxide solution (5 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (50 mL) was added to dilute the mixture and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL) and the organic fractions were combined, dried over anhydrous sodium sulfate, and were filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 12 × 3 cm) on neutralized silica gel to give the pyrimidine product **S3o** as a white solid (1.17 g, 88%).

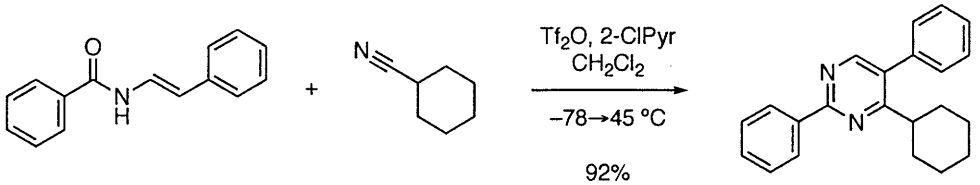
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.42–8.37 (m, 2H, Ar**H**), 7.48–7.38 (m, 3H, Ar**H**), 4.27 (t, 2H, J = 5.1 Hz, $CH_2CH_2C\mathbf{H}_2O$), 2.98 (t, 2H, J = 6.7 Hz, $C\mathbf{H}_2CH_2CH_2O$), 2.20–2.14 (m, 2H, $CH_2C\mathbf{H}_2CH_2O$), 1.46 (s, 9H, $C(C\mathbf{H}_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	163.3, 154.8, 150.4, 147.6, 138.6,129.4, 128.5, 127.7, 66.3, 38.2, 28.3, 28.1, 22.1.
FTIR (neat) cm^{-1}:	3065 (w), 2955 (m), 2868 (w), 1558 (m), 1429 (m), 1406 (s), 1366 (m), 1353 (m).
HRMS (ESI):	calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$: 269.1654, found: 269.1653.
TLC (20% EtOAc in hexanes), R_f:	0.67 (UV, CAM).



4-Pent-4-ynyl-2-phenyl-7,8-dihydro-6*H*-pyrano[3,2-*d*]pyrimidine (S3p, Table 2, entry 16):

Trifluoromethanesulfonic anhydride (89 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1j** (100 mg, 0.490 mmol, 1 equiv), nitrile **S2g** (50 mg, 0.54 mmol, 1.1 equiv) and 2-chloropyridine (56 μL, 0.59 mmol, 1.2 equiv) in dichloromethane (1.6 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3p** as a colorless oil (107 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.36–8.33 (m, 2H, Ar**H**), 7.48–7.38 (m, 3H, Ar**H**), 4.28 (t, 2H, J = 5.1 Hz, $CH_2CH_2C\mathbf{H}_2O$), 2.98 (t, 2H, J = 6.6 Hz, $C\mathbf{H}_2CH_2CH_2O$), 2.92 (t, 2H, J = 7.2 Hz, $C\mathbf{H}_2CH_2CH_2CCH$), 2.37 td, 2H, J = 7.1, 2.6 Hz, $CH_2CH_2C\mathbf{H}_2CCH$), 2.20–2.14 (m, 2H, $CH_2C\mathbf{H}_2CH_2O$), 2.08 (quint, 2H, J = 7.4 Hz, $CH_2C\mathbf{H}_2CH_2CCH$), 2.01 (1H, t, J = 2.7 Hz, $CH_2CH_2CH_2CC\mathbf{H}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.2, 155.9, 149.7, 146.9, 138.4, 129.5, 128.6, 127.7, 84.5, 68.8, 66.9, 30.4, 28.1, 26.0, 22.2, 18.5.
FTIR (neat) cm^{-1}:	3297 (s), 3066 (m), 2939 (s), 2117 (w), 1587 (s), 1569 (s), 1411 (s), 1202 (m).
HRMS (ESI):	calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279.1497, found: 279.1496.
TLC (20% EtOAc in hexanes), R_f:	0.41 (UV, CAM).

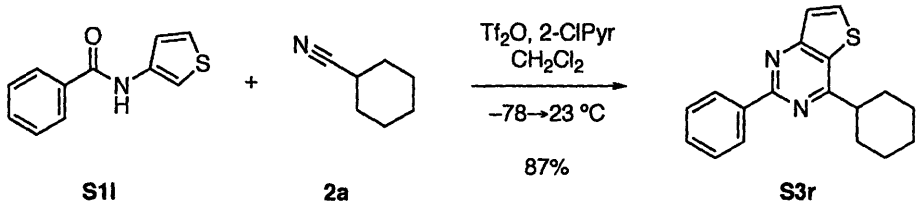


S1k **2a** **S3q**

4-Cyclohexyl-2,5-diphenyl-pyrimidine (S3q, Table 2, entry 17):

Trifluoromethanesulfonic anhydride (90 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1k** (110 mg, 0.493 mmol, 1 equiv), nitrile **2a** (269 mg, 2.47 mmol, 5.00 equiv) and 2-chloropyridine (56 μL, 0.59 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction vessel was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3q** as a white solid (142 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.59 (s, 1H, Ar**H**), 8.57–8.54 (m, 2H, Ar**H**), 7.55–7.44 (m, 6H, Ar**H**), 7.38–7.35 (m, 2H, Ar**H**), 2.90 (tt, 1H, J = 11.5, 3.5 Hz, ^{c}C$_6$H$_{11}$), 1.94–1.69 (m, 7H, ^{c}C$_6$H$_{11}$), 1.37 (qt, 1H, J = 12.8, 3.2 Hz, ^{c}C$_6$H$_{11}$), 1.30–1.20 (m, 2H, ^{c}C$_6$H$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	171.6, 163.1, 157.4, 138.2, 136.6, 131.7, 130.6, 129.4, 128.9, 128.7, 128.3, 128.1, 42.0, 32.2, 26.3, 26.1.
FTIR (neat) cm^{-1}:	3060 (w), 2929 (s), 2853 (m), 1586 (w), 1568 (s), 1525 (s), 1425 (s), 1378 (m).
HRMS (ESI):	calcd for $C_{22}H_{23}N_2$ $[M+H]^+$: 315.1861, found: 315.1861.
TLC (20% EtOAc in hexanes), R_f:	0.69 (UV, CAM).

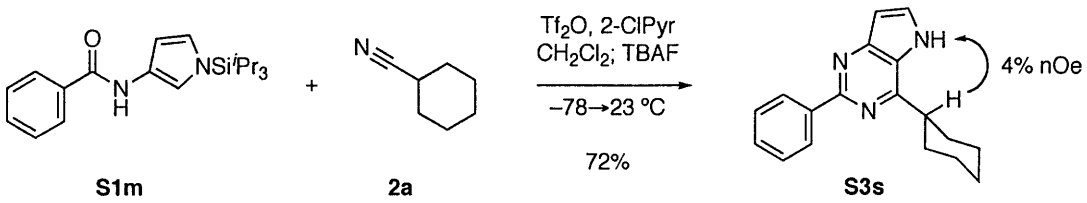


S1l **2a** **S3r**

4-Cyclohexyl-2-phenyl-thieno[3,2-*d*]pyrimidine (S3r, Table 2, entry 18):

Trifluoromethanesulfonic anhydride (72 μL, 0.43 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1l** (80 mg, 0.39 mmol, 1 equiv), nitrile **2a** (47 mg, 0.54 mmol, 1.1 equiv) and 2-chloropyridine (45 μL, 0.47 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3r** as a pale yellow solid (101 mg, 87%).

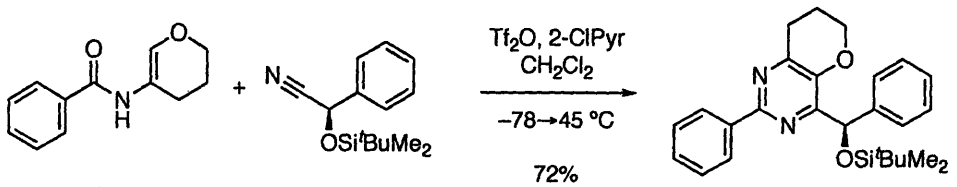
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.60–8.58 (m, 2H, Ar**H**), 7.92 (d, 1H, J = 5.5 Hz, Ar**H**), 7.60 (d, 1H, J = 5.5 Hz, Ar**H**), 7.54–7.48 (m, 3H, Ar**H**), 3.05 (tt, 1H, J = 11.5, 3.8 Hz, ^{c}C$_6$**H**$_{11}$), 2.10–1.81 (m, 7H, ^{c}C$_6$**H**$_{11}$), 1.56–1.38 (m, 3H, ^{c}C$_6$**H**$_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	168.8, 162.0, 161.4, 138.7, 134.5, 130.3, 128.7, 128.5, 127.4, 125.4, 46.3, 31.3, 26.5, 26.2.
FTIR (neat) cm^{-1}:	2928 (m), 2852 (w), 1535 (s), 1365 (w), 1341 (w).
HRMS (ESI):	calcd for $C_{18}H_{19}N_2S$ $[M+H]^+$: 295.1269, found: 295.1259.
TLC (20% EtOAc in hexanes), R_f:	0.52 (UV, CAM).



4-Cyclohexyl-2-phenyl-5*H*-pyrrolo[3,2-*d*]pyrimidine (S3s, Table 2, entry 19):

Trifluoromethanesulfonic anhydride (37 μL, 0.23 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **S1m** (70 mg, 0.20 mmol, 1 equiv), nitrile **2a** (46 mg, 0.41 mmol, 2.00 equiv) and 2-chloropyridine (39 μL, 0.41 mmol, 2.00 equiv) in dichloromethane (0.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (1 mL) was introduced to neutralize the trifluoromethanesulfonate salts, followed by TBAF (204 μL, 1.00 equiv, 1.0 M) to protodesilylate the pyrimidine product. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10→40% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3s** as a pale tan solid (41 mg, 72%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.57–8.52 (m, 2H, Ar**H**), 8.45 (s, 1H, N**H**), 7.54–7.47 (m, 3H, Ar**H**), 7.45–7.40 (m, 1H, Ar**H**), 6.79 (dd, 1H, J = 3.1, 2.0 Hz, Ar**H**), 3.05 (tt, 1H, J = 11.4, 3.5 Hz, $^cC_6\mathbf{H}_{11}$), 2.09–1.80 (m, 7H, $^cC_6\mathbf{H}_{11}$), 1.54–1.38 (m, 3H, $^cC_6\mathbf{H}_{11}$).
^{13}C NMR (125 MHz, DMF-d_7, 20 °C) δ:	157.9, 156.9, 151.9, 141.1, 133.6, 130.0, 129.3, 128.6, 125.2, 102.9, 42.4, 32.2, 27.3, 27.0.
FTIR (neat) cm^{-1}:	3073 (m), 3019 (m), 2924 (s), 2849 (s), 1996 (w), 1738 (w), 1609 (m), 1543 (s), 1445 (m), 1386 (s).
HRMS (ESI):	calcd for $C_{18}H_{20}N_3$ $[M+H]^+$: 278.1657, found: 278.1656.
TLC (40% EtOAc in hexanes), R_f:	0.38 (UV, CAM).



S1j **S2h** **S3t**, 96% ee

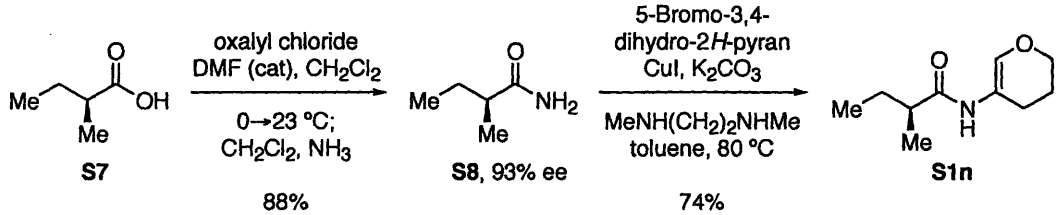
(*R*)-4-[(*tert*-Butyl-dimethyl-silanyloxy)-phenyl-methyl]-2-phenyl-7,8-dihydro-6*H*-pyrano[3,2-*d*]pyrimidine (S3t, Table 2, entry 20):

Trifluoromethanesulfonic anhydride (54 μL, 0.33 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **Slj** (60 mg, 0.30 mmol, 1 equiv), nitrile **S2h**[6] (219 mg, 0.885 mmol, 3.00 equiv) and 2-chloropyridine (34 μL, 0.35 mmol, 1.2 equiv) in dichloromethane (1.0 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, and the resulting solution was allowed to warm to ambient temperature for 5 min. before being placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction vessel was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3t** as a colorless oil (91 mg, 72%, 96% ee). The ee of the product was determined by chiral HPLC analysis of the corresponding desilylated alcohol. The enantiomeric excess of the pyrimidine product was determined to be 95% ee by chiral HPLC analysis [Chiralpak AD-H; 2.5 mL/min; 7% ^{i}PrOH in hexanes; t_R (minor) = 6.74 min., t_R (major) = 9.95 min].

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.44–8.38 (m, 2H, Ar**H**), 7.62–7.57 (m, 2H, Ar**H**), 7.48–7.38 (m, 3H, Ar**H**), 7.35–7.30 (m, 2H, Ar**H**), 7.27–7.24 (m, 1H, Ar**H**), 6.20 (s, 1H, C**H**OTBS), 4.32–4.21 (m, 2H, $CH_2CH_2CH_2O$), 3.03–2.92 (m, 2H, $CH_2CH_2CH_2O$), 2.20–2.11 (m, 2H, $CH_2CH_2CH_2O$), 0.95 (s, 9H, $Si(CH_3)_2C(CH_3)_3$), 0.05 (s, 3H, $Si(CH_3)_2C(CH_3)_3$), 0.00 (s, 3H, $Si(CH_3)_2C(CH_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.4, 156.0, 151.3, 145.7, 142.6, 138.3, 129.5, 128.5, 128.1, 127.8, 127.3, 127.0, 71.8, 66.8, 28.2, 26.0, 22.0, 18.5, –4.5, –4.7.
FTIR (neat) cm^{-1}:	3065 (m), 3032 (m), 2954 (s), 2886 (s), 2856 (s), 1957 (w), 1819 (w), 1586 (m), 1564 (s), 1409 (s), 1252 (s).

[6] The nitrile **S2h** was prepared by silylation of the corresponding commercially available cyanohydrin. The optical activity of the starting cyanohydrin was determined to be 96% ee by chiral HPLC analysis.

HRMS (ESI):	calcd for $C_{26}H_{33}N_2O_2Si$ $[M+H]^+$: 433.2311, found: 433.2303.
TLC (20% EtOAc in hexanes), R_f:	0.67 (UV, CAM).



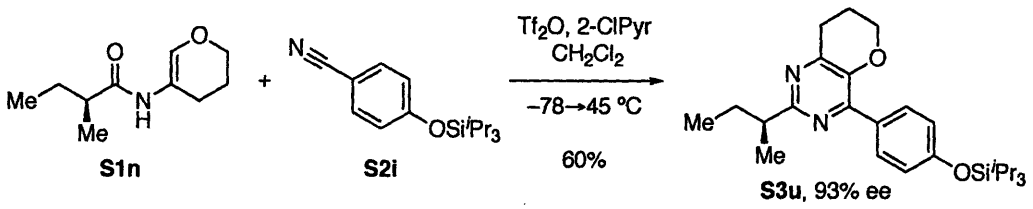
(*S*)-*N*-(5,6-Dihydro-4*H*-pyran-3-yl)-2-methyl-butyramide (S1n, Table 2, entry 21):

Oxalyl chloride (1.30 g, 10.3 mmol, 1.05 equiv) was added over 1 minute via syringe to a stirred solution of (*S*)-(+)-2-methylbutyric acid (**S7**, 1.0 g, 9.8 mmol, 1 equiv) and *N*,*N*-dimethylformamide (10 μL) in dichloromethane (33 mL) in an ice-bath at 0 °C. The reaction mixture was removed from the ice-bath after 15 min. and allowed to warm to ambient temperature. After 1.5 h, gas evolution had ceased and dichloromethane saturated with ammonia (33 mL) was added via cannula at ambient temperature. Water (10 mL) was added after 5 min. to remove ammonium salts and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL), the organic layers were combined and dried over anhydrous sodium sulfate and filtered, and the volatiles were removed under reduced pressure to afford pure primary amide **S8** as a white solid (870 mg, 88%). The enantiomeric excess of the amide was determined to be 93% ee by chiral HPLC analysis [Chiralpak AD-H; 1.0 mL/min; 7% ^{i}PrOH in hexanes; t_R (minor) = 14.2 min., t_R (major) = 15.7 min]. The primary amide (850 mg, 8.40 mmol, 1 equiv) was then combined with 5-Bromo-3,4-dihydro-2*H*-pyran[7] (1.1 g, 7.0 mmol, 0.83 equiv), copper iodide (160 mg, 0.840 mmol, 0.100 equiv), *N*,*N*'-dimethylethylenediamine (148 mg, 1.68 mmol, 0.200 equiv), and potassium carbonate (1.97 g, 14.3 mmol, 1.70 equiv) in toluene (8.4 mL) in a pressure vessel. The resulting reaction mixture was placed in a preheated oil bath at 80 °C and maintained at that temperature. After 16 h, the solution was removed from the bath and allowed to cool to ambient temperature. The crude mixture was diluted with ethyl acetate (30 mL) and filtered through celite; the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% EtOAc in hexanes; SiO_2: 25 × 3 cm) on silica gel to give the amide product **S1n** as a white solid (950 mg, 74%). The copper catalyzed C–N bond formation occurred without loss of optical activity as confirmed by measuring the enantiomeric excess of the corresponding pyrimidine **S3u** (see page S24).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	6.93 (s, 1H, C=C**H**), 6.15 (br s, 1H, N**H**), 3.95 (t, 2H, J = 5.3 Hz, $CH_2CH_2CH_2O$), 2.26–2.22 (m, 2H, $CH_2CH_2CH_2O$), 2.16–2.07 (m, 1H, $CH(CH_3)CH_2CH_3$), 1.98–1.92 (m, 2H, $CH_2CH_2CH_2O$), 1.74–1.64 (m, 1H, $CH(CH_3)CH_2CH_3$), 1.51–1.42 (m, 1H, $CH(CH_3)CH_2CH_3$), 1.16 (d, 3H, J = 6.7 Hz, $CH(CH_3)CH_2CH_3$), 0.94 (t, 3H, J = 7.4 Hz, $CH(CH_3)CH_2CH_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	175.8, 139.5, 113.7, 65.4, 43.3, 27.6, 23.9, 22.1, 17.7, 12.1.

[7] Bonner, W. A.; Werth, P. J.; Roth, J. M. *J. Org. Chem.* **1962**, *27*, 1575.

FTIR (neat) cm^{-1}:	3292 (w), 2968 (m), 2936 (m), 2878 (w), 1727 (s), 1699 (m), 1651 (s), 1510 (m), 1463 (m), 1382 (w), 1165 (m).
HRMS (ESI):	calcd for $C_{10}H_{18}NO_2$ $[M+H]^+$: 184.1332, found: 184.1337.
TLC (40% EtOAc in hexanes), R_f:	0.34 (UV, CAM).



(*S*)-2-*sec*-Butyl-4-[4-(triisopropyl-silanyloxy)-phenyl]-7,8-dihydro-6*H*-pyrano[3,2-*d*]pyrimidine (S3u, Table 2, entry 21):

Trifluoromethanesulfonic anhydride (79 μL, 0.48 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **Sln** (80 mg, 0.44 mmol, 1 equiv), nitrile **S2i** (361 mg, 1.31 mmol, 3.00 equiv) and 2-chloropyridine (50 μL, 0.52 mmol, 1.2 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, and the resulting solution was allowed to warm to ambient temperature for 5 min. before being placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction vessel was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10→20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyrimidine product **S3u** as a colorless oil (115 mg, 60%). The enantiomeric excess of the pyrimidine product was determined to be 93% ee by protodesilylation and chiral HPLC analysis [Chiralpak AD-H; 2.0 mL/min; 3% ^{i}PrOH in hexanes; t_R (major) = 9.36 min., t_R (minor) = 11.1 min] of the corresponding alcohol.[8]

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ: 8.16–8.12 (m, 2H, Ar**H**), 6.97–6.93 (m, 2H, Ar**H**), 4.28 (t, 2H, J = 5.1 Hz, $CH_2CH_2C\mathbf{H}_2O$), 2.98–2.87 (m, 3H, $\mathbf{CH}_2CH_2CH_2O$, $C\mathbf{H}(CH_3)CH_2CH_3$), 2.20–2.15 (m, 2H, $CH_2\mathbf{CH}_2CH_2O$), 1.96–1.86 (m, 1H, $CH(CH_3)C\mathbf{H}_2CH_3$), 1.70–1.61 (m, 1H, $CH(CH_3)\mathbf{CH}_2CH_3$), 1.34–1.26 (m, 6H, $CH(\mathbf{CH}_3)CH_2CH_3$, $Si(C\mathbf{H}(CH_3)_2)_3$), 1.14 (d, 18H, J = 7.5 Hz, $Si(CH(\mathbf{CH}_3)_2)_3$), 0.90 (t, 3H, J = 7.4 Hz, $CH(CH_3)CH_2\mathbf{CH}_3$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ: 165.5, 157.7, 151.4, 150.9, 145.6, 131.3, 128.9, 119.5, 66.7, 44.2, 29.6, 28.4, 22.1, 20.0, 18.1, 12.9, 12.4.

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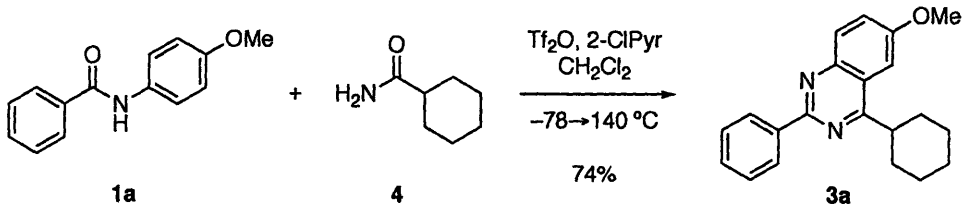
[8] The use of the (*S*)-*N*-(4-methoxyphenyl)-2-methylbutyramide variant of amide **S1n** as the substrate with the same nitrile (**S2i**, 1.1 equiv) under standard conditions (B or C, see text) provided the corresponding quinazoline in 58% yield (condition C) but with complete racemization (0%ee). This is likely due to the compounded effect of the low reactivity of the amide and the nitrile in addition to the likely slower rate of cyclization of intermediate **6** (Scheme 5) leading to quinazolines.

FTIR (neat) cm^{-1}:	2961 (s), 2868 (s), 1605 (s), 1558 (m), 1541 (w), 1508 (s), 1463 (m), 1270 (s).
HRMS (EI):	calcd for $C_{26}H_{40}N_2O_2Si$ $[M]^+$: 440.2859, found: 440.2865.
TLC (20% EtOAc in hexanes), R_f:	0.37 (UV, CAM)

Direct conversion of secondary amide 1a and primary amide 4 to quinazoline 3a.



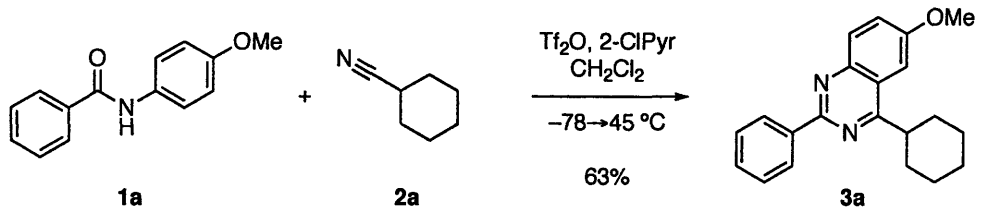
<u>4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (eq 2):</u>

Trifluoromethanesulfonic anhydride (193 μL, 1.17 mmol, 2.30 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (115 mg, 0.506 mmol, 1 equiv), cyclohexanecarboxamide **4** (71 mg, 0.56 mmol, 1.1 equiv) and 2-chloropyridine (125 μL, 1.32 mmol, 2.60 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath for 5 min. and warmed to 0 °C. The resulting solution was warmed to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **3a** as a white solid (119 mg, 74%).

See 4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (3a, Table 2, entry 1) experimental page for spectroscopic data.

In situ IR analysis of the conversion of amide 1a and nitrile 2a to quinazoline 3a:

All reactions were performed in a reaction vessel under an atmosphere of argon with the React-IR probe submerged completely in the reaction mixture.

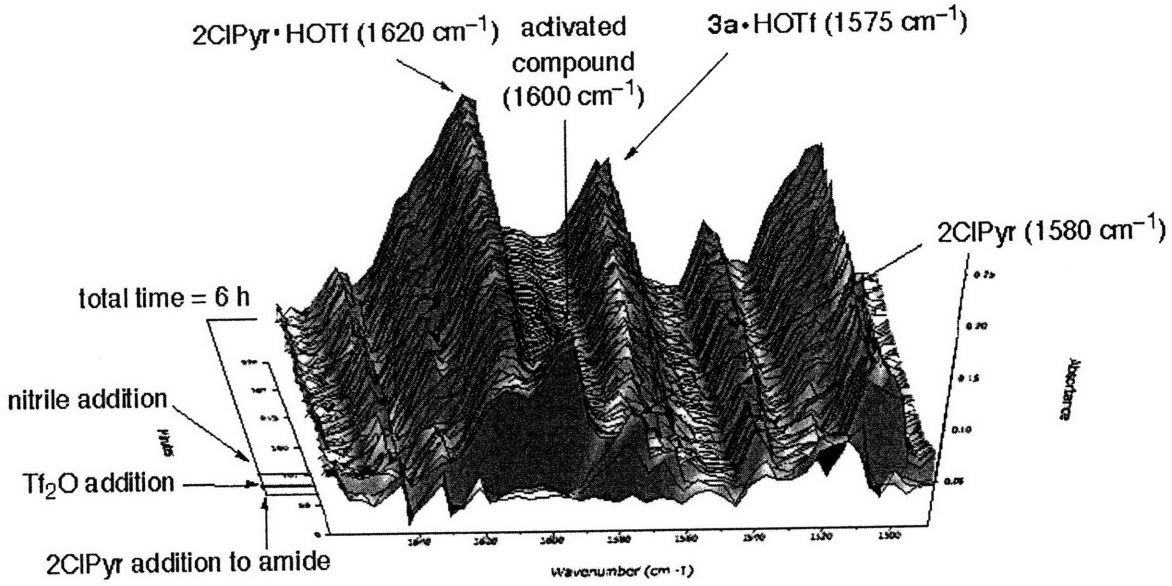


1a **2a** **3a**

<u>4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (3a):</u>

In situ IR monitoring of the addition of trifluoromethanesulfonic anhydride (96 μL, 0.58 mmol, 1.1 equiv) via syringe over 1 min to a mixture of amide **1a** (120 mg, 0.528 mmol, 1 equiv) and 2-chloropyridine (60 μL, 0.63 mmol, 1.2 equiv) in dichloromethane (2.7 mL) at 0 °C revealed consumption of both amide **1a** and 2-chloropyridine with concomitant appearance of a persistent band at 1600 cm^{-1} corresponding to the activated compound. After 5 min., nitrile **2a** (63 mg, 0.58 mmol, 1.1 equiv) was added via syringe, and the resulting solution was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 6 h, the reaction vessel was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **3a** as a white solid (106 mg, 63%).[9]

[9] Dines, T. J.; MacGregor, L. D.; Rochester, C. H. *Spectrochimica Acta Part A* **2003**, *59*, 3205.



Control IR Experiments:

Assignment of the 2-chloropyridine and the 2-chloropyridinium triflate characteristic stretches:

1) In situ IR monitoring of the addition of trifluoromethanesulfonic acid (47 μL, 0.53 mmol, 1 equiv) via syringe to a solution of 2-chloropyridine (50 μL, 0.53 mmol, 1 equiv, 1580 cm^{-1}) in CH_2Cl_2 (2.2 mL) at 0 °C resulted in the expected 2-chloropyridinium triflate salt (1620 cm^{-1}).

*Assignment of the 4-Cyclohexyl-6-methoxy-2-phenyl-quinazolin-1-ium triflate (**3a**•HOTf) characteristic stretch:*

2) In situ IR monitoring of the addition of trifluoromethanesulfonic acid (78 μL, 0.88 mmol, 2.0 equiv) via syringe to a solution of quinazoline **3a** (140 mg, 0.29 mmol, 1 equiv, 1550 cm^{-1}) and 2-chloropyridine (50 μL, 0.53 mmol, 1 equiv, 1580 cm^{-1}) in CH_2Cl_2 (2.2 mL) at 0 °C resulted in the expected mixture containing 2-chloropyridinium triflate salt (1620 cm^{-1}) and the 4-cyclohexyl-6-methoxy-2-phenyl-quinazolin-1-ium triflate salt (**3a**•HOTf, 1575 cm^{-1}).

3) The same characteristic resonance for **3a**•HOTf was observed in the absence of 2-chloropyridine. In situ IR monitoring of the addition of trifluoromethanesulfonic acid (43 μL, 0.49 mmol, 1 equiv) to a solution of quinazoline **3a** (140 mg, 0.29 mmol, 1 equiv, 1550 cm^{-1}) in CH_2Cl_2 (2.2 mL) at 0 °C resulted in the expected 4-cyclohexyl-6-methoxy-2-phenyl-quinazolin-1-ium triflate salt (**3a**•HOTf, 1575 cm^{-1}).

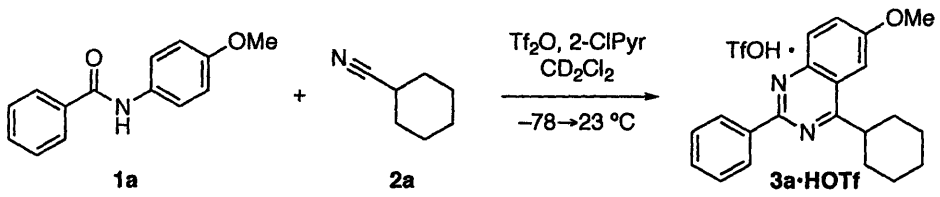
Assignment of the characteristic stretch at 1600 cm^{-1} to the activated intermediate in the presence of 2-chloropyridine:

4) Trifluoromethanesulfonic anhydride (96 μL, 0.58 mmol, 1.1 equiv) was added via syringe over 1 min to a solution of amide **1a** (120 mg, 0.528 mmol, 1 equiv) in dichloromethane (2.7 mL) at 0 °C. After 5 min., 2-chloropyridine (60 μL, 0.63 mmol, 1.2 equiv) was added via

syringe resulting in the appearance of the characteristic stretch at 1600 cm^{-1}. The nitrile **2a** (63 mg, 0.58 mmol, 1.1 equiv) was immediately added via syringe, and the resulting solution was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 3 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **3a** as a white solid (58 mg, 35%). This non-ideal procedure (order of reagent addition and time) was used to verify the involvement of 2-chloropyridine in the formation of the activated intermediate resulting in the observed stretch at 1600 cm^{-1}.

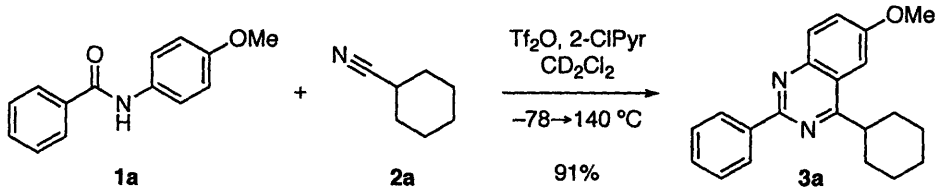
5) Additionally, in situ IR monitoring of the addition of trifluoromethanesulfonic acid (73 μL, 0.44 mmol, 1 equiv) via syringe to 2-chloropyridine (42 μL, 0.44 mmol, 1 equiv, 1580 cm^{-1}) in CH_2Cl_2 (2.2 mL) at ambient temperature resulted in no observable change. The band at 1580 cm^{-1} related to 2-chloropyridine persisted with out loss in intensity. After 4.5 h, water (70 μL, 4.4 mmol, 10 equiv) was added via syringe and as expected the 2-chloropyridine stretch (1580 cm^{-1}) disappeared completely with a concomitant appearance of a band consistent with 2-chloropyridinium triflate salt (1620 cm^{-1}).

^{1}H and ^{19}F NMR monitoring of the conversion of amide 1a and nitrile 2a to quinazoline 3a:



4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (3a•HOTf):

Trifluoromethanesulfonic anhydride (80 μL, 0.48 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (100 mg, 0.440 mmol, 1 equiv) and 2-chloropyridine (50 μL, 0.53 mmol, 1.2 equiv) in CD_2Cl_2 (1.5 mL) at –78 °C. After 5 min the reaction vessel was placed in an ice-water bath and warmed to 0 °C. ^{1}H (500 MHz) and ^{19}F (282 MHz) NMR analysis revealed broad resonances. Additionally, complete consumption of 2-chloropyridine and the starting amide **1a** was confirmed. ^{19}F NMR was informative and revealed a broad peak corresponding to a triflate ion at δ–79.6 along with remaining trifluoromethanesulfonic anhydride (δ–72.4, ~16%). The nitrile **2a** (53 mg, 0.48 mmol, 1.1 equiv) was added via syringe. After 5 min., ^{1}H and ^{19}F NMR analysis revealed a small set of resonances consistent with the protonated quinazoline product **3a**•HOTf along with dominant resonances corresponding to those observed during activation of the amide as described above. Again, the ^{19}F NMR was informative and revealed predominantly a broad resonance corresponding to a triflate ion at δ–79.6 along with unreacted trifluoromethanesulfonic anhydride (13%) at δ–72.4. While a trace amount of the product was observed, the best conditions for the synthesis of **3a** involve heating to 140 °C.



4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline (3a):

Trifluoromethanesulfonic anhydride (80 μL, 0.48 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1a** (100 mg, 0.440 mmol, 1 equiv), nitrile **2a** (53 mg, 0.48 mmol, 1.1 equiv) and 2-chloropyridine (50 μL, 0.53 mmol, 1.2 equiv) in CD_2Cl_2 (1.5 mL) at –78 °C. After 5 min., the reaction vessel was placed in an ice-water bath for 5 min. and warmed to 0 °C; the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and a sample was subject to ^{1}H (500 MHz) and ^{19}F NMR (282 MHz) analysis. Complete conversion to the desired product was observed by this crude ^{1}H NMR analysis. The observed resonances corresponded to 2-chloropyridium trifluoromethane-sulfonate, protonated quinazoline **3a**•HOTf, and the remaining nitrile **2a**. ^{19}F NMR analysis of the crude reaction mixture revealed only a broad resonance corresponding to triflate anion at δ–79.6 and weak resonance at δ–72.4 for the trace amount of remaining trifluoromethanesulfonic anhydride. Aqueous sodium hydroxide solution (1 mL, 1N)

was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinazoline product **3a** as a white solid (127 mg, 91%).

Control ^{1}H and ^{19}F NMR Experiments:

Assignment of the 2-chloropyridinium triflate resonances:

1) Addition of trifluoromethanesulfonic acid (1 equiv) via syringe to 2-chloropyridine (1 equiv) in CD_2Cl_2 (700 μL) at 23 °C followed by ^{1}H and ^{19}F NMR analysis revealed the formation of the expected 2-chloropyridinium triflate. ^{1}H NMR (500 MHz) δ: 15.8 (br-s, 1H), 8.76 (br-m, 1H), 8.54 (m, 1H), 8.02–7.98 (m, 2H). ^{19}F NMR (282 MHz) δ: –79.3.

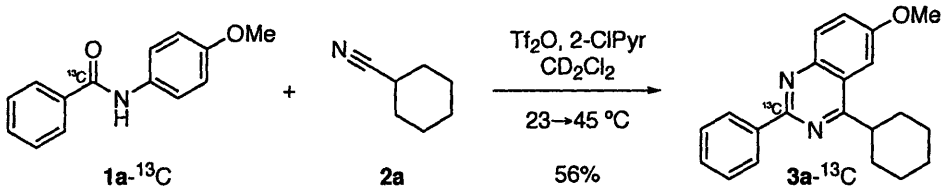
2) Consistent with the IR experiments described above, the addition of trifluoromethanesulfonic anhydride (32 μL, 0.19 mmol, 1.1 equiv) via syringe to a solution of 2-chloropyridine (17 μL, 0.18 mmol, 1 equiv) in CD_2Cl_2 (600 μL) at 23 °C under an atmosphere of argon followed by ^{1}H and ^{19}F NMR analysis revealed no change after 24 h. Importantly, ^{19}F NMR (282 MHz) analysis only reveals a persistent resonance at δ–72.4 (Tf_2O). After 24 hours, water (50 μL) was added to this sample to give the expected 2-chloropyridinium triflate (δ–79.5).

*Assignment of the 4-Cyclohexyl-6-methoxy-2-phenyl-quinazolin-1-ium triflate (**3a**•HOTf) resonances:*

3) Addition of trifluoromethanesulfonic acid (56 μL, 0.63 mmol, 2.0 equiv) via syringe to a solution of 2-chloropyridine (36 μL, 0.38 mmol, 1.2 equiv) and quinazoline **3a** (100 mg, 0.310 mmol, 1 equiv) in CD_2Cl_2 (1 mL) at 23 °C followed by ^{1}H and ^{19}F NMR analysis revealed the formation of the expected 2-chloropyridinium triflate and the 4-cyclohexyl-6-methoxy-2-phenyl-quinazolin-1-ium triflate (**3a**•HOTf). ^{1}H NMR (500 MHz) δ: ^{1}H NMR (500 MHz) δ:14.9 (br-s, 2.6H), 9.05 (br-s, 2.2H), 8.72 (dd, 1.1H, J = 5.5, 1.8 Hz), 8.70–8.63 (m, 3.0H), 8.28 (ddd, 1.0H, J = 8.2, 7.7, 1.9 Hz), 7.92 (dd, 0.9H, J = 9.3, 2.6 Hz), 7.82–7.75 (m, 2.8H), 7.75–7.70 (m, 2.0H), 7.61 (d, 1.1H, J = 2.7 Hz), 4.10 (s, 3.0H), 3.74 (tt, 1.1H, J = 11.4, 3.4 Hz), 2.14–1.90 (m, 7.2H), 1.70–1.59 (m, 2.1H), 1.48 (qt, 1.1H, J = 13.0, 3.5 Hz). ^{19}F NMR (282 MHz) δ: –79.6.

4) Addition of trifluoromethanesulfonic acid (56 μL, 0.63 mmol, 2.0 equiv) via syringe to a solution of quinazoline **3a** (100 mg, 0.310 mmol, 1 equiv) in CD_2Cl_2 (1 mL) at 23 °C followed by ^{19}F NMR analysis of the mixture suggests *mono*-protonation to give the quinazolinium triflate **3a**•HOTf. ^{19}F NMR (282 MHz) δ: –78.0, –79.1.

^{13}C NMR monitoring of the conversion of amide 1a-^{13}C and nitrile 2a to quinazoline 3a-^{13}C:



1a-^{13}C **2a** **3a-^{13}C**

<u>**4-Cyclohexyl-6-methoxy-2-phenyl-quinazoline-^{13}C (3a-^{13}C):**</u>

2-Chloropyridine (50 μL, 0.53 mmol, 1.2 equiv) was added via syringe to a solution of amide[10] **1a**-^{13}C (^{13}C=O, 100 mg, 0.439 mmol, 1 equiv) in CD_2Cl_2 (1.1 mL) at ambient temperature in an NMR tube under an atmosphere of argon. A sharp resonance corresponding to the carbonyl of amide **1a**-^{13}C (δ166.0) was observed. Trifluoromethanesulfonic anhydride (80 μL, 0.48 mmol, 1.1 equiv) was added via syringe at 23 °C and the ^{13}C NMR spectrum of the resulting mixture was immediately recorded. The starting amide was completely consumed and a new and persistent broad resonance was detected (δ149.8). Addition of nitrile **2a** (53 mg, 0.48 mmol, 1.1 equiv) at 23 °C and immediate ^{13}C NMR monitoring led to observation of two new sharp resonance at δ166.9 and δ96.9 along with the remaining broad resonance at δ149.8 (~0.9:0.4,1.0, respectively). After 2 h heating of the mixture at 45 °C, the sample was cooled to 23 °C and the ^{13}C NMR analysis of the reaction mixture revealed a dominant new resonance at δ155.1 attributed to the desired product quinazoline **3a**-^{13}C•HOTf and disappearance of the broad resonance at δ149.8. The resonances at δ166.9 and δ96.9 were weak (~5%) but remained detectable. The assignment of the resonance at δ155.1 to **3a**-^{13}C•HOTf was confirmed independently by protonation of a sample of product **3a**-^{13}C with TfOH (1 equiv) in CD_2Cl_2. The NMR tube was placed in a 45 °C oil bath and maintained at that temperature for an additional 14 h. At this time, the only dominant 13C resonance was that attributed to the desired product quinazoline **3a**-^{13}C•HOTf (δ155.1). An aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL103, was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the isotopically enriched quinazoline product **3a**-^{13}C as a white solid (79 mg, 56%).

---

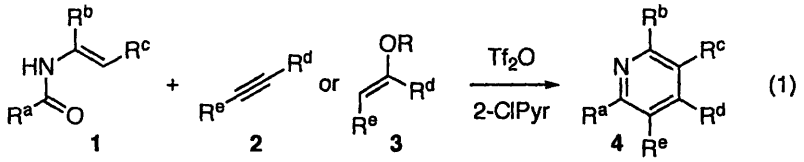
[10] Amide **1a**-^{13}C was readily prepared from the commercially available benzoic acid-*carboxy*-^{13}C (99% atom % ^{13}C, Ph$^{13}CO_2H$).

Chapter III

Direct Synthesis of Pyridine Derivatives

Introduction and Background

As discussed in Chapter I, the pyridine substructure is one of the most prevalent heterocycles found in natural products, pharmaceuticals, and functional materials.[1] Many powerful methodologies for the synthesis of these heterocycles rely on condensation of amines and carbonyl compounds or cycloaddition reactions.[2,3] Cross-coupling chemistry also allows introduction of substituents to activated heterocycles.[4] Our two-step pyridine synthesis[5] (Chapter I) requires a ruthenium catalyst and can provide di- or tri-substituted pyridines. Herein we report a mild and convergent, transition-metal free, single-step procedure for the conversion of readily available *N*-vinyl and *N*-aryl amides[6] to the corresponding substituted pyridines and quinolines, respectively (eq 1).



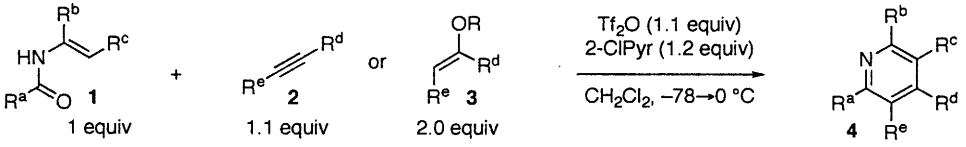
(1)

Results and Discussion

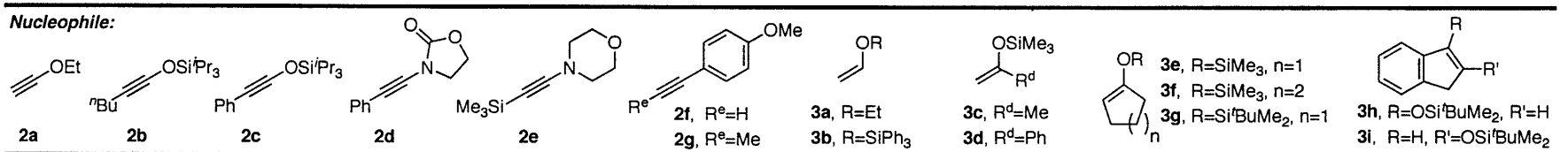
In earlier chapters of this thesis we reported a two-step synthesis of pyridines and a single-step synthesis of pyrimidines from readily available amides.[5] These methodologies were made possible in part due to the recognition of the unique electrophilic activation[5b] of amides with trifluoromethanesulfonic anhydride (Tf_2O)[7] in the presence of 2-chloropyridine (2-ClPyr) as the base additive.[8] A variety of amides were employed in our pyrimidine synthesis using nitriles as σ-nucleophiles.[5b] The current study focuses on the direct condensation of amides **1** with a wide range of π-nucleophiles (**2** or **3**) to provide the corresponding pyridine derivatives **4** (eq 1) in a single step.

We began our studies by investigating the use of alkoxy and silyloxy acetylenes in direct condensation with amides upon activation with Tf_2O and 2-ClPyr (eq 2).[5b] Under optimum reaction conditions, these electron-rich π-nucleophiles provided the desired pyridine and quinoline derivatives in one step from the corresponding *N*-vinyl and *N*-aryl amides (Table 1, **4a-e**). Similarly, the use of ynamide **2d** and ynamine **2e** readily provided the 4-amino pyridine derivatives in a single step (Table 1, **4f-l**). While phenyl acetylene was not sufficiently

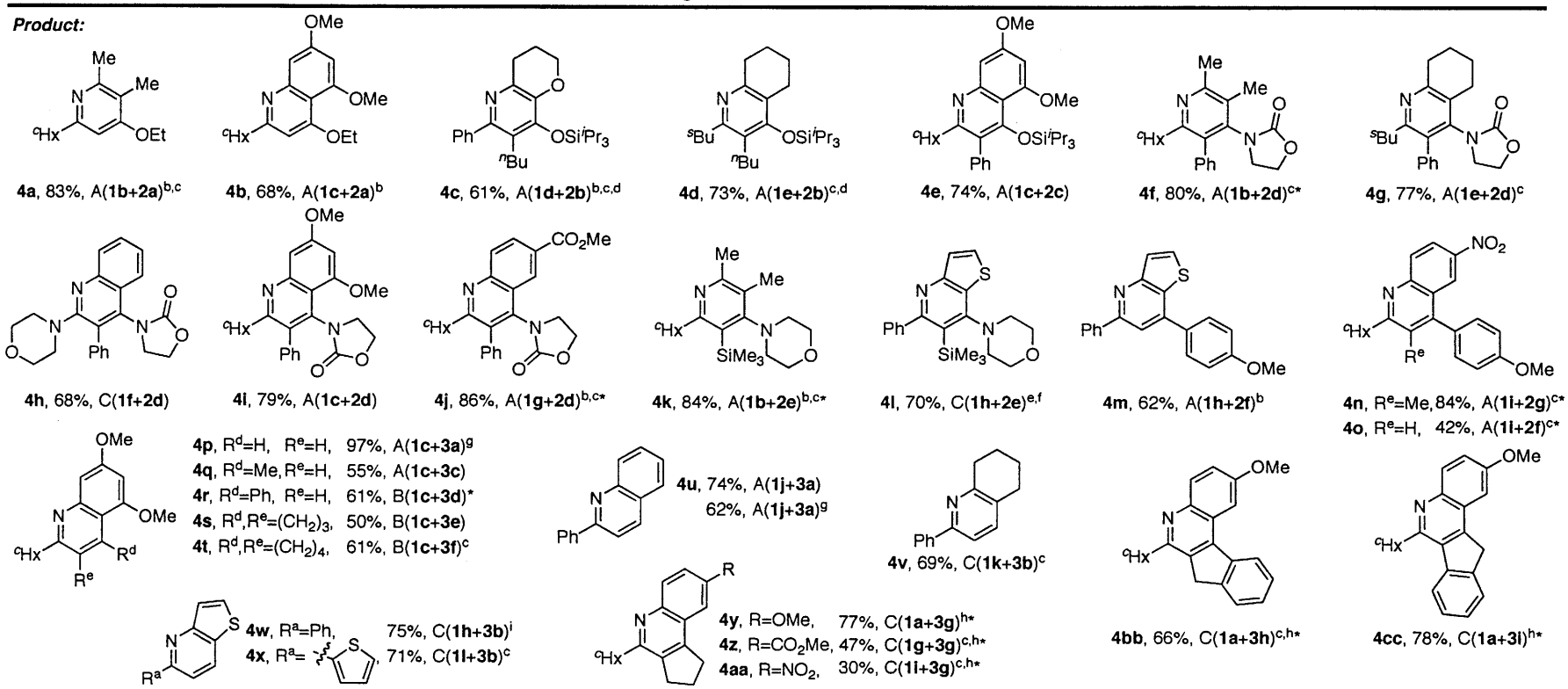
Table 1. Single-Step Synthesis of Pyridine Derivatives by Condensation of π-Nucleophiles with Amides.[a]



Nucleophile:

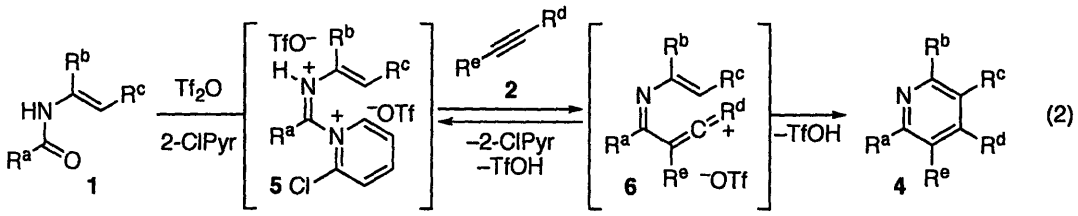


Product:



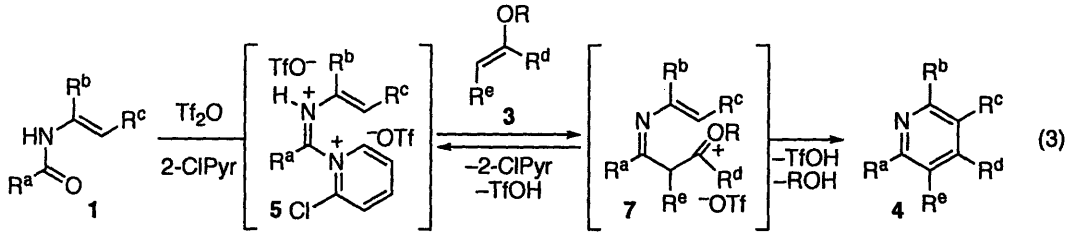
[a] Average of two experiments. Uniform conditions unless otherwise noted: Tf_2O (1.1 equiv), 2-ClPyr (1.2 equiv), nucleophile (**2** or **3**), CH_2Cl_2, heating: A = 23 °C, 1 h; B = 45 °C, 1 h; C = 140 °C, 20 min. [b] nucleophile (2.0 equiv). [c] 2-ClPyr (2.0 equiv). [d] only 10 min at 23 °C. [e] 2-ClPyr (5.0 equiv). [f] only 1 min heating, nucleophile (3.0 equiv). [g] nucleophile (1.1 equiv). [h] heated for 1 h. [i] 45% yield using **3a** with condition A. * Reactions performed by my colleague, Omar K. Ahmad.

nucleophilic, the more electron rich derivatives **2f** and **2g** served as π-nucleophiles in this pyridine synthesis (Table 1, **4m-o**). Importantly, both electron-rich and electron-deficient *N*-aryl amides can be condensed with π-nucleophiles **2a-g** (Table 1, compare **4i** and **4j**).



(2)

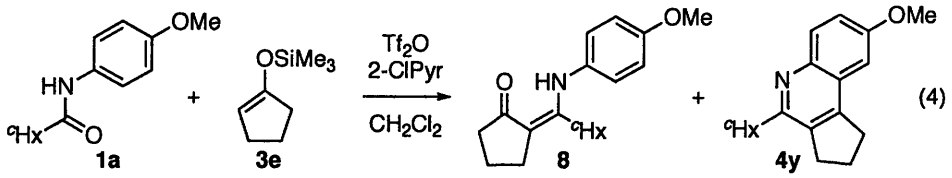
Based on mechanistic findings in our pyrimidine synthesis,[5b] we propose this single-step pyridine synthesis proceeds by π-nucleophilic addition of acetylenes **2a-g** to an activated electrophile **5**[9] followed by expulsion of 2-ClPyr•HOTf and annulation of the highly reactive intermediate **6** (eq 2). The condensation of the terminal alkyne **2f** with an *N*-(4-nitrophenyl) amide gave the desired quinoline **4o** in low yield (Table 1, 42% yield) along with 32% yield of cyclohex-1-yl-3-(4-methoxyphenyl)-propynone, the hydrolysis product of the corresponding alkynyl imine.[10] This observation suggests competitive deprotonation of intermediate **6** (R^e=H) when cyclization to heterocycle **4** is slow.



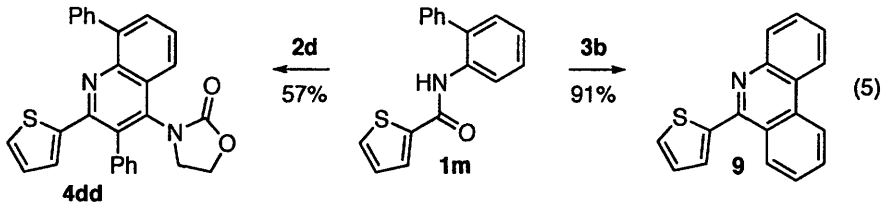
(3)

We next examined the direct condensation of enol ethers with *N*-vinyl and *N*-aryl amides (eq 3). While ethyl vinyl ether (**3a**) could be used as a π-nucleophile when heating is not required (Table 1, **4p** and **4u**), we found triphenylsilyl vinyl ether (**3b**) to provide superior results in more challenging cases (Table 1, **4v-x**). The use of excess nucleophile can be beneficial and provides an improved yield of the product (Table 1, **4u**). Importantly, the use of silyl ether **3b** in place of ethyl vinyl ether **3a** eliminates the competitive addition of EtOH, generated in conversion of **7** to **4** (eq 3), to the activated intermediate **5**. Both acyclic and cyclic trimethylsilyl

enol ethers can be used in direct condensation with amides (Table 1, **4q-t**). However, when desilylation competes with cyclization of oxonium ion **7** (eq 3), the use of more robust silyl enol ether derivatives is preferred. Condensation of amide **1a** with enol ether **3e** at 23 °C predominantly gave the vinylogous amide **8** (eq 4, 78%, **8**:**4y**, >99:1, reaction performed by my colleague, Omar K. Ahmad) while heating the reaction mixture at 140 °C for 2 h[11] provided the desired quinoline (eq 4, 53%, **4y**:**8**, >99:1, reaction performed by my colleague, Omar K. Ahmad).

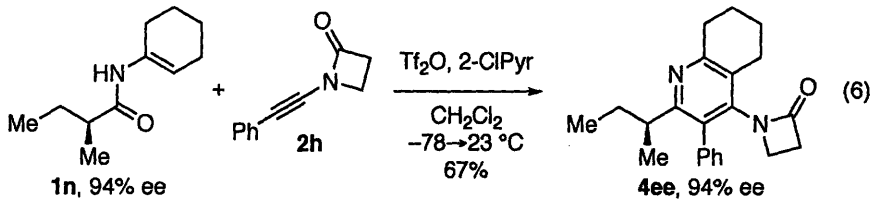


Consistent with cyclization of intermediate **7** (eq 3), exposure of amide **8** to the standard reaction conditions provided <10% yield of **4y**. Whereas the use of triisopropylsilyl ether derivatives was not optimal due to slow cyclization, the use of *tert*-butyldimethylsilyl ethers and microwave irradiation extends this chemistry to less reactive amide substrates (Table 1, **4y-cc**). The use of enol ethers as the π-nucleophile in conjunction with electron deficient *N*-aryl amides (Table 1, compare **4y-aa**) in this azaheterocycle synthesis is less efficient as compared to the use of acetylenic derivatives as the nucleophile (vide supra). Additionally, it should be noted that formamides do not give the corresponding pyridines with alkynyl or alkenyl π-nucleophiles due to rapid isocyanide formation.



The example shown in equation 5 highlights the greater efficiency of this chemistry when nucleophilic acetylenes are employed in place of enol derivatives. Activation of amide **1m** under standard conditions and the use of silyl enol ether **3b** provided the intramolecular annulation product **9** rather than the expected quinoline product. However, activation of amide **1m** under identical conditions and the use of nucleophile **2d** provided the desired quinoline derivative **4dd**

without detectable formation of phenanthridine **9** (eq 5). The synthesis of pyridine **4ee** from the corresponding *N*-vinyl amide **1n** without loss of optical activity (eq 6) is noteworthy and is consistent with our prior observations.[5b]



Conclusion

Herein we describe a single-step and convergent procedure for the synthesis of pyridine derivatives. This chemistry is compatible with a wide range of *N*-vinyl/aryl amides and π-nucleophiles. This methodology alleviates the need for isolation of activated amide derivatives and provides rapid access to highly substituted pyridines with predictable control of substituent introduction. The versatility of this chemistry offers a valuable addendum to methodology for azaheterocycle synthesis.[12] Future work in this area will focus on intramolecular trapping of electrophilic activated amide intermediates with σ- and π-nucleophiles to generate polycyclic azaheterocycles.

(1) (a) Jones, G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V.; McKillop, A., Eds; Pergamon: Oxford, 1996; Vol. 5; p 167. (b) Henry, G. D. *Tetrahedron* **2004**, *60*, 6043. (c) Michael, J. P. *Nat. Prod. Rep.* **2005**, *22*, 627.

(2) (a) Boger, D. L. *J. Heterocycl. Chem.* **1998**, *35*, 1003. (b) Jayakumar, S.; Ishar, M. P. S.; Mahajan, M. P. *Tetrahedron* **2002**, *58*, 379. (c) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285. (d) Varela, J. A.; Saá, C. *Chem. Rev.* **2004**, *104*, 3787.

(3) (a) Varela, J. A.; Castedo, L.; Saá, C. *J. Org. Chem.* **2003**, *68*, 8595. (b) Sangu, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2004**, *6*, 353. (c) Zhang, X.; Campo, M. A.; Yao, T.; Larock, R. C. *Org. Lett.* **2005**, *7*, 763. (d) McCormick, M. M.; Duong, H. A.; Zuo, G.; Louie, J. *J. Am. Chem. Soc.* **2005**, *127*, 5030 and references therein.

(4) Chinchilla, R.; Nájera, C.; Yus, M. *Chem. Rev.* **2004**, *104*, 2667.

(5) (a) Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 4592. (b) Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 14254.

(6) (a) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (b) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p. 1051. (c) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (d) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.

(7) (a) For elegant prior studies on amide activation, see: Charette, A. B.; Grenon, M. *Can. J. Chem.* **2001**, *79*, 1694. (b) Review: Baraznenok, I. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 3077.

(8) Myers, A. G.; Tom, N. J.; Fraley, M. E.; Cohen, S. B.; Madar, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 6072.

(9) For discussion of the structure and chemistry of **5**, see ref. 6b.

(10) See the Experimental Section for details.

(11) Shorter reaction times gave a mixture of amide **8** and product **4y**.

(12) Movassaghi, M.; Hill, M. D.; Ohmad, O. K. *J. Am. Chem. Soc.* **2007**, *129*, 10096.

Experimental Section

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure.[2] 2-chloropyridine was distilled from calcium hydride and stored sealed under an argon atmosphere. The starting amides were prepared by acylation of the corresponding anilines[3] or via previously reported copper–catalyzed C–N bond–forming reactions.[4,5] Ethoxy acetylene (**2a**) was purchased from Aldrich as a solution in hexanes and purified by kugelrohr distillation before use (% wt. in hexanes determined by ^{1}H NMR analysis, ~47% wt.). Silyloxy acetylenes **2b** and **2c** were prepared according to Sun, J.; Kozmin., S. A. *Angew. Chem. Int. Ed.* **2006**, *45*, 4991. Ynamide **2d** was prepared according to Buissonneaud, D.; Cintrat, J.-C. *Tetrahedron Lett.* **2006**, *47*, 3139. Silyl enol ether **3b** was prepared according to Schaumann, E.; Tries, F. *Synthesis* **2002**, 191.

Instrumentation. All reaction conducted at 140 °C were performed in a CEM Discover Lab Mate microwave reactor. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer or a Bruker 400 AVANCE spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, C_6HD_5: δ 7.16).

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

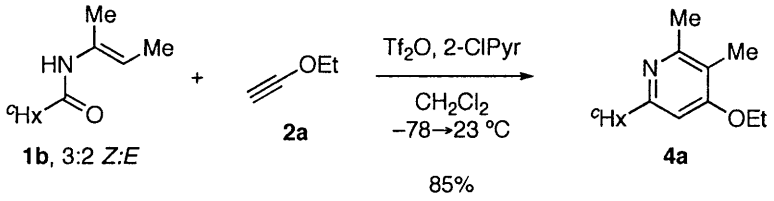
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(3) For a general procedure, see: DeRuiter, J.; Swearingen, B. E.; Wandrekar, V.; Mayfield, C. A. *J. Med. Chem.* **1989**, *32*, 1033.

(4) For the general procedure used for the synthesis of all *N*-vinyl amides, see: Jiang, L.; Job, G. E.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 3667.

(5) For related reports, see: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (b) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (c) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (d) Beletskaya, I. P.; Cheprakov, A. V. *Coordin. Chem. Rev.* **2004**, *248*, 2337. (e) Dehli, J. R.; Legros, J.; Bolm, C. *Chem. Commun.* **2005**, 973.

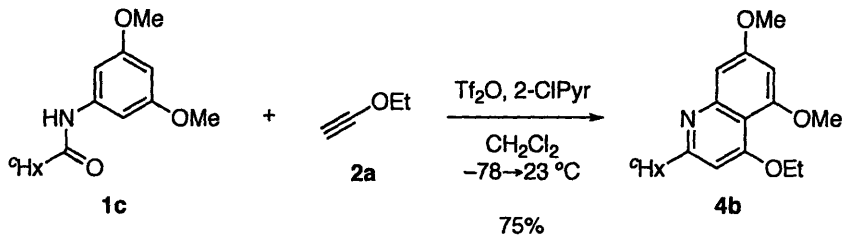
Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), integration, coupling constant(s) in Hertz, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer or a Bruker 400 AVANCE spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.2, benzene-d_6: δ 128.0). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Chiral HPLC analysis was performed on an Agilent 1100 Series HPLC with a Whelk-O1 (*S*,*S*) column. We thank Dr. Li Li at the Massachusetts Institute of Technology Department of Chemistry instrumentation facility for obtaining mass spectroscopic data.



6-Cyclohexyl-4-ethoxy-2,3-dimethylpyridine (4a, Table 1):

Trifluoromethanesulfonic anhydride (50 μL, 0.30 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1b** (50 mg, 0.28 mmol, 1 equiv) and 2-chloropyridine (52 μL, 0.55 mmol, 2.0 equiv) in dichloromethane (900 μL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ethyl ethynyl ether (**2a**, 82 mg, 0.55 mmol, 2.0 equiv, 47% wt. in hexane) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc/1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4a** as a pale yellow solid (55 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	6.48 (s, 1H, Ar**H**), 4.06 (q, 2H, J = 7.0 Hz, $OC\mathbf{H}_2CH_3$), 2.66–2.58 (m, 1H, $^cC_6\mathbf{H}_{11}$), 2.46 (s, 3H, $C\mathbf{H}_3$), 2.10 (s, 3H, $C\mathbf{H}_3$), 1.98–1.93 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.86–1.80 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.77–1.71 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.48–1.38 (m, 7H, $^cC_6\mathbf{H}_{11}$, $OCH_2C\mathbf{H}_3$), 1.32–1.24 (m, 1H, $^cC_6\mathbf{H}_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	164.7, 163.4, 156.5, 117.2, 101.0, 63.5, 47.0, 33.5, 26.8, 26.3, 22.8, 14.8, 10.9.
FTIR (neat) cm^{-1}:	3231 (w), 3064 (w), 2955 (s), 2865 (s), 1726 (w), 1634 (m), 1594 (w), 1535 (s), 1498 (s), 1475 (s), 1240 (m).
HRMS (ESI):	calcd for $C_{15}H_{24}NO$ $[M+H]^+$: 234.1852, found: 234.1844.
TLC (20% EtOAc in hexanes), R_f:	0.27 (UV, $KMnO_4$).

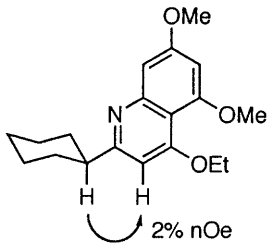


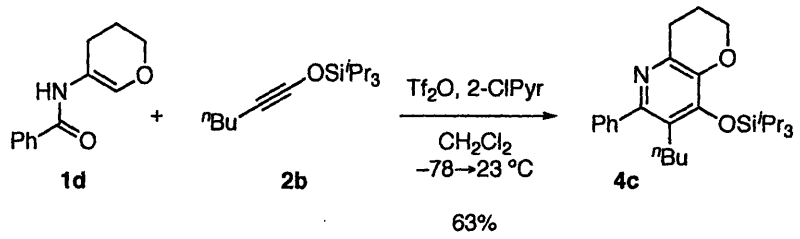
2-Cyclohexyl-4-ethoxy-5,7-dimethoxyquinoline (4b, Table 1):

Trifluoromethanesulfonic anhydride (83 μL, 0.50 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (120 mg, 0.456 mmol, 1 equiv) and 2-chloropyridine (52 μL, 0.55 mmol, 1.2 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, ethyl ethynyl ether (**2a**, 128 mg, 0.91 mmol, 2.0 equiv, 50% wt. in hexane) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 30% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **4b** as a white solid (110 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	6.97 (br s, 1H, Ar**H**), 6.51 (s, 1H, Ar**H**), 6.44 (d, 1H, J = 2.3 Hz, Ar**H**), 4.22 (q, 2H, J = 7.0 Hz, $OC\mathbf{H}_2CH_3$), 3.93 (s, 3H, $OC\mathbf{H}_3$), 3.91 (s, 3H, $OC\mathbf{H}_3$), 2.82–2.72 (m, 1H, $^cC_6\mathbf{H}_{11}$), 2.04–1.99 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.90–1.85 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.80–1.74 (m, 1H, $^cC_6\mathbf{H}_{11}$), 1.60–1.51 (m, 5H, $^cC_6\mathbf{H}_{11}$, $OCH_2C\mathbf{H}_3$), 1.50–1.41 (m, 2H, $^cC_6\mathbf{H}_{11}$), 1.32 (tt, 1H, J = 12.7, 3.5 Hz, $^cC_6\mathbf{H}_{11}$).
^{13}C NMR (125 MHz, DMF-d_7, 20 °C) δ:	168.6, 164.0, 161.0, 158.2, 152.8, 107.6, 100.2, 98.2, 98.2, 64.4, 56.3, 55.7, 47.9, 33.1, 26.7, 26.3, 14.7.
FTIR (neat) cm^{-1}:	2929 (m), 2851 (w), 1725 (w), 1615 (s), 1591 (s), 1451 (m), 1404 (m), 1382 (m), 1206 (m), 1155 (s).
HRMS (ESI):	calcd for $C_{19}H_{26}NO_3$ $[M+H]^+$: 316.1907, found: 316.1904.
TLC (40% EtOAc in hexanes), R_f:	0.54 (UV, $KMnO_4$).

nOe data:



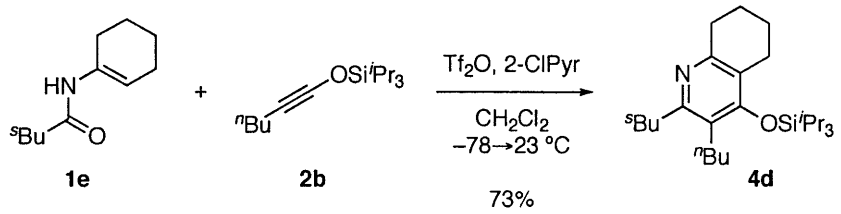


7-Butyl-6-phenyl-8-(triisopropylsilyloxy)-3,4-dihydro-2*H*-pyrano[3,2-*b*]pyridine (4c, Table 1):

Trifluoromethanesulfonic anhydride (72 μL, 0.43 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1d** (80 mg, 0.39 mmol, 1 equiv) and 2-chloropyridine (75 μL, 0.79 mmol, 2.0 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynol **2b**[6] (200 mg, 0.788 mmol, 2.00 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 10 min., triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4c** as a clear oil (110 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.40–7.30 (m, 5H, Ar**H**), 4.18 (t, 2H, J = 5.1 Hz, $CH_2CH_2C\mathbf{H}_2O$), 2.95 (t, 2H, J = 6.6 Hz, $C\mathbf{H}_2CH_2CH_2O$), 2.56–2.50 (m, 2H, $C\mathbf{H}_2CH_2$ CH_2CH_3), 2.15–2.09 (m, 2H, $CH_2C\mathbf{H}_2CH_2O$), 1.45–1.38 (m, 2H, $CH_2C\mathbf{H}_2CH_2CH_3$), 1.35–1.27 (m, 3H, $Si(C\mathbf{H}(CH_3)_2)_3$), 1.25–1.15 (m, 2H, CH_2CH_2 $C\mathbf{H}_2CH_3$), 1.11 (d, 18H, J = 7.4 Hz, $Si(CH$ $(C\mathbf{H}_3)_2)_3$), 0.76 (t, 3H, J = 7.3 Hz, CH_2CH_2 $CH_2C\mathbf{H}_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 20 °C) δ:	152.4, 149.9, 141.6, 141.0, 140.5, 129.1, 128.1, 127.3, 125.9, 65.8, 32.3, 28.3, 27.2, 23.0, 22.7, 18.3, 14.6, 13.9.
FTIR (neat) cm^{-1}:	2981 (w), 2927 (s), 2852 (m), 1731 (w), 1588 (s), 1575 (s), 1468 (m), 1328 (m), 1217 (m), 1123 (s).
HRMS (ESI):	calcd for $C_{18}H_{22}NO_2$ $[M–Si(^iPr)_3+2H]^+$: 284.1645, found: 284.1644.
TLC (20% EtOAc in hexanes), R_f:	0.21 (UV, $KMnO_4$).

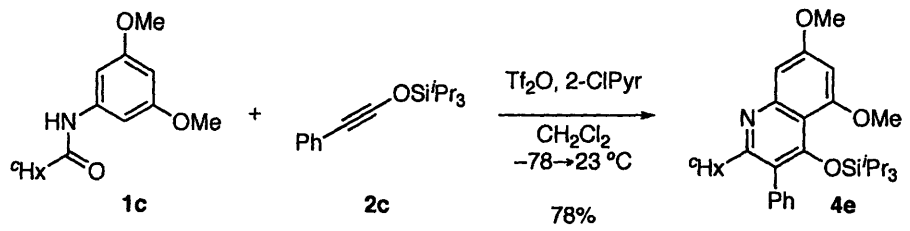
[6] For preparation of **2b** and **2c**, see Sun, J.; Kozmin., S. A. *Angew. Chem. Int. Ed.* **2006**, *45*, 4991.



2-*sec*-Butyl-3-butyl-4-(triisopropylsilyloxy)-5,6,7,8-tetrahydroquinoline (4d, Table 1):

Trifluoromethanesulfonic anhydride (80 μL, 0.49 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1e** (80 mg, 0.44 mmol, 1 equiv) and 2-chloropyridine (84 μL, 0.88 mmol, 2.0 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynol **2b** (123 mg, 0.485 mmol, 1.10 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 10 min., triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 3% EtOAc and 0.5% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4d** as a clear oil (134 mg, 73%).

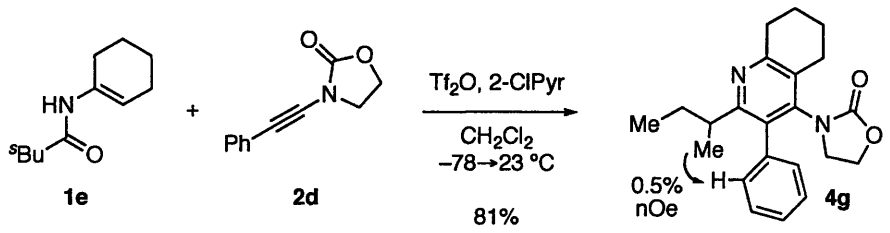
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	2.92–2.79 (m, 3H), 2.70–2.50 (m, 4H), 1.85–1.70 (m, 5H), 1.62–1.53 (m, 1H), 1.43–1.30 (m, 7H), 1.21 (d, 3H, J = 6.8 Hz, $CH_3CH_2CHCH_3$), 1.10 (d, 18H, J = 7.5 Hz, $Si(CH(CH_3)_2)_3$), 0.95–0.92 (m, 3H), 0.79 (t, 3H, J = 7.4 Hz, $CH_3CH_2CHCH_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	162.3, 159.8, 155.3, 123.7, 120.4, 38.0, 33.5, 33.0, 30.1, 26.4, 24.4, 23.4, 23.3, 22.9, 21.0, 18.2, 14.6, 14.3, 12.7.
FTIR (neat) cm^{-1}:	3257 (w), 3090 (w), 2958 (s), 2933 (s), 2869 (s), 1631 (w), 1612 (w), 1502 (s), 1464 (m), 1427 (m), 1210 (w).
HRMS (ESI):	calcd for $C_{26}H_{48}NOSi$ $[M+H]^+$: 418.3500, found: 418.3510.
TLC (20% EtOAc in hexanes), R_f:	0.76 (UV, $KMnO_4$).



2-Cyclohexyl-5,7-dimethoxy-3-phenyl-4-(triisopropylsilyloxy)quinoline (4e, Table 1):

Trifluoromethanesulfonic anhydride (69 μL, 0.42 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (100 mg, 0.380 mmol, 1 equiv) and 2-chloropyridine (43 μL, 0.46 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynol **2c**[6] (115 mg, 0.418 mmol, 1.10 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 4% EtOAc and 0.5% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **4e** as a clear oil (154 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.41–7.30 (m, 5H, Ar**H**), 6.97 (d, 1H, J = 2.4 Hz, Ar**H**), 6.41 (d, 1H, J = 2.4 Hz, Ar**H**), 3.95 (s, 3H, O**CH$_3$**), 3.82 (s, 3H, O**CH$_3$**), 2.58 (tt, 1H, J = 11.1, 3.5 Hz, ^{c}C$_6$**H$_{11}$**), 1.75–1.55 (m, 7H, ^{c}C$_6$**H$_{11}$**), 1.28 (qt, 1H, J = 13.0, 3.4 Hz, ^{c}C$_6$**H$_{11}$**), 1.12–1.00 (m, 2H, ^{c}C$_6$**H$_{11}$**), 0.83 (d, 18H, J = 7.2 Hz, Si(CH(C**H$_3$**)$_2$)$_3$), 0.75–0.67 (m, 3H, Si(C**H**(CH$_3$)$_2$)$_3$).
^{13}C NMR (100 MHz, $CDCl_3$, 20 °C) δ:	166.7, 160.2, 157.9, 157.5, 152.6, 137.3, 132.8, 128.2, 127.2, 123.9, 110.4, 100.3, 97.5, 55.6, 55.0, 42.8, 32.3, 26.6, 26.1, 18.1, 14.2.
FTIR (neat) cm^{-1}:	3057 (w), 2942 (s), 2865 (s), 1619 (s), 1567 (s), 1465 (m), 1451 (m), 1375 (s), 1358 (s), 1250 (m), 1207 (s).
HRMS (ESI):	calcd for $C_{32}H_{46}NO_3Si$ $[M+H]^+$: 520.3241, found: 520.3245.
TLC (10% EtOAc in hexanes), R_f:	0.32 (UV, $KMnO_4$).



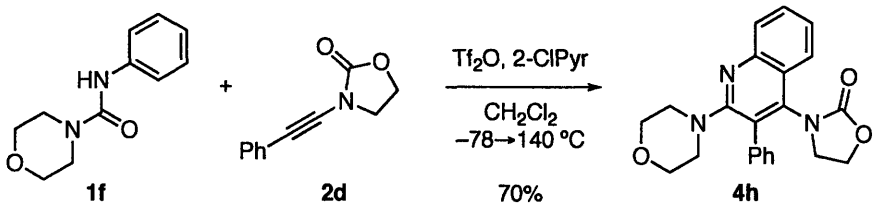
3-(2-*sec*-Butyl-3-phenyl-5,6,7,8-tetrahydroquinolin-4-yl)oxazolidin-2-one (4g, Table 1):

Trifluoromethanesulfonic anhydride (80 μL, 0.49 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1e** (80 mg, 0.44 mmol, 1 equiv) and 2-chloropyridine (84 μL, 0.88 mmol, 2.0 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamide **2d**Error! Bookmark not defined. (91 mg, 0.49 mmol, 1.1 equiv) was added as a solid in one portion and the reaction flask was rapidly purged and sealed under an argon atmosphere. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 30% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4g** as a white solid (126 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, minor atropisomer noted by *) δ:7.48–7.37 (m, 3H, Ar**H**; 3H, Ar**H***), 7.33–7.28 (m, 1H, Ar**H**; 1H, Ar**H***), 7.20–7.16 (m, 1H, Ar**H**; 1H, Ar**H***), 4.28–4.21 (m, 1H, NCH_2CH_2O; 1H, NCH_2CH_2O*), 3.86–3.80 (m, 1H, NCH_2CH_2O; 1H, NCH_2CH_2O*), 3.59–3.48 (m, 1H, NCH_2CH_2O; 1H, NCH_2CH_2O*), 3.14–3.03 (m, 1H, NCH_2CH_2O; 1H, NCH_2CH_2O*), 3.03–2.80 (m, 3H, $CH_2CH_2CH_2CH_2$; 3H, $CH_2CH_2CH_2CH_2$*), 2.69–2.60 (m, 1H, $CH_3CH_2CHCH_3$; 1H, $CH_3CH_2CHCH_3$*), 2.59–2.51 (m, 1H, $CH_2CH_2CH_2CH_2$; 1H, $CH_2CH_2CH_2CH_2$*), 1.97–1.62 (m, 5H, $CH_2CH_2CH_2CH_2$, $CH_3CH_2CHCH_3$; 5H, $CH_2CH_2CH_2CH_2$*, $CH_3CH_2CHCH_3$*), 1.60–1.37 (m, 1H, $CH_3CH_2CHCH_3$; 1H, $CH_3CH_2CHCH_3$*), 1.23 (d, 3H, J = 6.7 Hz, $CH_3CH_2CHCH_3$), 0.99 (d, 3H, J = 6.8 Hz, $CH_3CH_2CHCH_3$*), 0.82 (t, 3H, J = 7.4 Hz, $CH_3CH_2CHCH_3$*), 0.58 (t, 3H, J = 7.3Hz, $CH_3CH_2CHCH_3$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ: 162.4, 162.2, 158.5, 158.5, 156.5, 156.5, 141.0, 140.9, 136.5, 136.4, 132.8, 132.7, 130.1, 129.9, 129.1, 129.1, 129.0, 129.0, 128.2, 128.1, 127.9, 127.7, 62.9, 46.1, 45.9, 39.7, 38.8, 38.8, 33.1, 29.9, 29.1, 24.4, 22.9, 22.9, 22.5, 20.9, 20.9, 12.7, 12.3.

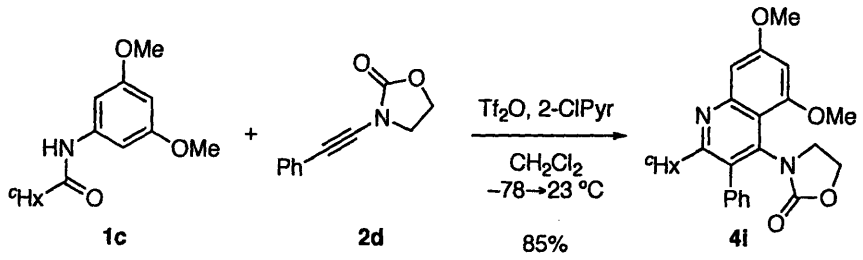
FTIR (neat) cm^{-1}:	2959 (m), 2933 (m), 1753 (s), 1603 (w), 1575 (w), 1481 (w), 1440 (m), 1409 (m), 1230 (m), 1181 (w).
HRMS (ESI):	calcd for $C_{22}H_{27}N_2O_2$ $[M+H]^+$: 351.2067, found: 351.2057.
TLC (30% EtOAc in hexanes), R_f:	0.29 (UV, $KMnO_4$).



3-(2-Morpholino-3-phenylquinolin-4-yl)oxazolidin-2-one (4h, Table 1):

Trifluoromethanesulfonic anhydride (40 μL, 0.24 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of urea **1f** (46 mg, 0.22 mmol, 1 equiv) and 2-chloropyridine (25 μL, 0.27 mmol, 1.2 equiv) in dichloromethane (750 μL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamide **2d** (83 mg, 0.44 mmol, 1.1 equiv) was added as a solid in one portion and the reaction flask was rapidly purged and sealed under an argon atmosphere. The resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before triethylamine (300 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **4h** as a white solid (58 mg, 70%).

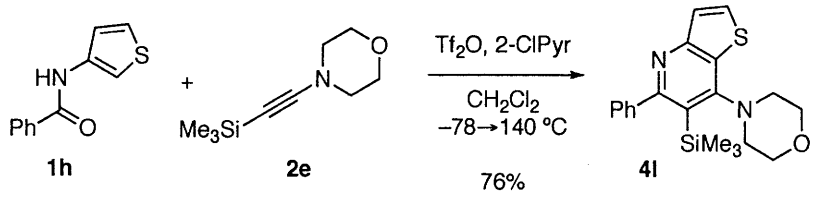
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.93–7.90 (m, 1H, Ar**H**), 7.73–7.69 (m, 1H, Ar**H**), 7.66 (qd, 1H, J = 6.9, 1.5 Hz, Ar**H**), 7.63–7.58 (m, 1H, Ar**H**), 7.55–7.47 (m, 3H, Ar**H**), 7.45–7.41 (m, 2H, Ar**H**), 4.46–4.40 (m, 1H, NCH_2CH_2O), 4.08–4.02 (m, 1H, NCH_2CH_2O), 3.64–3.52 (m, 5H, NCH_2CH_2O, $N(CH_2CH_2)_2O$), 3.22–3.13 (m, 4H, $N(CH_2CH_2)_2O$), 3.04–2.99 (m, 1H, NCH_2CH_2O).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	159.6, 157.8, 147.8, 140.4, 135.6, 130.3, 129.6, 129.5, 128.8, 128.7, 128.6, 128.3, 128.2, 125.3, 122.5, 122.2, 66.7, 63.2, 49.7, 46.1.
FTIR (neat) cm^{-1}:	3490 (w), 3060 (m), 2965 (m), 2893 (m), 2849 (m), 2248 (w), 1755 (s), 1587 (s), 1491 (s), 1409 (s), 1238 (s), 1117 (s).
HRMS (ESI):	calcd for $C_{22}H_{22}N_3O_3$ $[M+H]^+$: 376.1656, found: 376.1668.
TLC (40% EtOAc in hexanes), R_f:	0.28 (UV, $KMnO_4$).



3-(2-Cyclohexyl-5,7-dimethoxy-3-phenylquinolin-4-yl)oxazolidin-2-one (4i, Table 1):

Trifluoromethanesulfonic anhydride (69 μL, 0.42 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (100 mg, 0.380 mmol, 1 equiv) and 2-chloropyridine (43 μL, 0.46 mmol, 1.2 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamide **2d** (78 mg, 0.42 mmol, 1.1 equiv) was added as a solid in one portion, and the reaction flask was rapidly purged and sealed under an argon atmosphere. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **4i** as a white solid (140 mg, 85%).

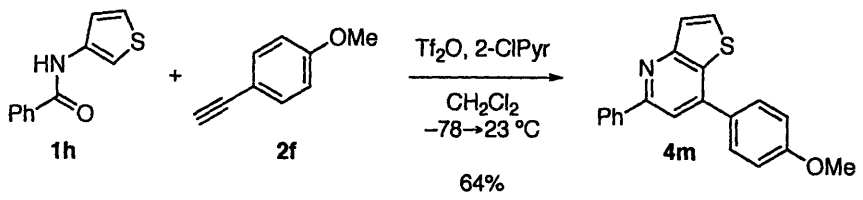
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.49–7.40 (m, 4H, Ar**H**), 7.23–7.19 (m, 1H, Ar**H**), 7.11 (d, 1H, J = 2.3 Hz, Ar**H**), 6.57 (d, 1H, J = 2.3 Hz, Ar**H**), 4.33–4.28 (m, 1H, NCH_2CH_2O), 3.97 (s, 3H, OCH_3), 3.96–3.89 (m, 4H, OCH_3, NCH_2CH_2O), 3.76–3.70 (m, 1H, NCH_2CH_2O), 3.24–3.18 (m, 1H, NCH_2CH_2O), 2.67–2.60 (m, 1H, $^cC_6H_{11}$), 1.91–1.74 (m, 3H, $^cC_6H_{11}$), 1.63–1.60 (m, 2H, $^cC_6H_{11}$), 1.35–1.10 (m, 4H, $^cC_6H_{11}$), 1.09–0.99 (m, 1H, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	166.4, 160.9, 157.8, 156.0, 152.3, 138.5, 136.3, 133.4, 130.3, 128.8, 128.7, 127.9, 127.8, 111.4, 101.2, 99.9, 62.9, 56.6, 55.8, 47.8, 43.2, 32.5, 32.2. 26.5, 26.5, 26.0.
FTIR (neat) cm^{-1}:	2924 (m), 2850 (w), 1745 (s), 1617 (s), 1573 (s), 1479 (w), 1446 (w), 1423 (m), 1407 (m), 1249 (m).
HRMS (ESI):	calcd for $C_{26}H_{29}N_2O_4$ $[M+H]^+$: 433.2122, found: 433.2107.
TLC (40% EtOAc in hexanes), R_f:	0.31 (UV, $KMnO_4$).



4-(5-Phenyl-6-(trimethylsilyl)thieno[3,2-*b*]pyridin-7-yl)morpholine (4l, Table 1):

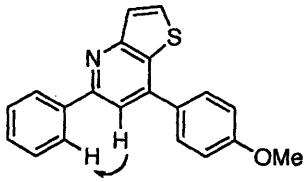
Trifluoromethanesulfonic anhydride (89 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1h** (100 mg, 0.492 mmol, 1 equiv) and 2-chloropyridine (233 μL, 2.45 mmol, 5.00 equiv) in dichloromethane (1.6 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamine **2e** (270 mg, 1.48 mmol, 3.00 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 1 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc was 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivatives **4l** as a pale yellow oil (138 mg, 76%).

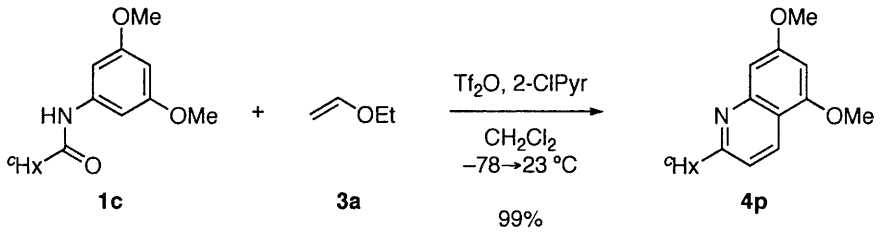
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.74–7.72 (m, 1H, Ar**H**), 7.62–7.60 (m, 1H, Ar**H**), 7.50–7.47 (m, 2H, Ar**H**), 7.45–7.40 (m, 3H, Ar**H**), 3.98–3.95 (m, 4H, $N(CH_2C\mathbf{H}_2)_2O$), 3.42 (br s, 4H, $N(C\mathbf{H}_2CH_2)_2O$), 0.05 (s, 9H, $Si(C\mathbf{H}_3)_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	181.1, 166.3, 161.8, 158.7, 144.6, 130.6, 129.7, 128.3, 128.3, 125.9, 125.8, 67.0, 51.9, 2.6.
FTIR (neat) cm^{-1}:	2955 (m), 2894 (m), 2856 (m), 1572 (w), 1515 (s), 1471 (s), 1445 (m), 1337 (s), 1259 (s), 1113 (s).
HRMS (ESI):	calcd for $C_{20}H_{25}N_2OSSi$ $[M+H]^+$: 369.1451, found: 369.1452.
TLC (30% EtOAc in hexanes), R_f:	0.44 (UV, $KMnO_4$).



7-(4-Methoxyphenyl)-5-phenylthieno[3,2-*b*]pyridine (4m, Table 1):

Trifluoromethanesulfonic anhydride (80 μL, 0.49 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1h** (90 mg, 0.44 mmol, 1 equiv) and 2-chloropyridine (50 μL, 0.53 mmol, 1.2 equiv) in dichloromethane (1.5 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the acetylene **2f** (117 mg, 0.886 mmol, 2.00 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4m** as a pale yellow oil (90 mg, 64%).

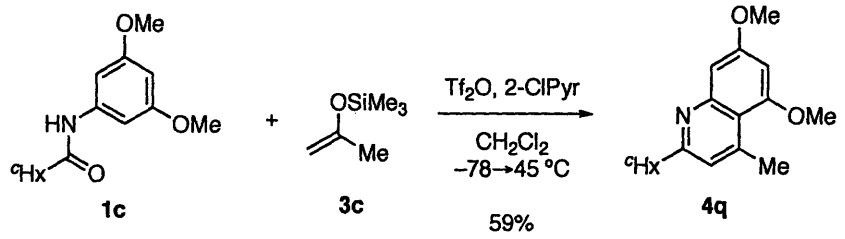
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.13–8.09 (m, 2H, Ar**H**), 7.82–7.77 (m, 3H, Ar**H**), 7.73 (s, 1H, Ar**H**), 7.70 (d, 1H, J = 5.5 Hz, Ar**H**), 7.55–7.50 (m, 2H, Ar**H**), 7.46 (tt, 1H, J = 7.4, 1.3 Hz, Ar**H**), 7.12–7.09 (m, 2H, Ar**H**), 3.92 (s, 3H, OCH_3).
^{13}C NMR (100 MHz, $CDCl_3$, 20 °C) δ:	160.6, 157.3, 156.5, 144.7, 140.0, 131.2, 130.9, 130.5, 129.5, 129.0, 129.0, 127.5, 126.1, 115.7, 114.7, 55.6.
FTIR (neat) cm^{-1}:	3061 (w), 2931 (w), 2836 (w), 1996 (w), 1608 (m), 1565 (m), 1513 (s), 1357 (m), 1294 (m), 1257 (s), 1031 (m).
HRMS (ESI):	calcd for $C_{20}H_{16}NOS$ $[M+H]^+$: 318.0947, found: 318.0944.
TLC (20% EtOAc in hexanes), R_f:	0.37 (U V, $KMnO_4$).
nOe data:	 15% nOe



5,7-dimethoxy-2-phenylquinoline (4p, Table 1):

Trifluoromethanesulfonic anhydride (55 μL, 0.33 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (80 mg, 0.30 mmol, 1 equiv) and 2-chloropyridine (35 μL, 0.37 mmol, 1.2 equiv) in dichloromethane (1.0 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the vinyl ether **3a** (24 mg, 0.33 mmol, 1.1 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline product **4p** as a pale yellow solid (81 mg, 99%).

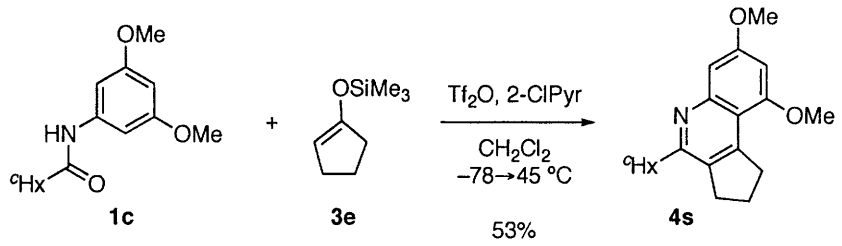
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.36 (d, 1H, J = 8.5 Hz, Ar**H**), 7.16 (d, 1H, J = 8.7 Hz, Ar**H**), 7.00 (d, 1H, J = 2.1 Hz, Ar**H**), 6.47 (d, 1H, J = 2.3 Hz, Ar**H**), 3.97 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 2.87 (tt, 1H, J = 12.0, 3.5 Hz, $^cC_6H_{11}$), 2.06–2.0 (m, 2H, $^cC_6H_{11}$), 1.94–1.86 (m, 2H, $^cC_6H_{11}$), 1.82–1.76 (m, 1H, $^cC_6H_{11}$), 1.62 (qd, 2H, J = 12.6, 3.0 Hz, $^cC_6H_{11}$), 1.48 (qt, 2H, J = 12.6, 3.2 Hz, $^cC_6H_{11}$), 1.35 (qt, 1H, J = 12.8, 3.5 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	167.8, 156.2, 135.3, 131.2, 127.9, 116.5, 115.4, 99.7, 97.5, 55.9, 55.8, 47.8, 33.1, 26.8, 26.3.
FTIR (neat) cm^{-1}:	2929 (s), 2852 (m), 1643 (m), 1624 (s), 1608 (s), 1580 (s), 1511 (w), 1452 (m), 1397 (m), 1205 (s), 1151 (s).
HRMS (ESI):	calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1645, found: 272.1644.
TLC (20% EtOAc in hexanes), R_f:	0.28 (UV, $KMnO_4$).



2-Cyclohexyl-5,7-dimethoxy-4-methylquinoline (4q, Table 1):

Trifluoromethanesulfonic anhydride (76 μL, 0.46 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (110 mg, 0.418 mmol, 1 equiv) and 2-chloropyridine (48 μL, 0.50 mmol, 1.2 equiv) in dichloromethane (1.4 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3c** (109 mg, 0.836 mmol, 2.00 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 3% EtOAc and 1% Et_3N→10% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline product **4q** as a white solid (70 mg, 59%).

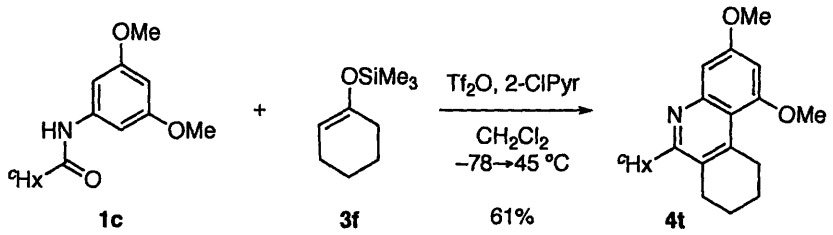
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	6.98 (s, 1H, Ar**H**), 6.88 (s, 1H, Ar**H**), 6.44 (s, 1H, Ar**H**), 3.92 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 2.83–2.74 (m, 4H, CH_3, $^cC_6H_{11}$), 2.02–1.96 (m, 2H, $^cC_6H_{11}$), 1.91–1.84 (m, 2H, $^cC_6H_{11}$), 1.80–1.74 (m, 1H, $^cC_6H_{11}$), 1.59 (qd, 2H, J = 12.7, 3.3 Hz, $^cC_6H_{11}$), 1.51–1.40 (m, 2H, $^cC_6H_{11}$), 1.32 (qt, 1H, J = 12.5, 3.4 Hz, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	166.8, 160.4, 158.7, 151.4, 145.9, 119.6, 115.4, 100.5, 97.9, 55.6, 55.6, 47.5, 33.0, 26.7, 26.3, 24.6.
FTIR (neat) cm^{-1}:	2998 (w), 2927 (s), 2851 (m), 1692 (w), 1619 (s), 1593 (s), 1452 (m), 1405 (m), 1252 (m), 1155 (m).
HRMS (ESI):	calcd for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1802, found: 286.1804.
TLC (20% EtOAc in hexanes), R_f:	0.46 (UV, $KMnO_4$).



4-Cyclohexyl-7,9-dimethoxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinoline (4s, Table 1):

Trifluoromethanesulfonic anhydride (76 μL, 0.46 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (110 mg, 0.418 mmol, 1 equiv) and 2-chloropyridine (48 μL, 0.51 mmol, 1.2 equiv) in dichloromethane (1.4 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3e** (131 mg, 0.836 mmol, 2.00 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 0.5% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline product **4s** as a white solid (69 mg, 53%).

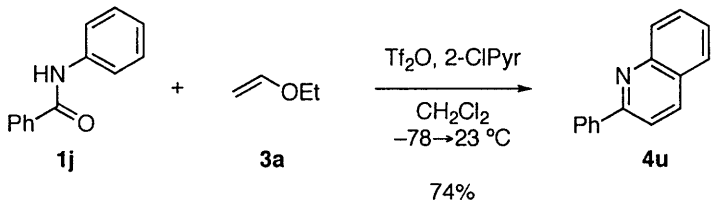
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.00 (s, 1H, Ar**H**), 6.41 (s, 1H, Ar**H**), 3.92 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.52–3.44 (m, 2H, $CH_2CH_2CH_2$), 3.04–2.96 (m, 2H, $CH_2CH_2CH_2$), 2.88–2.80 (m, 1H, $^cC_6H_{11}$), 2.18–2.10 (m, 2H, $CH_2CH_2CH_2$), 1.94–1.70 (m, 7H, $^cC_6H_{11}$), 1.48–1.36 (m, 3H, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	163.3, 160.0, 157.4, 150.2, 149.9, 133.0, 113.9, 100.1, 97.5, 55.7, 55.6, 44.6, 35.4, 31.4, 30.5, 26.9, 26.2, 24.5.
FTIR (neat) cm^{-1}:	2998 (w), 2928 (s), 2850 (m), 1621 (s), 1583 (s), 1508 (w), 1450 (m), 1414 (w), 1360 (m), 1251 (m), 1205 (s).
HRMS (ESI):	calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1958, found: 312.1961.
TLC (20% EtOAc in hexanes), R_f:	0.59 (UV, $KMnO_4$).



6-Cyclohexyl-1,3-dimethoxy-7,8,9,10-tetrahydrophenanthridine (4t, Table 1):

Trifluoromethanesulfonic anhydride (76 μL, 0.46 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1c** (110 mg, 0.418 mmol, 1 equiv) and 2-chloropyridine (79 μL, 0.84 mmol, 2.0 equiv) in dichloromethane (1.4 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3f** (142 mg, 0.836 mmol, 2.00 equiv) was added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a preheated oil bath at 45 °C and maintained at that temperature. After 1 h, the reaction mixture was allowed to cool to ambient temperature and aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 0.5% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline product **4t** as a white solid (83 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	6.96 (d, 1H, J = 2.5 Hz, Ar**H**), 6.43 (d, 1H, J = 2.5 Hz, Ar**H**), 3.93 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.42–3.48 (m, 2H, CH_2CH_2 CH_2CH_2), 3.00–2.93 (m, 1H, $^cC_6H_{11}$), 2.87–2.82 (m, 2H, $CH_2CH_2CH_2CH_2$), 1.92–1.73 (m, 11H, $^cC_6H_{11}$, $CH_2CH_2CH_2CH_2$), 1.48–1.37 (m, 3H, $^cC_6H_{11}$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	165.6, 159.2, 158.6, 149.5, 143.6, 125.6, 114.9, 101.0, 98.2, 55.6, 55.6, 41.8, 32.1, 30.5, 27.1, 26.7, 26.4, 23.1, 22.6.
FTIR (neat) cm^{-1}:	2926 (s), 2851 (m), 1617 (s), 1577 (m), 1449 (m), 1406 (w), 1307 (w), 1245 (m), 1206 (s), 1157 (s).
HRMS (ESI):	calcd for $C_{21}H_{28}NO_2$ $[M+H]^+$: 326.2115, found: 326.2105.
TLC (20% EtOAc in hexanes), R_f:	0.59 (UV, $KMnO_4$).

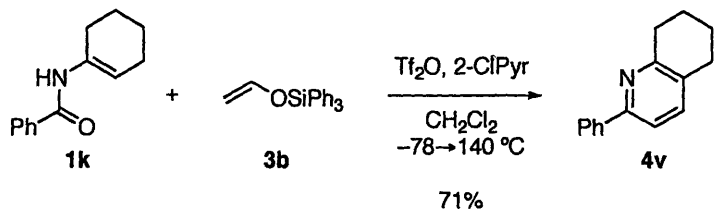


2-Phenylquinoline (4u,Table 1):

Trifluoromethanesulfonic anhydride (92 μL, 0.56 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1j** (100 mg, 0.507 mmol, 1 equiv) and 2-chloropyridine (58 μL, 0.61 mmol, 1.2 equiv) in dichloromethane (1.7 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the vinyl ether **3a** (73 mg, 1.0 mmol, 2.0 equiv) was added via syringe. The resulting solution was allowed to warm to ambient temperature. After 1 h, aqueous sodium hydroxide solution (1 mL, 1N) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline product **4u** as a white solid (77 mg, 74%).[7]

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.25 (d, 1H, J = 8.5 Hz, Ar**H**), 8.21–8.16 (m, 3H, Ar**H**), 7.90 (d, 1H, J = 8.5 Hz, Ar**H**), 7.85 (d, 1H, J = 8.2 Hz, Ar**H**), 7.75 (ddd, 1H, J = 8.5, 7.0, 1.5 Hz, Ar**H**), 7.57–7.52 (m, 3H, Ar**H**), 7.48 (tt, 1H, J = 7.3, 1.2 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.5, 148.4, 139.8, 137.0, 129.9, 129.9, 129.5, 129.0, 127.8, 127.7, 127.3, 126.5, 119.2.
FTIR (neat) cm^{-1}:	3189 (s), 3055 (w), 2091 (s), 1617 (w), 1597 (s), 1491 (m), 1447 (s).
HRMS (EI):	calcd for $C_{15}H_{11}N$ $[M]^+$: 205.0886, found: 205.0885.
Analysis	calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82, found: C, 87.55; H, 5.37; N, 6.84.
TLC (20% EtOAc in hexanes), R_f:	0.51 (UV, CAM).

[7] For a two-step synthesis of **4u**, see Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 4592.

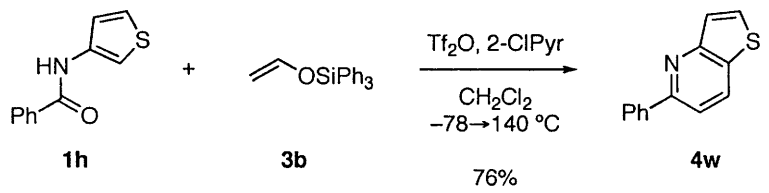


2-Phenyl-5,6,7,8-tetrahydroquinoline (4v, Table 1):

Trifluoromethanesulfonic anhydride (57 μL, 0.34 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1k** (63 mg, 0.31 mmol, 1 equiv) and 2-chloropyridine (59 μL, 0.63 mmol, 2.0 equiv) in dichloromethane (1.1 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3b**[8] (189 mg, 0.626 mmol, 2.00 equiv) was added, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 3% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4v** as a pale yellow solid (46 mg, 71%).[7]

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	7.97–7.94 (m, 2H, Ar**H**), 7.48–7.36 (m, 5H, Ar**H**), 3.00 (t, 2H, J = 6.4 Hz, CH_2), 2.82 (t, 2H, J = 6.4 Hz, CH_2), 1.98–1.91 (m, 2H, CH_2), 1.89–1.83 (m, 2H, CH_2).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	157.4, 154.9, 140.1, 137.6, 130.9, 128.8, 128.5, 127.0, 118.1, 33.1, 28.8, 23.4, 23.0.
FTIR (neat):	3061 (w), 3032 (w), 2935 (s), 2860 (m), 1590 (m), 1566 (m), 1460 (s), 1434 (m), 1253 (m).
HRMS (ESI):	calcd for $C_{15}H_{16}N$ $[M+H]^+$: 210.1277, found: 210.1279.
TLC (20% EtOAc in hexanes), R_f:	0.48 (UV, $KMnO_4$).

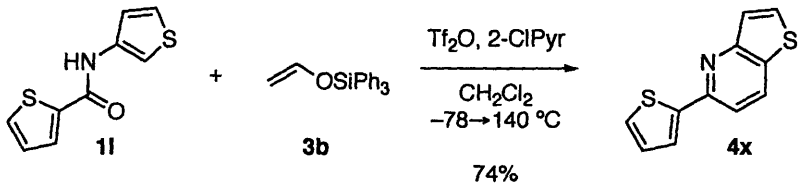
[8] For preparation of **3b** see Schaumann, E.; Tries, F. *Synthesis* **2002**, 191.



5-Phenylthieno[3,2-*b*]pyridine (4w, Table 1):

Trifluoromethanesulfonic anhydride (63 μL, 0.38 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1h** (70 mg, 0.34 mmol, 1 equiv) and 2-chloropyridine (39 μL, 0.41 mmol, 1.2 equiv) in dichloromethane (1.2 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3b** (208 mg, 0.688 mmol, 2.00 equiv) was added, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 10% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine product **4w**[7] as a pale yellow solid (55 mg, 76%).

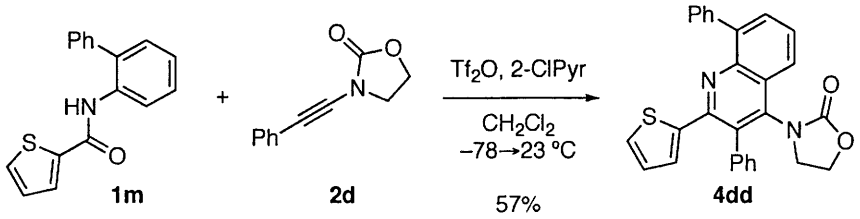
^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.26 (d, 1H, J = 8.6 Hz, Ar**H**), 8.08 (d, 2H, J = 7.3 Hz, Ar**H**), 7.78 (d, 1H, J = 5.5 Hz, C**H**S), 7.73 (d, 1H, J = 8.5 Hz, Ar**H**), 7.65 (d, 1H, J = 5.5 Hz, C**H**CHS)), 7.52 (t, 2H, J = 7.0 Hz, Ar**H**), 7.45 (t, 1H, J = 7.3 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	156.4, 155.5, 139.8, 131.7, 131.0, 131.0, 129.0, 128.9, 127.4, 125.5, 116.5.
FTIR (neat):	3071 (s), 1906 (w), 1564 (s), 1544 (s), 1397 (s), 1280 (s), 1158 (s).
HRMS (ESI):	calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0528, found: 212.0534.
TLC (20% EtOAc in hexanes), R_f:	0.53 (UV, $KMnO_4$).



5-(Thiophen-2-yl)thieno[3,2-*b*]pyridine (4x, Table 1):

Trifluoromethanesulfonic anhydride (69 μL, 0.42 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1l** (80 mg, 0.38 mmol, 1 equiv) and 2-chloropyridine (72 μL, 0.76 mmol, 2.0 equiv) in dichloromethane (1.3 mL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the enol ether **3b** (231 mg, 0.764 mmol, 2.00 equiv) was added, and the resulting solution was allowed to warm to ambient temperature for 5 min. before the reaction vessel was placed into a microwave reactor and heated to 140 °C. After 20 min., the reaction vessel was removed from the microwave reactor and allowed to cool to ambient temperature before triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc and 0.5% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4x** as a pale yellow solid (61 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$, 20°C):	8.18 (d, 1H, J = 8.5 Hz, Ar**H**), 7.76 (d, 1H, J = 5.5 Hz, Ar**H**), 7.68–7.65 (m, 2H, Ar**H**), 7.59 (dd, 1H, J = 5.5, 0.6 Hz, Ar**H**), 7.42 (dd, 1H, J = 5.1, 1.1 Hz, Ar**H**), 7.14 (dd, 1H, J = 5.0, 3.7 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20°C):	156.1, 150.6, 145.3, 131.5, 131.1, 131.0, 128.2, 127.6, 125.3, 125.1, 115.1.
FTIR (neat):	3098 (w), 2733 (w), 2453 (w), 1996 (w), 1564 (s), 1548 (s), 1437 (m), 1395 (s), 1159 (m).
HRMS (ESI):	calcd for $C_{11}H_8NS_2$ $[M+H]^+$: 218.0093, found: 218.0096.
TLC (20% EtOAc in hexanes), R_f:	0.50 (UV, $KMnO_4$).



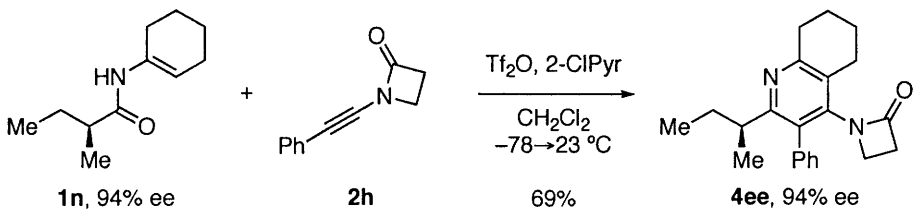
3-(3,8-Diphenyl-2-(thiophen-2-yl)quinolin-4-yl)oxazolidin-2-one (4dd, equation 5):

Trifluoromethanesulfonic anhydride (52 μL, 0.32 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1m** (80 mg, 0.29 mmol, 1 equiv) and 2-chloropyridine (33 μL, 0.34 mmol, 1.2 equiv) in dichloromethane (950 μL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamide **2d** (59 mg, 0.32 mmol, 1.1 equiv) was added as a solid in one portion and the reaction flask was rapidly purged and sealed under an argon atmosphere. The resulting solution was allowed to warm to ambient temperature. After 1 h, triethylamine (500 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% EtOAc/1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the quinoline derivative **4dd** as a pale yellow solid (73 mg, 57%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.87–7.81 (m, 4H, Ar**H**), 7.69–7.59 (m, 3H, Ar**H**), 7.57–7.52 (m, 3H, Ar**H**), 7.50–7.44(m, 2H, Ar**H**), 7.28–7.26 (m, 2H, Ar**H**), 6.74 (dd, 1H, J = 5.1, 3.9 Hz, Ar**H**), 6.28 (dd, 1H, J = 3.9, 1.1 Hz, Ar**H**), 4.51–4.45 (m, 1H, $NCH_2C\mathbf{H}_2O$), 4.07–4.01 (m, 1H, $NCH_2C\mathbf{H}_2O$), 3.90–3.84 (m, 1H, $NC\mathbf{H}_2CH_2O$), 3.41–3.35 (m, 1H, $NC\mathbf{H}_2CH_2O$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	157.3, 151.4, 146.1, 145.9, 141.3, 140.8, 138.9, 135.9, 132.2, 131.5, 131.2, 129.9, 129.9, 129.6, 129.2, 129.1, 128.9, 127.9, 127.8, 127.6, 124.7, 121.9, 63.2, 47.2.
FTIR (neat) cm^{-1}:	3060 (w), 2916 (w), 2249 (w), 1753 (s), 1601 (w), 1579 (m), 1479 (s), 1421 (s), 1231 (m).
HRMS (EI):	calcd for $C_{28}H_{21}N_2O_2S$ $[M+H]^+$: 449.1318, found: 449.1317.
TLC (50% EtOAc in hexanes), R_f:	0.43 (UV, $KMnO_4$)

Characterization of the product **9** (see text):

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	8.71 (d, 1H, J = 8.3 Hz, Ar**H**), 8.59 (dd, 2H, J = 7.9, 4.6 Hz, Ar**H**), 8.22 (d, 1H, J = 8.2 Hz, Ar**H**), 7.89 (t, 1H, J = 7.5 Hz, Ar**H**), 7.78–7. 65 (m, 4H, Ar**H**), 7.58 (dd, 1H, J = 5.1, 1.0 Hz, Ar**H**), 7.25 (dd, 1H, J = 5.2, 3.6 Hz, Ar**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	154.2, 143.9, 142.7, 133.8, 130.8, 130.4, 129.5, 129.1, 128.3, 128.1, 127.6, 127.6, 127.2, 124.9, 123.7, 122.5, 122.1.
FTIR (neat) cm^{-1}:	3070 (m), 1956 (w), 1812 (w), 1734 (w), 1610 (m), 1577 (m), 1562 (s), 1519 (m), 1484 (s), 1458 (s), 1430 (s).
HRMS (EI):	calcd for $C_{17}H_{12}NS$ $[M+H]^+$: 262.0685, found: 262.0683.
TLC (20% EtOAc in hexanes), R_f:	0.51 (UV, $KMnO_4$).



(*S*)-1-(2-*sec*-butyl-3-phenyl-5,6,7,8-tetrahydroquinolin-4-yl)azetidin-2-one (4ee, equation 6):

Trifluoromethanesulfonic anhydride (15 μL, 0.091 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of amide **1n**[9] (15 mg, 0.083 mmol, 1 equiv) and 2-chloropyridine (16 μL, 0.17 mmol, 2.0 equiv) in dichloromethane (280 μL) at –78 °C. After 5 min., the reaction mixture was placed in an ice-water bath and warmed to 0 °C, the ynamide **2h** (16 mg, 0.091 mmol, 1.1 equiv) was added as a solid in one portion and the reaction flask was rapidly purged and sealed under an argon atmosphere. After 1 h, triethylamine (100 μL) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and was filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 20% EtOAc and 1% Et_3N in hexanes; SiO_2: 15 × 1.5 cm) on neutralized silica gel to give the pyridine derivative **4ee** as a pale yellow oil (19 mg, 69%). The enantiomeric excess of pyridine **4ee** was determined to be 94% ee by chiral HPLC analysis [Whelk-O1 (*S,S*); 0.5 mL/min; 1% ^{i}PrOH in hexanes containing 0.2% Et_3N; t_R (minor) = 55.0 min., t_R (major) = 61.2 min].

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ:	7.46–7.41 (m, 2H, Ar**H**), 7.41–7.36 (m, 1H, Ar**H**), 7.23–7.18 (m, 2H, Ar**H**), 2.95 (t, 2H, J = 6.3 Hz, $NC\mathbf{H}_2CH_2CO$), 2.85–2.62 (m, 7H, $NCH_2C\mathbf{H}_2CO$, $C\mathbf{H}_2CH_2CH_2C\mathbf{H}_2$, $CH_3CH_2C\mathbf{H}CH_3$), 1.96–1.73 (m, 5H, $CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2$, $CH_3C\mathbf{H}_2CHCH_3$), 1.50–1.40 (m, 1H, $CH_3C\mathbf{H}_2CHCH_3$), 1.11 (d, 3H, J = 6.8 Hz, $CH_3CH_2CHC\mathbf{H}_3$), 0.67 (t, 3H, J = 7.5 Hz, $C\mathbf{H}_3CH_2CHCH_3$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C) δ:	166.0, 161.6, 158.1, 140.9, 136.9, 130.9, 129.9, 129.7, 128.6, 128.6, 127.7, 126.6, 41.0, 38.6, 36.5, 33.2, 29.6, 25.3, 22.9, 22.7, 21.0, 12.5.
FTIR (neat) cm^{-1}:	2959 (m), 2933 (m), 2870 (w), 1757 (s), 1602 (w), 1570 (w), 1547 (m), 1432 (m), 1405 (m), 1379 (m), 1192 (m).
HRMS (ESI):	calcd for $C_{22}H_{27}N_2O$ $[M+H]^+$: 335.2118, found: 335.2115.

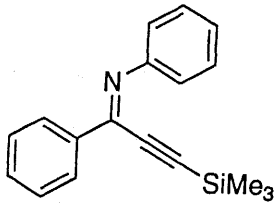
[9] The enantiomeric excess of amide **1n** was determined to be 94% ee by chiral HPLC analysis [Whelk-O1 (*S,S*); 1.0 mL/min; 3% ^{i}PrOH in hexanes; t_R (major) = 28.6 min., t_R(minor) = 32.5 min].

Appendix A

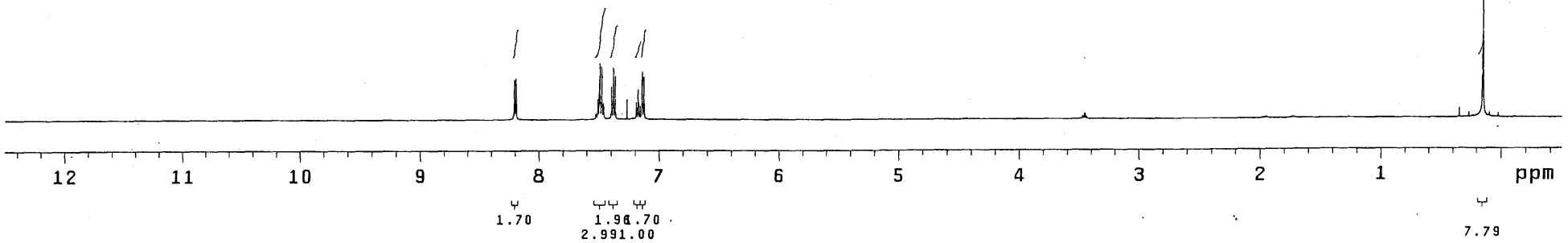
Spectra for Chapter I.

Solvent: CDCl3
Ambient temperature
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 500.2312691 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute

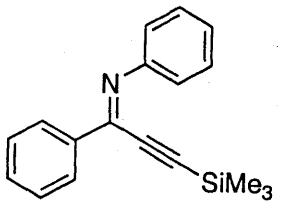


3a

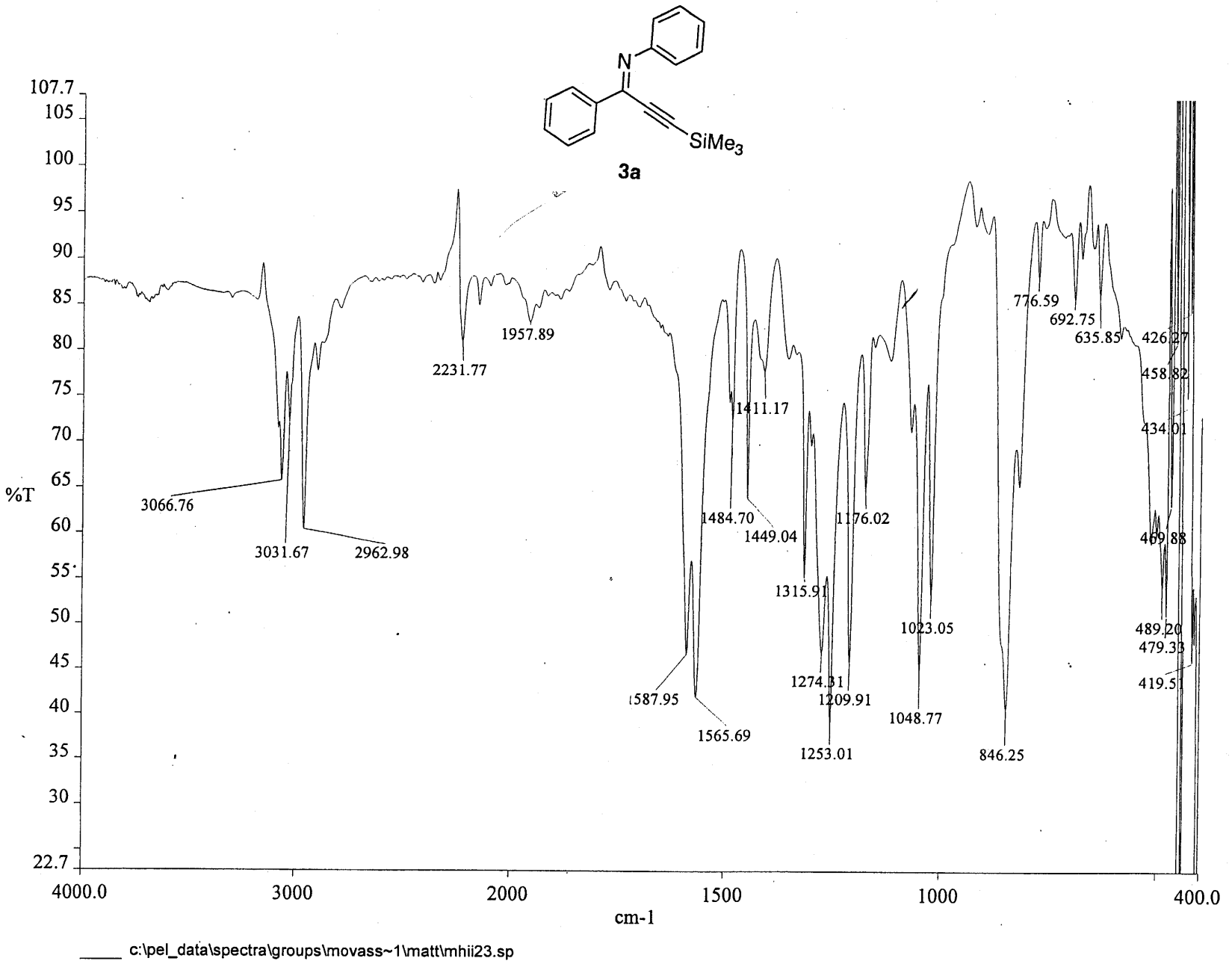


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
576 repetitions
OBSERVE C13, 125.7832286 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 16 minutes



3a


N
SiMe3
3a
%T
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100
95
90
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80
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50
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40
35
30
22.7
4000.0
3000
2000
1500
1000
400.0
cm-1
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2962.98
2231.77
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1587.95
1565.69
1484.70
1449.04
1411.17
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1048.77
1023.05
846.25
776.59
692.75
635.85
489.20
479.33
469.88
458.82
434.01
426.27
419.51
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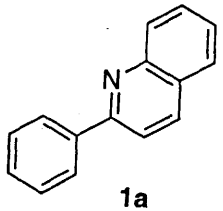
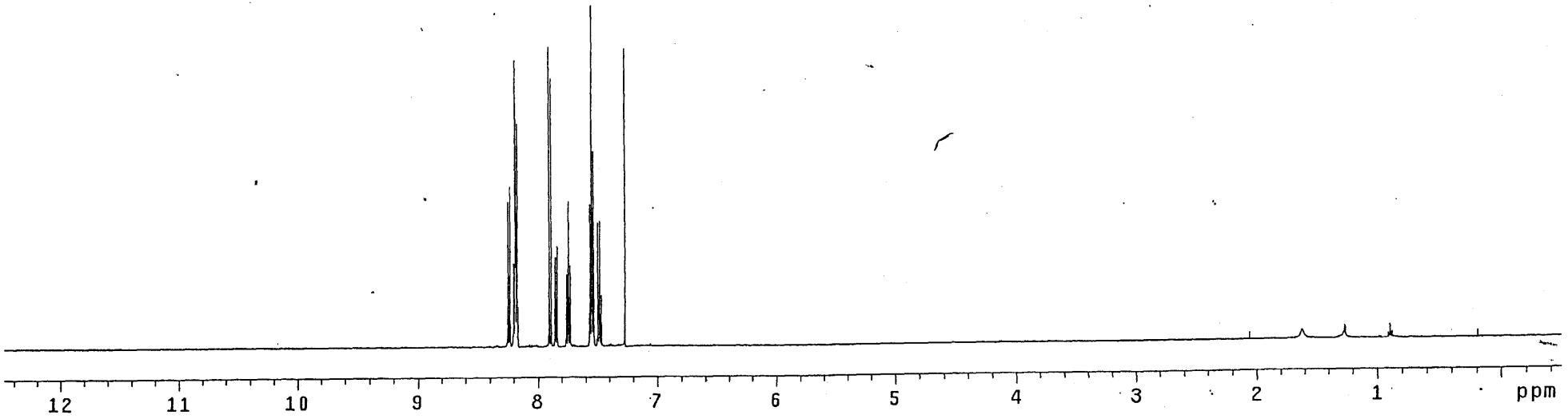
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537710 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec

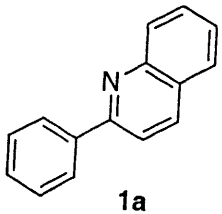


1a

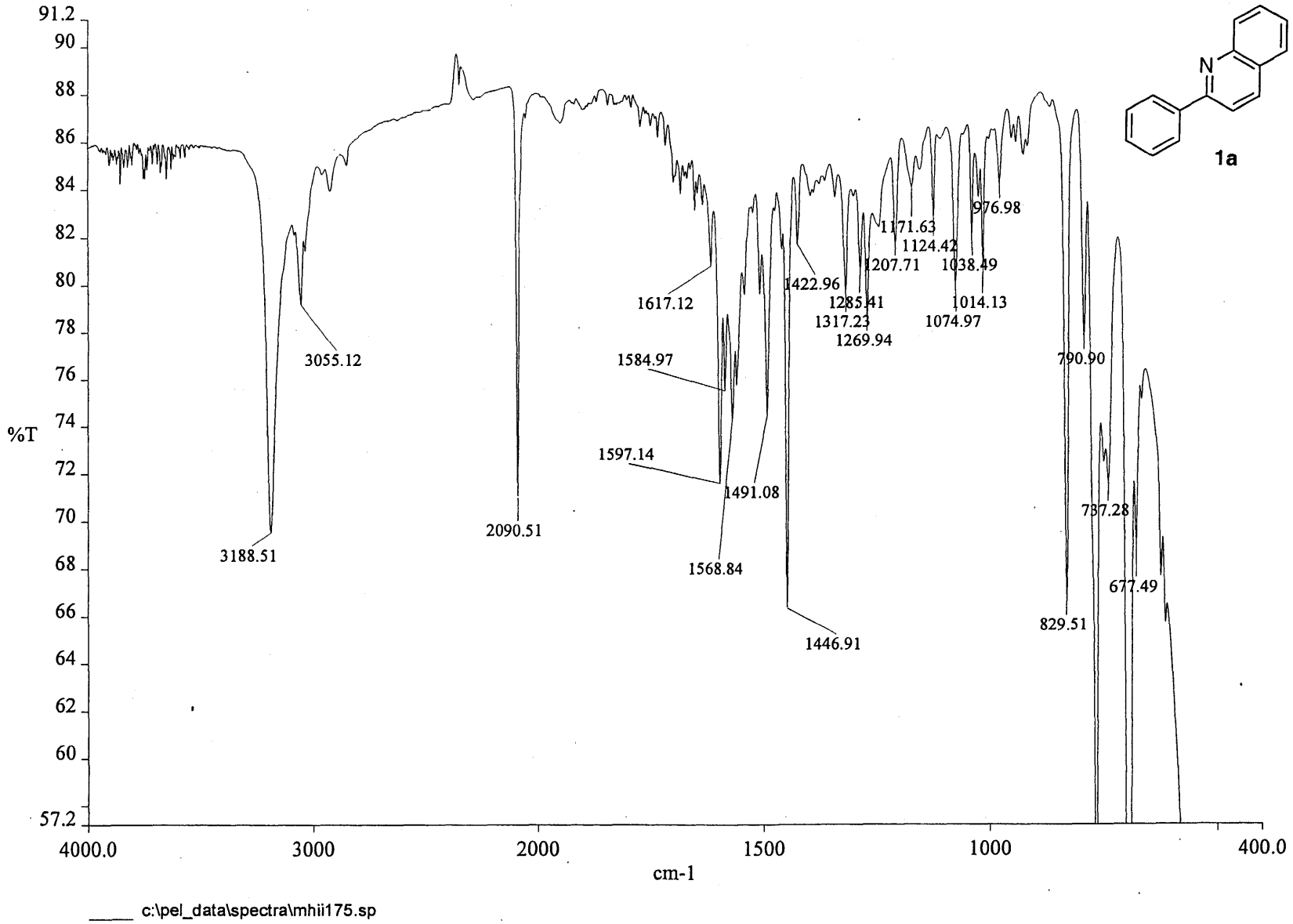


Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
100 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes



1a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86
84
82
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78
76
74
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70
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62
60
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%T
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3000
2000
1500
1000
400.0
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1597.14
1568.84
1491.08
1446.91
1422.96
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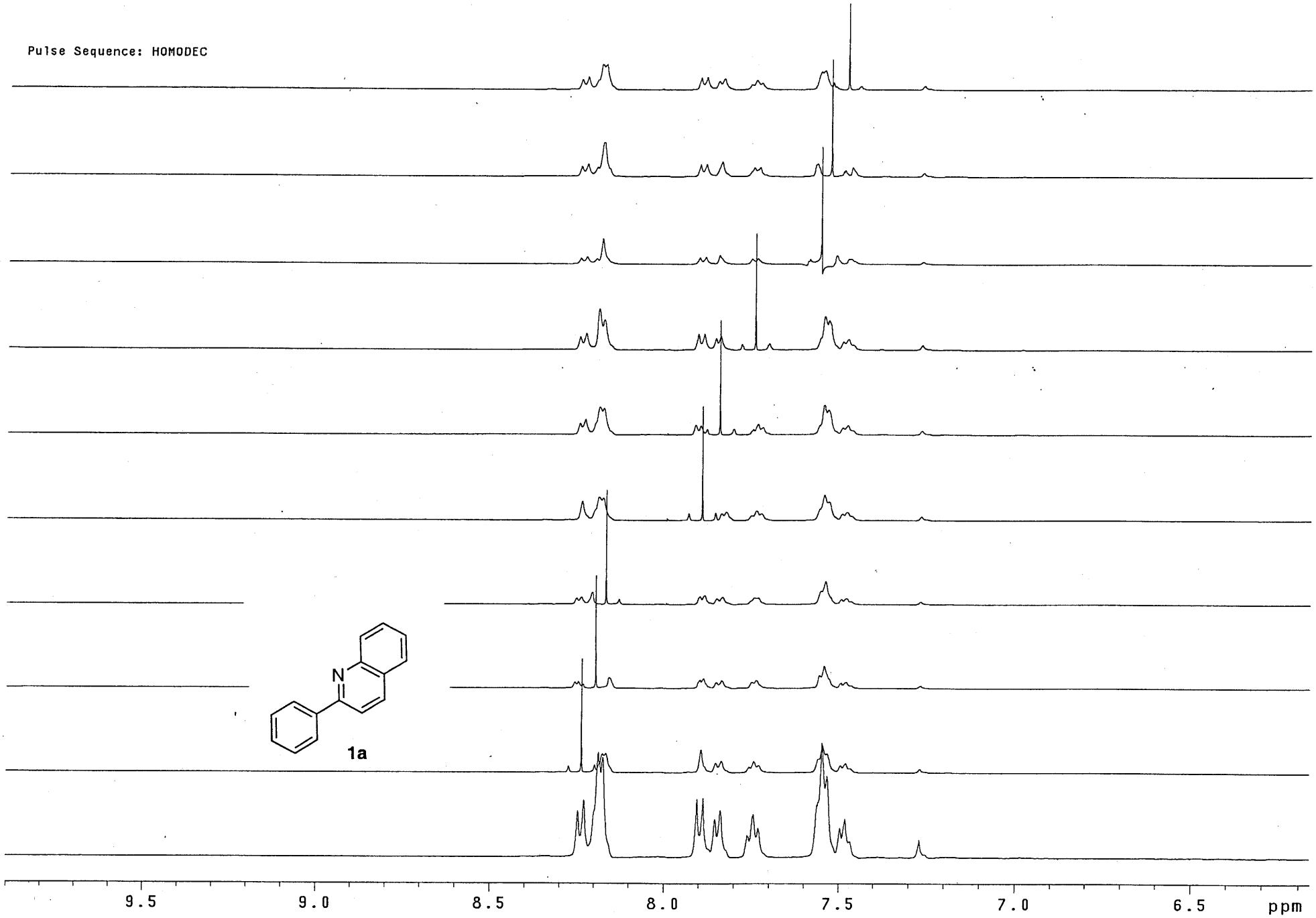
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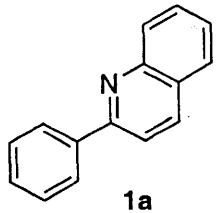
9.0
8.5
8.0
7.5
7.0
6.5
ppm



1a

CH3 carbons

CH2 carbons

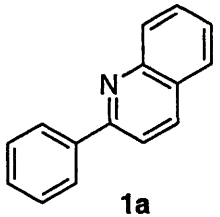
CH carbons

all protonated carbons

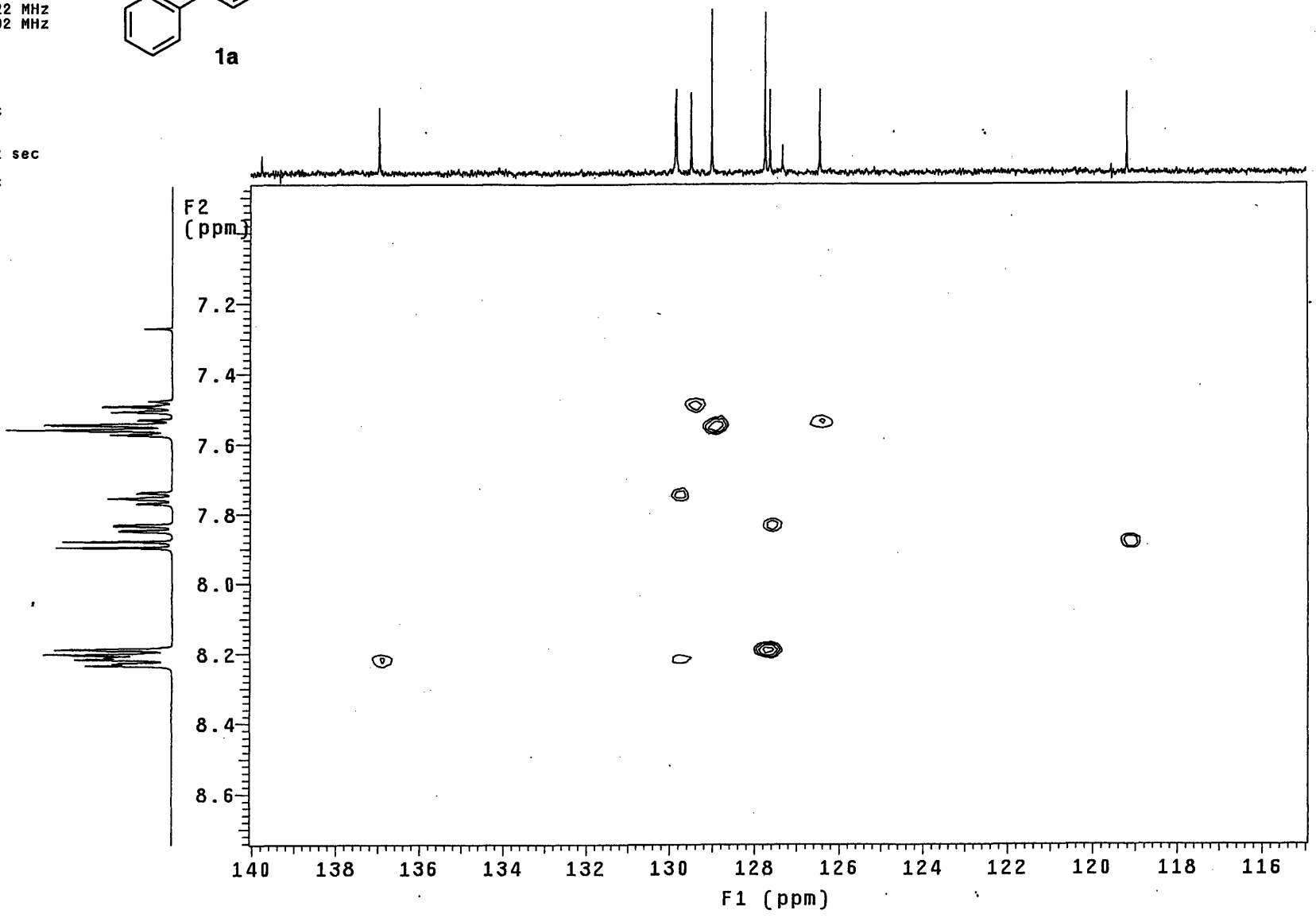
155 150 145 140 135 130 125 120 ppm

Pulse Sequence: HSQC
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

PULSE SEQUENCE: HSQC
Relax. delay 1.000 sec
Acq. time 0.100 sec
Width 5783.7 Hz
2D Width 19323.7 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 499.7537722 MHz
DECOUPLE C13, 125.6781902 MHz
Power 52 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Sq. sine bell 0.100 sec
Shifted by -0.100 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 23 min, 6 sec

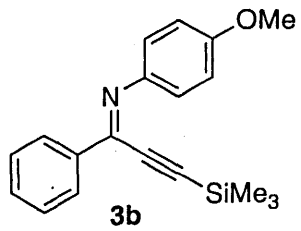


1a

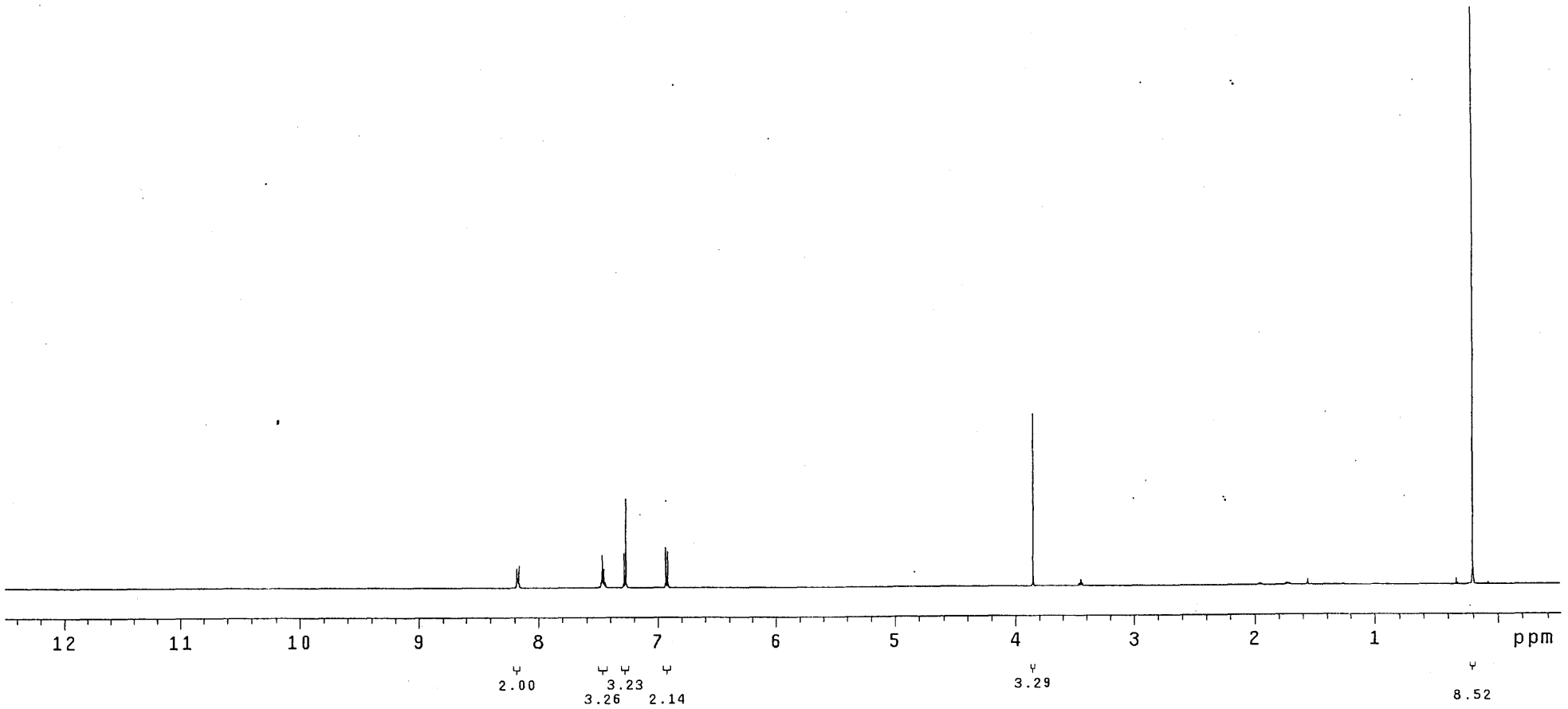


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537722 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec

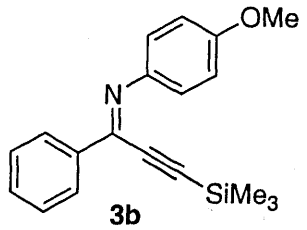


3b

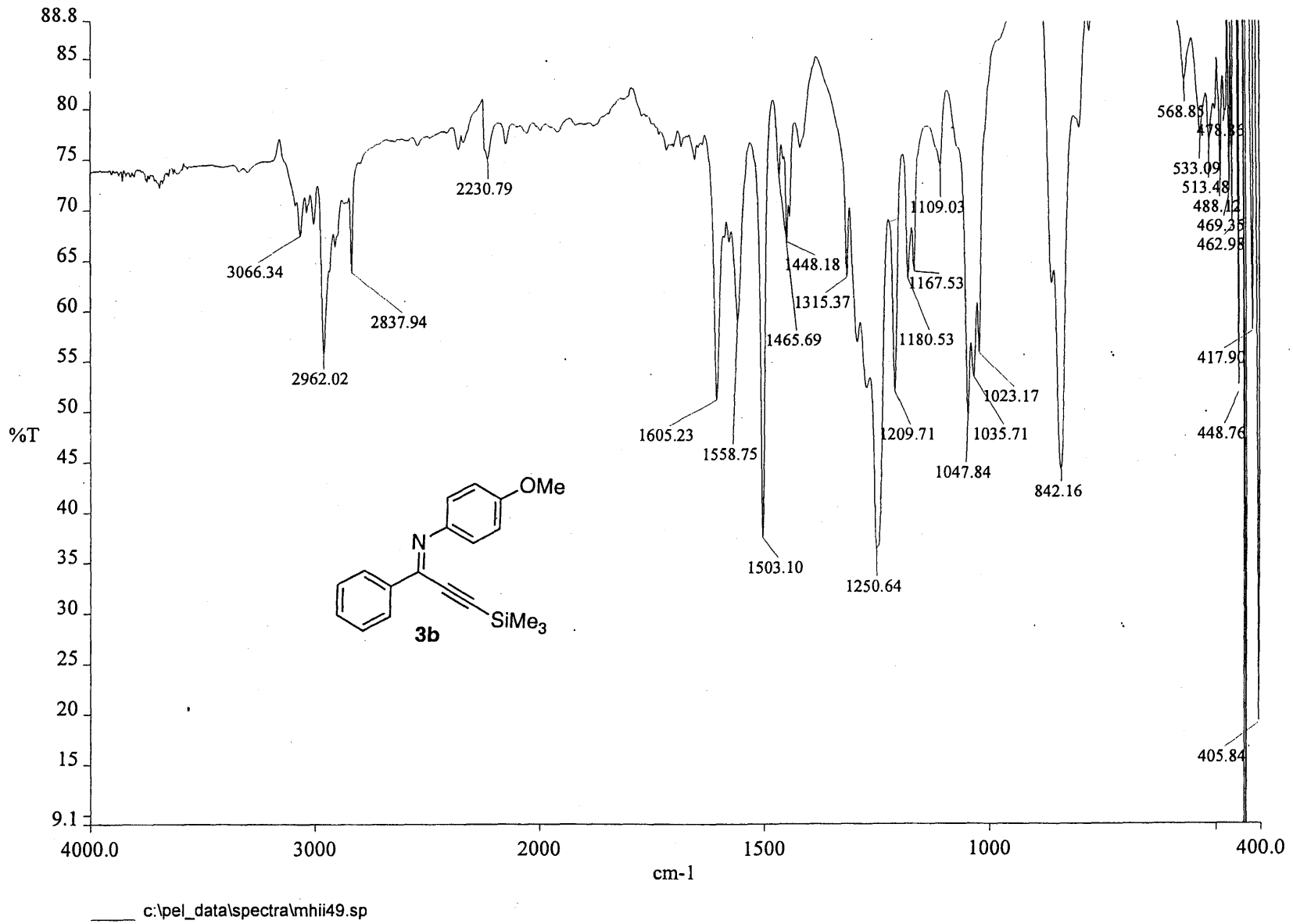


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
136 repetitions
OBSERVE C13, 125.7832337 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes

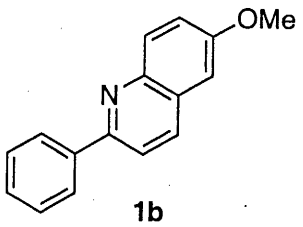


3b

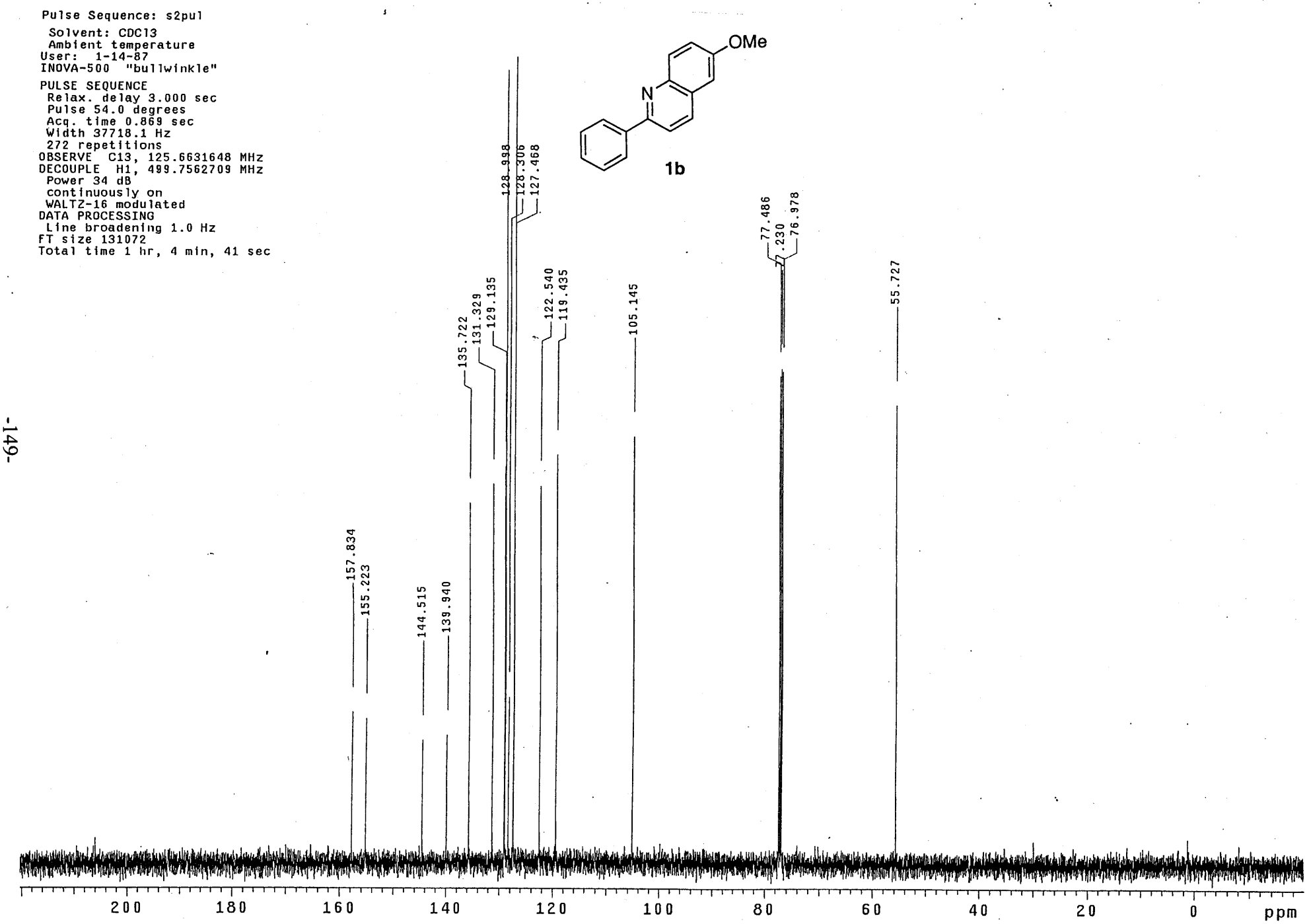

88.8
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
9.1
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3066.34
2962.02
2837.94
2230.79
1605.23
1558.75
1503.10
1465.69
1448.18
1315.37
1250.64
1209.71
1180.53
1167.53
1109.03
1047.84
1035.71
1023.17
842.16
568.85
533.09
513.48
488.12
469.35
462.98
448.76
417.90
405.84
OMe
N
SiMe3
3b
c:\pel_data\spectra\mhii49.sp

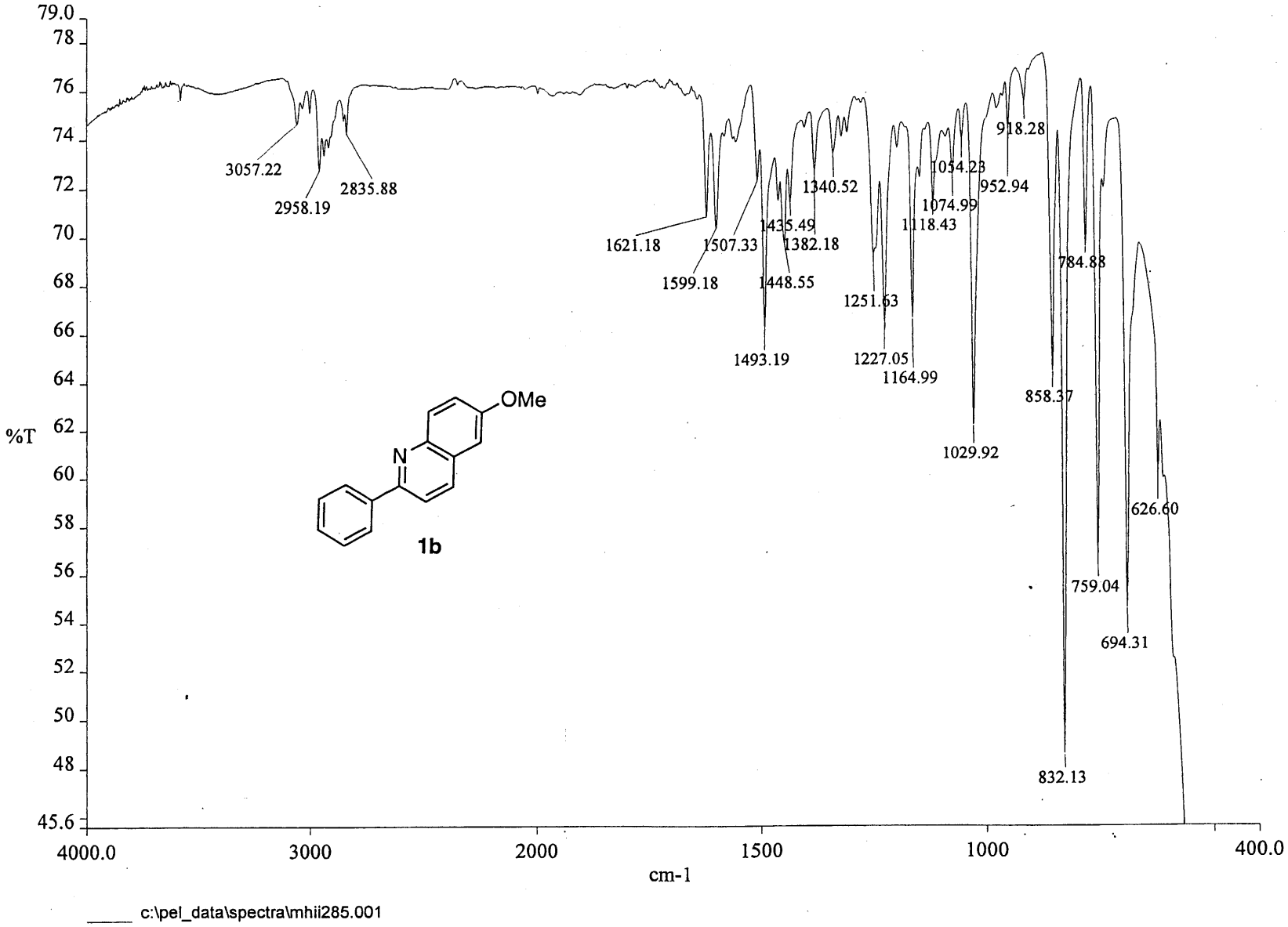
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-I-200A
INOVA-500 "zippy"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537722 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



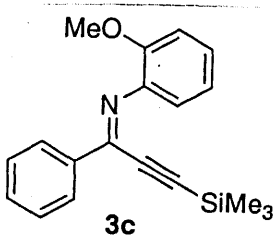
1b


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
272 repetitions
OBSERVE C13, 125.6631648 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 4 min, 41 sec
OMe
N
1b
157.834
155.223
144.515
139.940
135.722
131.329
129.135
128.938
128.306
127.468
122.540
119.435
105.145
77.486
77.230
76.978
55.727
200
180
160
140
120
100
80
60
40
20
0
ppm

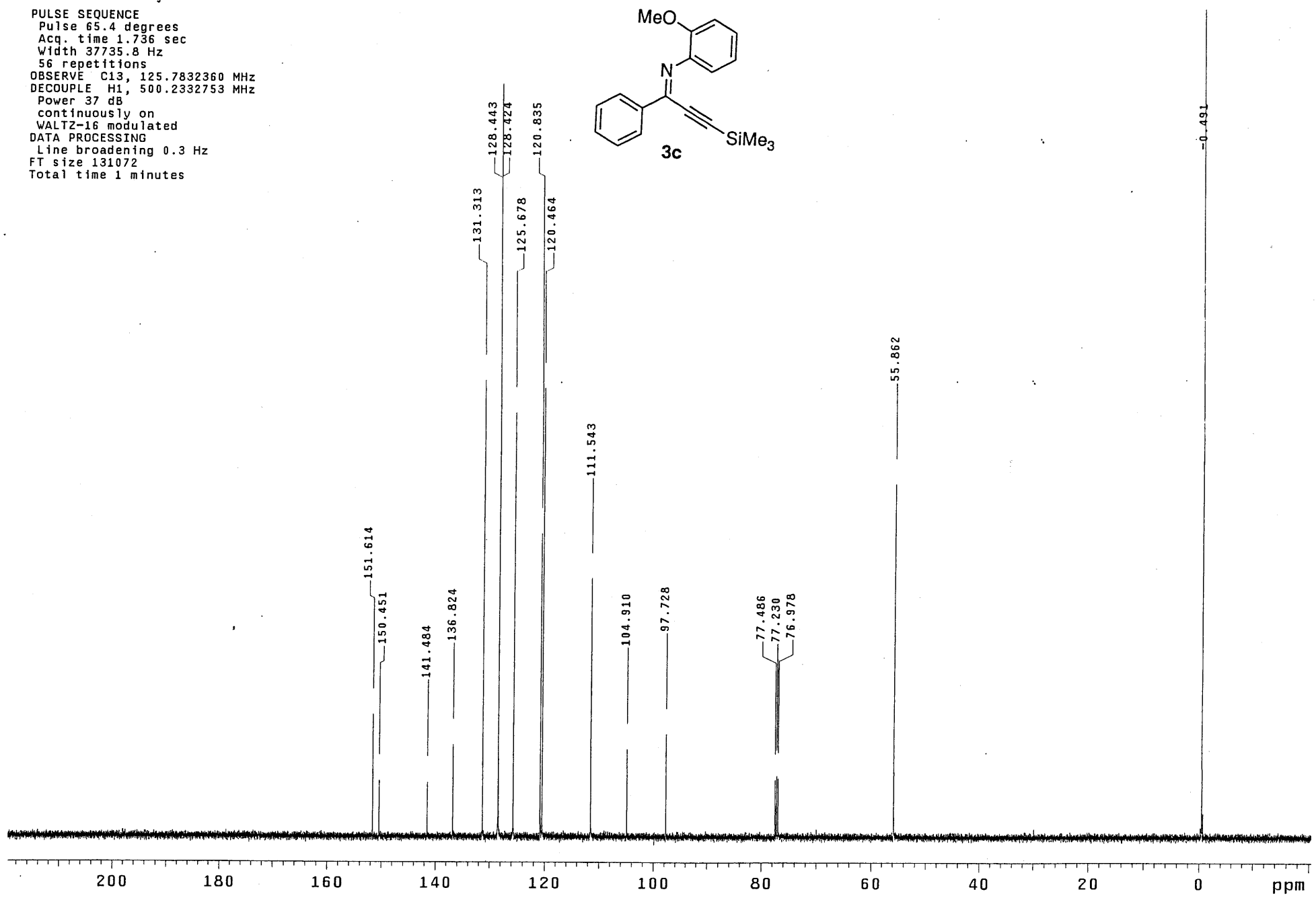

79.0
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
45.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3057.22
2958.19
2835.88
1621.18
1599.18
1507.33
1493.19
1448.55
1435.49
1382.18
1340.52
1251.63
1227.05
1164.99
1118.43
1074.99
1054.23
1029.92
952.94
918.28
858.37
832.13
784.88
759.04
694.31
626.60
OMe
N
1b
_____ c:\pel_data\spectra\mhii285.001

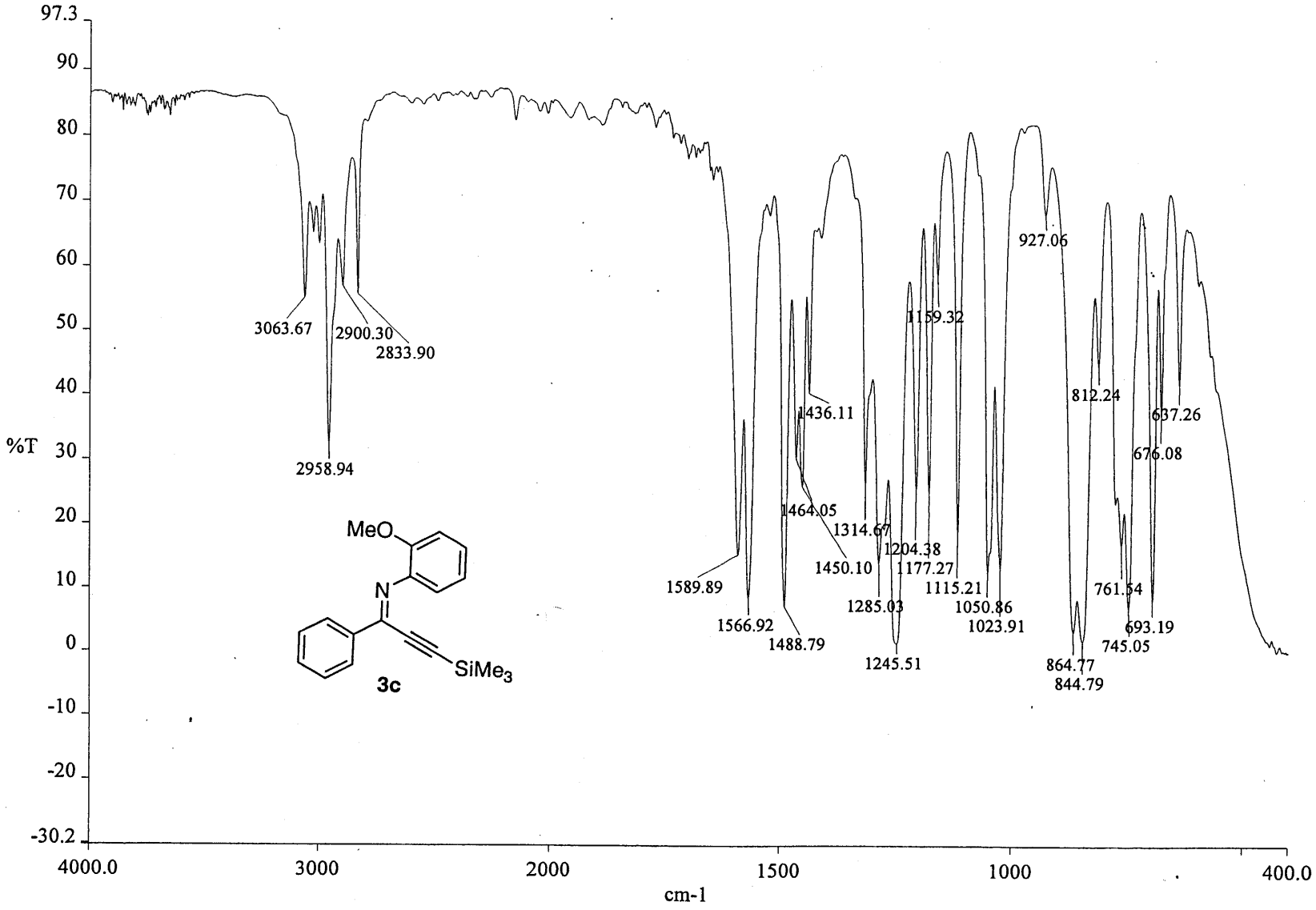
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



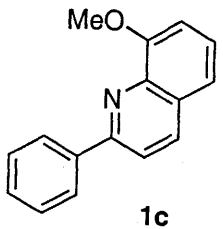
3c


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
56 repetitions
OBSERVE C13, 125.7832360 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes
MeO
N
SiMe3
3c
151.614
150.451
141.484
136.824
131.313
128.443
128.424
125.678
120.835
120.464
111.543
104.910
97.728
77.486
77.230
76.978
55.862
0.491
200
180
160
140
120
100
80
60
40
20
0
ppm

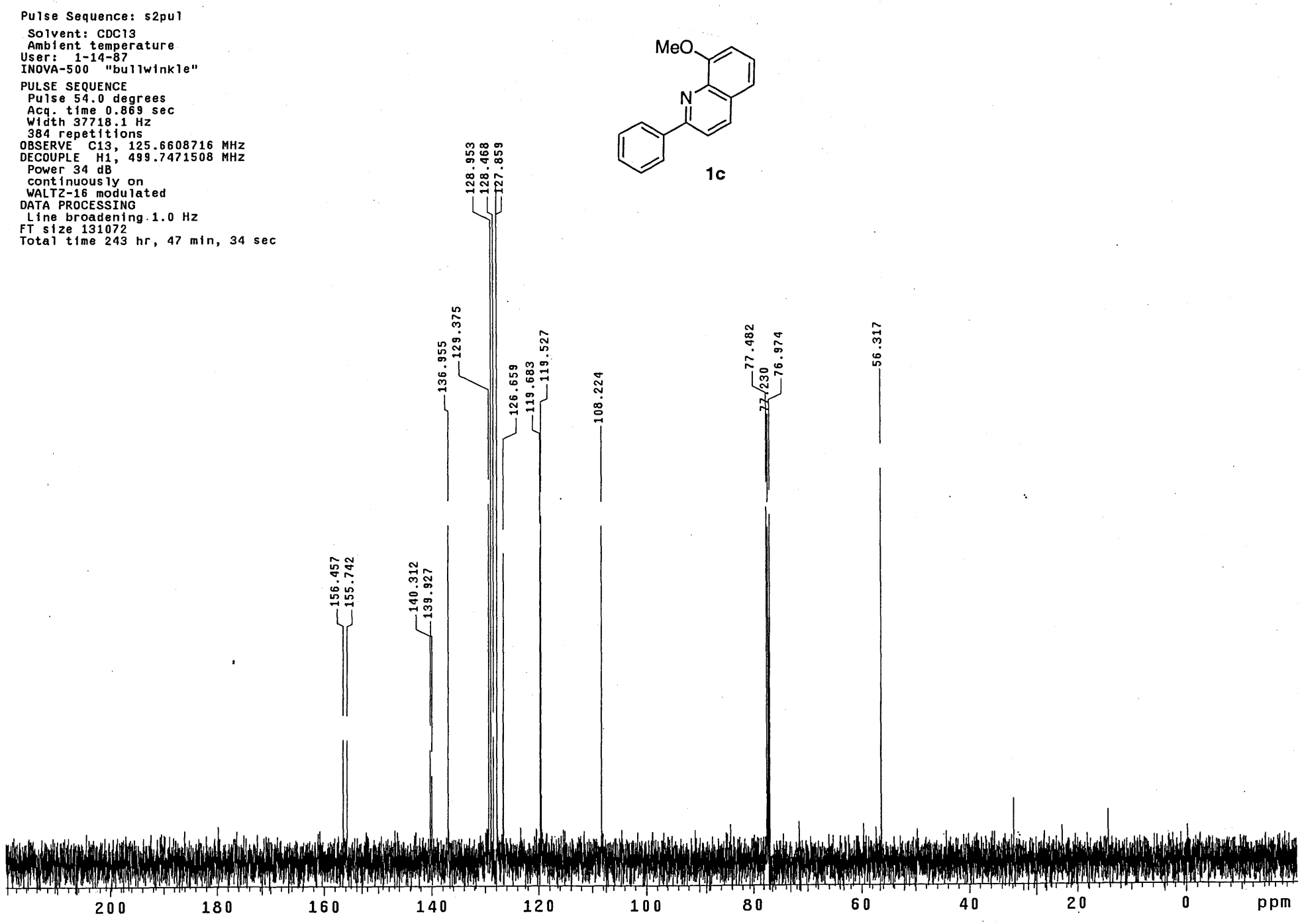

97.3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3063.67
2900.30
2833.90
2958.94
1589.89
1566.92
1488.79
1464.05
1436.11
1450.10
1314.67
1285.03
1245.51
1204.38
1177.27
1159.32
1115.21
1050.86
1023.91
927.06
864.77
844.79
812.24
761.54
745.05
693.19
676.08
637.26
MeO
N
SiMe3
3c
c:\pel_data\spectra\mhiii23.sp

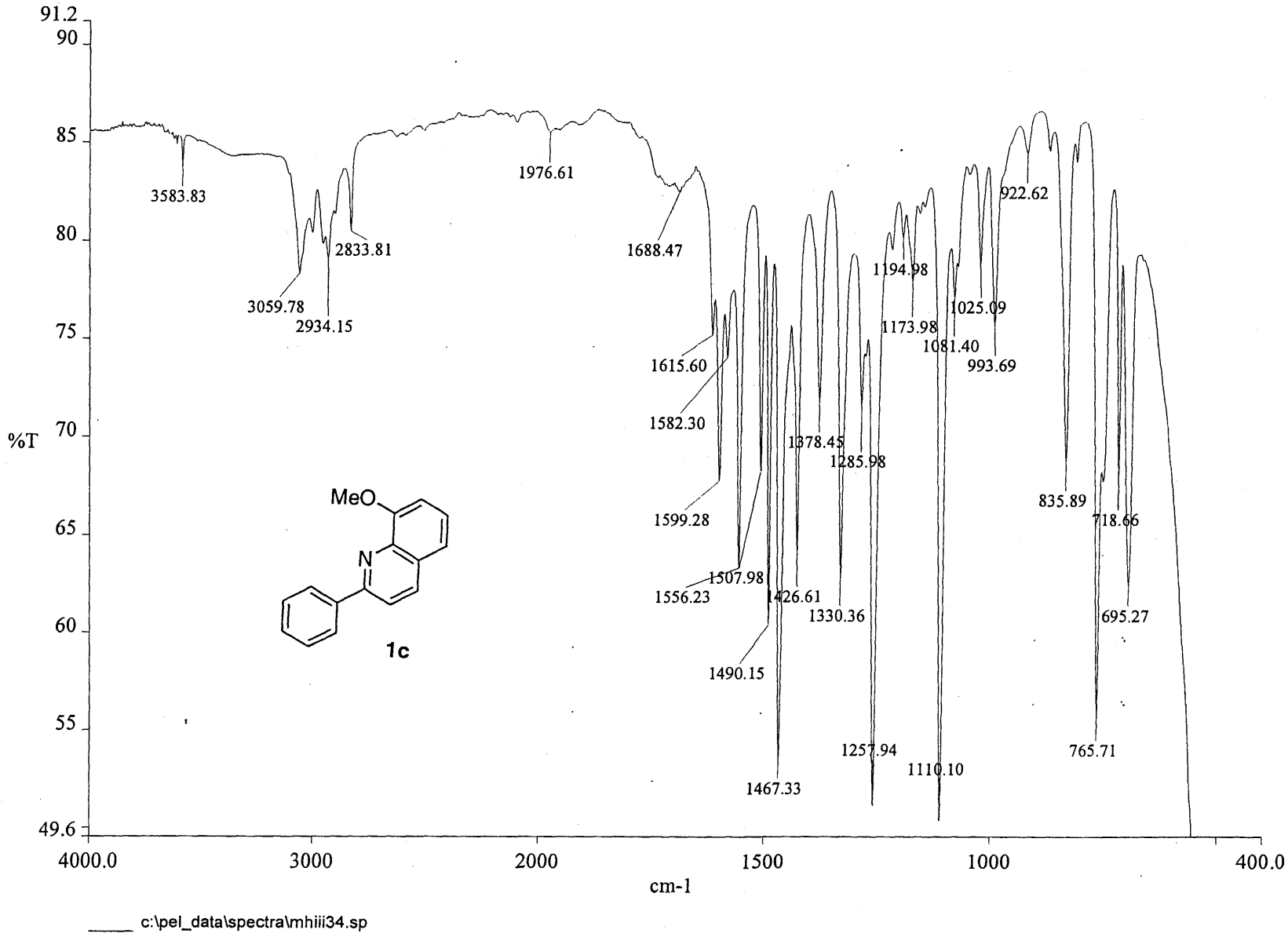
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

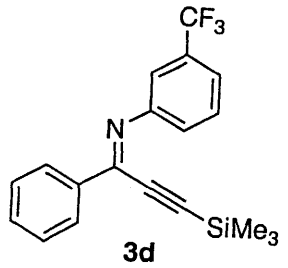


1c


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
384 repetitions
OBSERVE C13, 125.6608716 MHz
DECOUPLE H1, 499.7471508 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 243 hr, 47 min, 34 sec
MeO
N
1c
128.953
128.468
127.859
136.955
129.375
126.659
119.683
119.527
108.224
77.482
77.230
76.974
56.317
156.457
155.742
140.312
139.927
200
180
160
140
120
100
80
60
40
20
0
ppm


91.2
90
85
80
75
70
65
60
55
49.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3583.83
3059.78
2934.15
2833.81
1976.61
1688.47
1615.60
1582.30
1599.28
1556.23
1507.98
1490.15
1467.33
1426.61
1378.45
1330.36
1285.98
1257.94
1194.98
1173.98
1110.10
1081.40
1025.09
993.69
922.62
835.89
765.71
718.66
695.27
MeO
N
1c
c:\pel_data\spectra\mhiii34.sp

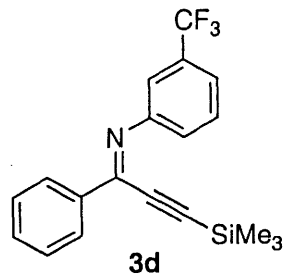
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-I-192column3
INOVA-500 "zippy"
PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537721 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec



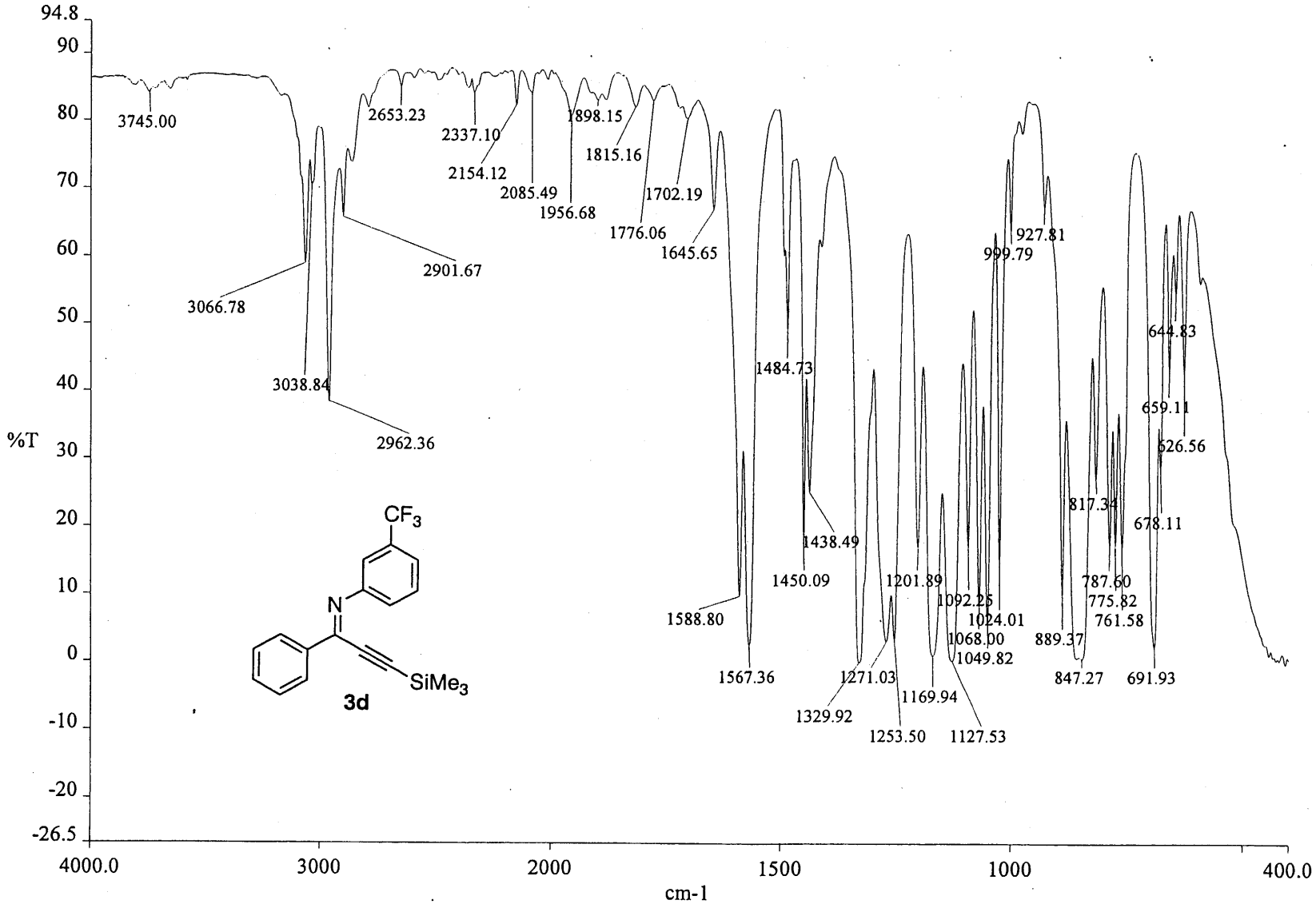
3d

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Pulse 54.0 degrees
Acq. time 0.959 sec
Width 50314.5 Hz
1808 repetitions
OBSERVE C13, 125.6631663 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 2 hr, 41 min, 20 sec

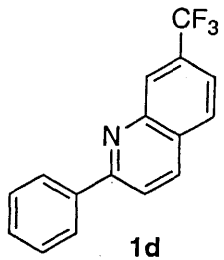


3d

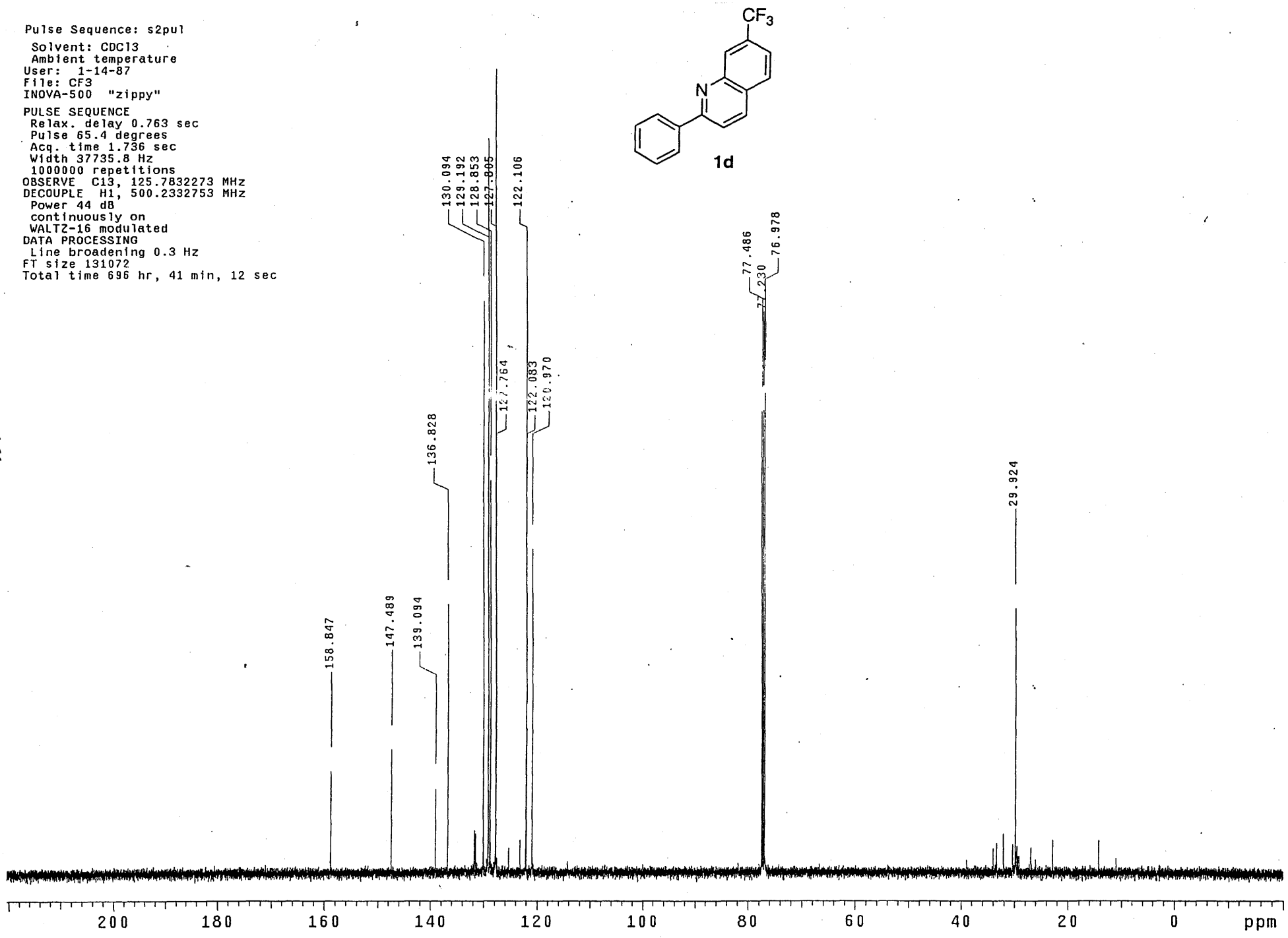

94.8
90
80
70
60
50
40
30
20
10
0
-10
-20
-26.5
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3745.00
3066.78
3038.84
2962.36
2901.67
2653.23
2337.10
2154.12
2085.49
1956.68
1898.15
1815.16
1776.06
1702.19
1645.65
1588.80
1567.36
1484.73
1450.09
1438.49
1329.92
1271.03
1253.50
1201.89
1169.94
1127.53
1092.25
1068.00
1049.82
1024.01
999.79
927.81
889.37
847.27
817.34
787.60
775.82
761.58
691.93
678.11
659.11
644.83
626.56
CF3
N
SiMe3
3d
c:\pel_data\spectra\mhi.sp

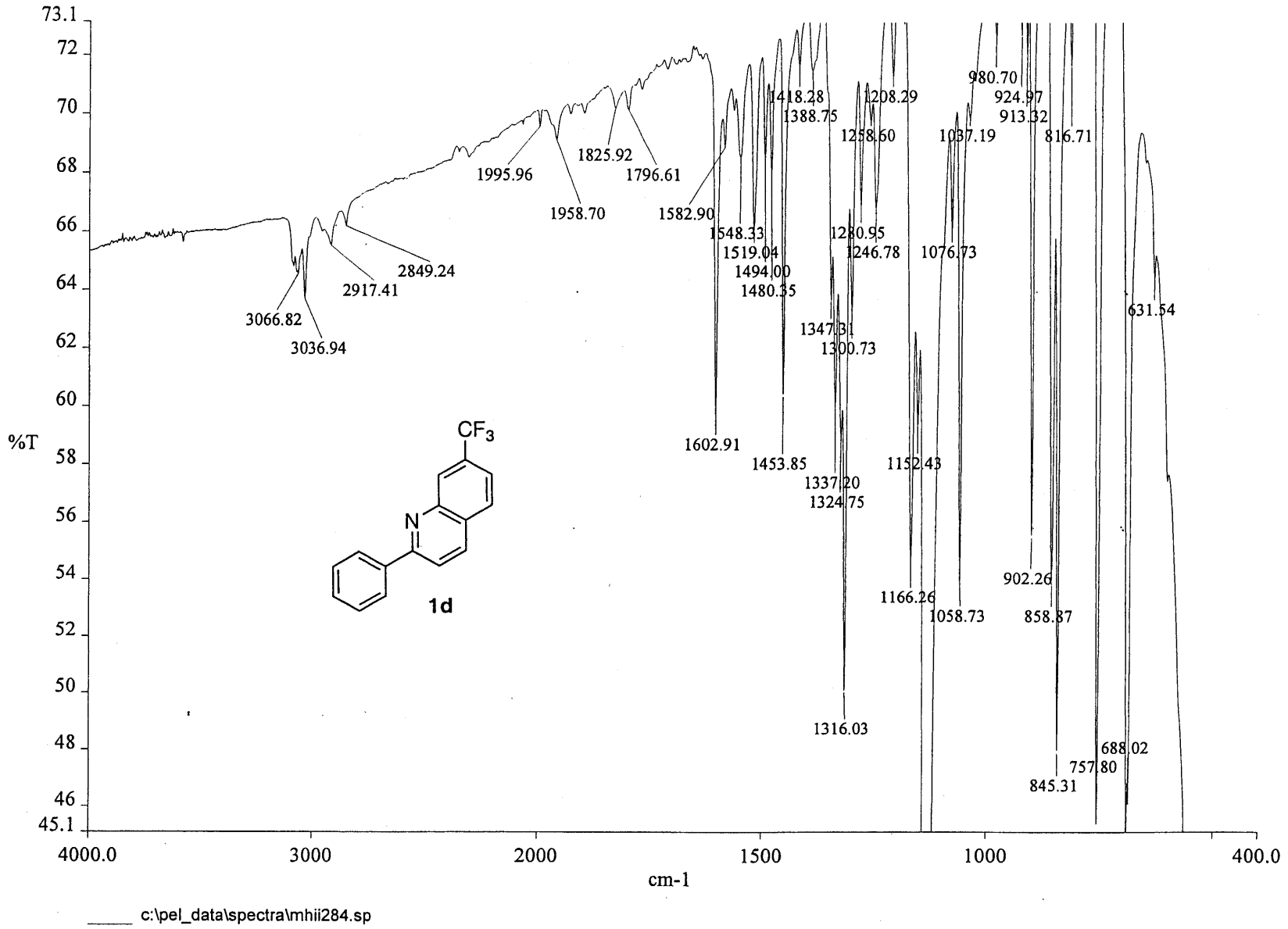
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537725 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec



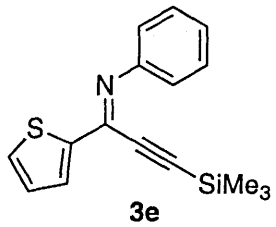
1d


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: CF3
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
1000000 repetitions
OBSERVE C13, 125.7832273 MHz
DECOUPLE H1, 500.2332753 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 696 hr, 41 min, 12 sec
CF3
N
1d
130.094
129.192
128.853
127.805
122.106
77.486
77.230
76.978
136.828
122.083
29.924
158.847
147.489
139.094
200
180
160
140
120
100
80
60
40
20
0
ppm


73.1
72
70
68
66
64
62
60
58
56
54
52
50
48
46
45.1
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3066.82
3036.94
2917.41
2849.24
1995.96
1958.70
1825.92
1796.61
1582.90
1602.91
1548.33
1519.04
1494.00
1480.35
1453.85
1418.28
1388.75
1347.31
1337.20
1324.75
1316.03
1300.73
1280.95
1246.78
1208.29
1258.60
1166.26
1152.43
1076.73
1058.73
1037.19
980.70
924.97
913.32
902.26
858.87
845.31
816.71
757.80
688.02
631.54
CF3
N
1d
c:\pel_data\spectra\mhii284.sp

Solvent: CDCl3
Ambient temperature
INOVA-500 "rocky"

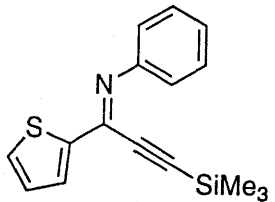
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 500.2312700 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute



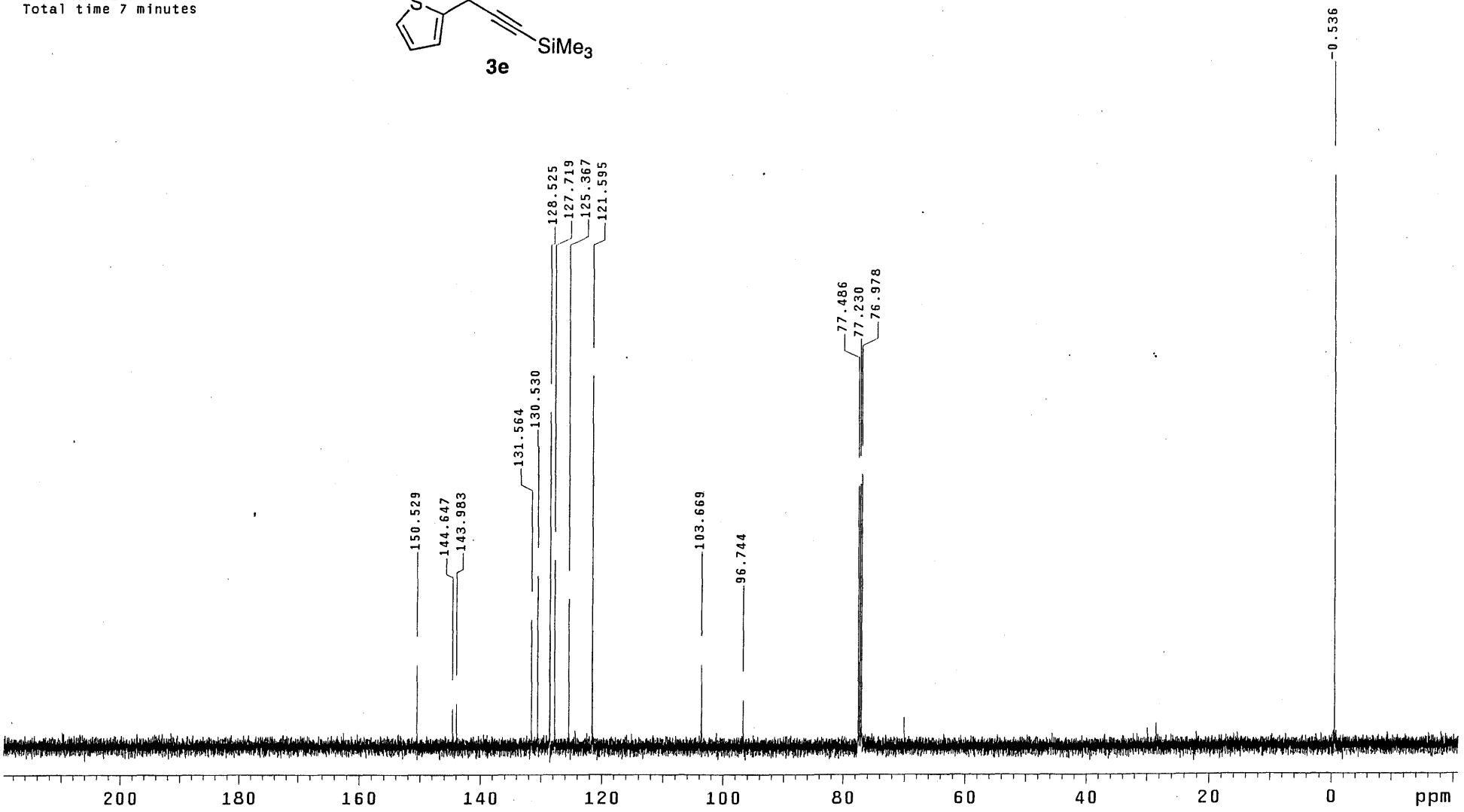
3e

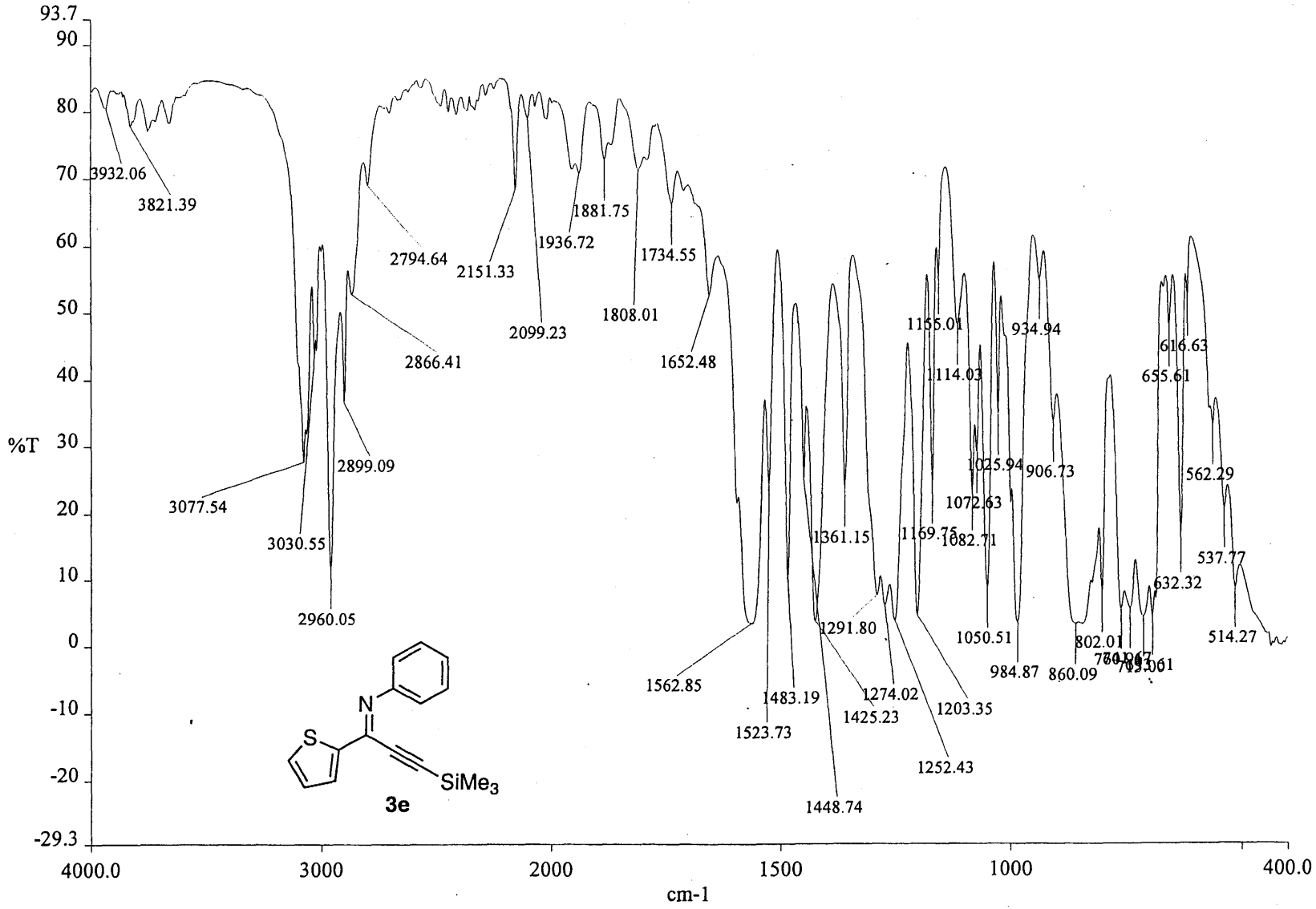
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
256 repetitions
OBSERVE C13, 125.7832280 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 7 minutes

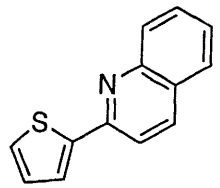


3e




93.7
90
80
70
60
50
40
30
20
10
0
-10
-20
-29.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3932.06
3821.39
2794.64
2151.33
1936.72
1881.75
1734.55
1808.01
2099.23
2866.41
1652.48
1155.01
934.94
616.63
655.61
114.03
3077.54
2899.09
3030.55
2960.05
1025.94
906.73
562.29
1072.63
1361.15
1169.75
1082.71
537.77
632.32
1291.80
1050.51
802.01
514.27
984.87
860.09
1562.85
1483.19
1274.02
1203.35
1425.23
1523.73
1252.43
1448.74
N
S
SiMe3
3e
c:\pel_data\spectra\mhii66.sp

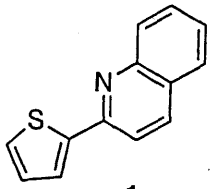
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446543 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec



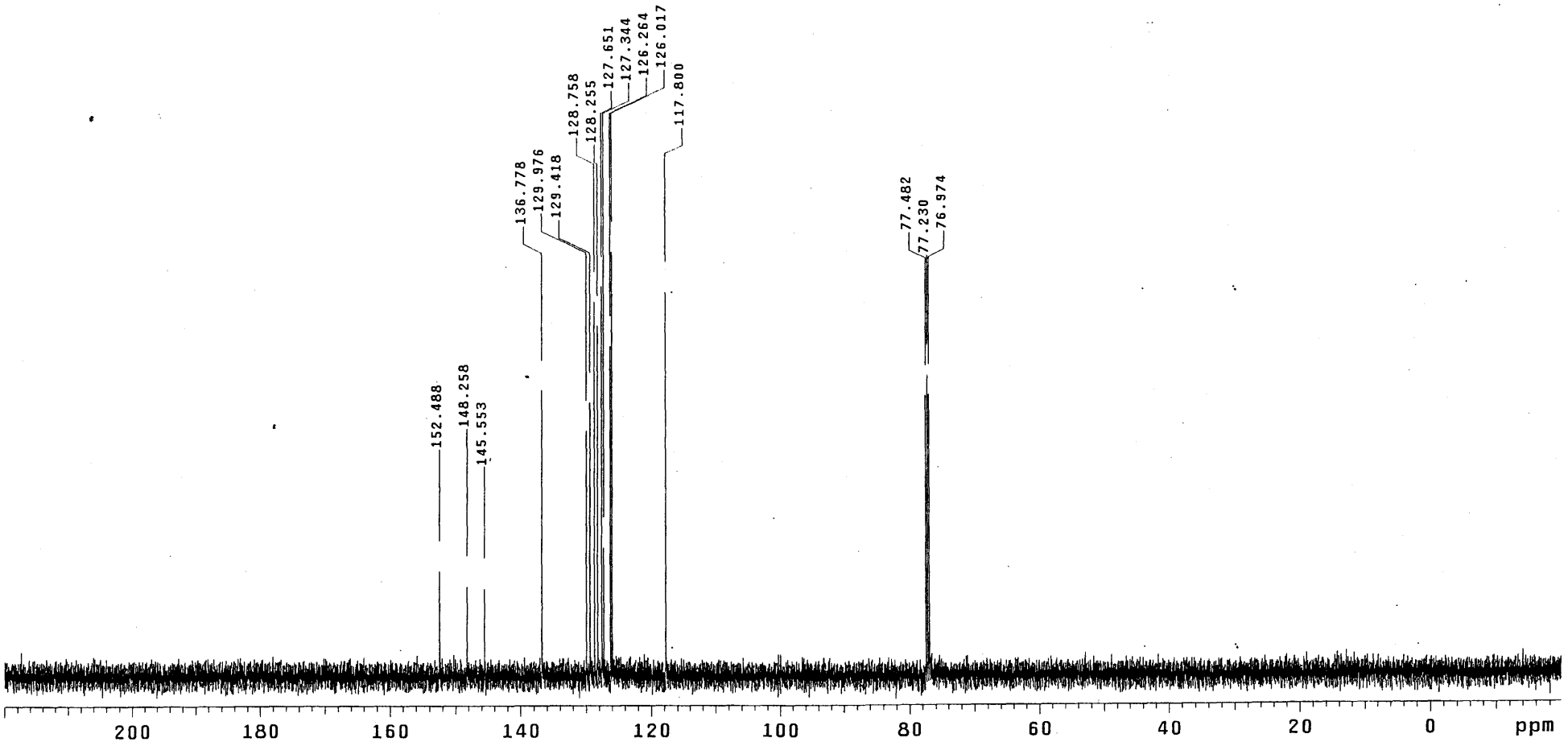
1e

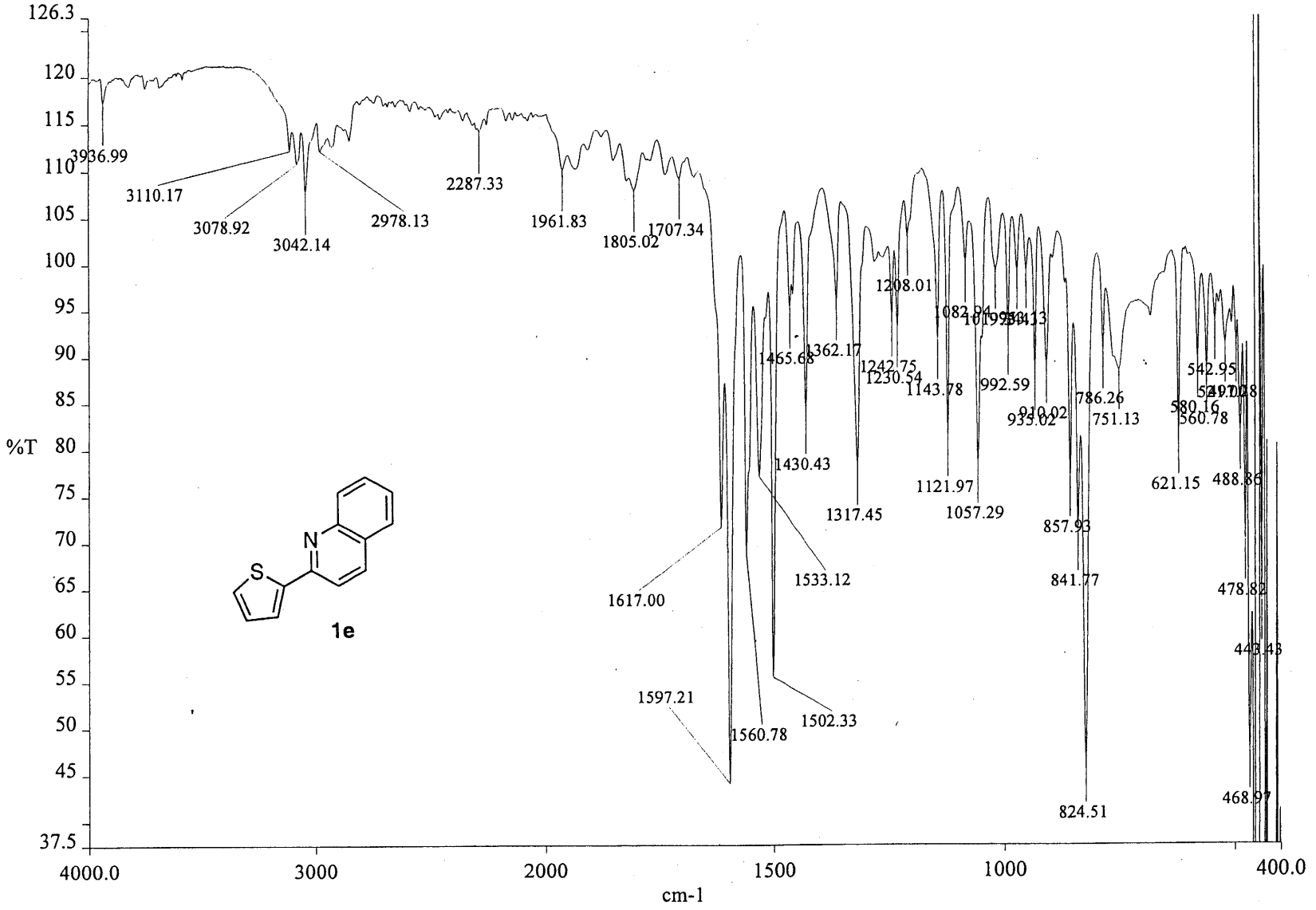
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
120 repetitions
OBSERVE C13, 125.7832337 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes



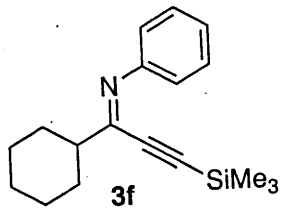
1e




126.3
120
115
110
105
100
95
90
85
%T 80
75
70
65
60
55
50
45
37.5
4000.0
3000
2000
1500
1000
400.0
cm-1
3936.99
3110.17
3078.92
3042.14
2978.13
2287.33
1961.83
1805.02
1707.34
1617.00
1597.21
1560.78
1533.12
1502.33
1465.68
1430.43
1362.17
1317.45
1242.75
1230.54
1208.01
1143.78
1121.97
1057.29
992.59
935.02
910.02
857.93
841.77
824.51
786.26
751.13
621.15
580.16
560.78
542.95
488.86
478.82
468.97
N
S
1e
c:\pel_data\spectra\mhii273.sp - mh-II-273 in CH2Cl2

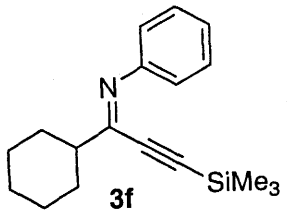
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537719 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec

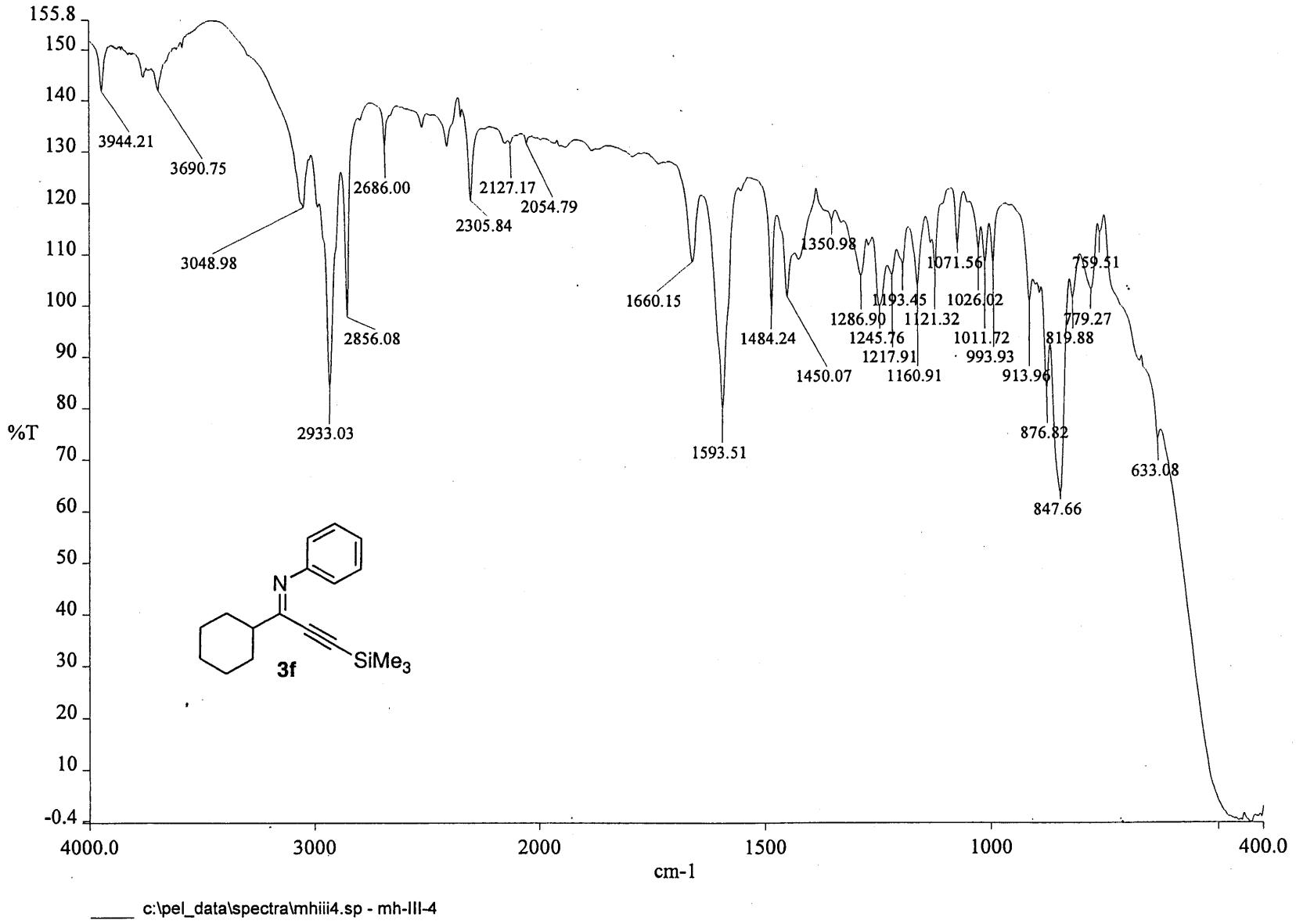


3f

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
208 repetitions
OBSERVE C13, 125.6631654 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 243 hr, 47 min, 34 sec

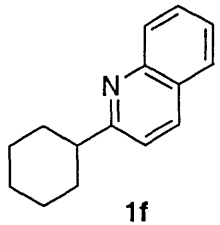


3f


155.8
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
-0.4
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3944.21
3690.75
3048.98
2686.00
2856.08
2933.03
2305.84
2127.17
2054.79
1660.15
1593.51
1484.24
1450.07
1350.98
1286.90
1245.76
1217.91
1193.45
1160.91
1121.32
1071.56
1026.02
1011.72
993.93
913.96
876.82
847.66
819.88
779.27
759.51
633.08
N
SiMe3
3f
c:\pel_data\spectra\mhiii4.sp - mh-III-4

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

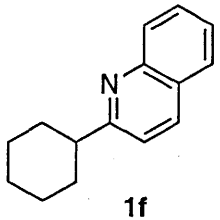
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



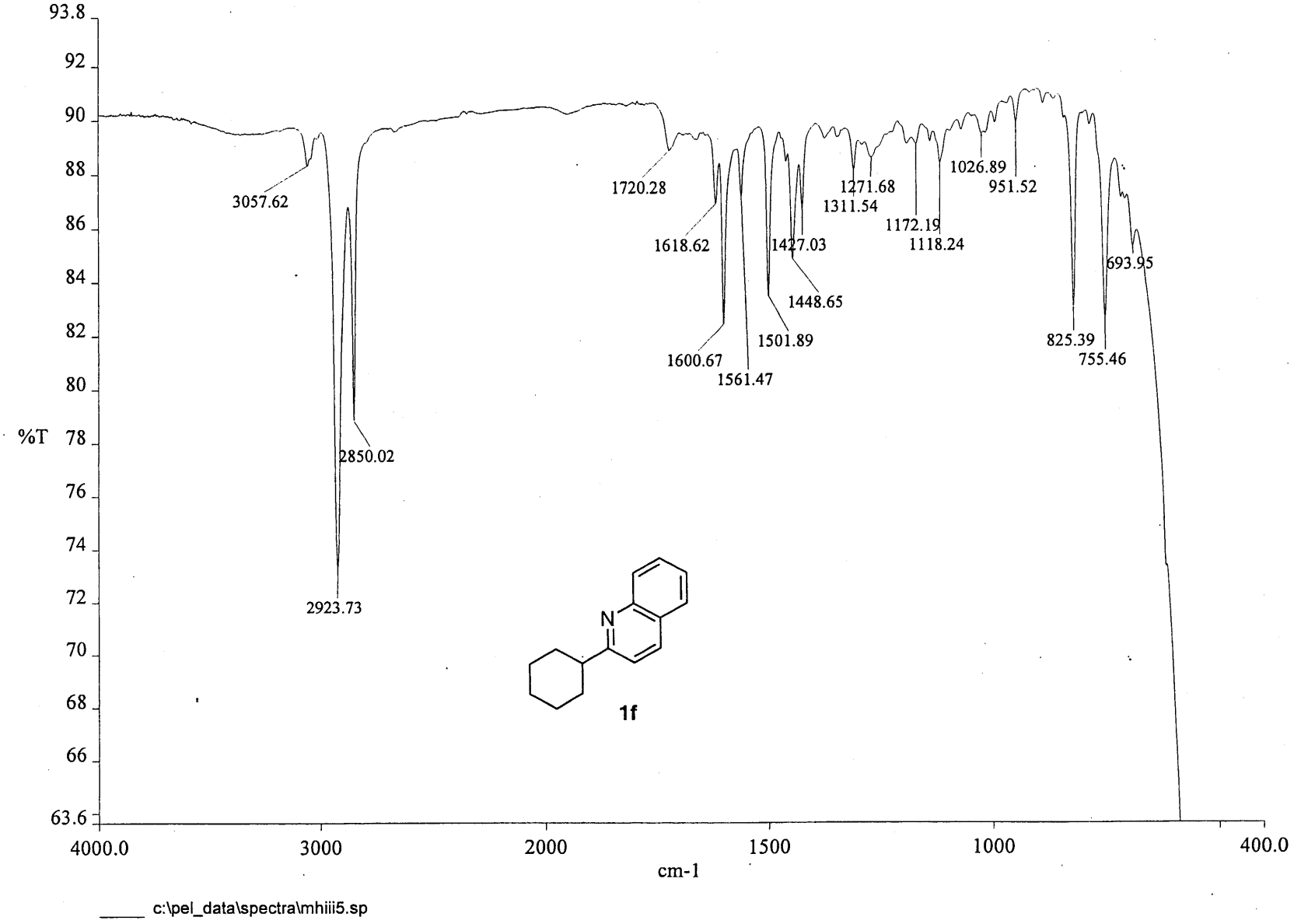
1f

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
416 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 12 minutes

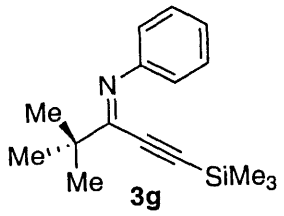


1f


93.8
92
90
88
86
84
82
80
78
76
74
72
70
68
66
63.6
%T
3057.62
2923.73
2850.02
1720.28
1618.62
1600.67
1561.47
1501.89
1448.65
1427.03
1311.54
1271.68
1172.19
1118.24
1026.89
951.52
825.39
755.46
693.95
N
1f
4000.0
3000
2000
1500
1000
400.0
cm-1
c:\pel_data\spectra\mhiii5.sp

Solvent: CDCl3
Ambient temperature
INOVA-500 "rocky"

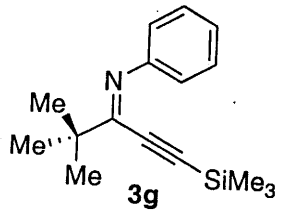
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 500.2312702 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute



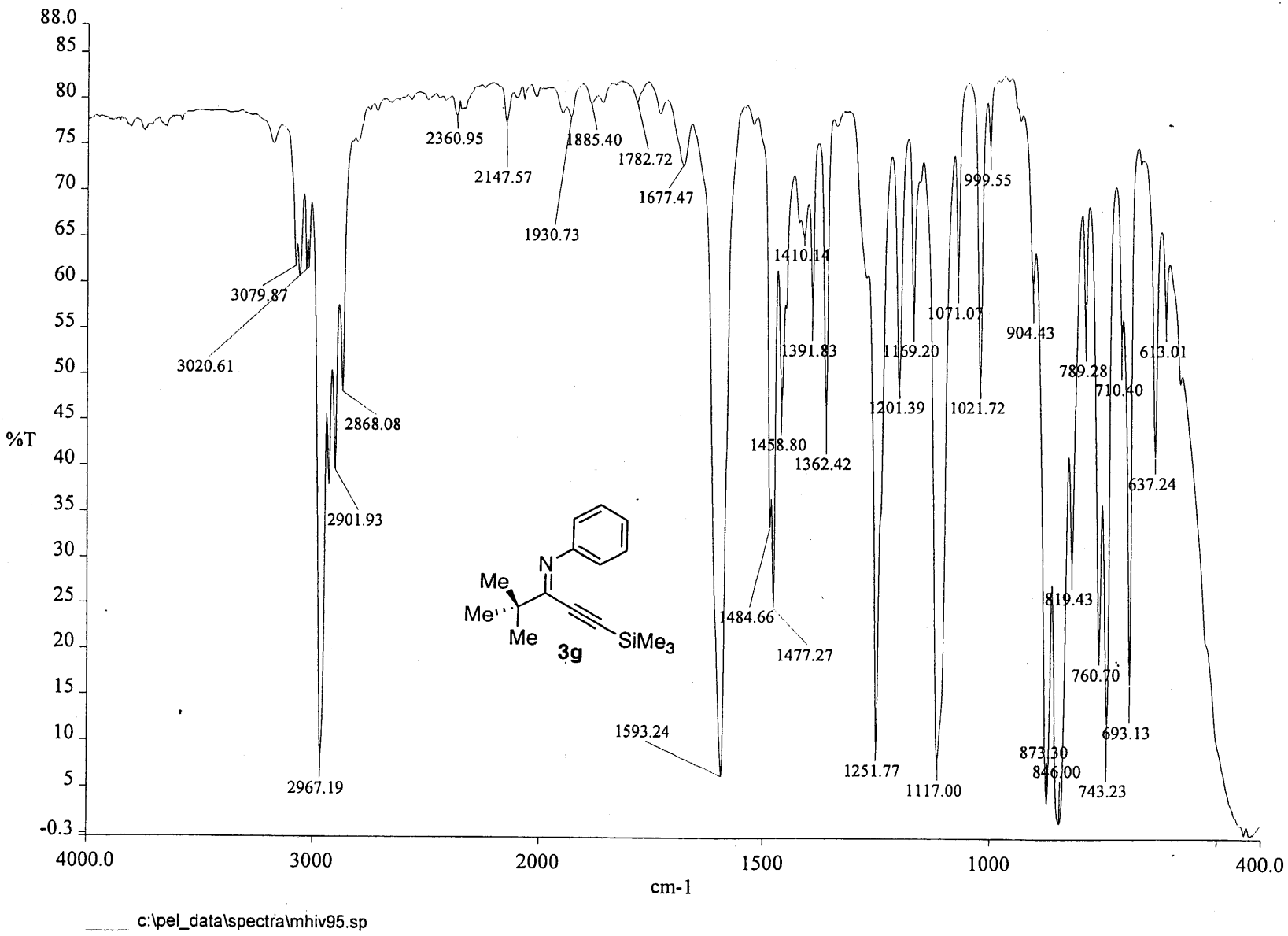
3g

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
160 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes

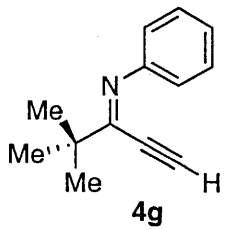


3g


88.0
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
-0.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3079.87
3020.61
2868.08
2901.93
2967.19
2360.95
2147.57
1930.73
1885.40
1782.72
1677.47
1593.24
1484.66
1477.27
1458.80
1410.14
1391.83
1362.42
1251.77
1201.39
1169.20
1117.00
1071.07
1021.72
999.55
904.43
873.30
846.00
819.43
789.28
760.70
743.23
710.40
693.13
637.24
613.01
N
Me
Me
Me
SiMe3
3g
c:\pel_data\spectra\mhiv95.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

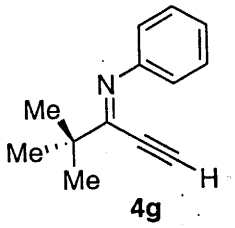
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



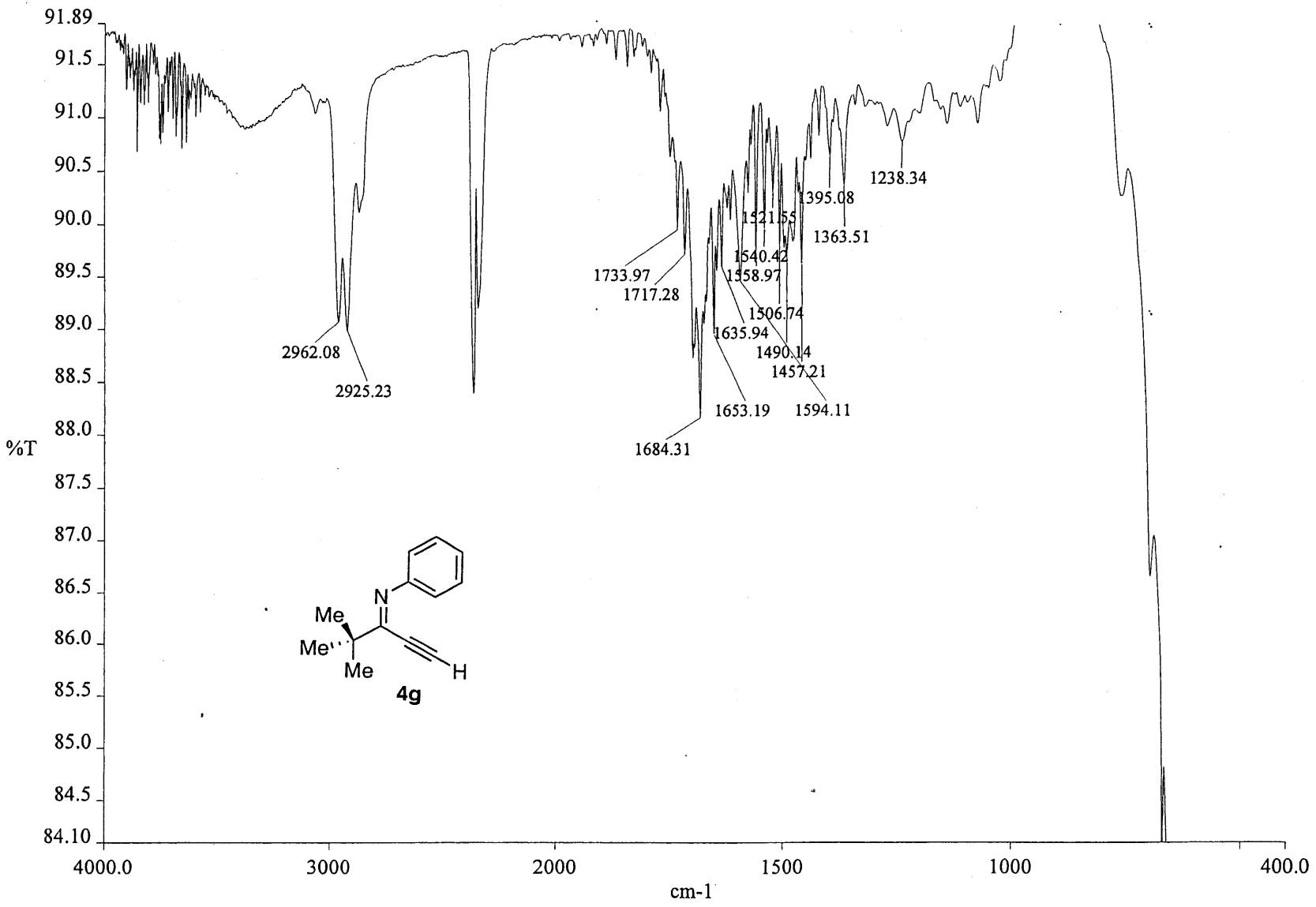
4g

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
32 repetitions
OBSERVE C13, 125.7832291 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

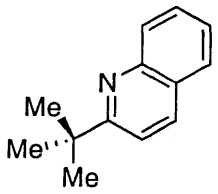


4g


91.89
91.5
91.0
90.5
90.0
89.5
89.0
88.5
88.0
87.5
87.0
86.5
86.0
85.5
85.0
84.5
84.10
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2962.08
2925.23
1733.97
1717.28
1684.31
1653.19
1635.94
1594.11
1558.97
1540.42
1521.55
1506.74
1490.14
1457.21
1395.08
1363.51
1238.34
N
Me
Me
Me
H
4g
c:\pel_data\spectra\mhiii177.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

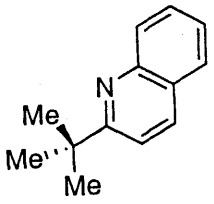
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446552 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



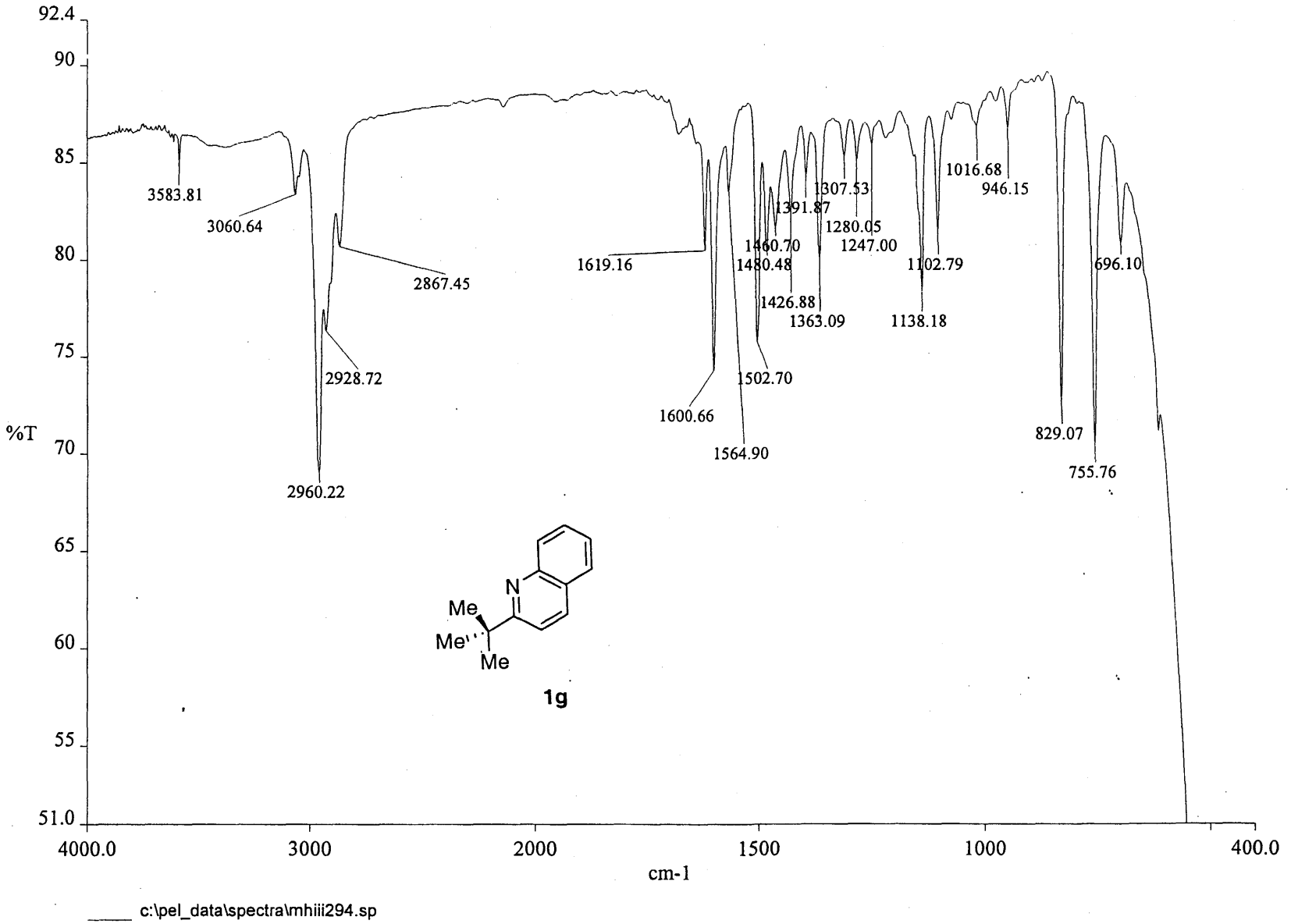
1g

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

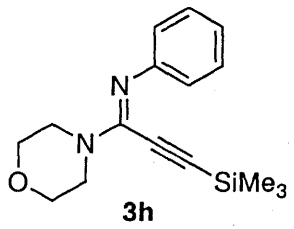
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
3112 repetitions
OBSERVE C13, 125.7832263 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 91 minutes



1g


92.4
90
85
80
75
70
65
60
55
51.0
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3583.81
3060.64
2867.45
2928.72
2960.22
1619.16
1600.66
1564.90
1502.70
1460.70
1480.48
1426.88
1391.87
1363.09
1307.53
1280.05
1247.00
1138.18
1102.79
1016.68
946.15
829.07
755.76
696.10
N
Me
Me
Me
1g
c:\pel_data\spectra\mhiii294.sp

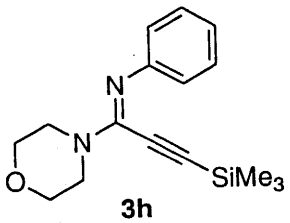
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-II-110fr12-14
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537708 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec



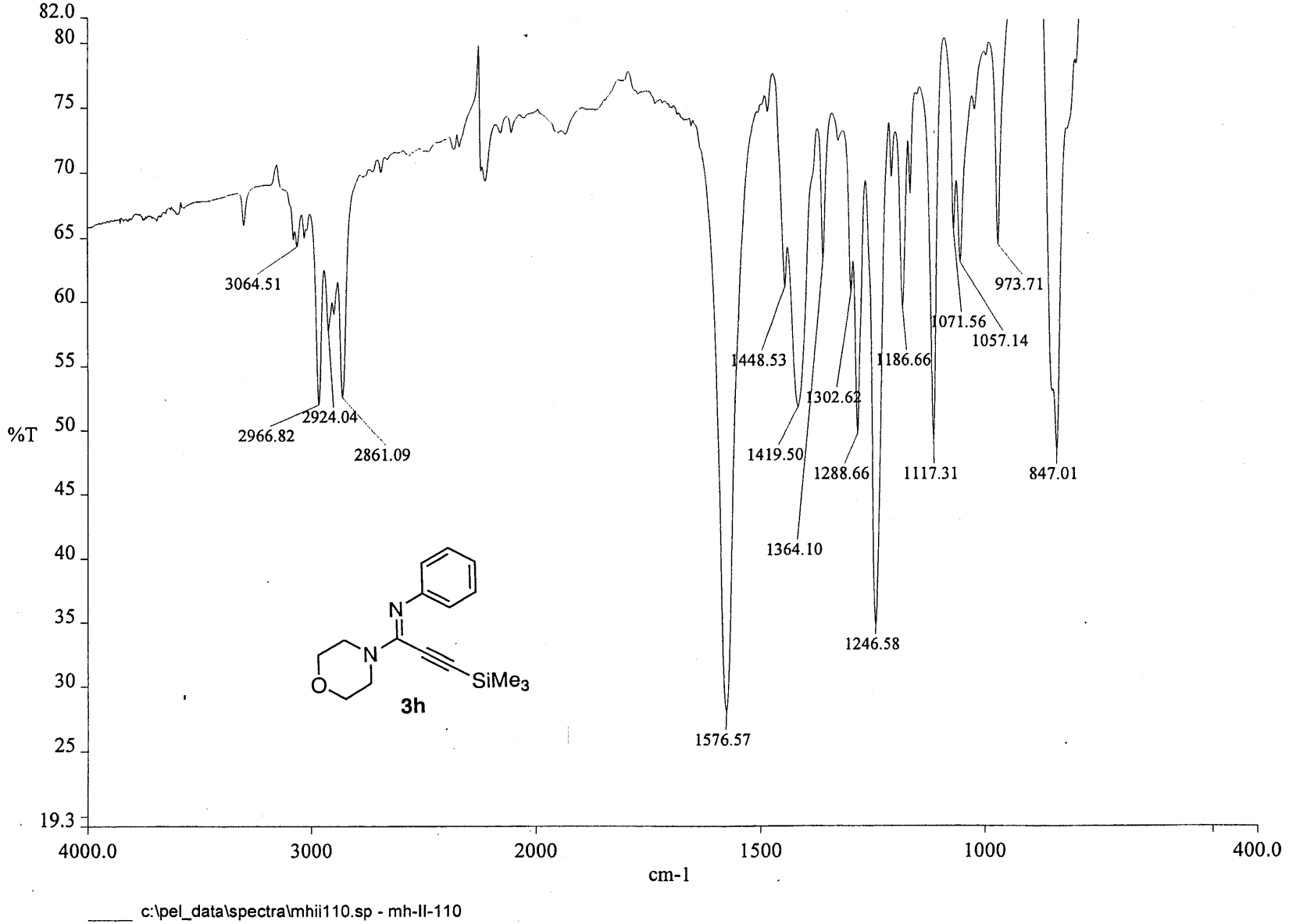
3h

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

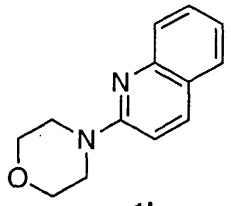
PULSE SEQUENCE
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
880 repetitions
OBSERVE C13, 125.6631607 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 243 hr, 47 min, 34 sec



3h


82.0
80
75
70
65
60
55
50
45
40
35
30
25
19.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3064.51
2966.82
2924.04
2861.09
1576.57
1448.53
1419.50
1364.10
1302.62
1288.66
1246.58
1186.66
1117.31
1071.56
1057.14
973.71
847.01
N
N
O
SiMe3
3h
c:\pel_data\spectra\mhii110.sp - mh-II-110

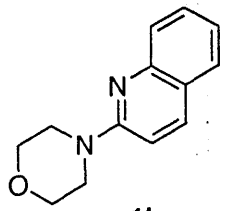
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-II-281
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



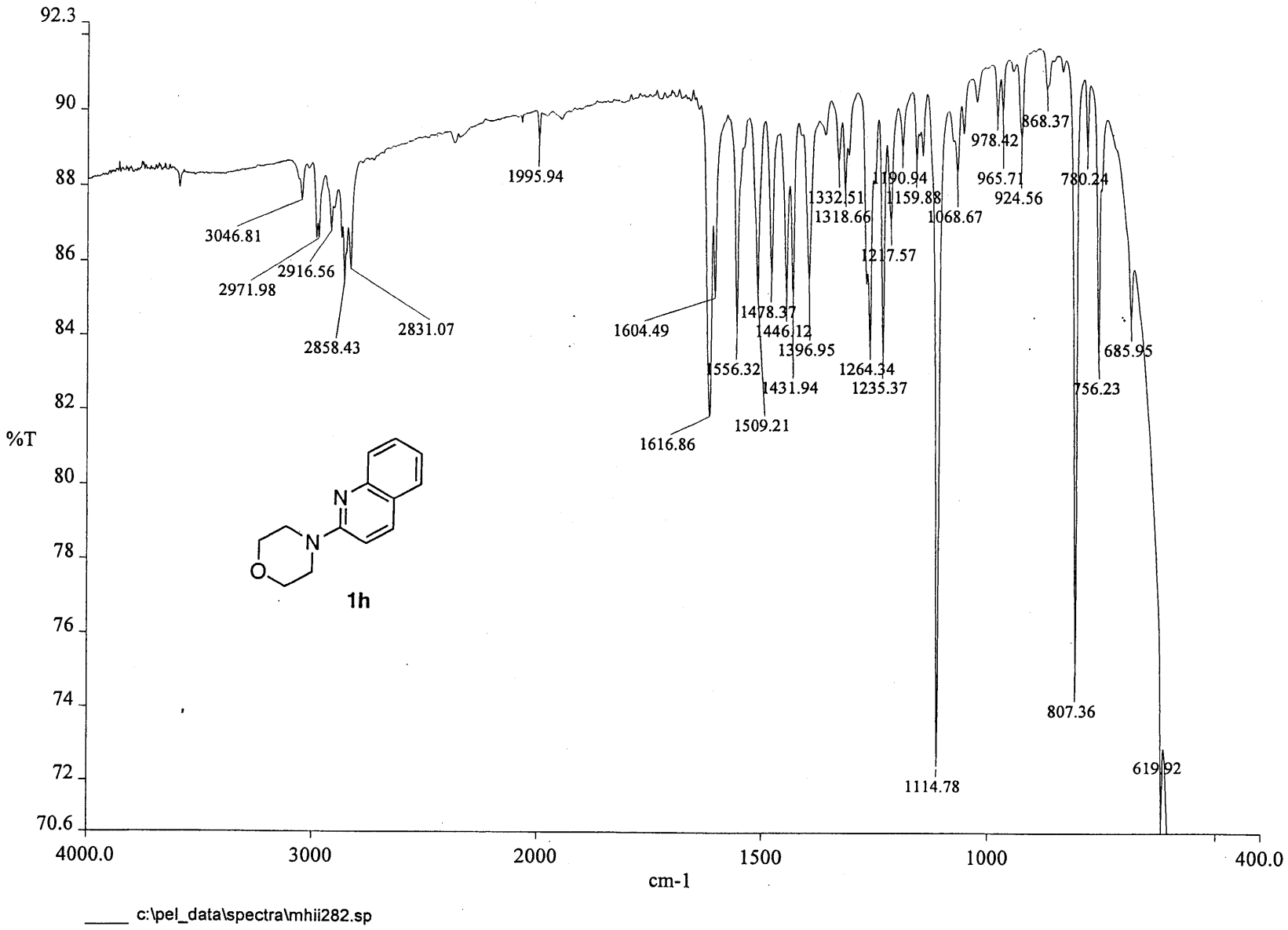
1h

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
8 repetitions
OBSERVE C13, 125.7832383 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

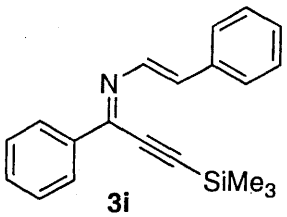


1h

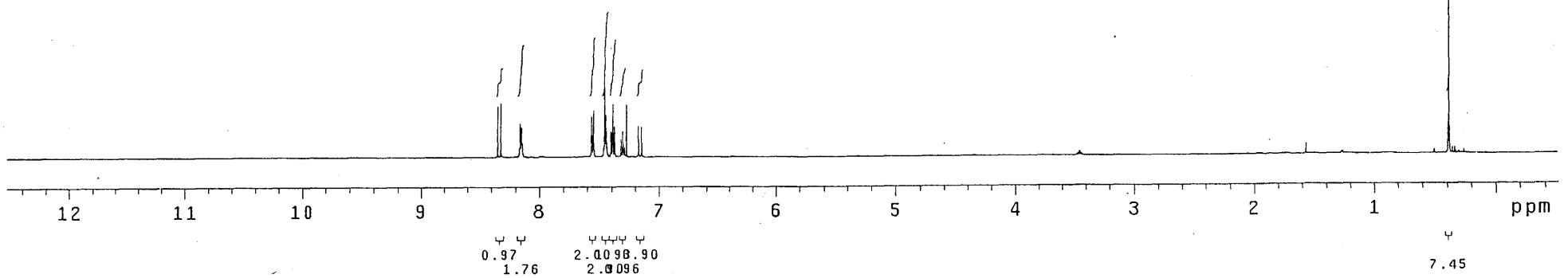

92.3
90
88
86
84
82
80
78
76
74
72
70.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3046.81
2971.98
2916.56
2858.43
2831.07
1995.94
1604.49
1616.86
1556.32
1509.21
1478.37
1446.12
1431.94
1396.95
1332.51
1318.66
1264.34
1235.37
1217.57
1190.94
1159.88
1114.78
1068.67
978.42
965.71
924.56
868.37
807.36
780.24
756.23
685.95
619.92
N
N
O
1h
c:\pel_data\spectra\mhii282.sp

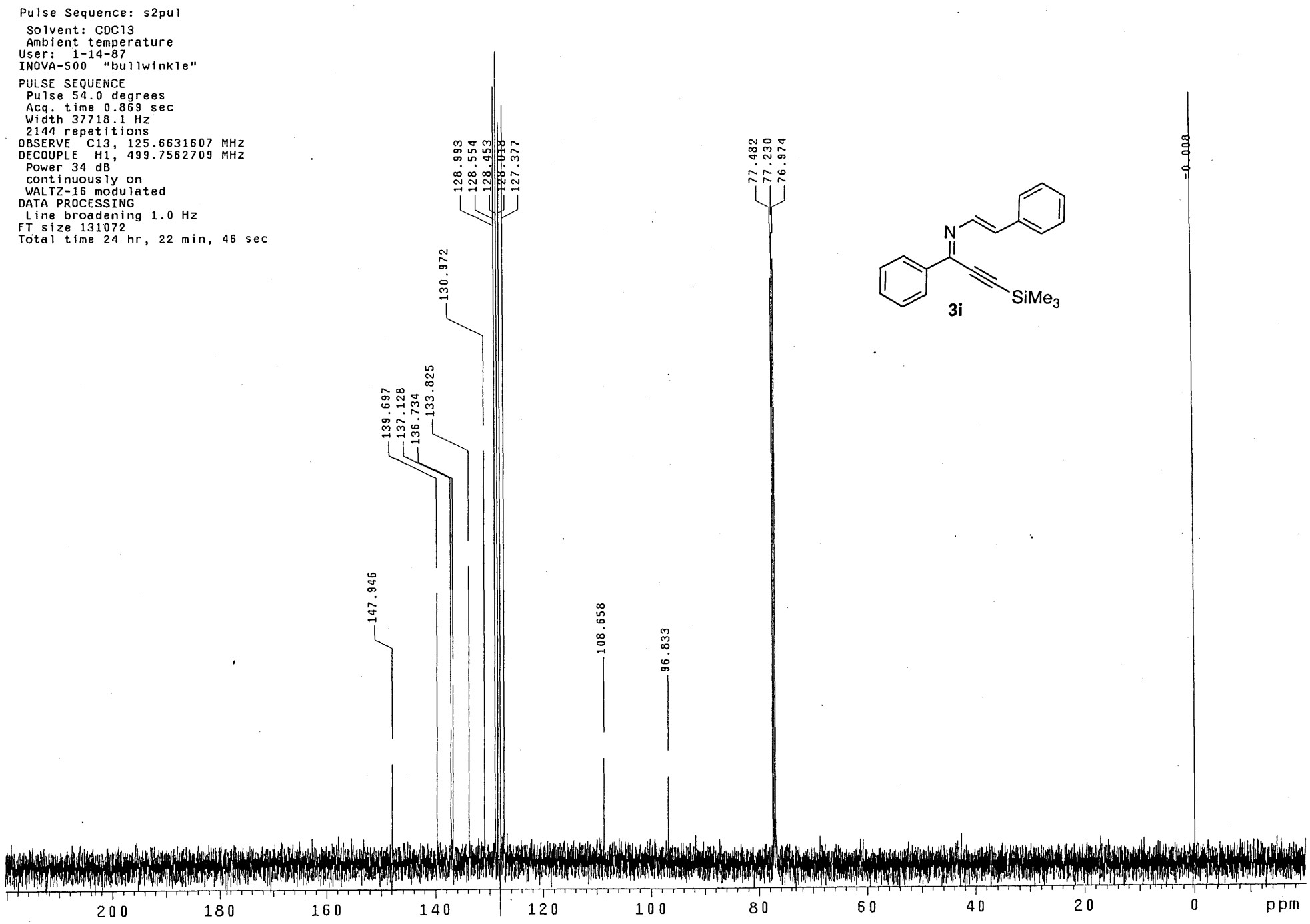
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

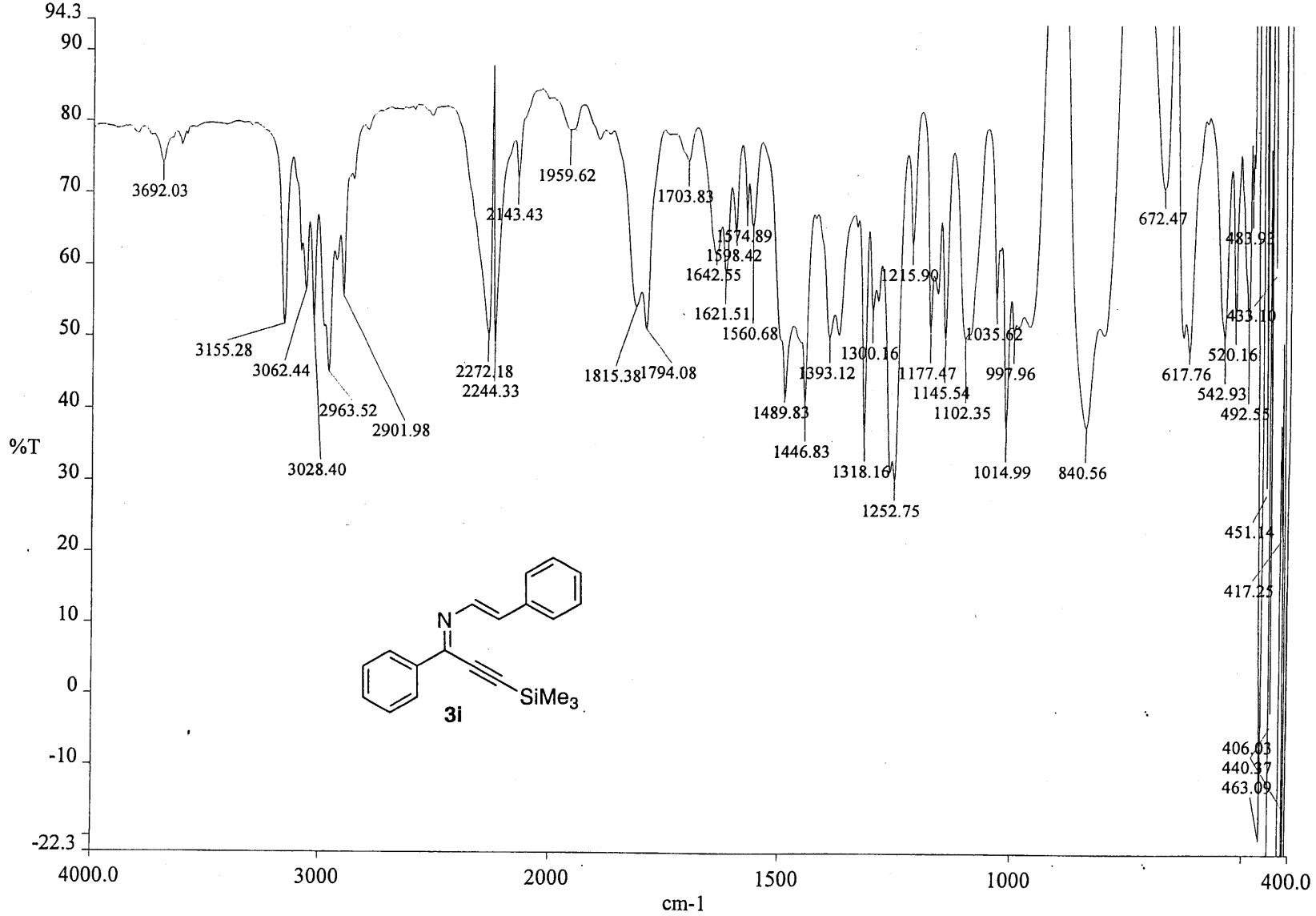
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537722 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec



3i

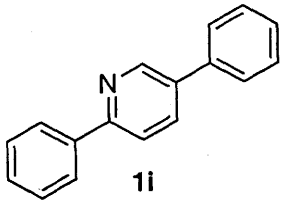



Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
2144 repetitions
OBSERVE C13, 125.6631607 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 24 hr, 22 min, 46 sec
147.946
139.697
137.128
136.734
133.825
130.972
128.993
128.554
128.453
128.018
127.377
108.658
96.833
77.482
77.230
76.974
0.008
N
SiMe3
3i
200
180
160
140
120
100
80
60
40
20
0
ppm

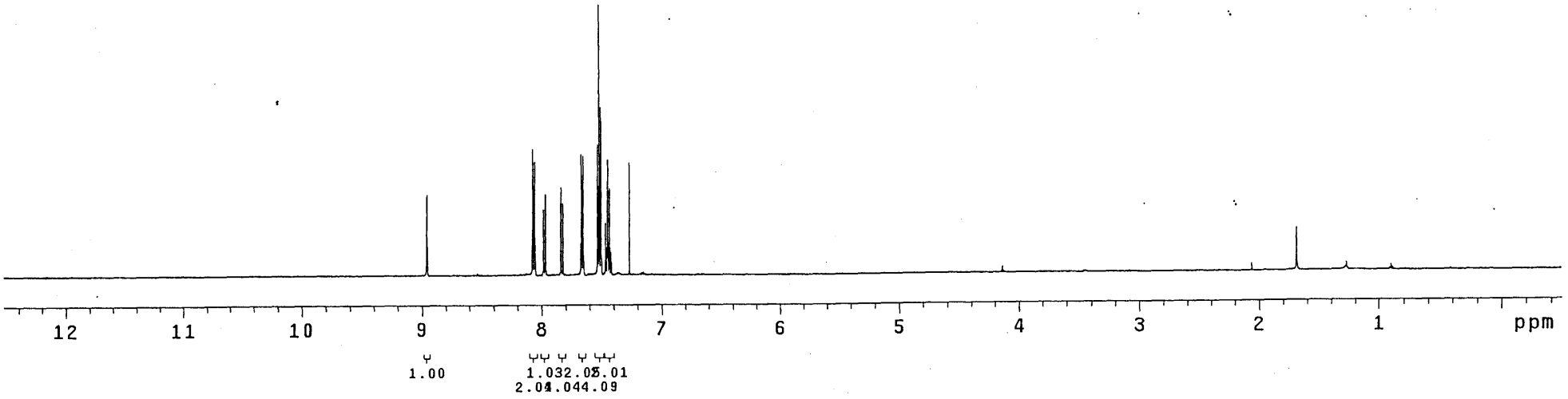

94.3
90
80
70
60
50
40
30
20
10
0
-10
-22.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3692.03
3155.28
3062.44
3028.40
2963.52
2901.98
2272.18
2244.33
2143.43
1959.62
1815.38
1794.08
1703.83
1642.55
1621.51
1598.42
1574.89
1560.68
1489.83
1446.83
1393.12
1318.16
1300.16
1252.75
1215.90
1177.47
1145.54
1102.35
1035.62
1014.99
997.96
840.56
672.47
617.76
542.93
520.16
492.55
483.93
433.10
451.14
417.25
406.03
440.37
463.09
N
SiMe3
3i
c:\pel_data\spectra\groups\movass~1\matt\mhii76.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 24 sec

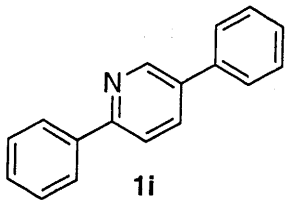


1i

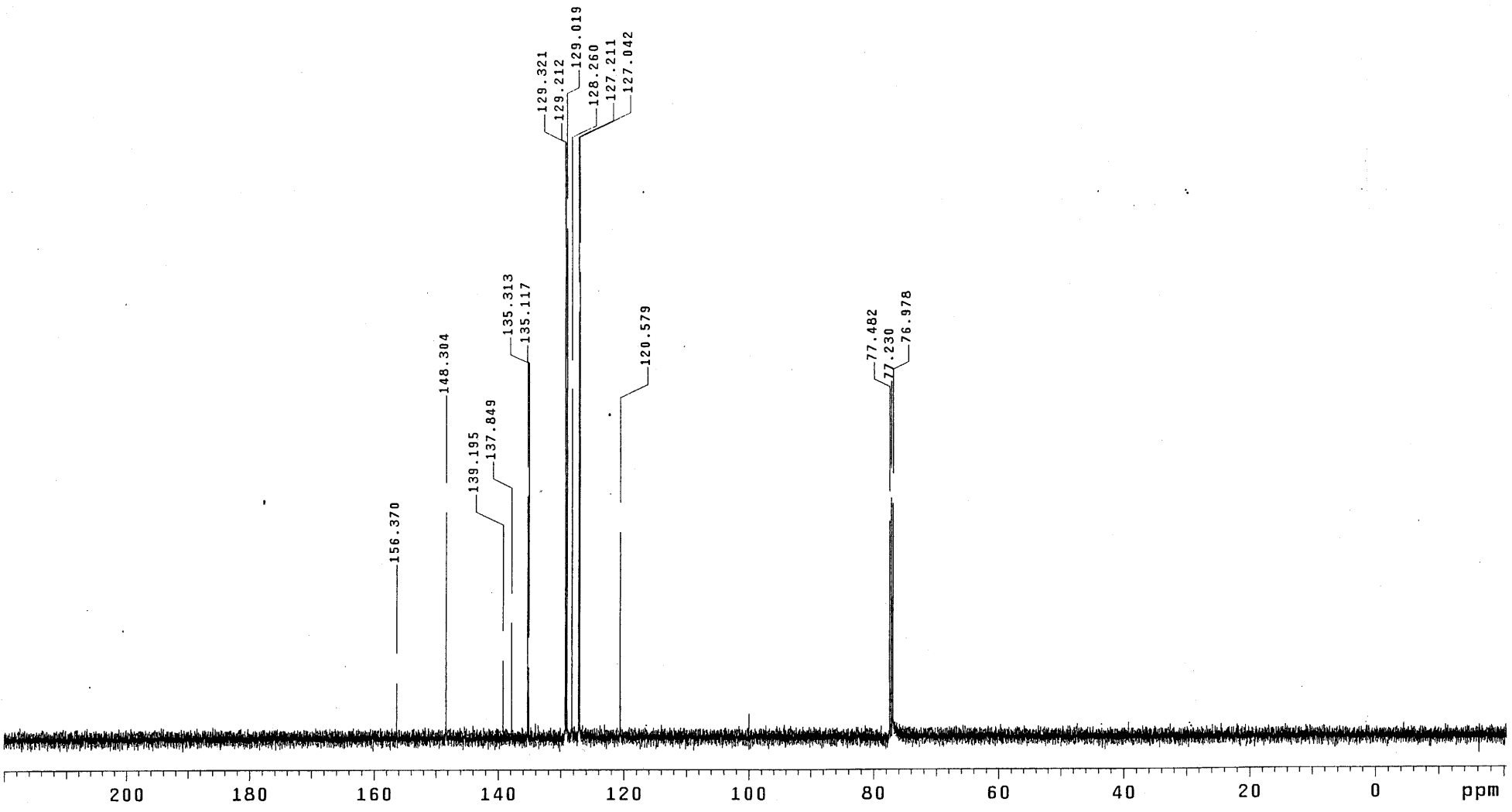


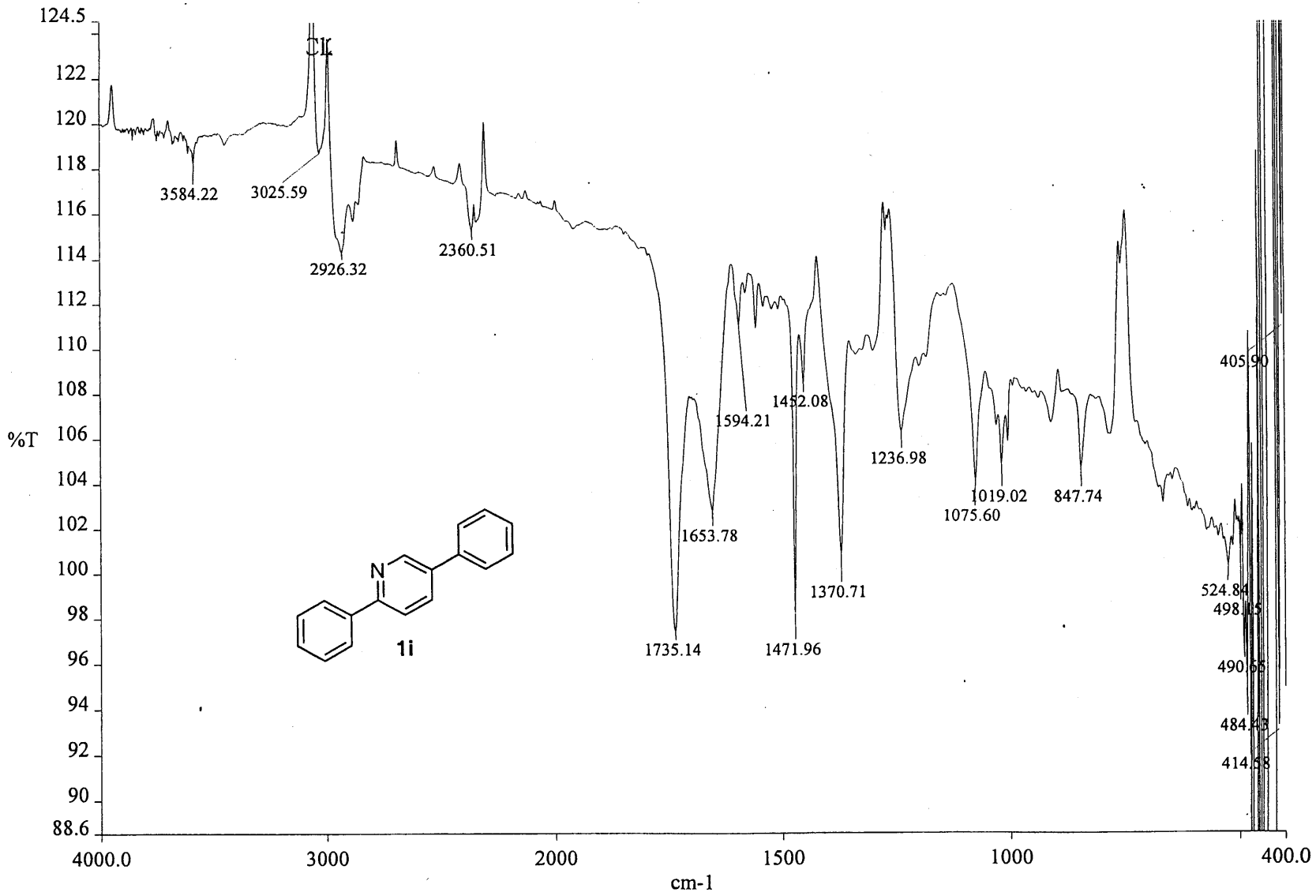
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
584 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 16 minutes



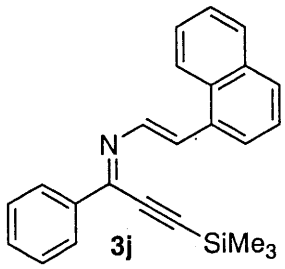
1i



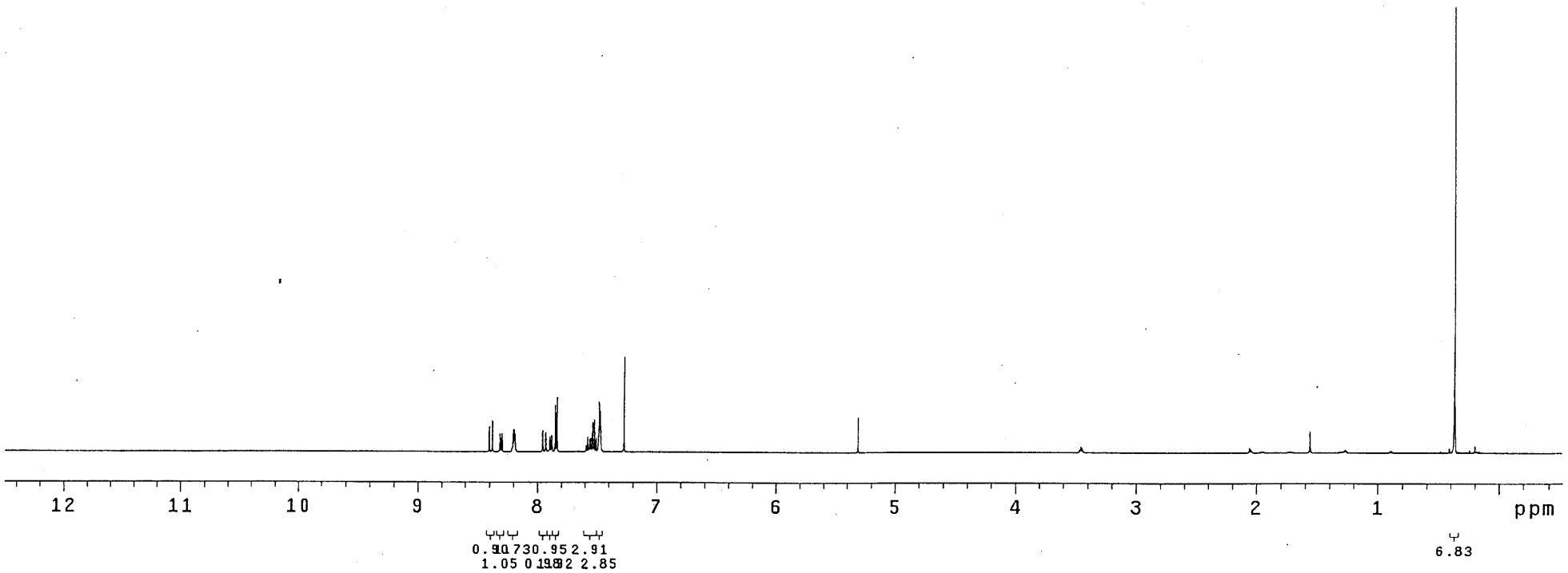

124.5
122
120
118
116
114
112
110
108
106
104
102
100
98
96
94
92
90
88.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3584.22
3025.59
2926.32
2360.51
1735.14
1653.78
1594.21
1471.96
1452.08
1370.71
1236.98
1075.60
1019.02
847.74
524.84
405.90
N
1i
c:\pel_data\spectra\mhii275.sp - mh-II-275 in CH2Cl2

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

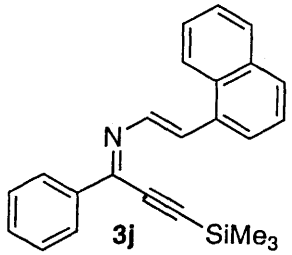


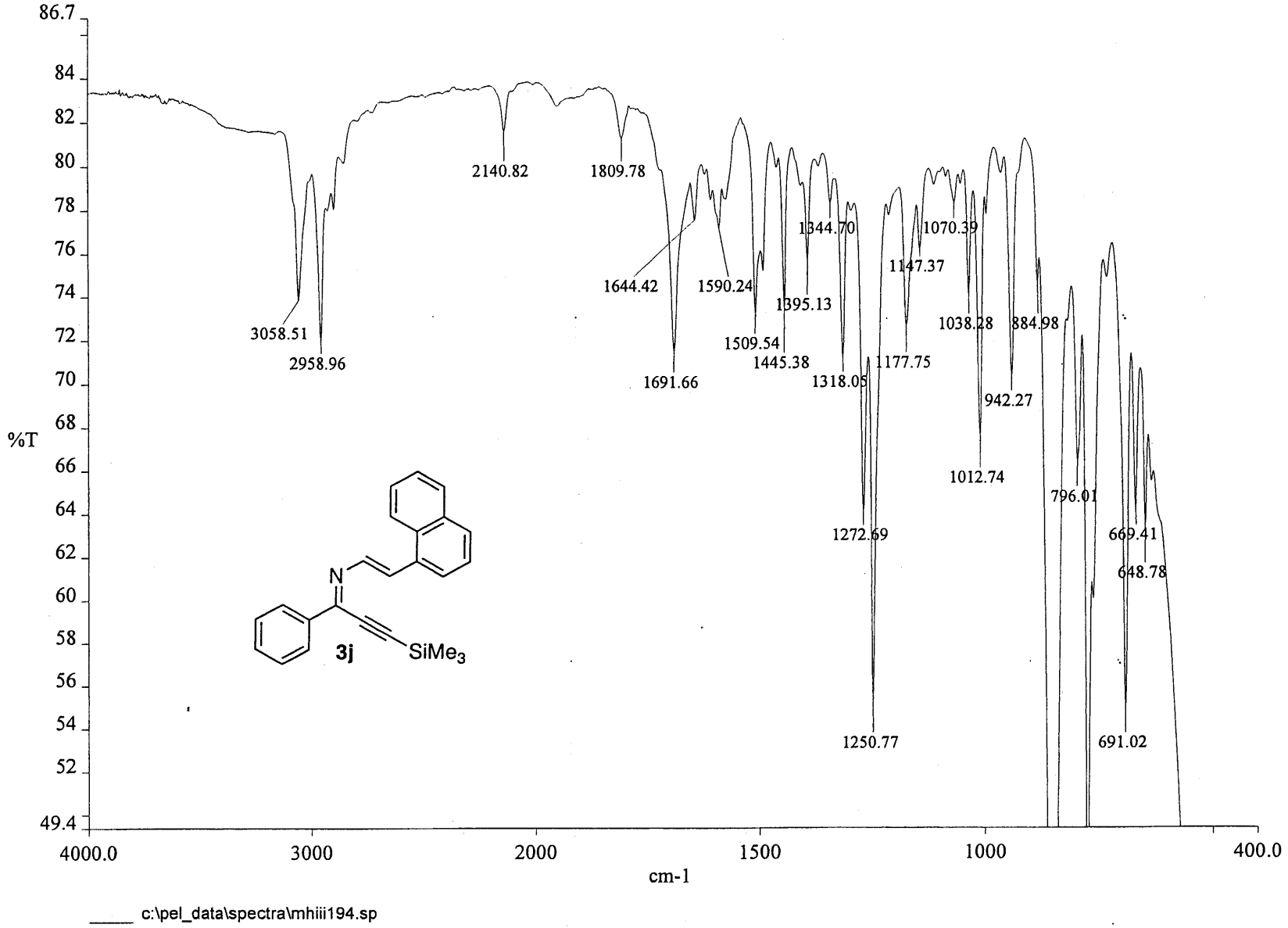
3j



Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-III-194carbon
INOVA-500 "rocky"

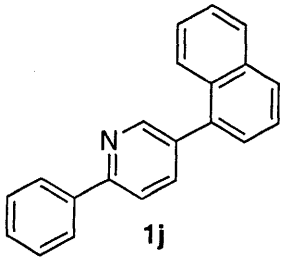
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
8 repetitions
OBSERVE C13, 125.7831641 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute



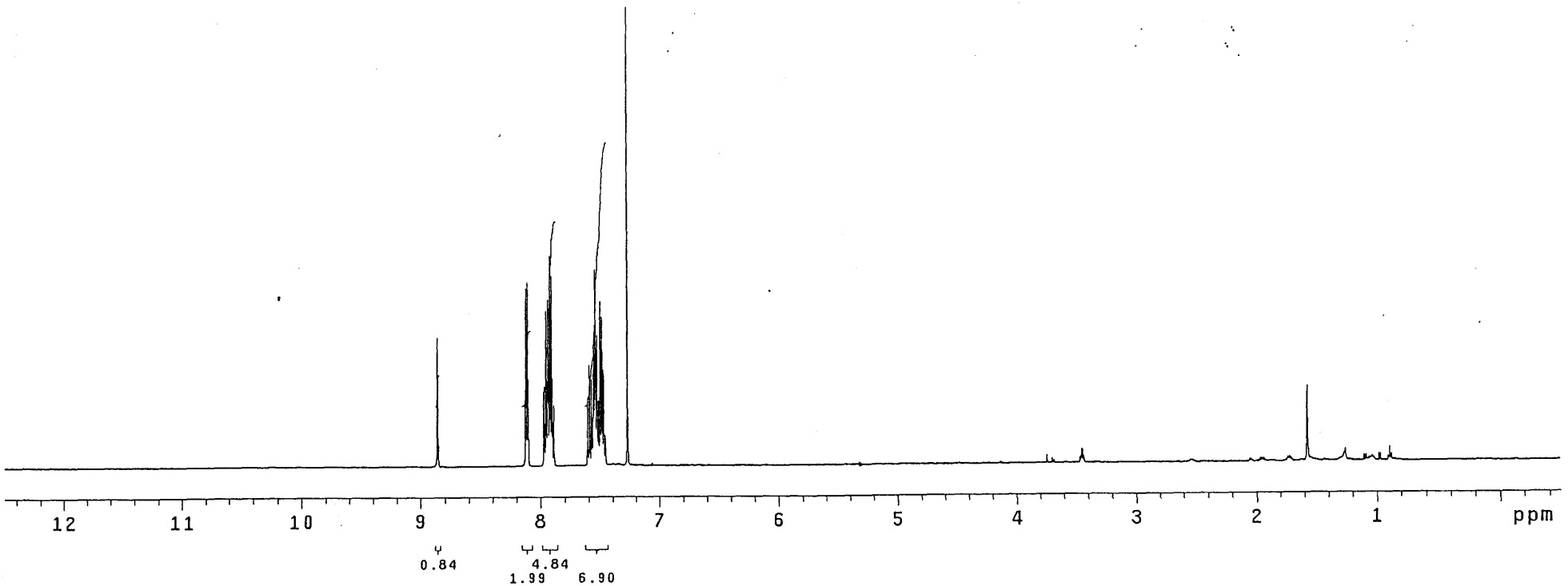

86.7
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
49.4
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3058.51
2958.96
2140.82
1809.78
1644.42
1691.66
1590.24
1509.54
1445.38
1395.13
1344.70
1318.05
1272.69
1250.77
1177.75
1147.37
1070.39
1038.28
1012.74
942.27
884.98
796.01
691.02
669.41
648.78
N
SiMe3
3j
c:\pel_data\spectra\mhiii194.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

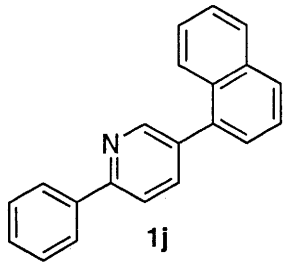


1j

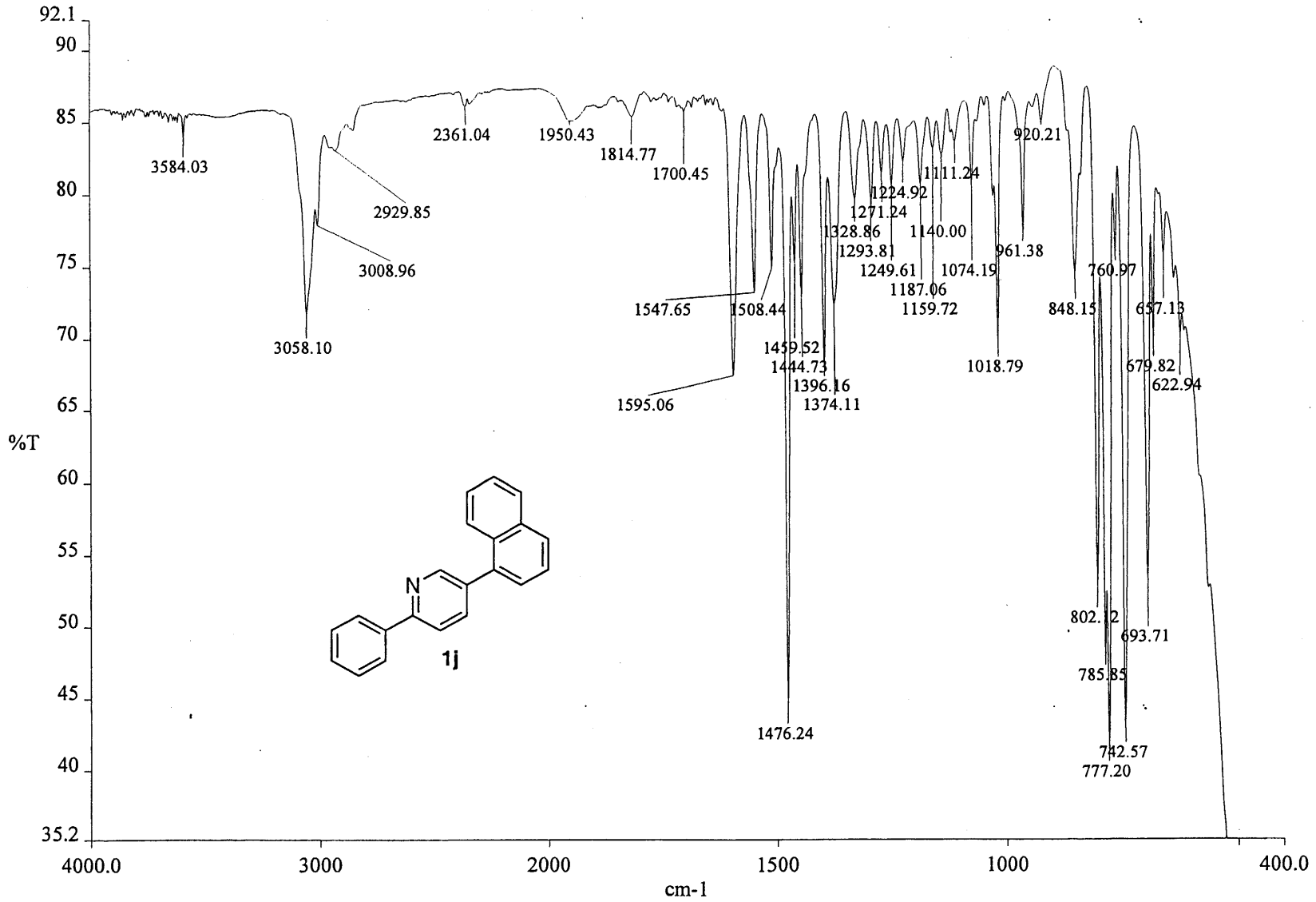


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
32 repetitions
OBSERVE C13, 125.7832326 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

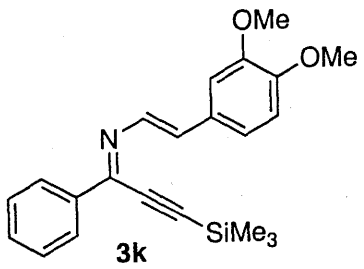


1j

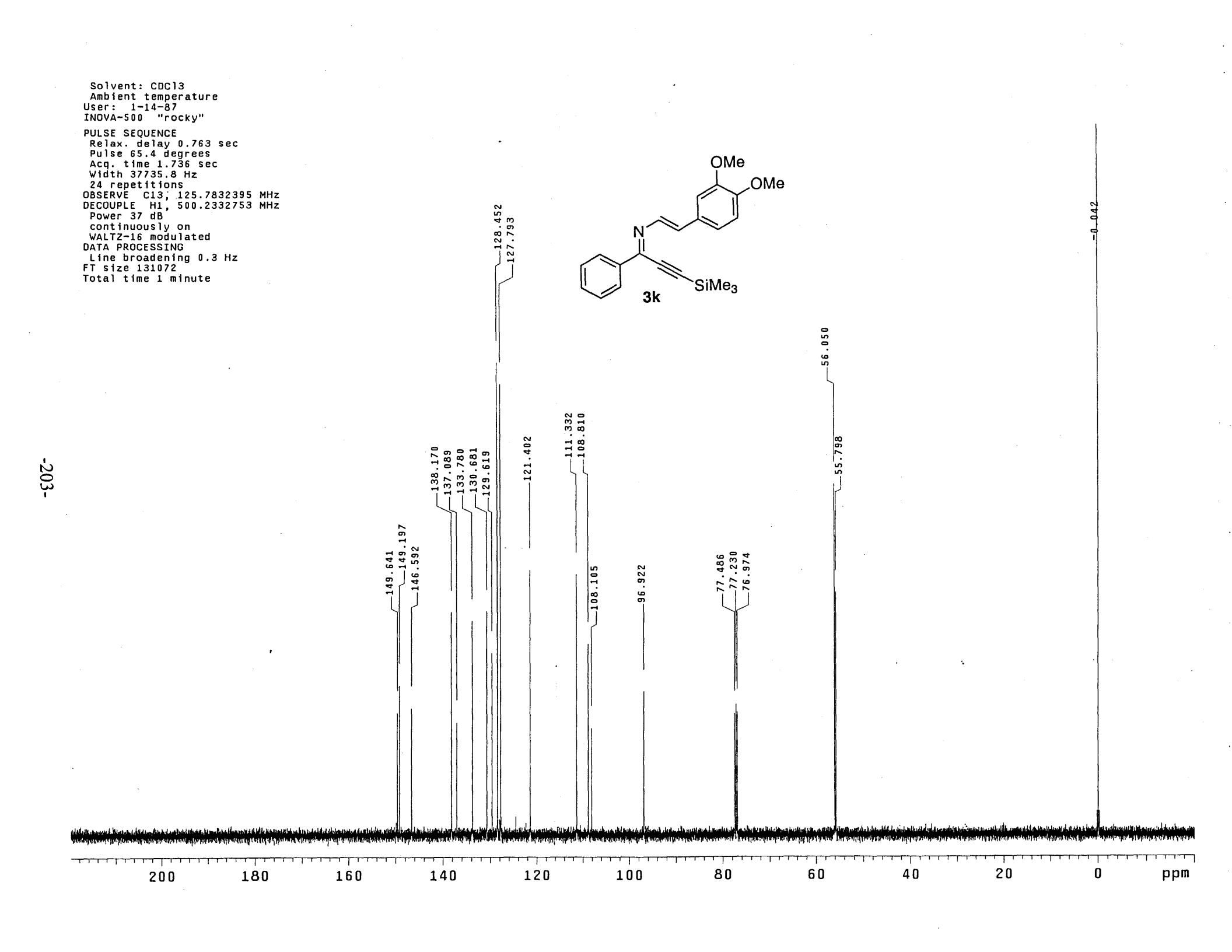

92.1
90
85
80
75
70
65
60
55
50
45
40
35.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3584.03
3058.10
2929.85
3008.96
2361.04
1950.43
1814.77
1700.45
1547.65
1595.06
1508.44
1459.52
1444.73
1396.16
1374.11
1476.24
1328.86
1293.81
1271.24
1249.61
1224.92
1187.06
1159.72
1140.00
1111.24
1074.19
1018.79
961.38
920.21
848.15
802.12
785.85
777.20
760.97
742.57
693.71
679.82
657.13
622.94
N
1j
c:\pel_data\spectra\mhiii201.sp

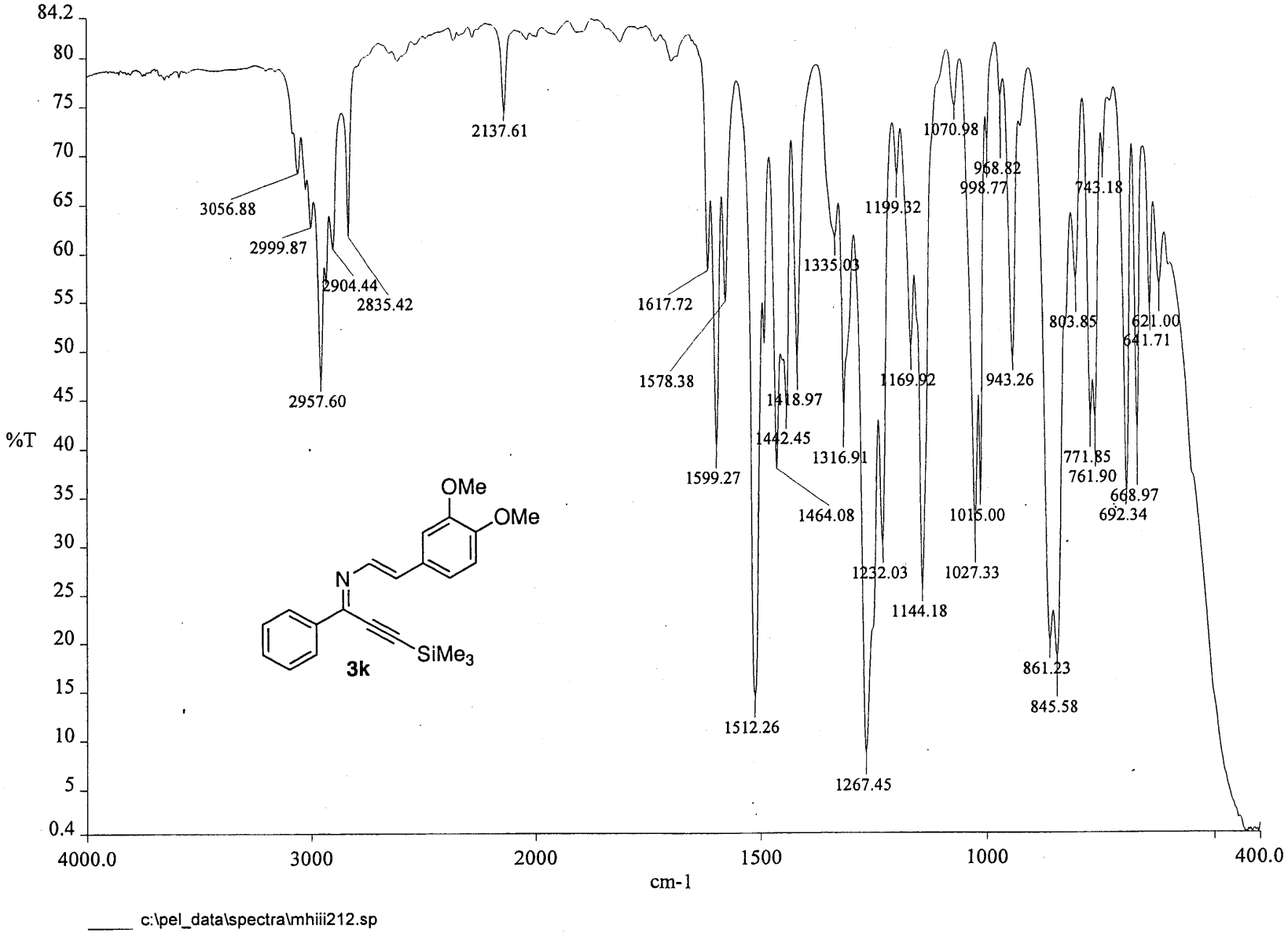
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



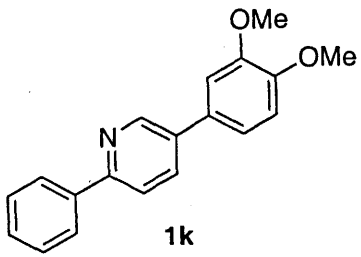
3k


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
24 repetitions
OBSERVE C13, 125.7832395 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
OMe
OMe
N
SiMe3
3k
149.641
149.197
146.592
138.170
137.089
133.780
130.681
129.619
128.452
127.793
121.402
111.332
108.810
108.105
96.922
77.486
77.230
76.974
56.050
55.798
-0.042
200
180
160
140
120
100
80
60
40
20
0
ppm

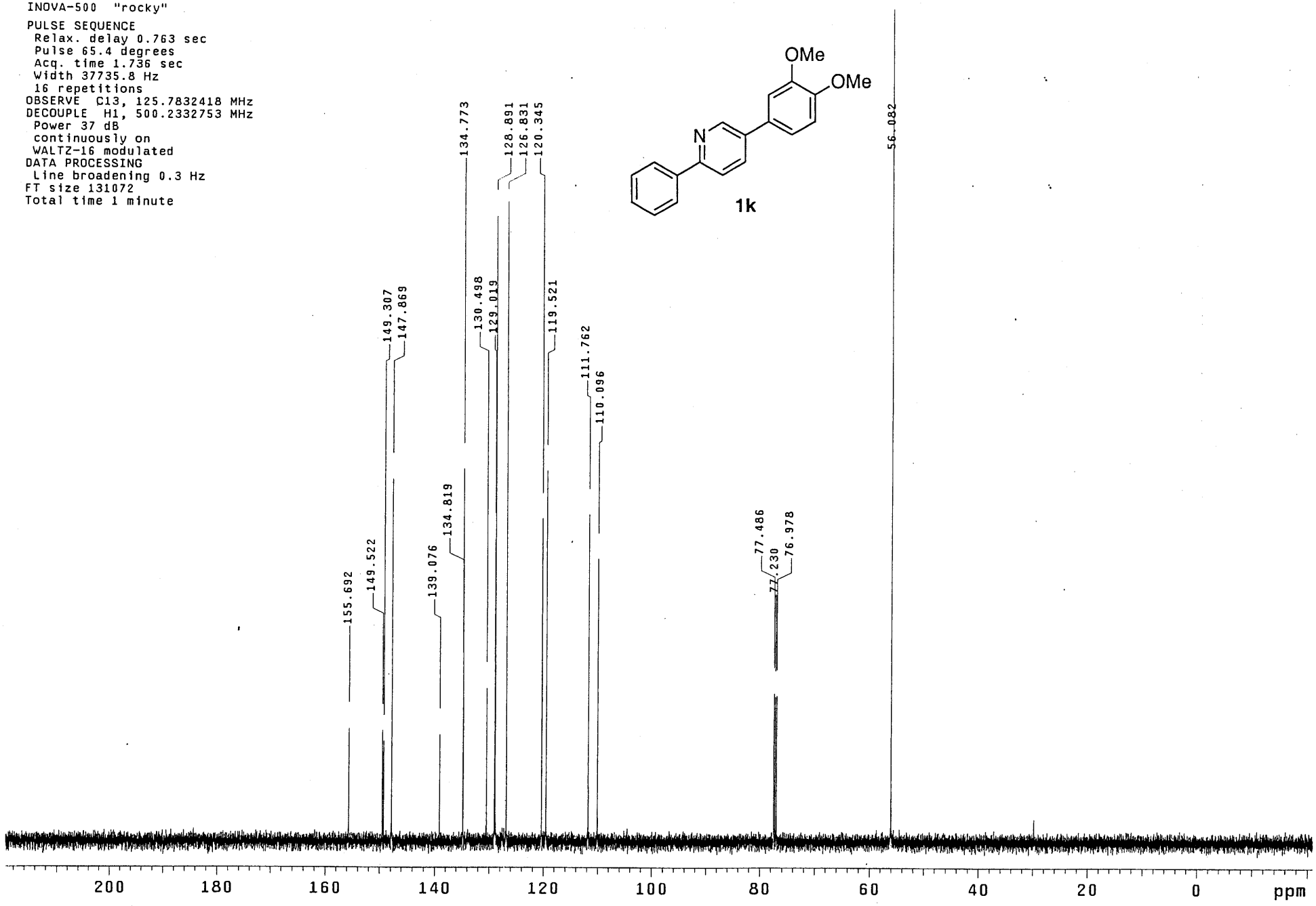

84.2
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.4
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3056.88
2999.87
2957.60
2904.44
2835.42
2137.61
1617.72
1578.38
1599.27
1512.26
1418.97
1442.45
1464.08
1335.03
1316.91
1267.45
1199.32
1232.03
1169.92
1144.18
1070.98
998.77
1015.00
1027.33
968.82
943.26
861.23
845.58
803.85
743.18
771.85
761.90
668.97
692.34
641.71
621.00
OMe
OMe
N
SiMe3
3k
c:\pel_data\spectra\mhiii212.sp

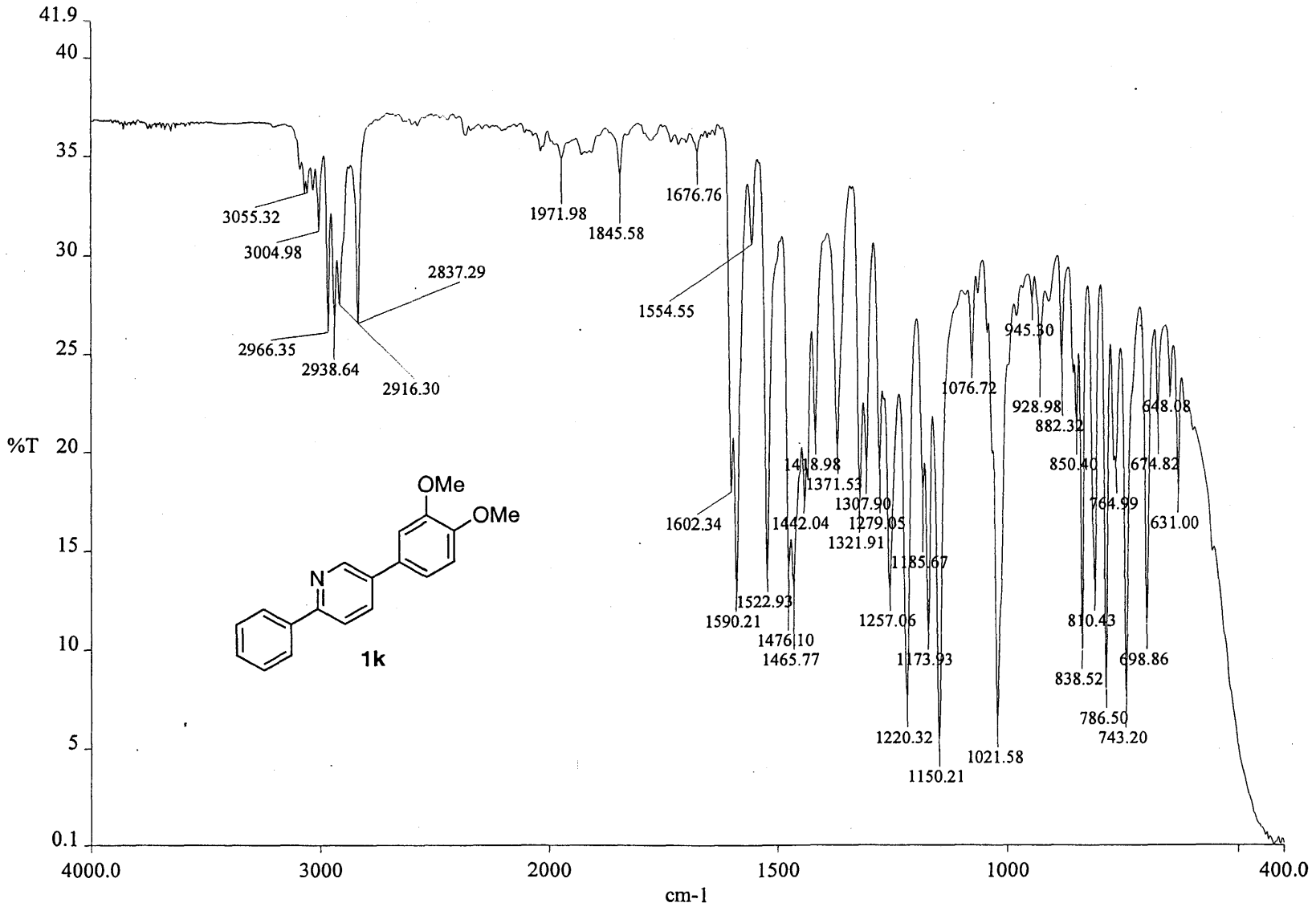
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

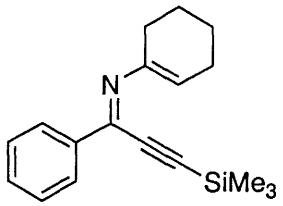


1k


Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-III-211carbon
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
16 repetitions
OBSERVE C13, 125.7832418 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
OMe
OMe
N
1k
155.692
149.522
149.307
147.869
139.076
134.819
134.773
130.498
129.019
128.891
126.831
120.345
119.521
111.762
110.096
77.486
77.230
76.978
56.082
200
180
160
140
120
100
80
60
40
20
0
ppm


41.9
40
35
30
25
20
15
10
5
0.1
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3055.32
3004.98
2966.35
2938.64
2916.30
2837.29
1971.98
1845.58
1676.76
1554.55
1602.34
1590.21
1522.93
1476.10
1465.77
1442.04
1418.98
1371.53
1321.91
1307.90
1279.05
1257.06
1220.32
1185.67
1173.93
1150.21
1076.72
1021.58
945.30
928.98
882.32
850.40
838.52
810.43
786.50
764.99
743.20
698.86
674.82
648.08
631.00
OMe
OMe
N
1k
c:\pel_data\spectra\mhiii211.001

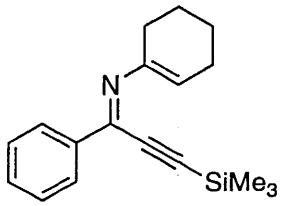
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



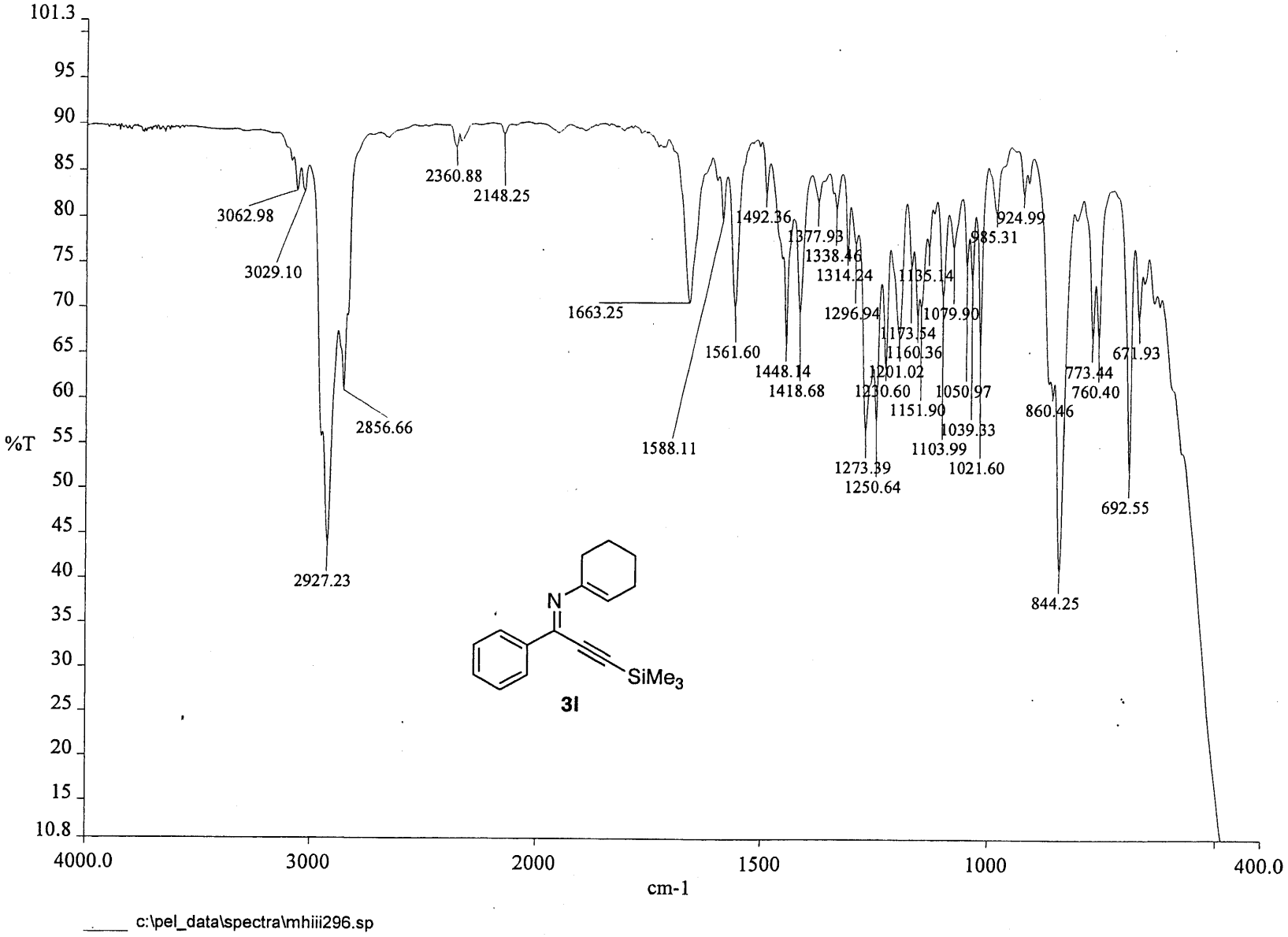
3l

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
344 repetitions
OBSERVE C13, 125.7832263 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 10 minutes



3l

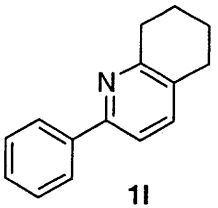


3l

c:\pel_data\spectra\mhiii296.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

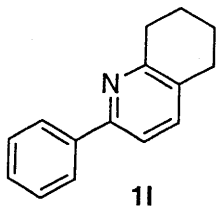
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
4 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



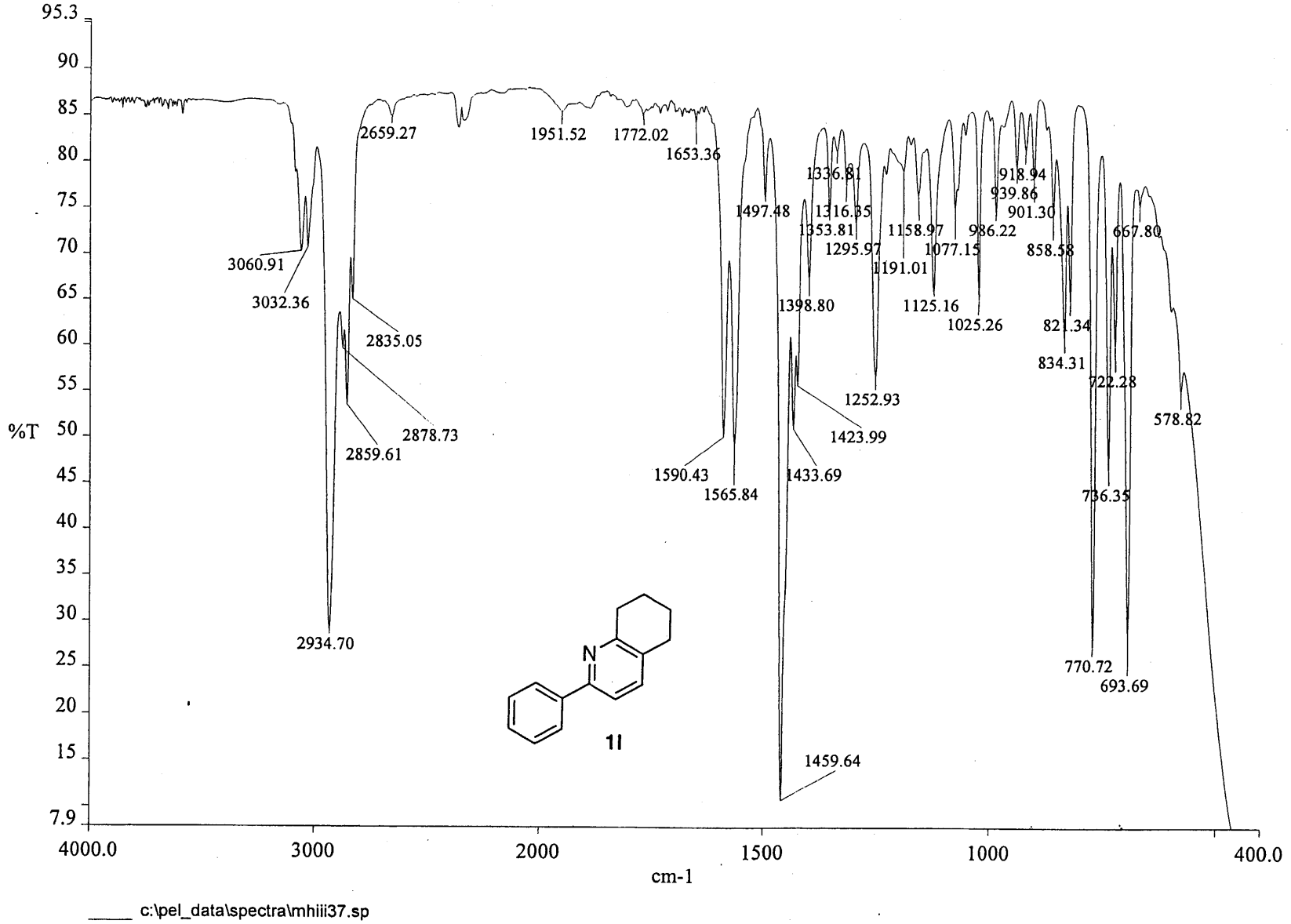
1l

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
24 repetitions
OBSERVE C13, 125.7832303 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

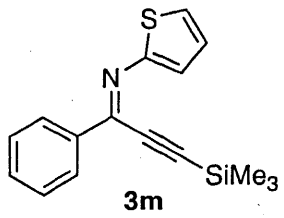


1l

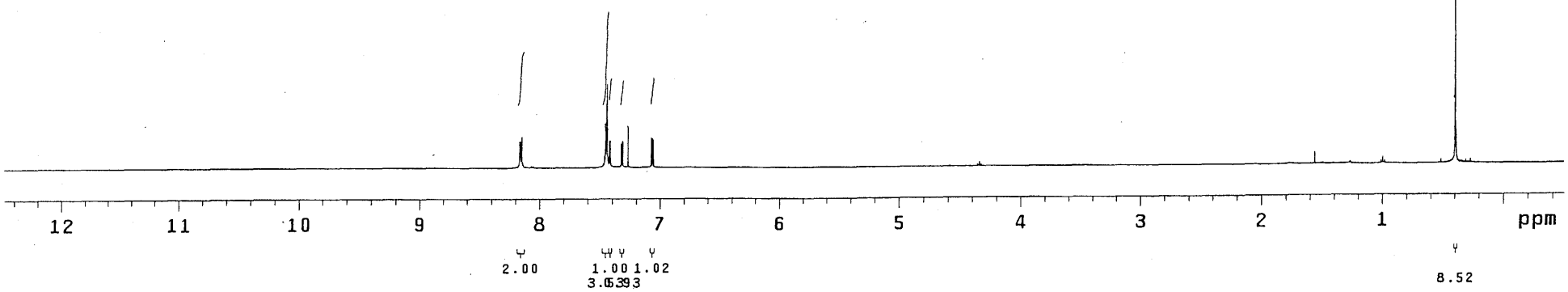

95.3
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
7.9
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3060.91
3032.36
2934.70
2859.61
2878.73
2835.05
2659.27
1951.52
1772.02
1653.36
1590.43
1565.84
1497.48
1459.64
1433.69
1423.99
1398.80
1353.81
1336.81
1316.35
1295.97
1252.93
1191.01
1158.97
1125.16
1077.15
1025.26
986.22
939.86
918.94
901.30
858.58
834.31
821.34
770.72
736.35
722.28
693.69
667.80
578.82
N
11
c:\pel_data\spectra\mhiii37.sp

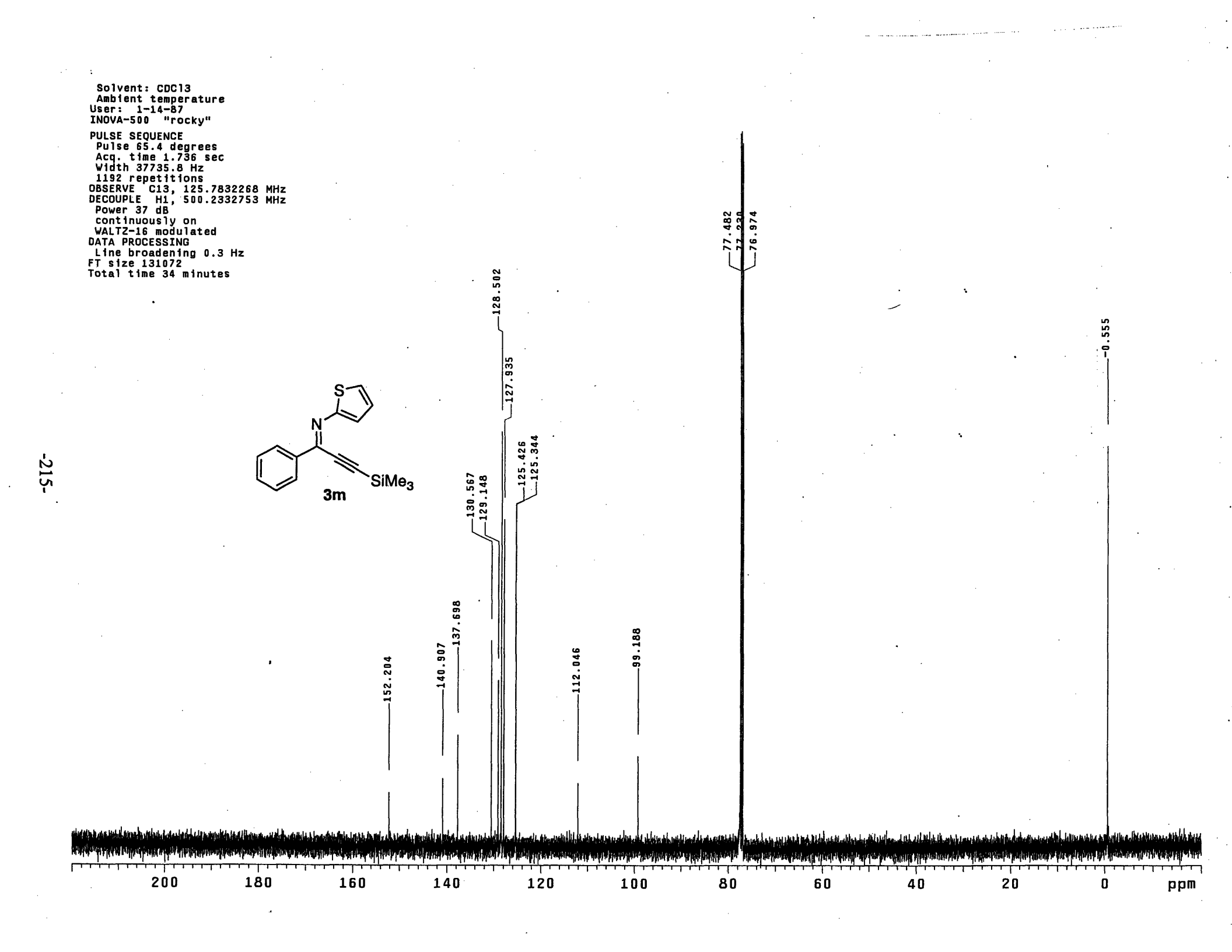
Solvent: CDCl3
Ambient temperature
INOVA-500 "rocky"

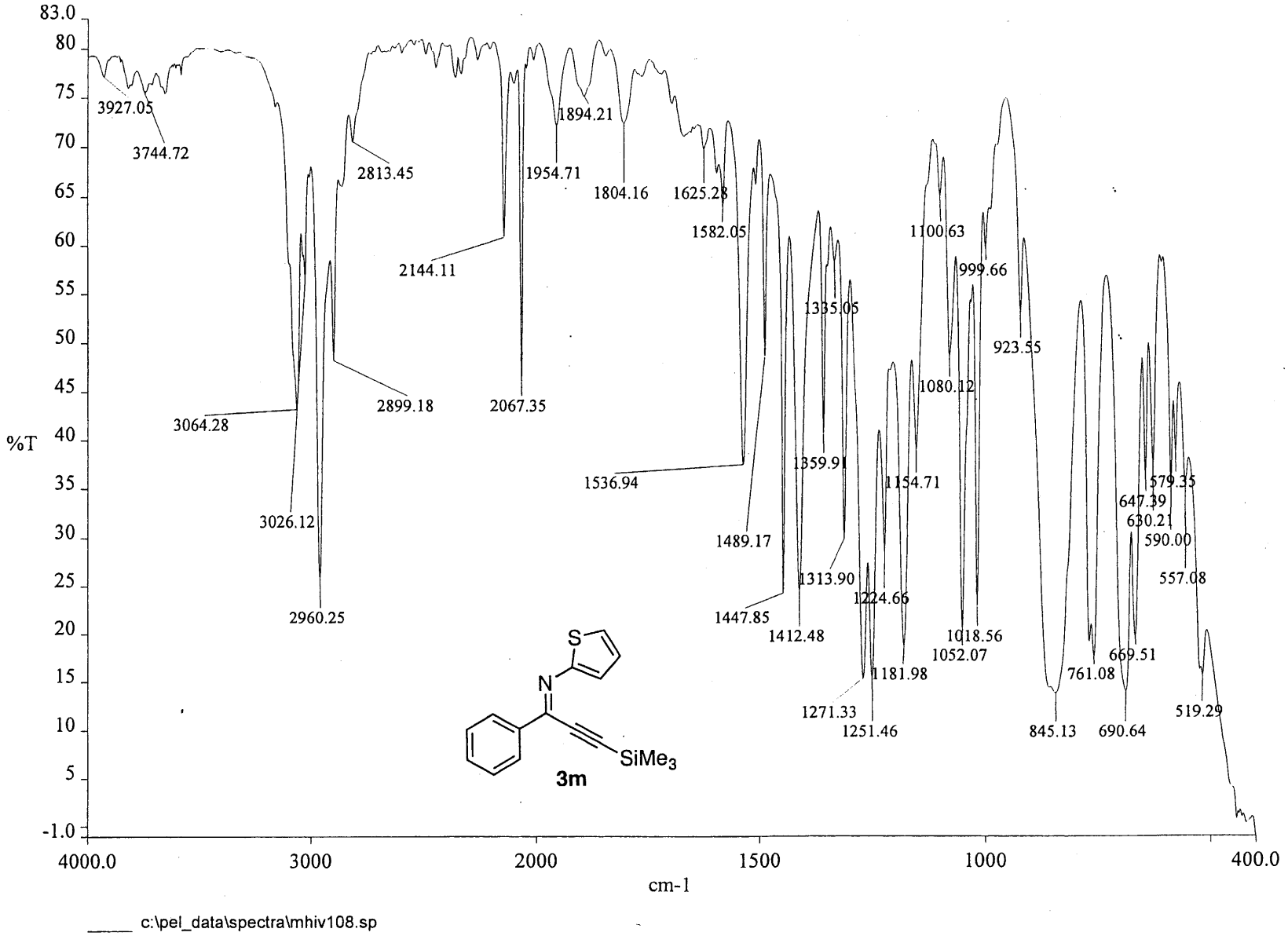
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 500.2312696 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute



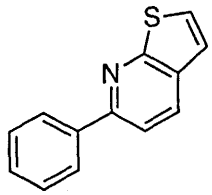
3m




Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
1192 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 34 minutes
S
N
SiMe3
3m
152.204
140.907
137.698
130.567
129.148
128.502
127.935
125.426
125.344
112.046
99.188
77.482
77.230
76.974
-0.555
200
180
160
140
120
100
80
60
40
20
0
ppm


83.0
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
-1.0
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3927.05
3744.72
2813.45
1894.21
1954.71
1804.16
1625.28
1582.05
2144.11
1100.63
999.66
1335.05
923.55
3064.28
2899.18
2067.35
1080.12
1536.94
1359.91
1154.71
579.35
647.39
630.21
590.00
3026.12
1489.17
1313.90
557.08
1224.66
2960.25
1447.85
1412.48
1018.56
1052.07
669.51
1181.98
761.08
1271.33
1251.46
845.13
690.64
519.29
S
N
SiMe3
3m
c:\pel_data\spectra\mhiv108.sp

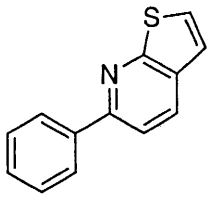
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446552 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



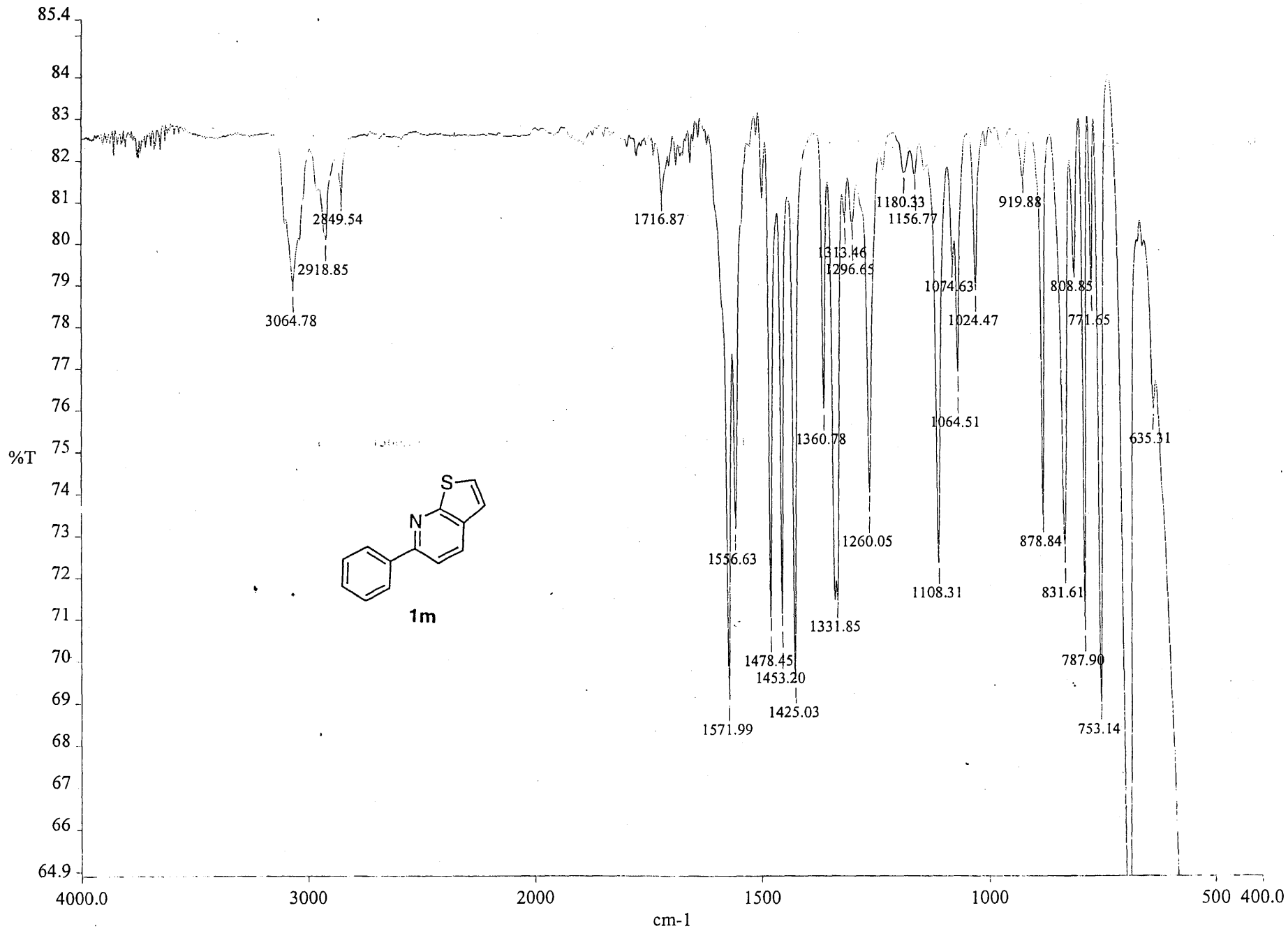
1m

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
208 repetitions
OBSERVE C13, 125.7832314 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6 minutes

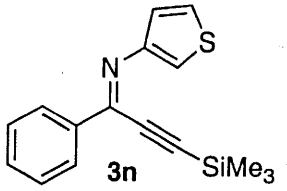


1m


85.4
84
83
82
81
80
79
78
77
76
75
74
73
72
71
70
69
68
67
66
64.9
%T
4000.0
3000
2000
1500
1000
500
400.0
cm-1
3064.78
2918.85
2849.54
1716.87
1571.99
1556.63
1478.45
1453.20
1425.03
1360.78
1331.85
1313.46
1296.65
1260.05
1180.33
1156.77
1108.31
1074.63
1064.51
1024.47
919.88
878.84
831.61
808.85
787.90
771.65
753.14
635.31
S
N
1m
c:\pel_data\spectra\mhii280.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

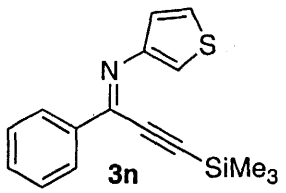
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



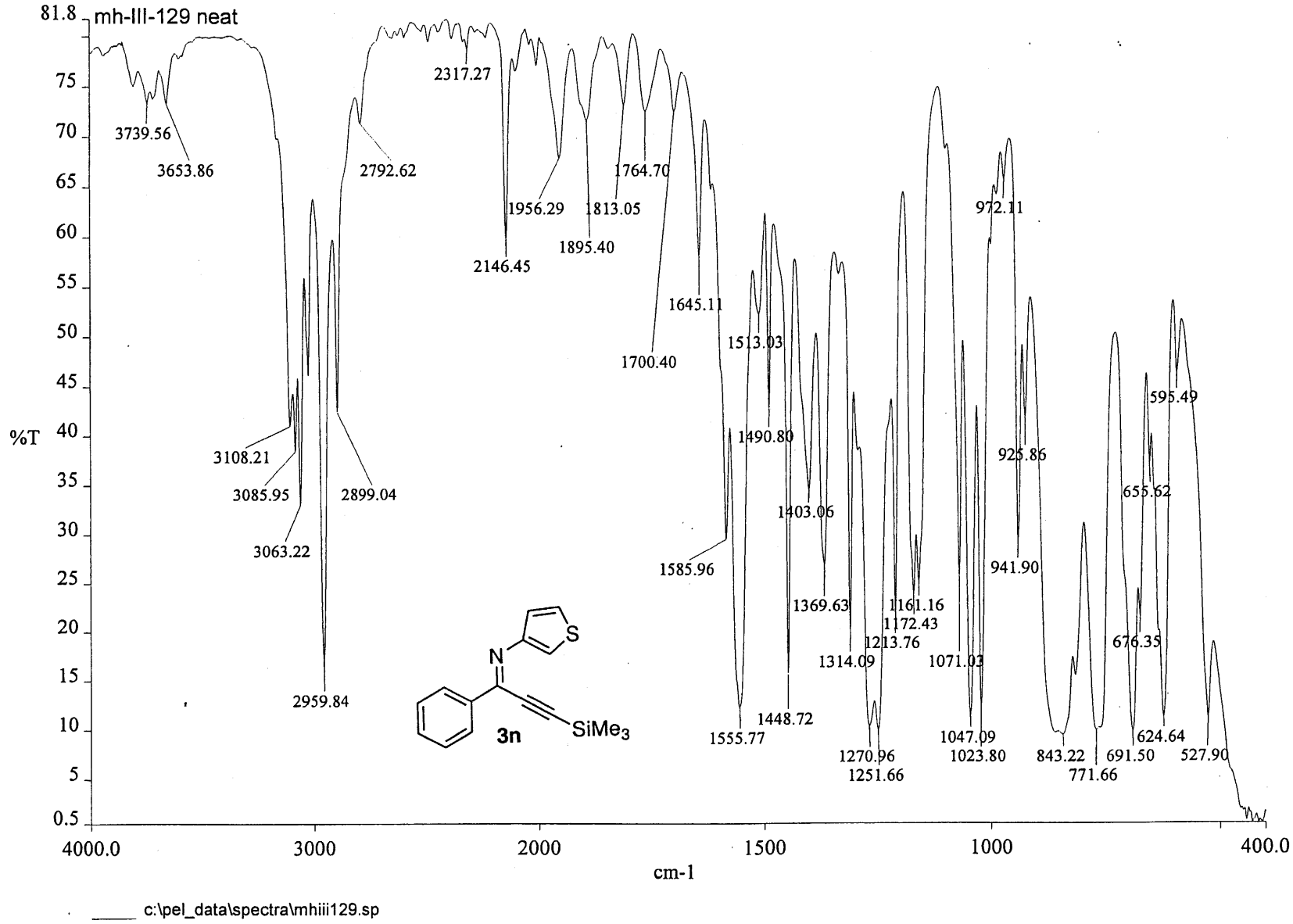
3n

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
24 repetitions
OBSERVE C13, 125.7832418 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

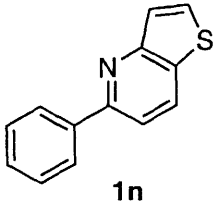


3n

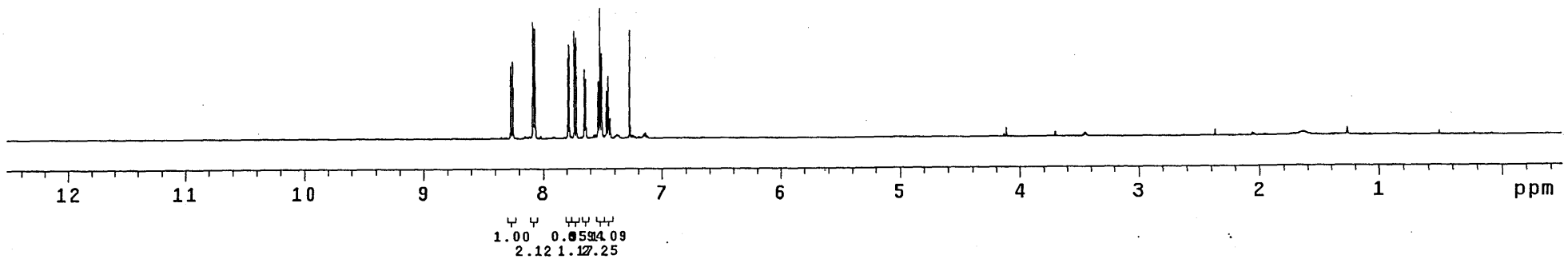

mh-III-129 neat
81.8
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.5
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3739.56
3653.86
2792.62
2317.27
1956.29
1813.05
1764.70
1895.40
2146.45
1645.11
1700.40
1513.03
1490.80
1585.96
1403.06
1369.63
1448.72
1555.77
1314.09
1270.96
1251.66
1161.16
1172.43
1213.76
1071.03
1047.09
1023.80
972.11
925.86
941.90
843.22
771.66
691.50
655.62
676.35
624.64
595.49
527.90
3108.21
3085.95
3063.22
2959.84
2899.04
N
S
SiMe3
3n
c:\pel_data\spectra\mhiii129.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-III-113
INOVA-500 "zippy"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446549 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

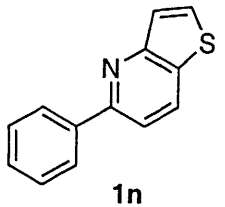


1n

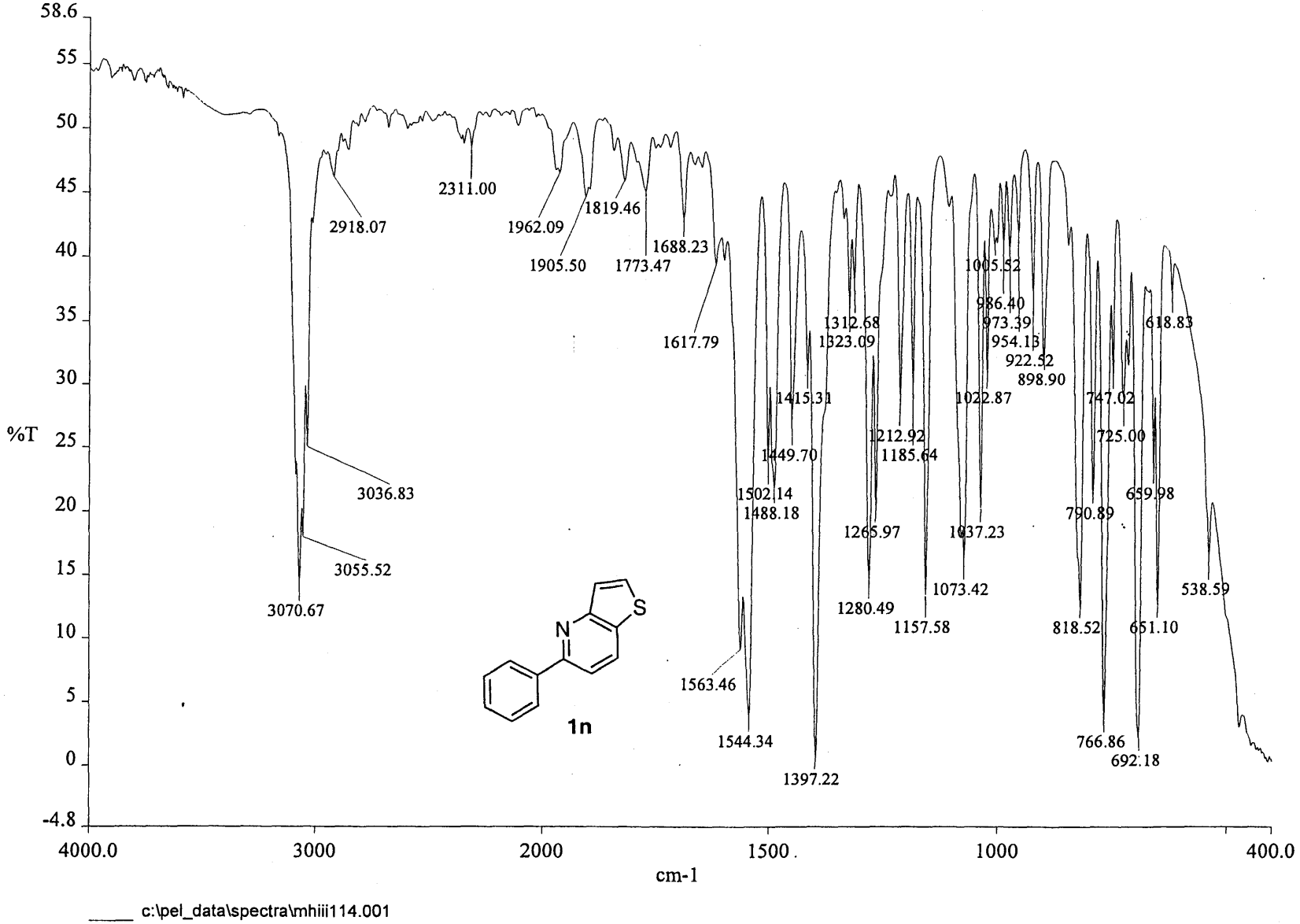


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
16 repetitions
OBSERVE C13, 125.7832458 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

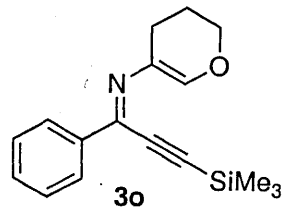


1n


58.6
55
50
45
40
35
30
25
20
15
10
5
0
-4.8
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2918.07
2311.00
1962.09
1819.46
1905.50
1773.47
1688.23
1617.79
3036.83
3055.52
3070.67
1502.14
1488.18
1449.70
1415.31
1312.68
1323.09
1212.92
1185.64
1265.97
1280.49
1157.58
1073.42
1037.23
1022.87
1005.52
986.40
973.39
954.13
922.52
898.90
747.02
725.00
790.89
659.98
618.83
538.59
818.52
651.10
766.86
692.18
1563.46
1544.34
1397.22
N
S
1n
c:\pel_data\spectra\mhiii114.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "mrhat"

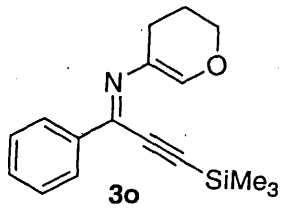
Relax. delay 5.000 sec
Pulse 34.1 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
6 repetitions
OBSERVE H1, 300.0986361 MHz
DATA PROCESSING
FT size 32768
Total time 2 min, 13 sec



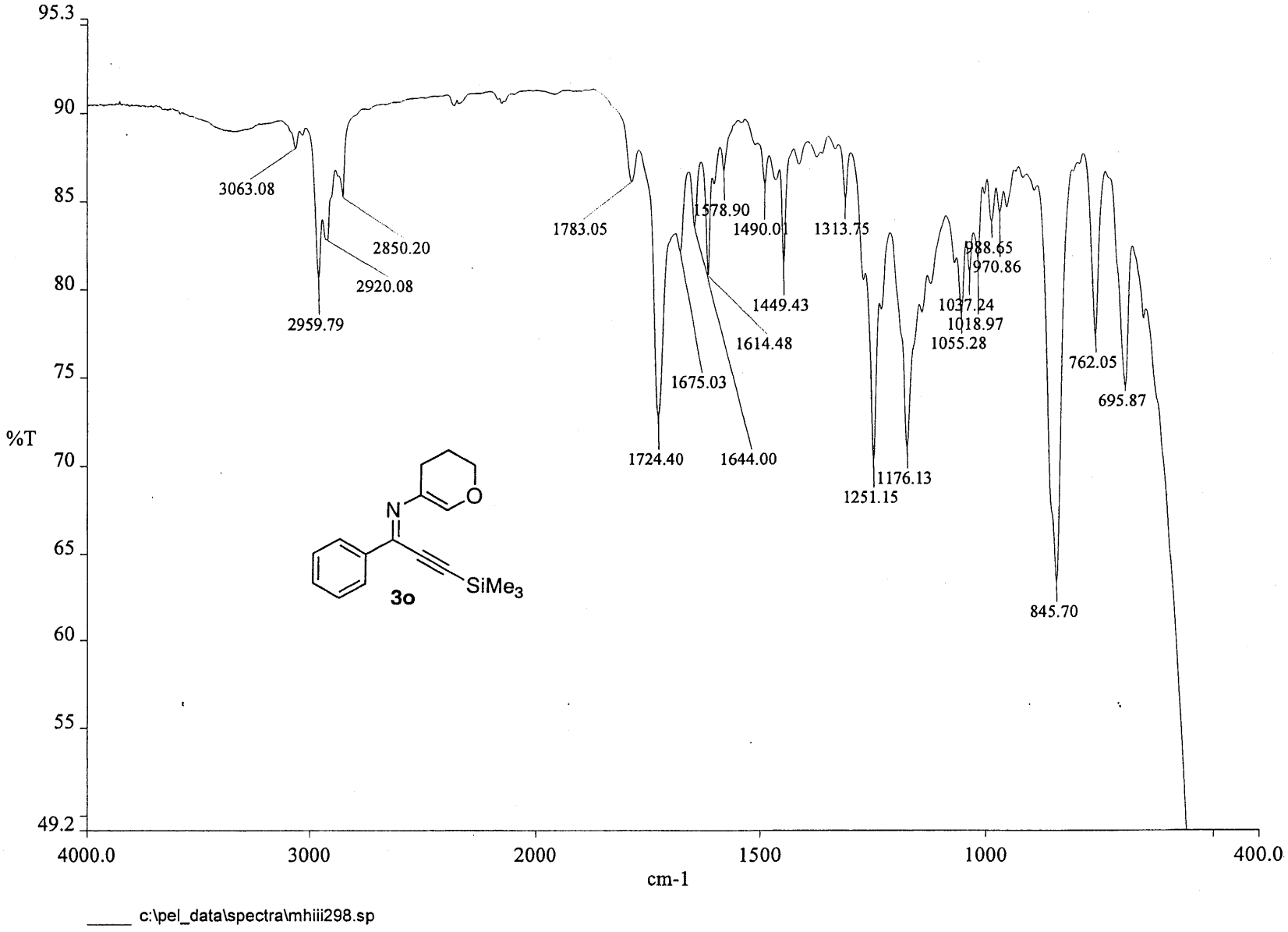
3o

Solvent: Benzene
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
744 repetitions
OBSERVE C13, 125.7831721 MHz
DECOUPLE H1, 500.2333204 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 12 minutes

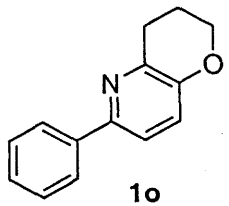


3o


95.3
90
85
80
75
70
65
60
55
49.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3063.08
2959.79
2920.08
2850.20
1783.05
1724.40
1675.03
1644.00
1614.48
1578.90
1490.01
1449.43
1313.75
1251.15
1176.13
1055.28
1037.24
1018.97
988.65
970.86
845.70
762.05
695.87
N
O
SiMe3
3o
_____ c:\pel_data\spectra\mhiii298.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

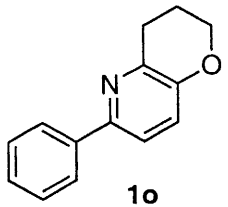
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446540 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



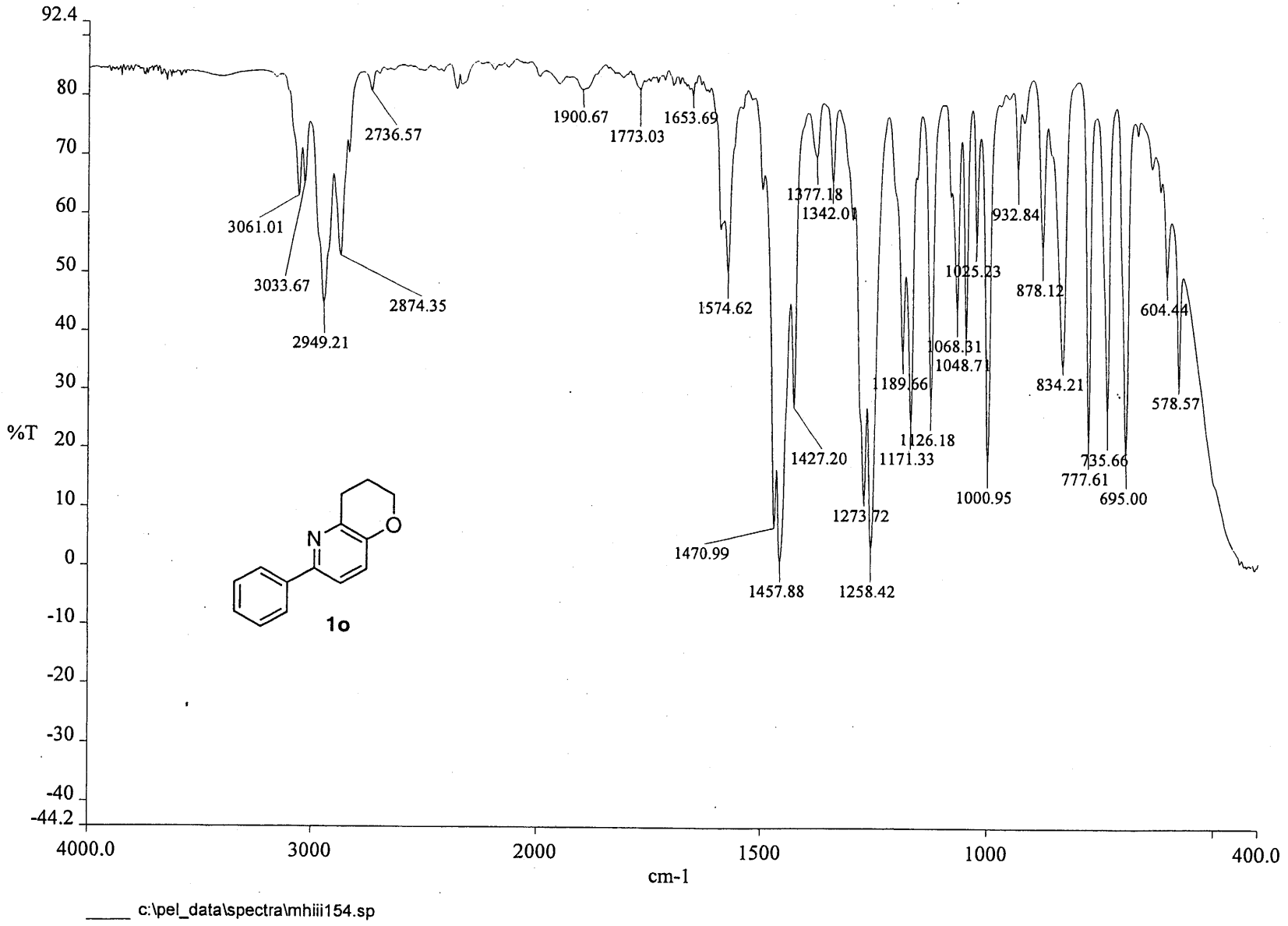
1o

Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
User: 1-14-87
File: mh-III-oxygen
INOVA-500 "zippy"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
1000000 repetitions
OBSERVE C13, 125.7831761 MHz
DECOUPLE H1, 500.2333204 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 280 hr, 14 min, 55 sec

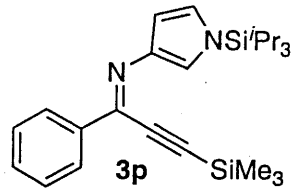


1o


92.4
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-44.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3061.01
3033.67
2949.21
2874.35
2736.57
1900.67
1773.03
1653.69
1574.62
1470.99
1457.88
1427.20
1377.18
1342.01
1273.72
1258.42
1189.66
1171.33
1126.18
1068.31
1048.71
1025.23
1000.95
932.84
878.12
834.21
777.61
735.66
695.00
604.44
578.57
N
O
1o
c:\pel_data\spectra\mhiii154.sp

Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
INOVA-500 "bullwinkle"

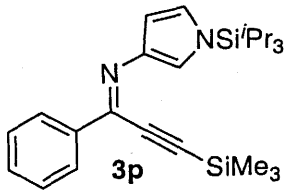
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446837 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



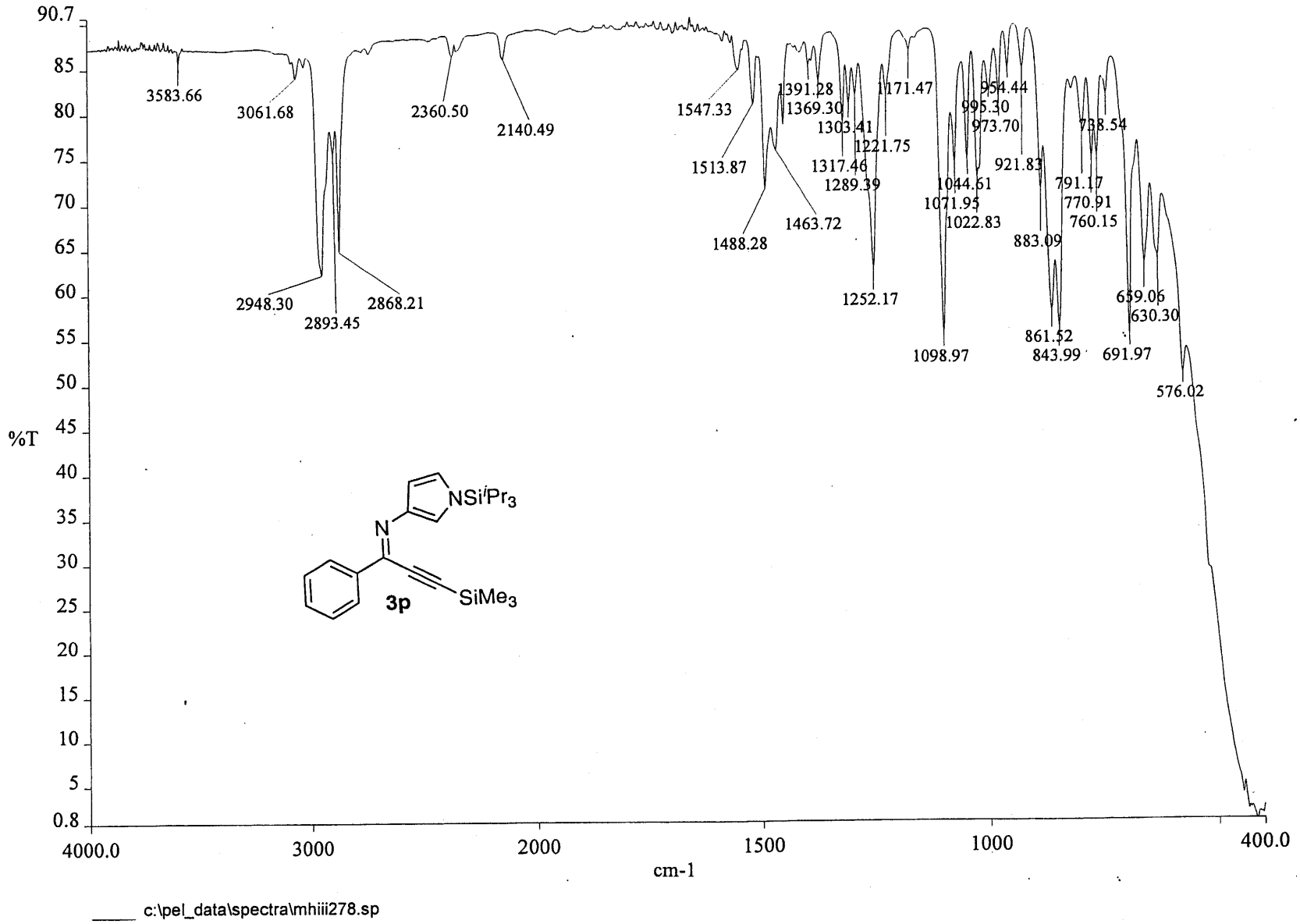
3p

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
40 repetitions
OBSERVE C13, 125.7832309 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

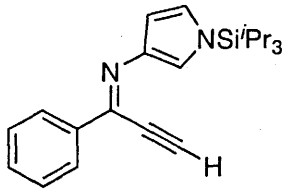


3p


90.7
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.8
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3583.66
3061.68
2360.50
2140.49
1547.33
1513.87
1488.28
1463.72
1391.28
1369.30
1303.41
1317.46
1289.39
1252.17
1221.75
1171.47
1098.97
1071.95
1044.61
1022.83
995.30
973.70
954.44
921.83
883.09
861.52
843.99
791.17
770.91
760.15
738.54
691.97
659.06
630.30
576.02
2948.30
2893.45
2868.21
NSi^{i}Pr$_3$
N
SiMe$_3$
3p
c:\pel_data\spectra\mhiii278.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

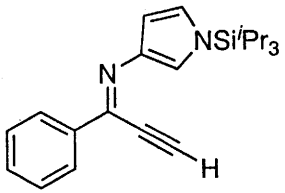
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



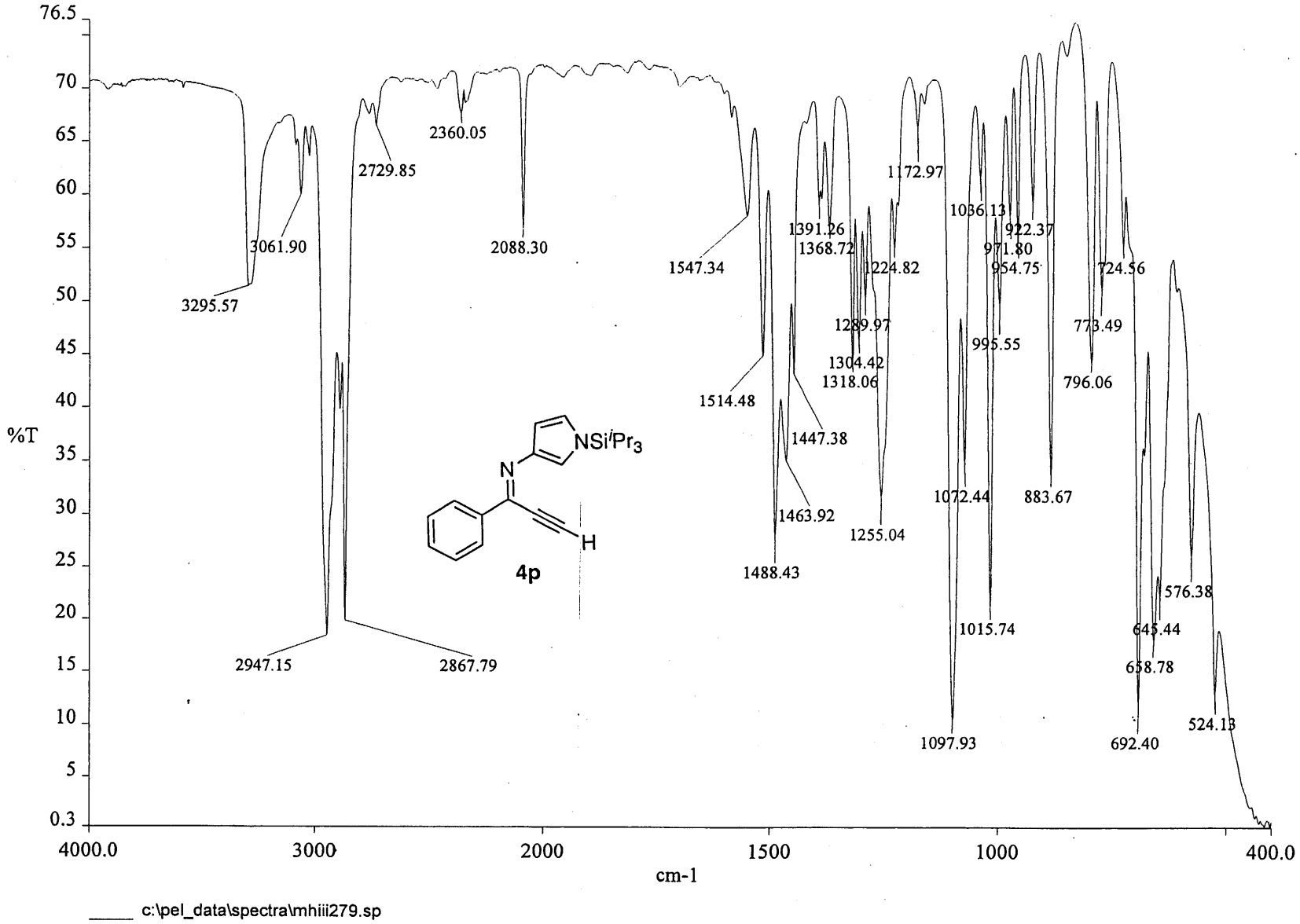
4p

Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
Mercury-300 "mrhat"

Pulse 30.3 degrees
Acq. time 2.501 sec
Width 22624.4 Hz
214 repetitions
OBSERVE C13, 75.4598148 MHz
DECOUPLE H1, 300.1001963 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 261 hr, 9 min, 1 sec

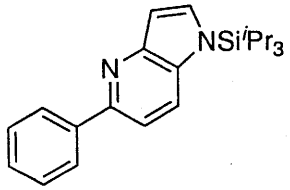


4p

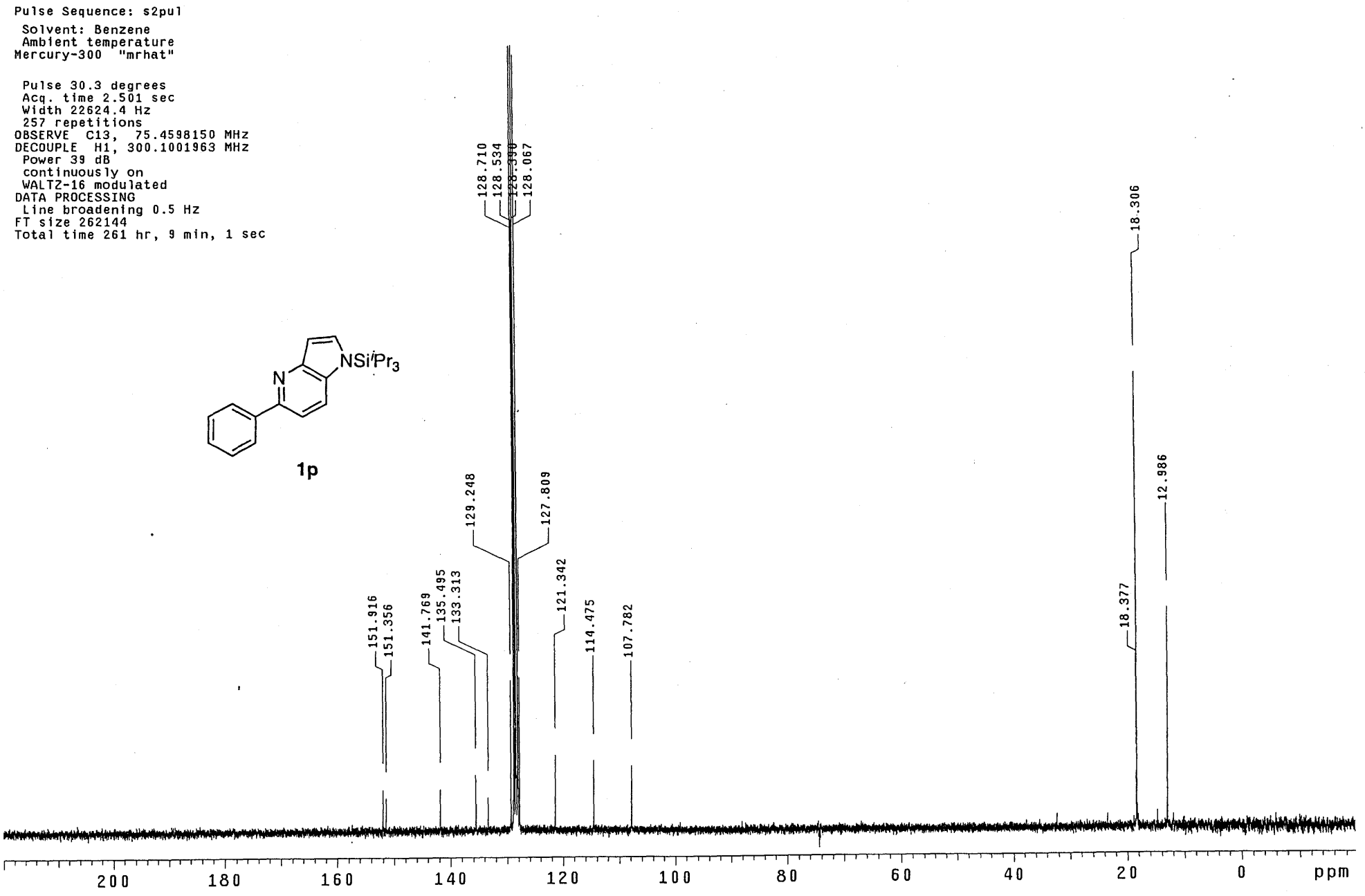

76.5
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3295.57
3061.90
2947.15
2867.79
2729.85
2360.05
2088.30
1547.34
1514.48
1488.43
1463.92
1447.38
1391.26
1368.72
1318.06
1304.42
1289.97
1255.04
1224.82
1172.97
1097.93
1072.44
1036.13
1015.74
995.55
971.80
954.75
922.37
883.67
796.06
773.49
724.56
692.40
658.78
645.44
576.38
524.13
NSi^{i}Pr$_3$
N
H
4p
c:\pel_data\spectra\mhiii279.sp

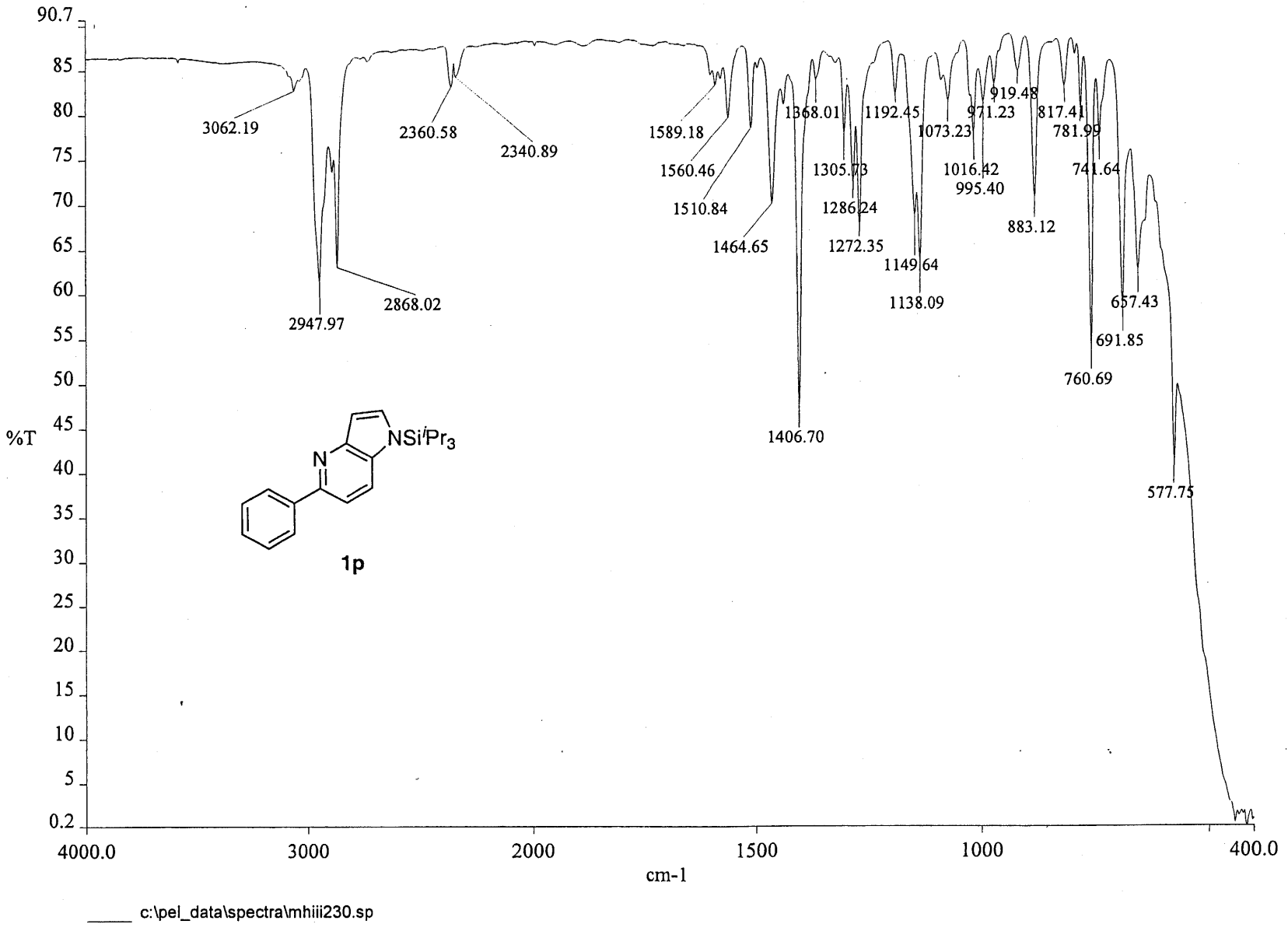
Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446834 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

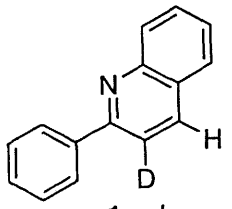


1p

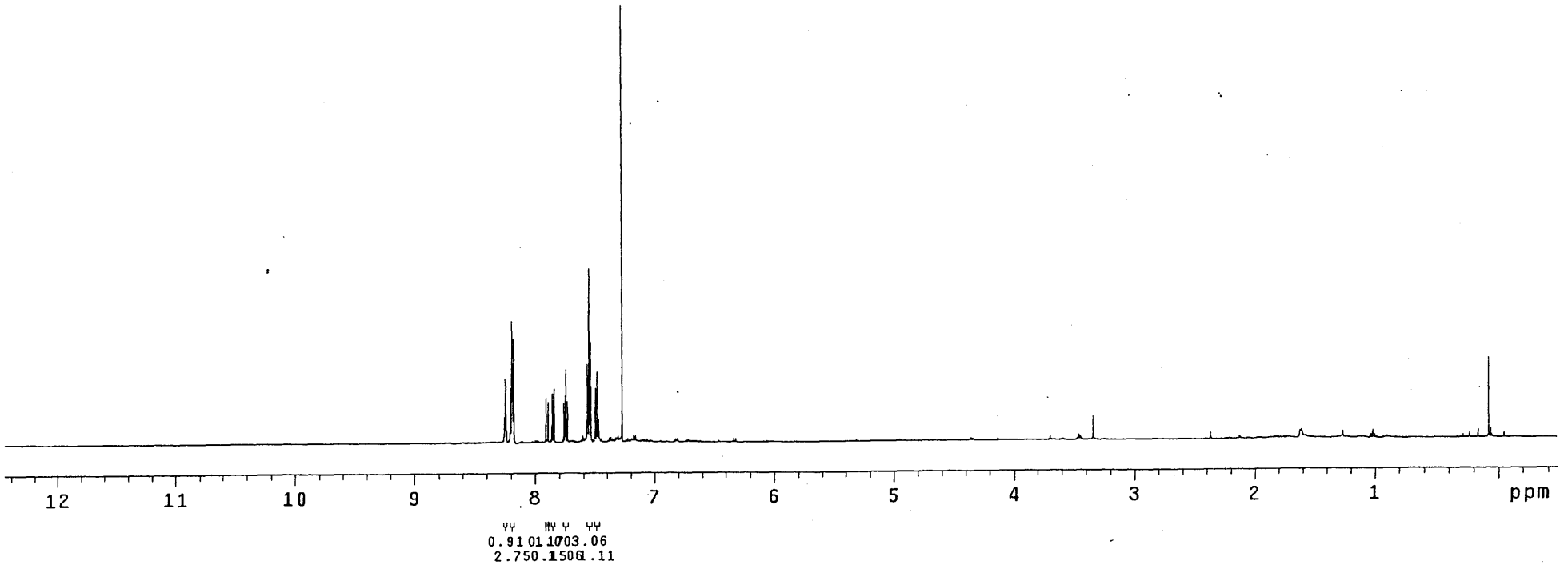

Pulse Sequence: s2pul
Solvent: Benzene
Ambient temperature
Mercury-300 "mrhat"
Pulse 30.3 degrees
Acq. time 2.501 sec
Width 22624.4 Hz
257 repetitions
OBSERVE C13, 75.4598150 MHz
DECOUPLE H1, 300.1001963 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 261 hr, 9 min, 1 sec
N
NSi^{i}Pr$_3$
1p
151.916
151.356
141.769
135.495
133.313
129.248
128.710
128.534
128.067
127.809
121.342
114.475
107.782
18.377
18.306
12.986
200
180
160
140
120
100
80
60
40
20
0
ppm


90.7
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3062.19
2947.97
2868.02
2360.58
2340.89
1589.18
1560.46
1510.84
1464.65
1406.70
1368.01
1305.73
1286.24
1272.35
1192.45
1149.64
1138.09
1073.23
1016.42
995.40
971.23
919.48
883.12
817.41
781.99
760.69
741.64
691.85
657.43
577.75
N
NSi^{i}Pr$_3$
1p
c:\pel_data\spectra\mhiii230.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-III-295
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446549 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec



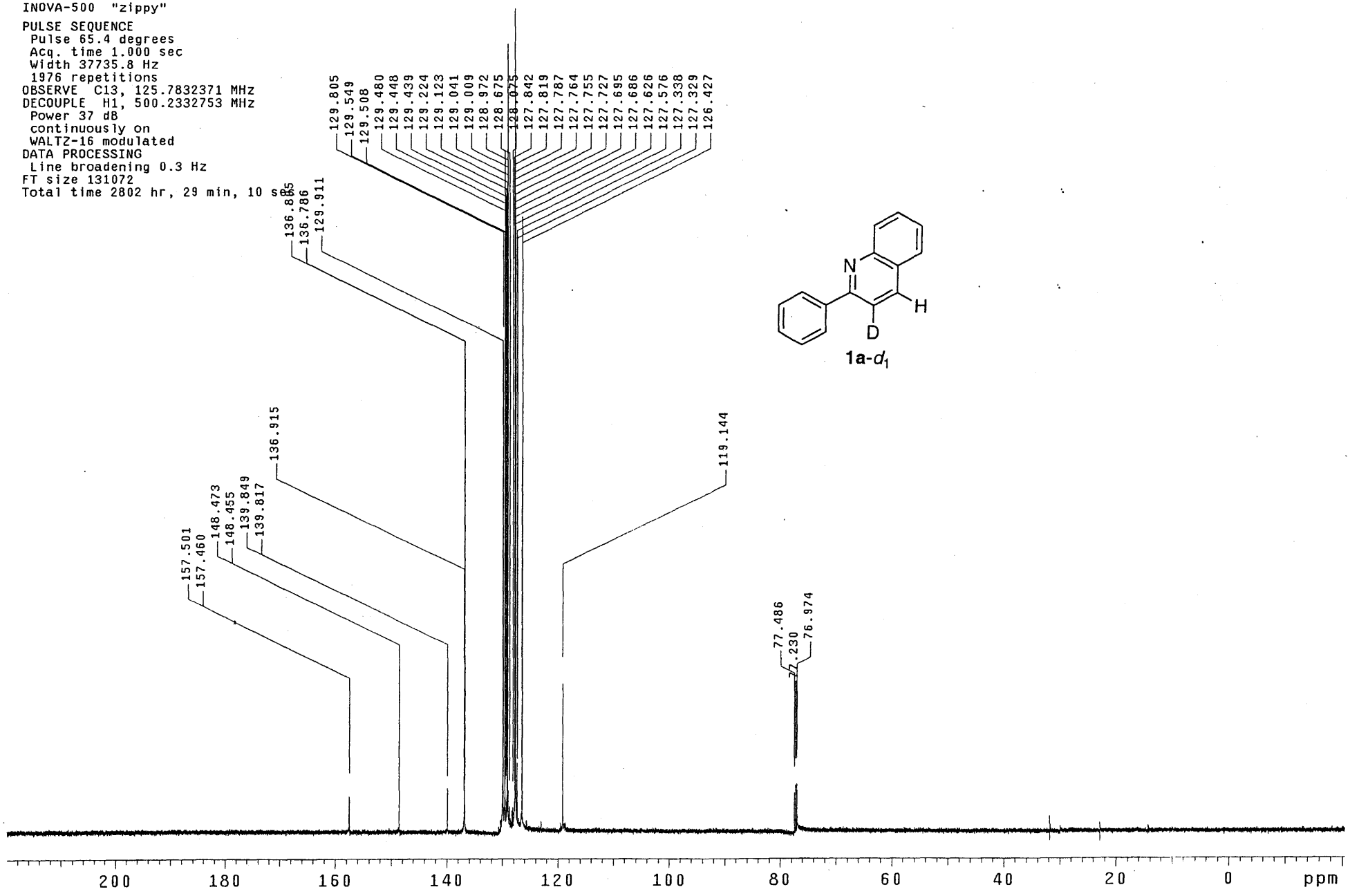
1a-d_1



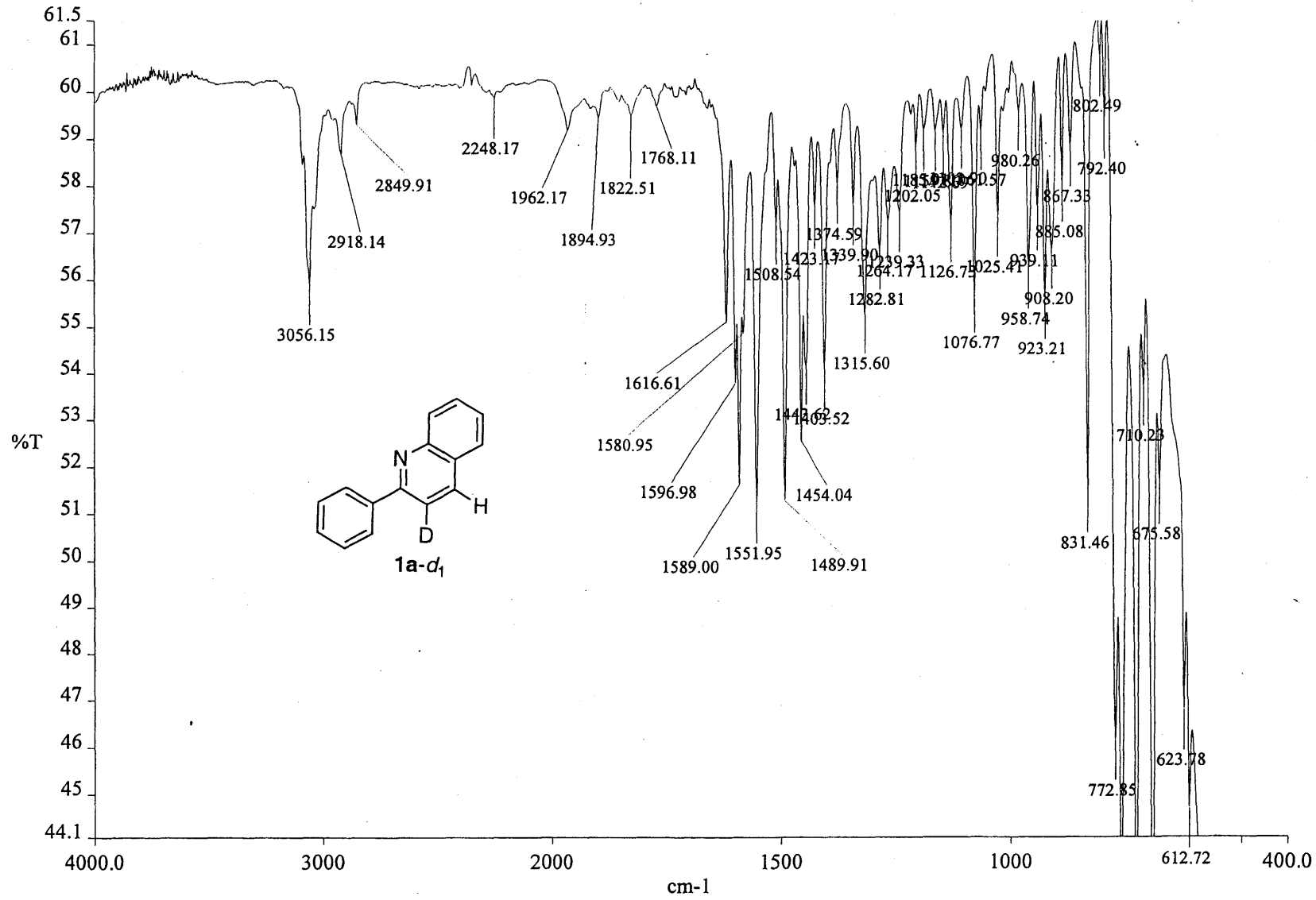
mh-III-295

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-III-295carbon
INOVA-500 "zippy"

PULSE SEQUENCE
Pulse 65.4 degrees
Acq. time 1.000 sec
Width 37735.8 Hz
1976 repetitions
OBSERVE C13, 125.7832371 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2802 hr, 29 min, 10 sec



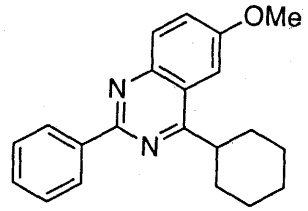
1a-d_1


61.5
61
60
59
58
57
56
55
54
53
52
51
50
49
48
47
46
45
44.1
%T
4000.0
3000
2000
1500
1000
612.72
400.0
cm-1
3056.15
2918.14
2849.91
2248.17
1962.17
1894.93
1822.51
1768.11
1616.61
1580.95
1596.98
1589.00
1551.95
1508.54
1489.91
1454.04
1443.62
1409.52
1374.59
1339.90
1315.60
1282.81
1264.17
1239.33
1202.05
1126.75
1076.77
1025.41
980.26
958.74
939.11
923.21
908.20
885.08
867.33
831.46
802.49
792.40
772.85
710.23
675.58
623.78
N
H
D
1a-d_1
_____ c:\pel_data\spectra\mhiii295.001

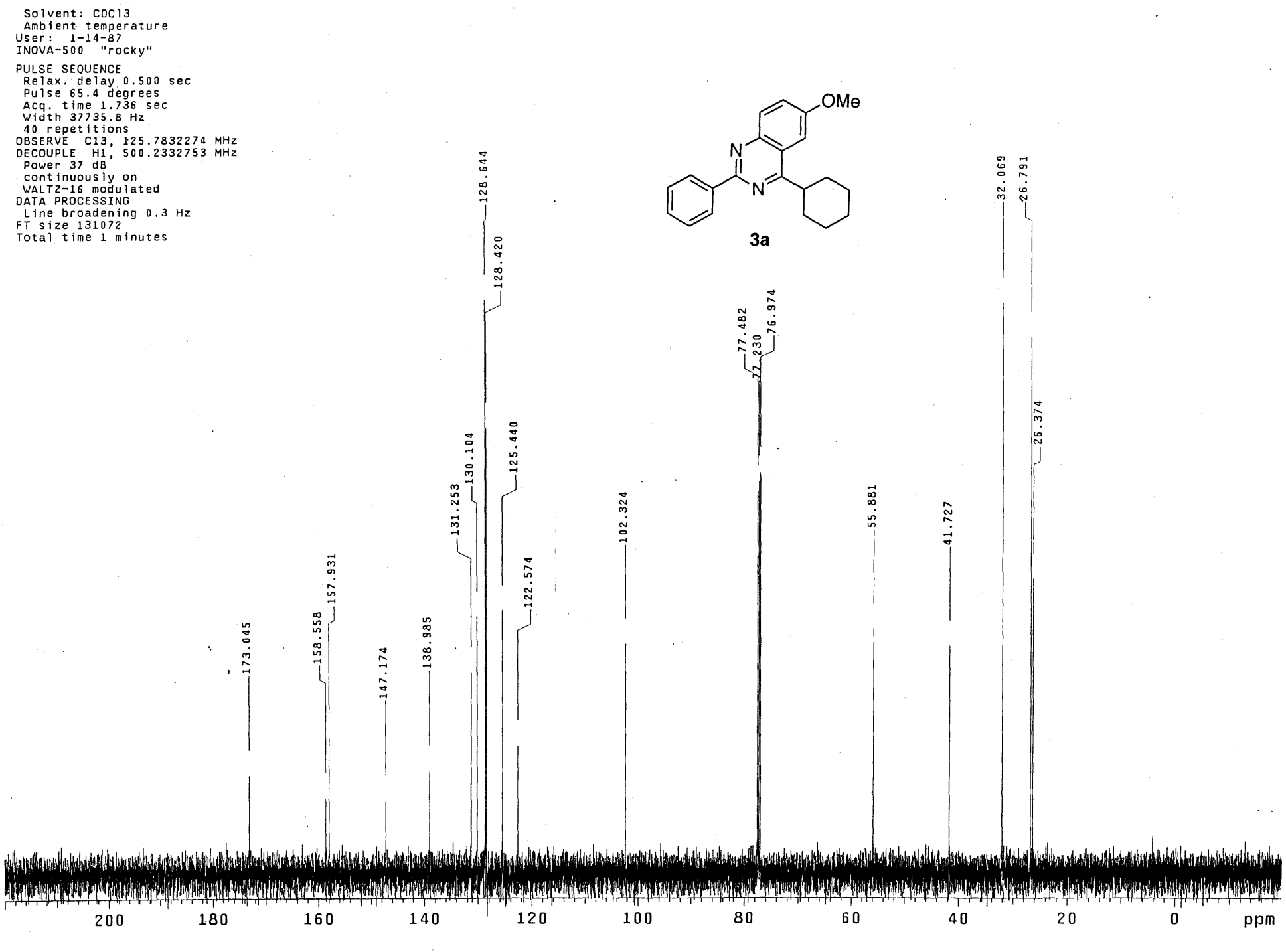
Appendix B

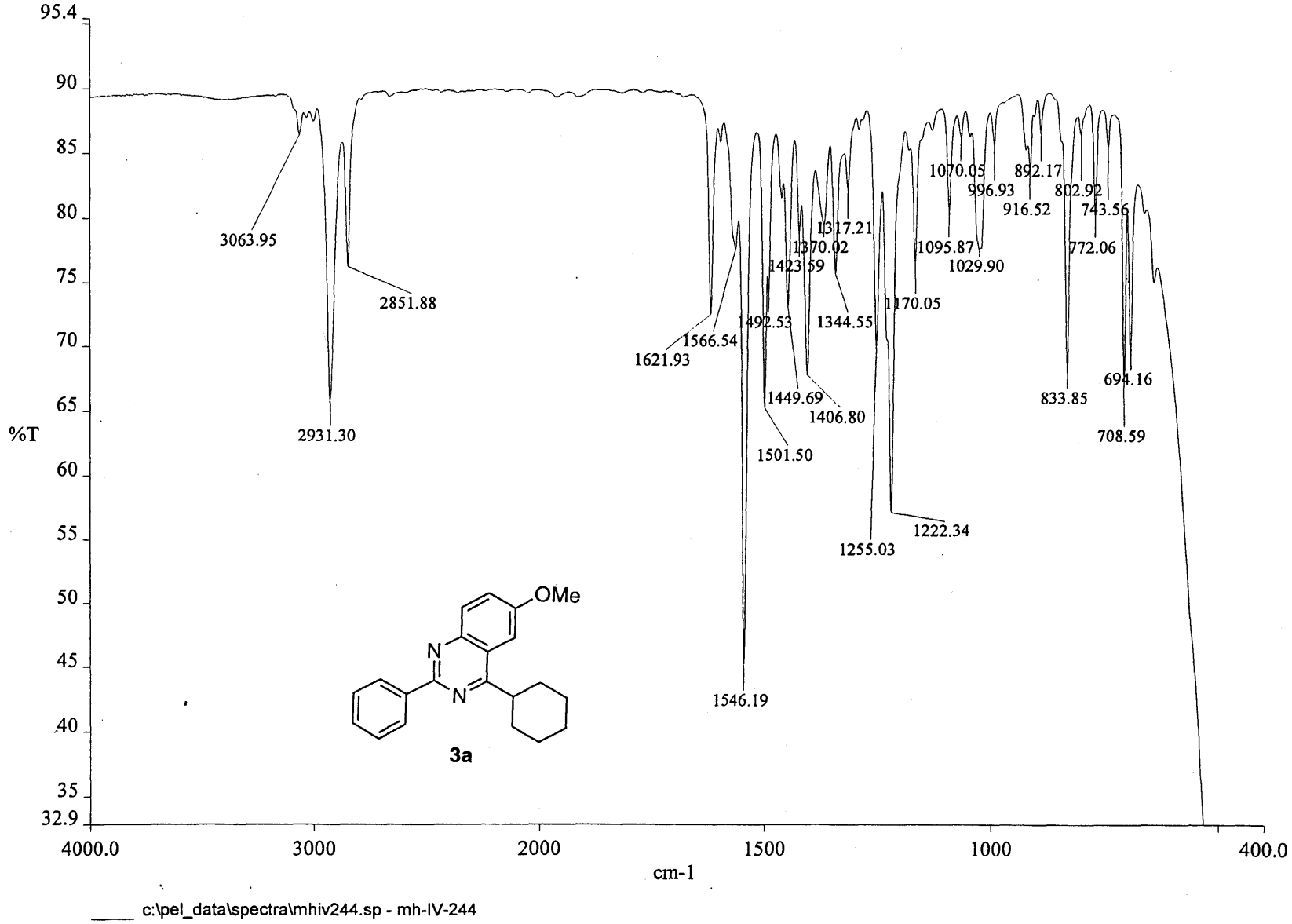
Spectra for Chapter II.

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-IV-244
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
4 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



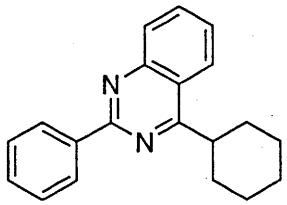
3a


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
40 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes
OMe
N
N
3a
173.045
158.558
157.931
147.174
138.985
131.253
130.104
128.644
128.420
125.440
122.574
102.324
77.482
77.230
76.974
55.881
41.727
32.069
26.791
26.374
200
180
160
140
120
100
80
60
40
20
0
ppm


95.4
90
85
80
75
70
65
60
55
50
45
40
35
32.9
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3063.95
2931.30
2851.88
1621.93
1566.54
1546.19
1501.50
1492.53
1449.69
1423.59
1406.80
1370.02
1344.55
1317.21
1255.03
1222.34
1170.05
1095.87
1070.05
1029.90
996.93
916.52
892.17
833.85
802.92
772.06
743.56
708.59
694.16
OMe
N
N
3a
c:\pel_data\spectra\mhiv244.sp - mh-IV-244

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-IV-255clean
INOVA-500 "bullwinkle"

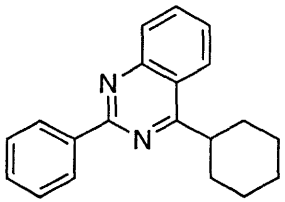
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



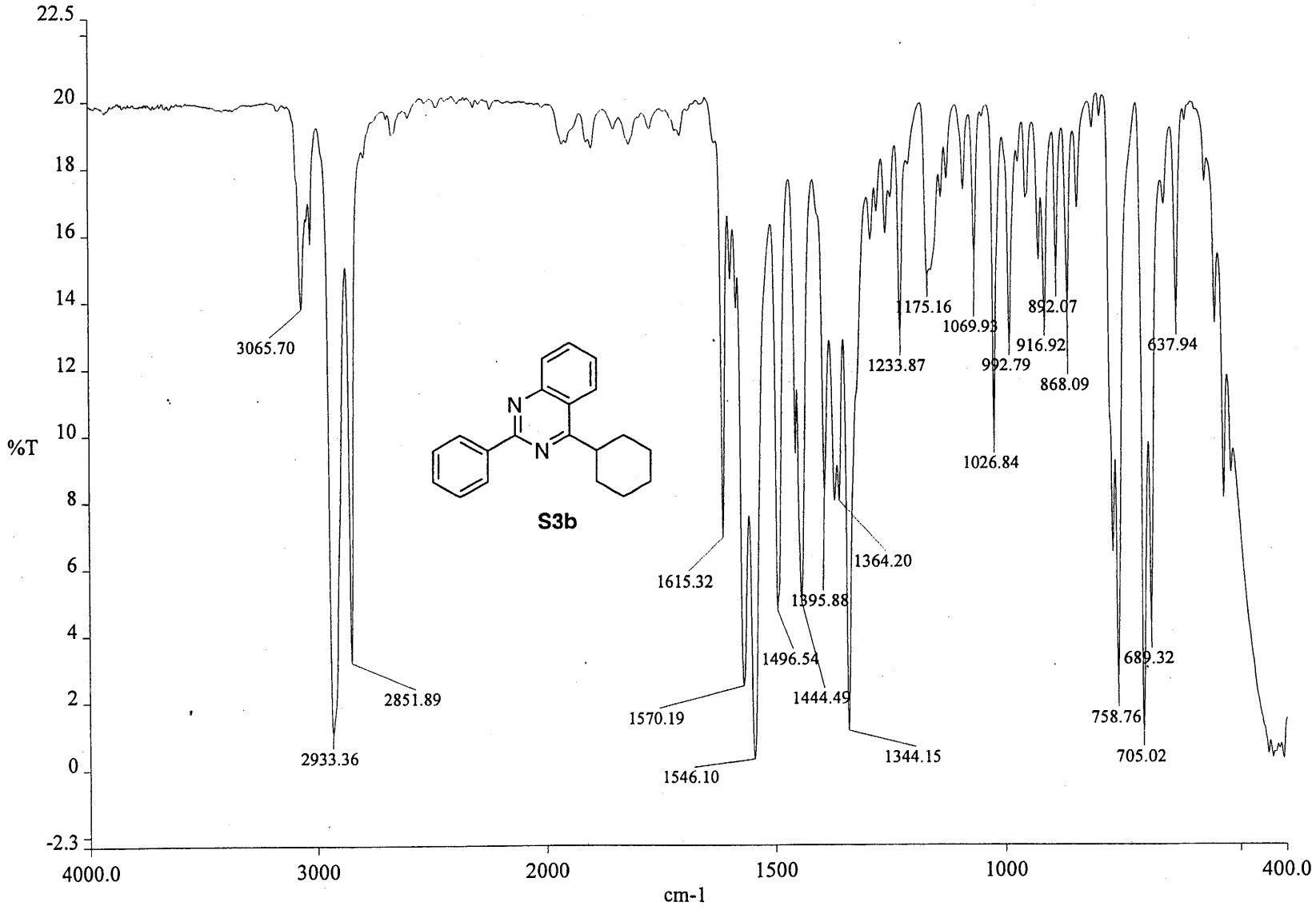
S3b

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
112 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes

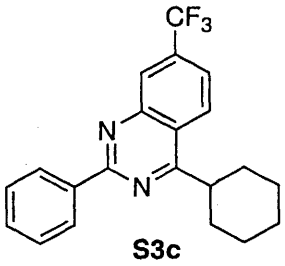


S3b

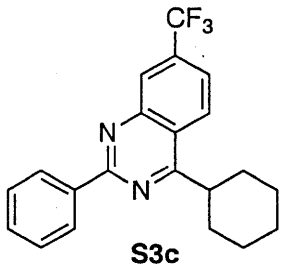

22.5
20
18
16
14
12
10
8
6
4
2
0
-2.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3065.70
2933.36
2851.89
1615.32
1570.19
1546.10
1496.54
1444.49
1395.88
1364.20
1344.15
1233.87
1175.16
1069.93
1026.84
992.79
916.92
892.07
868.09
758.76
705.02
689.32
637.94
N
N
S3b
c:\pel_data\spectra\mhiv255.001 - mh-IV-255

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



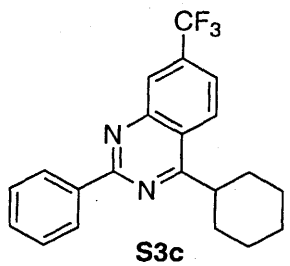
S3c



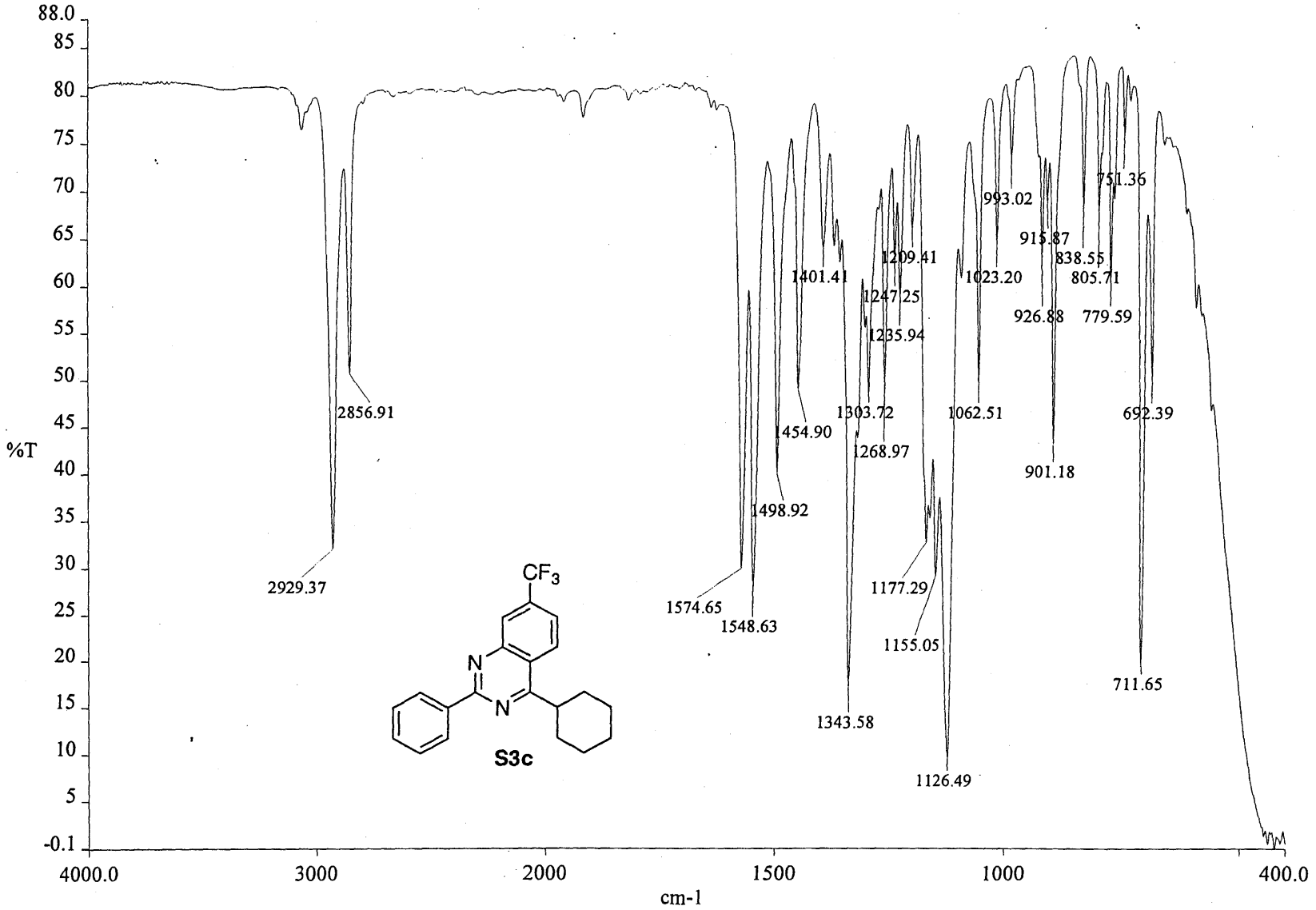
S3c

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-IV-265carbon
INOVA-500 "zippy"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
368 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6966 hr, 51 min, 36 sec

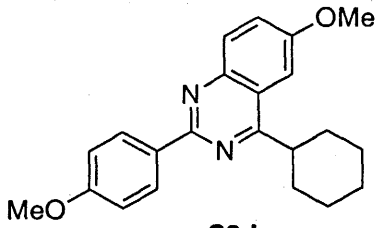


S3c


88.0
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
-0.1
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2929.37
2856.91
1574.65
1548.63
1498.92
1454.90
1401.41
1343.58
1303.72
1268.97
1247.25
1235.94
1209.41
1177.29
1155.05
1126.49
1062.51
1023.20
993.02
926.88
915.87
901.18
838.55
805.71
779.59
751.36
711.65
692.39
CF3
N
N
S3c
c:\pel_data\spectra\mhiv265.001 - mh-IV-265

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

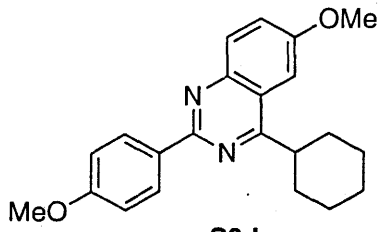
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



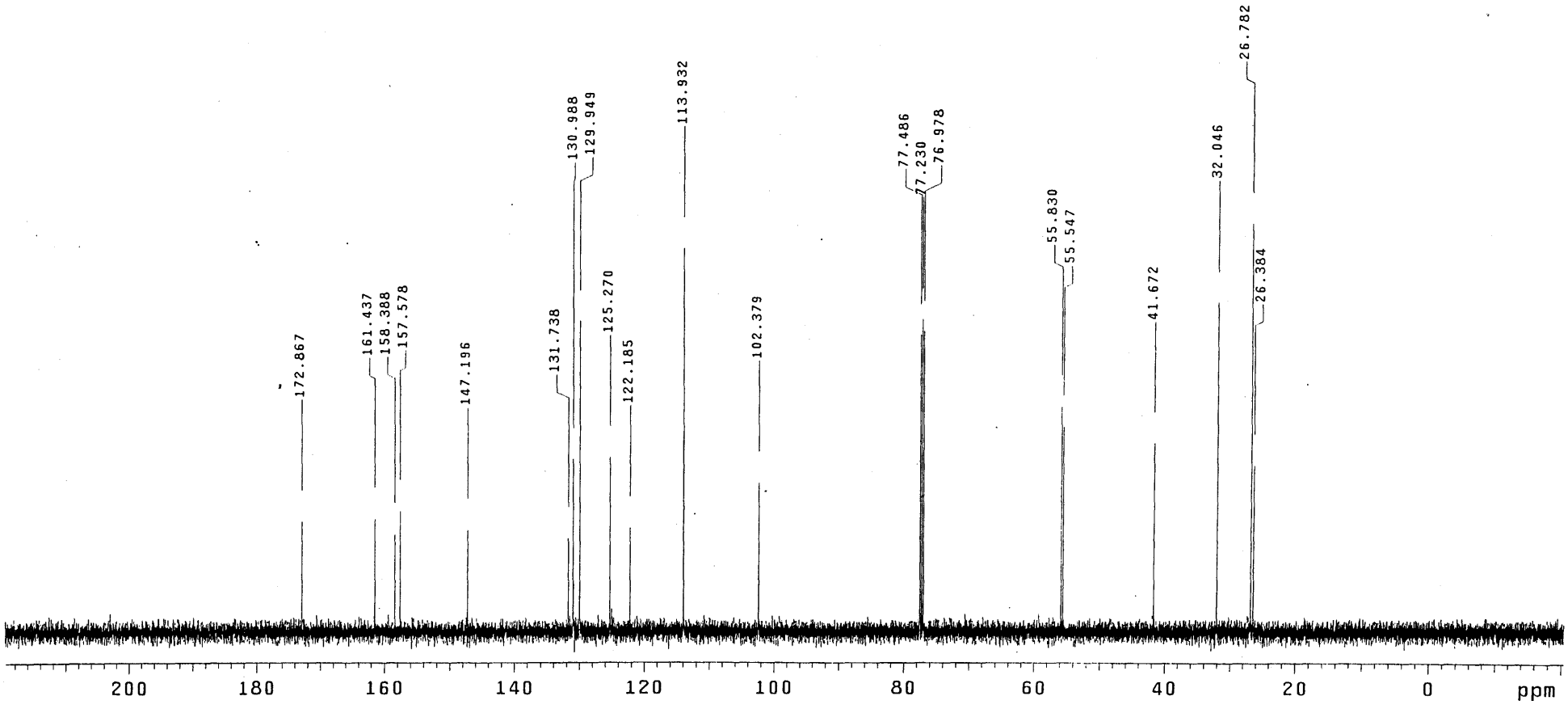
S3d

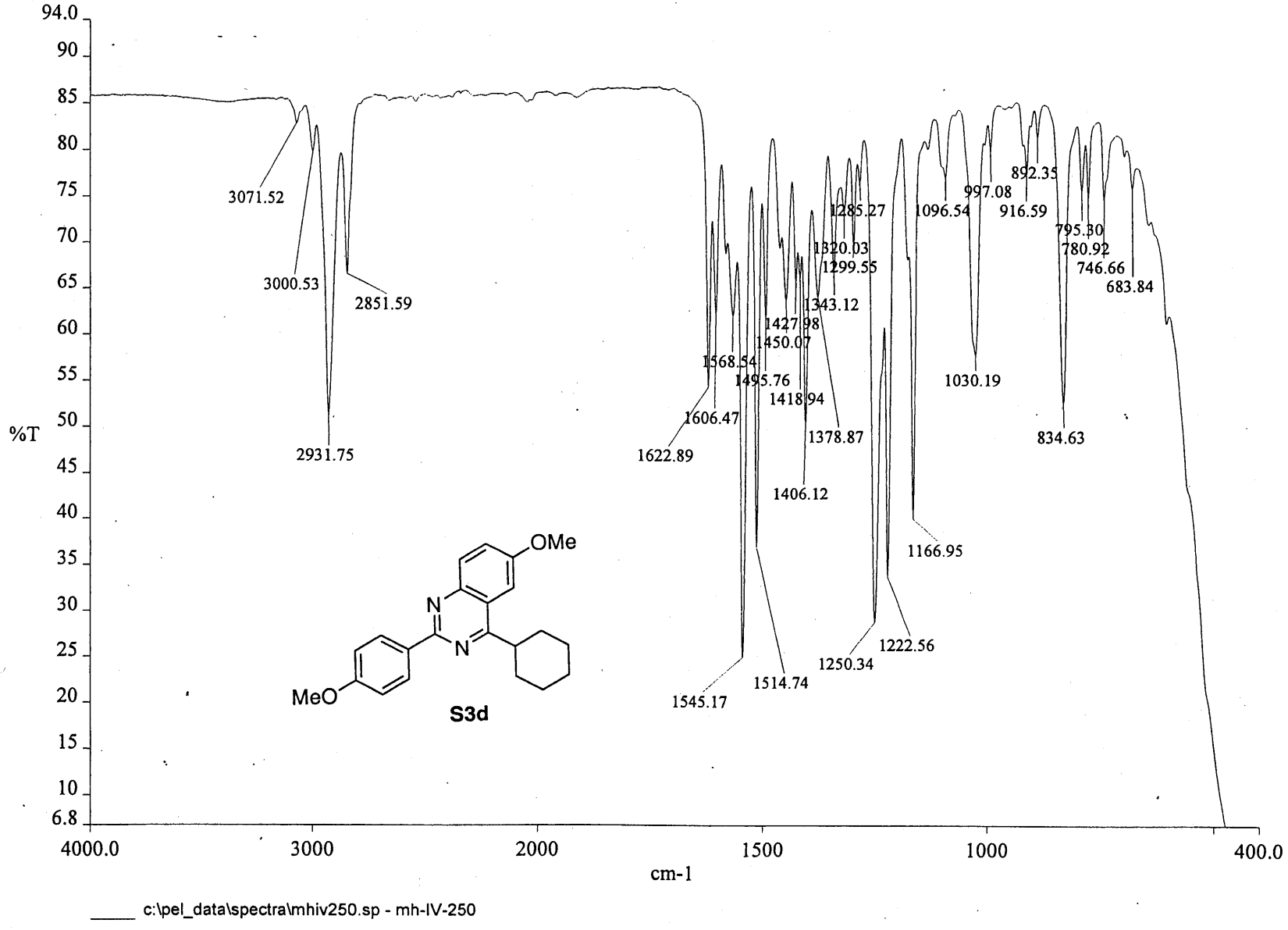
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
40 repetitions
OBSERVE C13, 125.7832297 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes



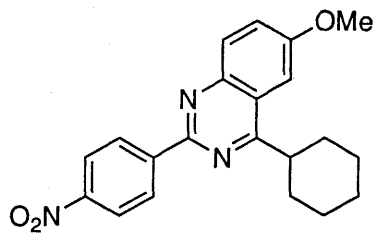
S3d




94.0
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
6.8
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3071.52
3000.53
2851.59
2931.75
1622.89
1606.47
1568.54
1545.17
1514.74
1495.76
1450.07
1427.98
1418.94
1406.12
1378.87
1343.12
1320.03
1299.55
1285.27
1250.34
1222.56
1166.95
1096.54
1030.19
997.08
916.59
892.35
834.63
795.30
780.92
746.66
683.84
OMe
MeO
N
N
S3d
c:\pel_data\spectra\mhiv250.sp - mh-IV-250

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

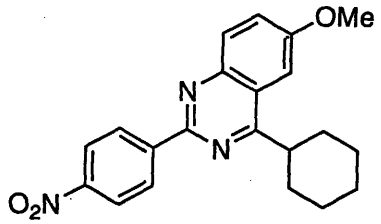
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



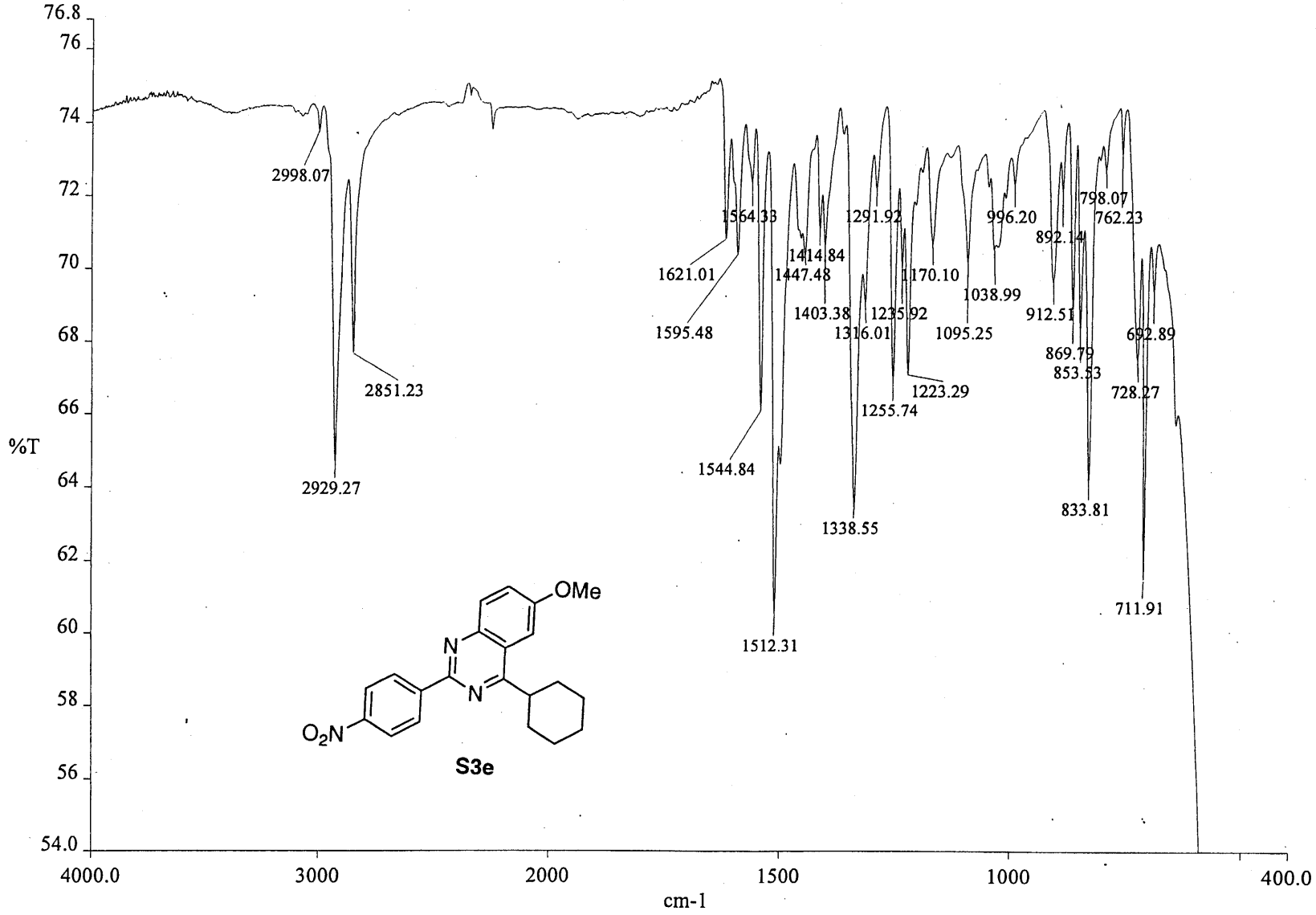
S3e

Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-IV-274carbon
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
648 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 27 minutes

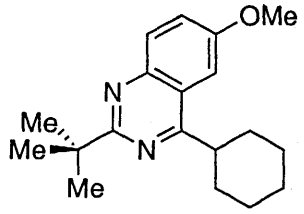


S3e


76.8
76
74
72
70
68
66
64
62
60
58
56
54.0
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2998.07
2929.27
2851.23
1621.01
1595.48
1564.33
1544.84
1512.31
1447.48
1414.84
1403.38
1338.55
1316.01
1291.92
1255.74
1235.92
1223.29
1170.10
1095.25
1038.99
996.20
912.51
892.14
869.79
853.53
833.81
798.07
762.23
728.27
711.91
692.89
OMe
N
N
O2N
S3e
c:\pel_data\spectra\mhiv274.001 - mh-IV-274

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

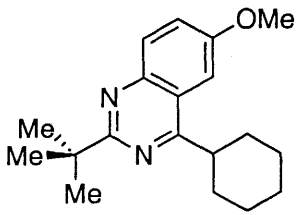
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



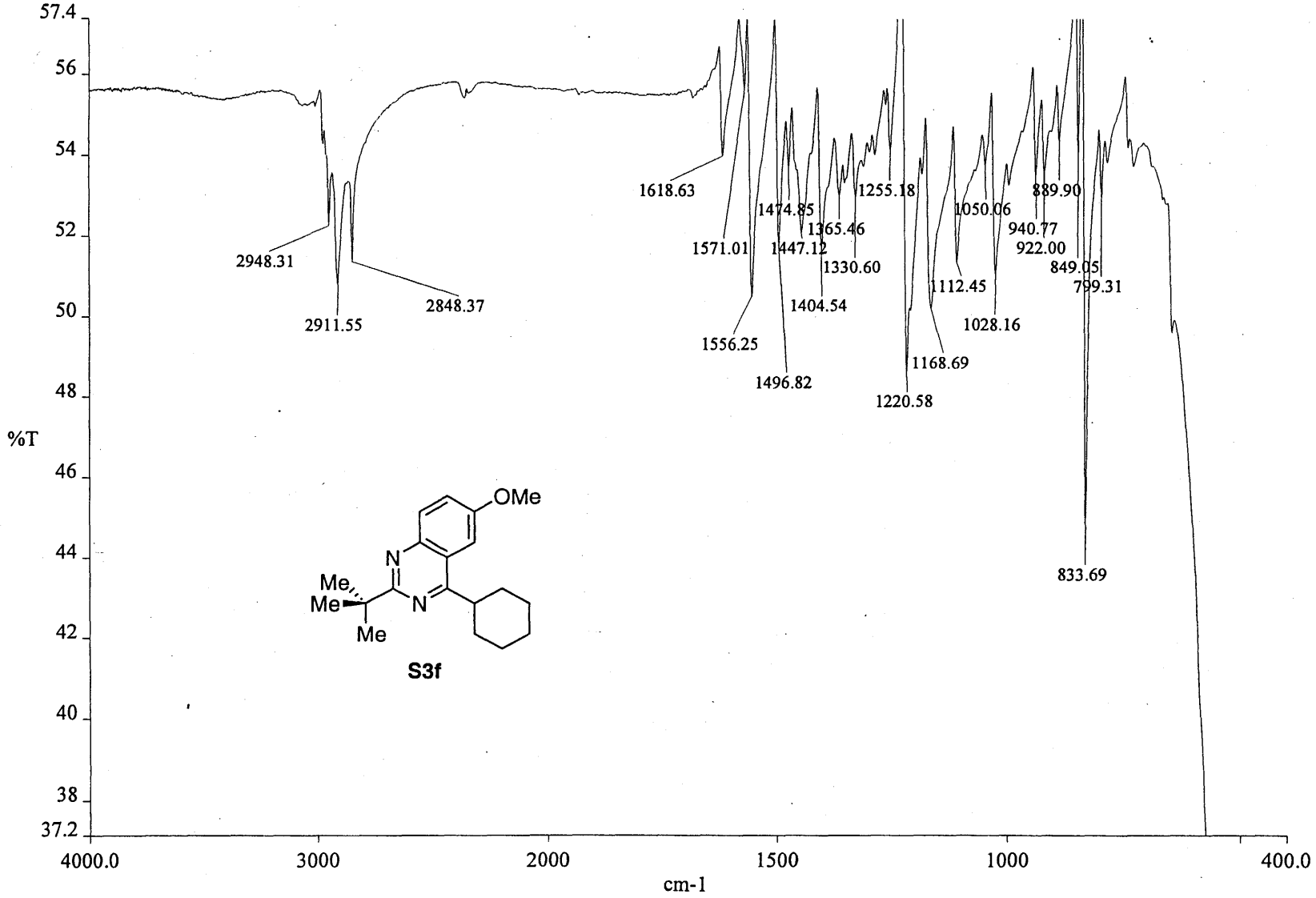
S3f

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

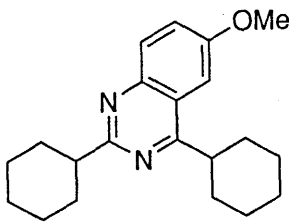
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
72 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2 minutes



S3f


57.4
56
54
52
50
48
46
44
42
40
38
37.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2948.31
2911.55
2848.37
1618.63
1571.01
1556.25
1496.82
1474.85
1447.12
1404.54
1365.46
1330.60
1255.18
1220.58
1168.69
1112.45
1050.06
1028.16
940.77
922.00
889.90
849.05
833.69
799.31
OMe
N
N
Me
Me
Me
S3f
c:\pel_data\spectra\mhii263.001 - mh-IV-263

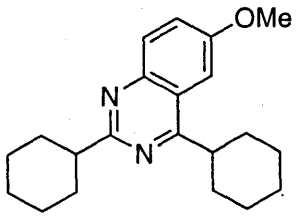
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-IV-273fr12-22
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
3 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



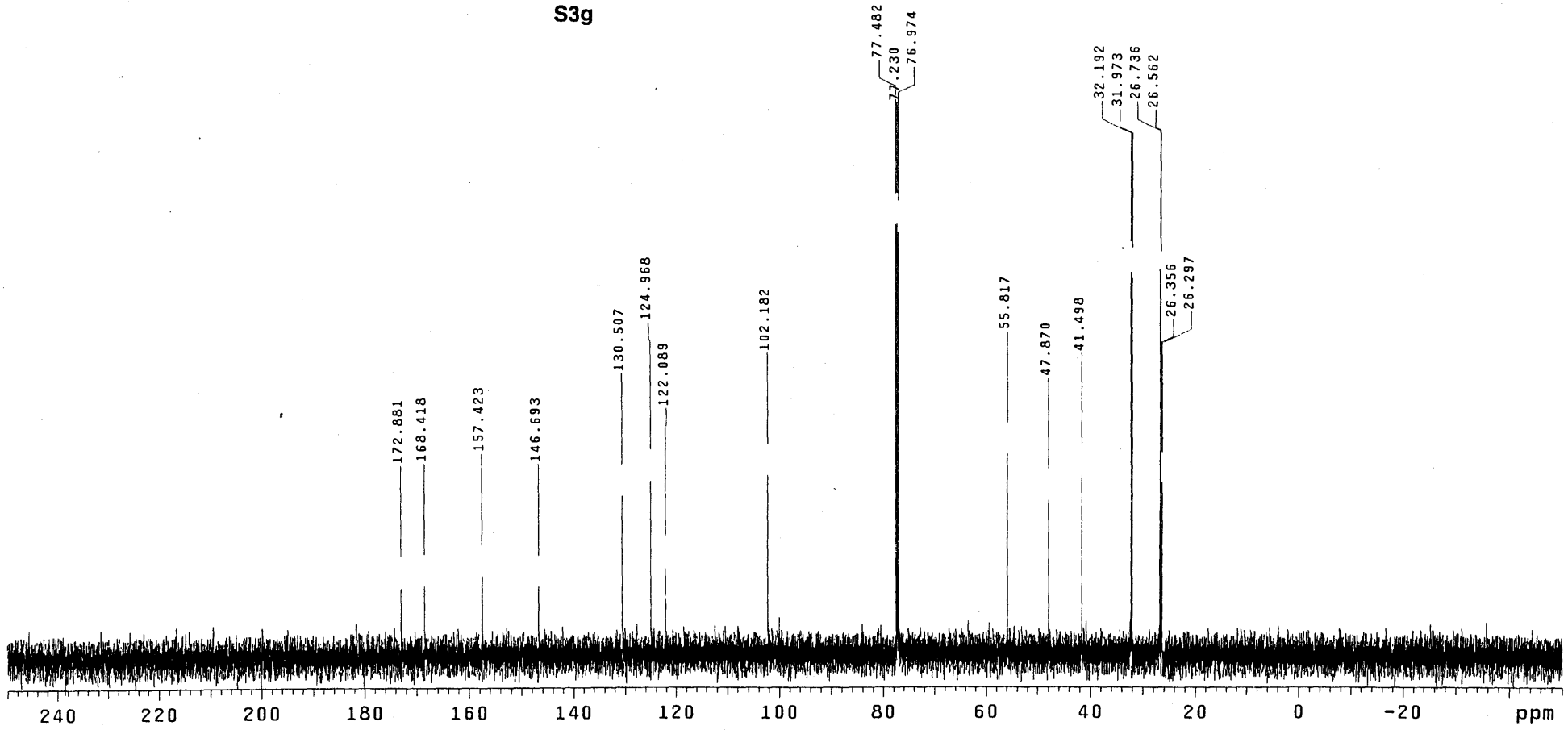
S3g

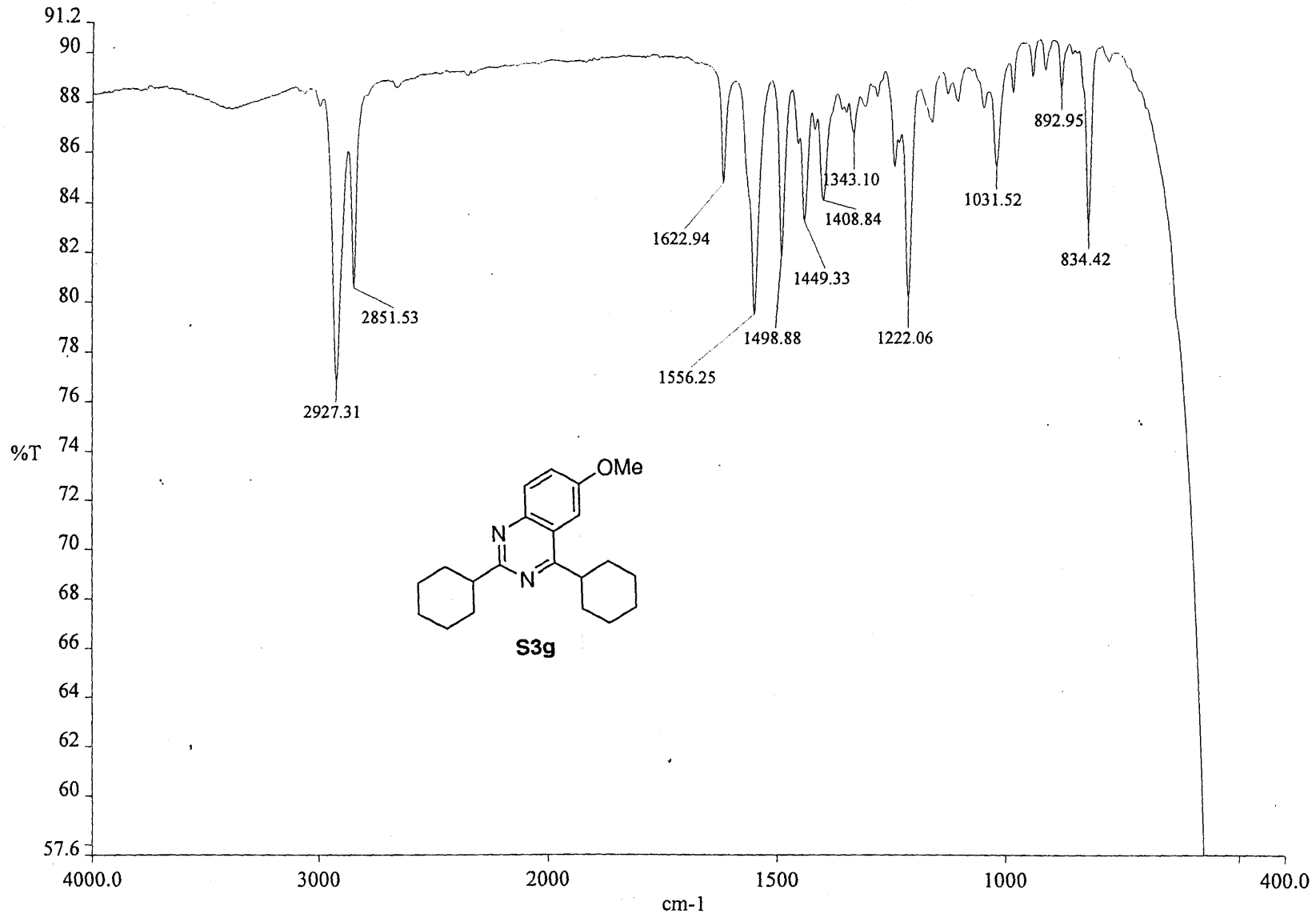
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
88 repetitions
OBSERVE C13, 125.7832286 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes



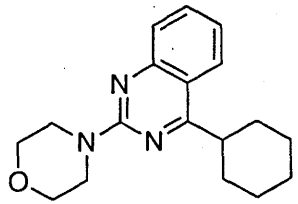
S3g




91.2
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
57.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2927.31
2851.53
1622.94
1556.25
1498.88
1449.33
1408.84
1343.10
1222.06
1031.52
892.95
834.42
OMe
N
N
S3g
c:\pel_data\spectra\mhiv273.sp - mh-IV-273

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-V-65clean
INOVA-500 "bullwinkle"

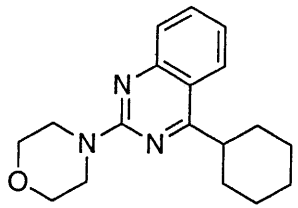
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



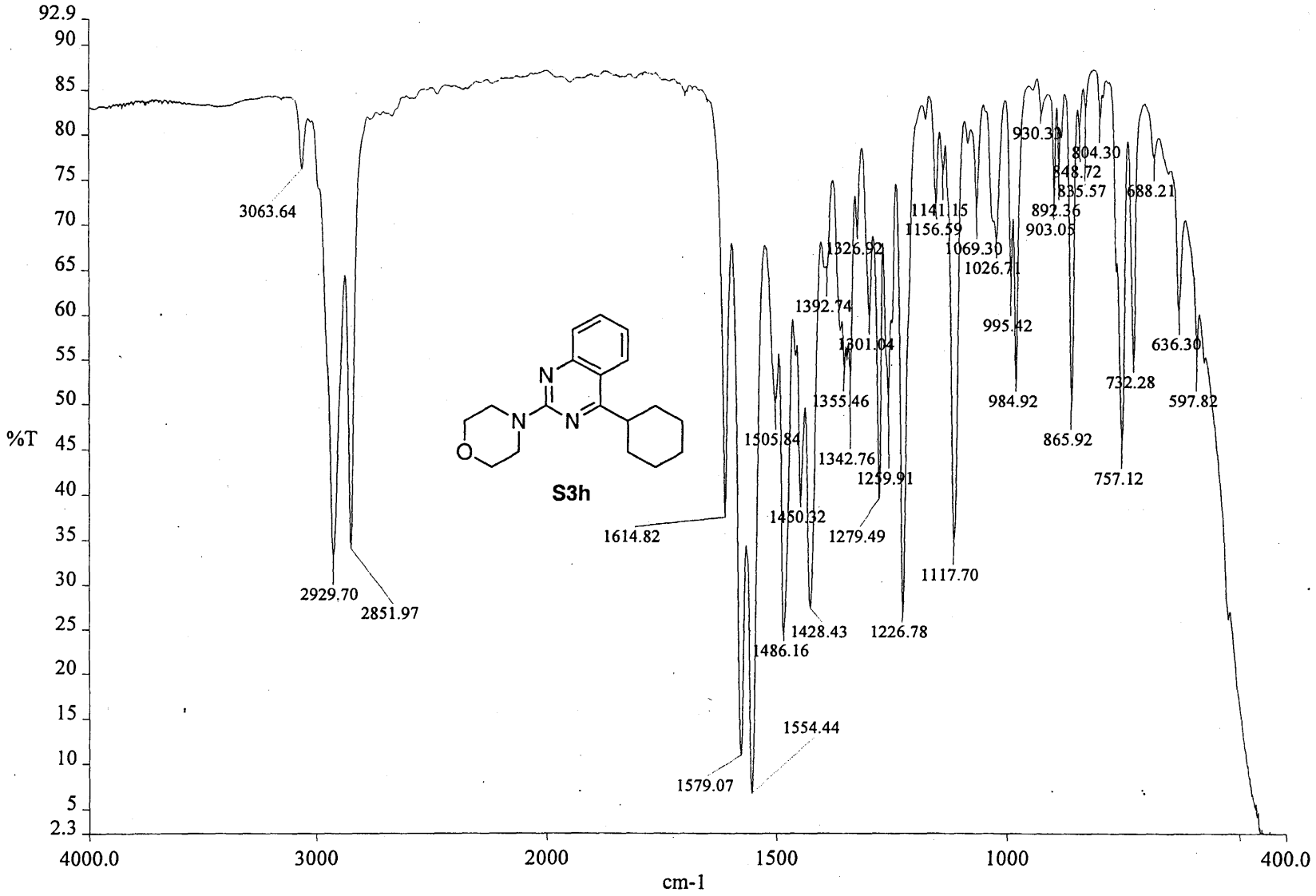
S3h

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
152 repetitions
OBSERVE C13, 125.7832297 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 5 minutes

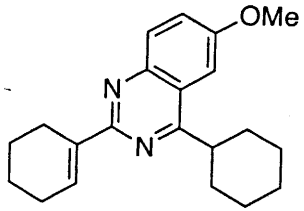


S3h


92.9
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
2.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3063.64
2929.70
2851.97
1614.82
1579.07
1554.44
1505.84
1486.16
1450.32
1428.43
1392.74
1355.46
1342.76
1326.92
1301.04
1279.49
1259.91
1226.78
1156.59
1141.15
1117.70
1069.30
1026.71
995.42
984.92
930.39
903.05
892.36
865.92
848.72
835.57
804.30
757.12
732.28
688.21
636.30
597.82
S3h
c:\pel_data\spectra\mhv65.sp - mh-V-65

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

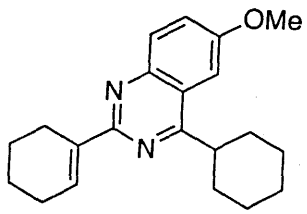
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



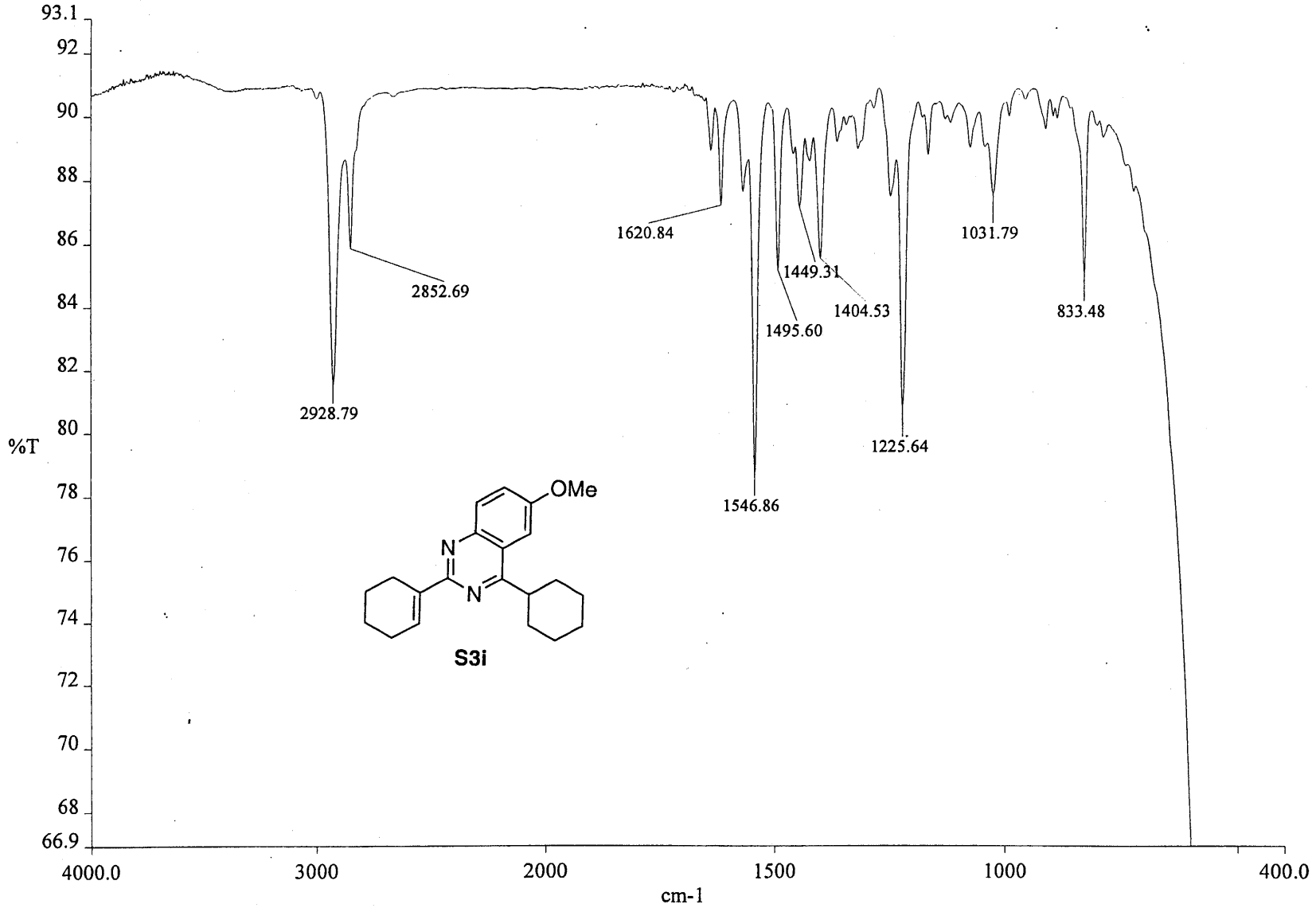
S3i

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
48 repetitions
OBSERVE C13, 125.7832286 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2 minutes

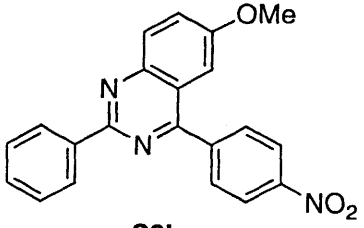


S3i

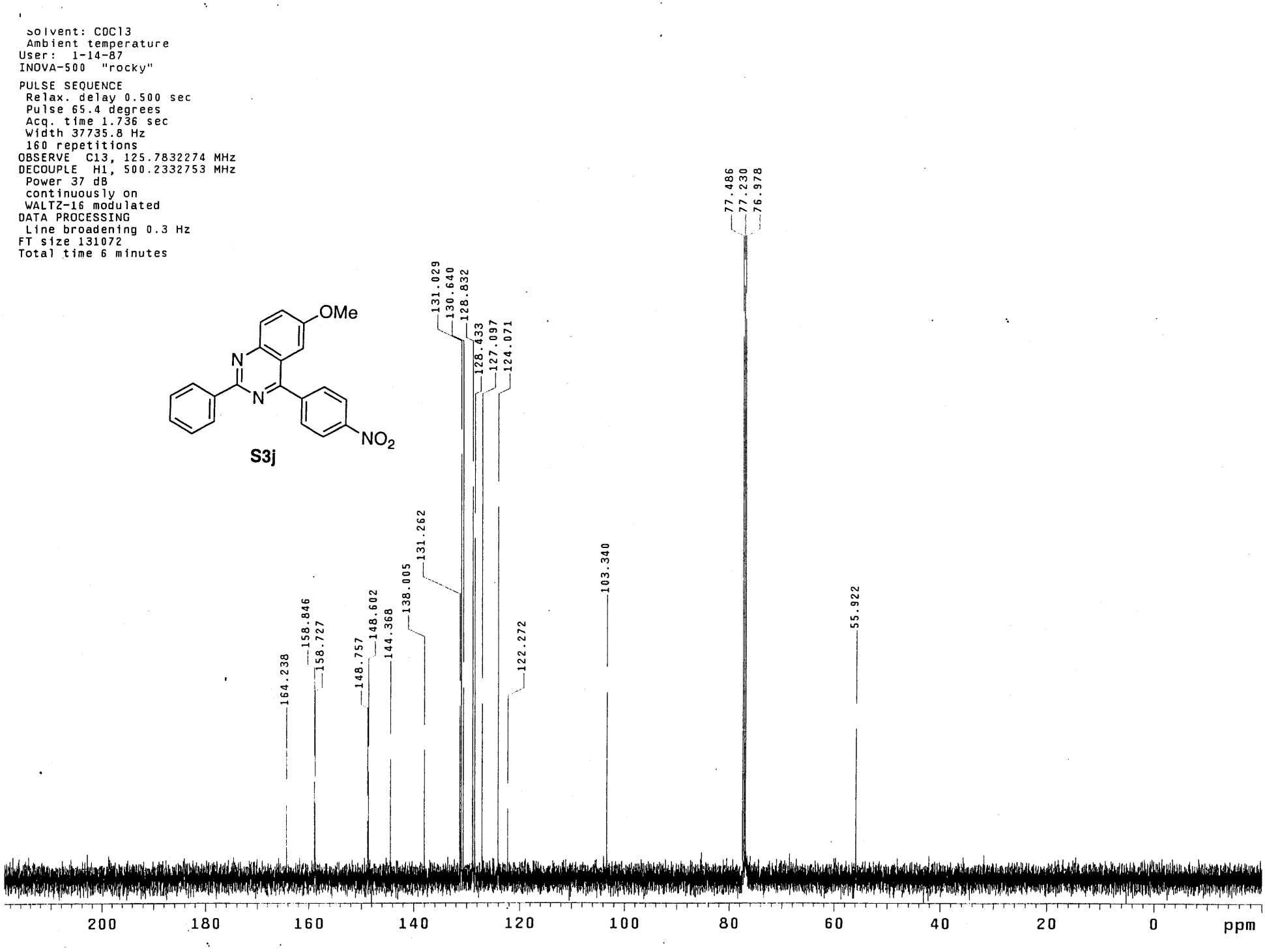

93.1
92
90
88
86
84
82
80
78
76
74
72
70
68
66.9
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2928.79
2852.69
1620.84
1546.86
1495.60
1449.31
1404.53
1225.64
1031.79
833.48
OMe
N
N
S3i
c:\pel_data\spectra\mhiv283.001 - mh-IV-283

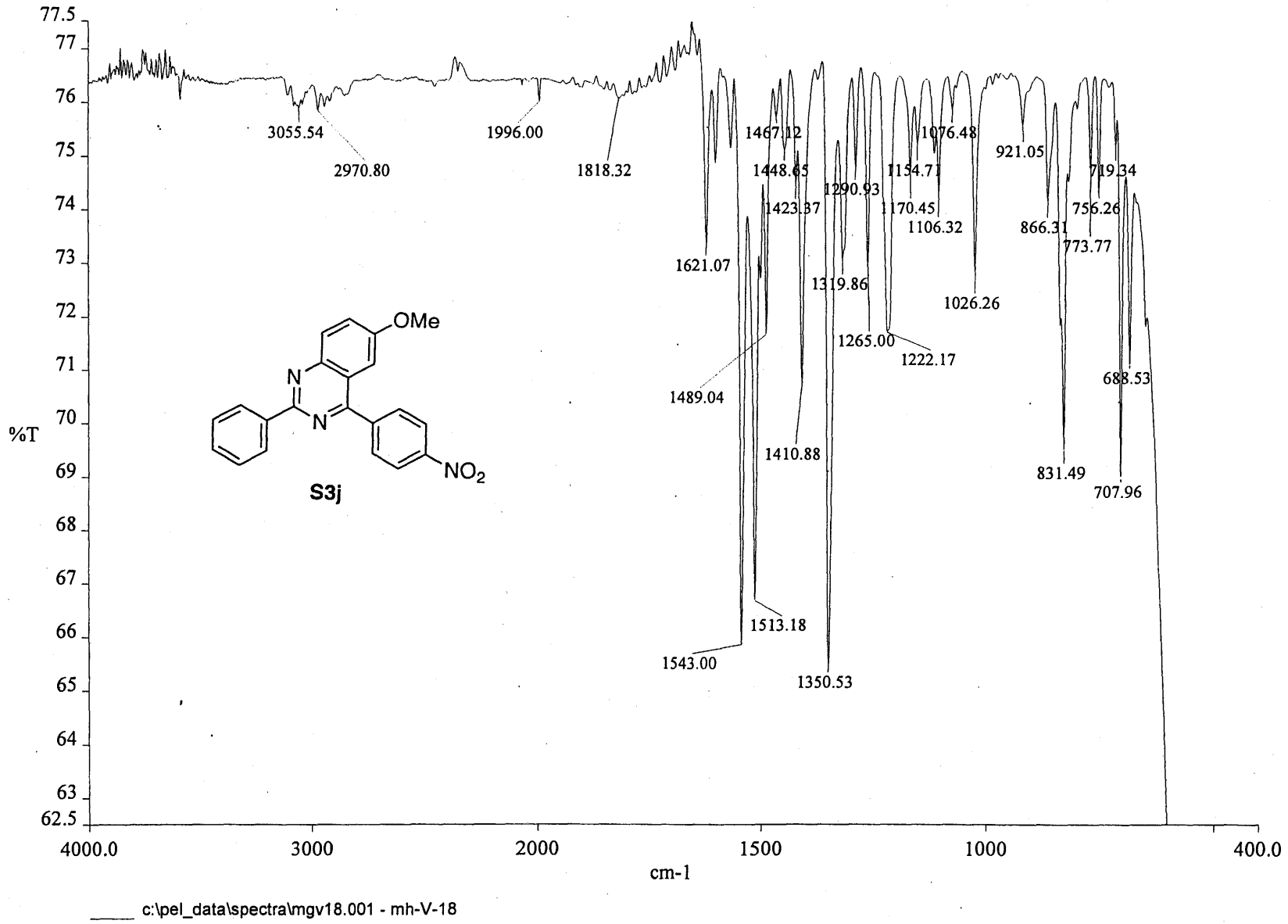
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



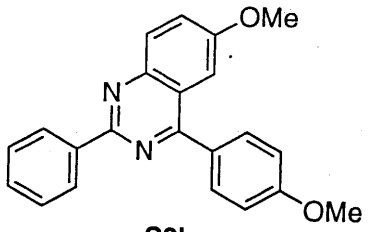
S3j


solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
160 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6 minutes
OMe
N
N
NO2
S3j
77.486
77.230
76.978
131.029
130.640
128.832
128.433
127.097
124.071
131.262
138.005
148.602
144.368
148.757
158.846
158.727
164.238
122.272
103.340
55.922
200
180
160
140
120
100
80
60
40
20
0
ppm

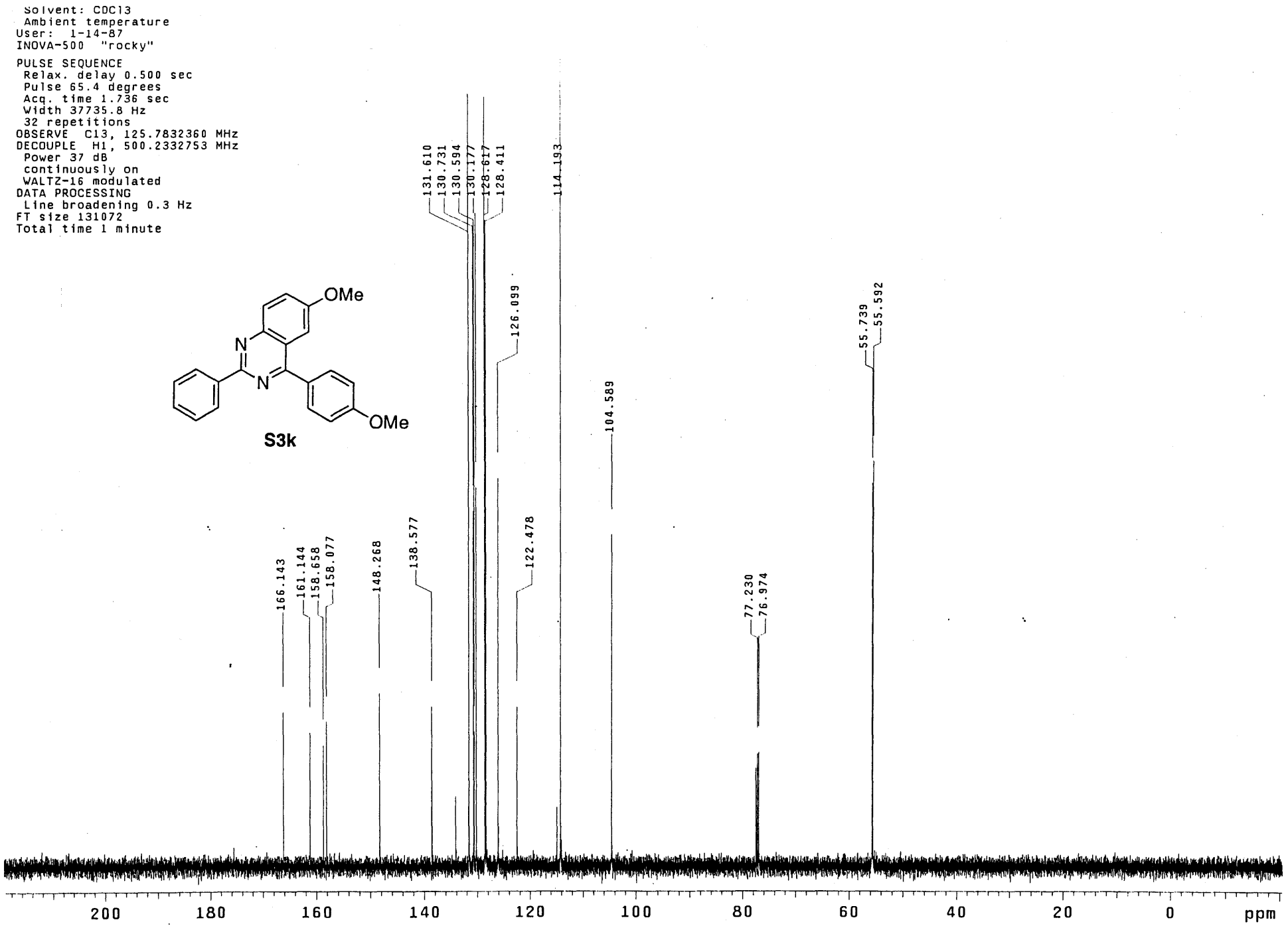

77.5
77
76
75
74
73
72
71
70
69
68
67
66
65
64
63
62.5
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3055.54
2970.80
1996.00
1818.32
1621.07
1543.00
1513.18
1489.04
1467.12
1448.65
1423.37
1410.88
1350.53
1319.86
1290.93
1265.00
1222.17
1170.45
1154.71
1106.32
1076.48
1026.26
921.05
866.31
831.49
773.77
756.26
719.34
707.96
688.53
OMe
N
N
NO2
S3j
c:\pel_data\spectra\mgv18.001 - mh-V-18

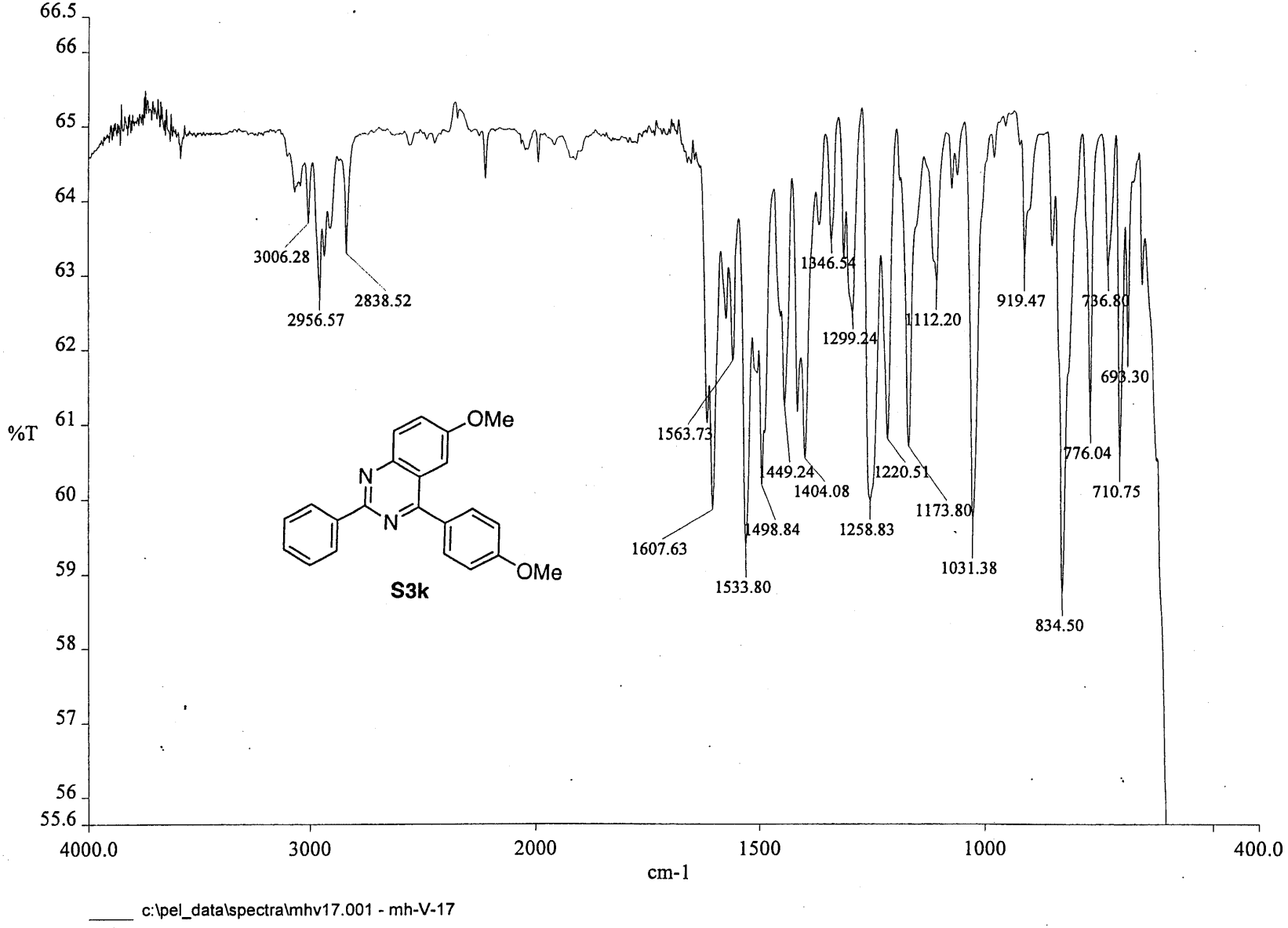
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
9 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



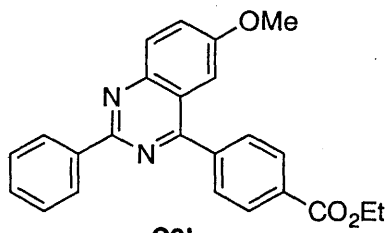
S3k


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
32 repetitions
OBSERVE C13, 125.7832360 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
OMe
N
N
OMe
S3k
131.610
130.731
130.594
130.177
128.617
128.411
114.193
126.099
104.589
55.739
55.592
166.143
161.144
158.658
158.077
148.268
138.577
122.478
77.230
76.974
200
180
160
140
120
100
80
60
40
20
0
ppm

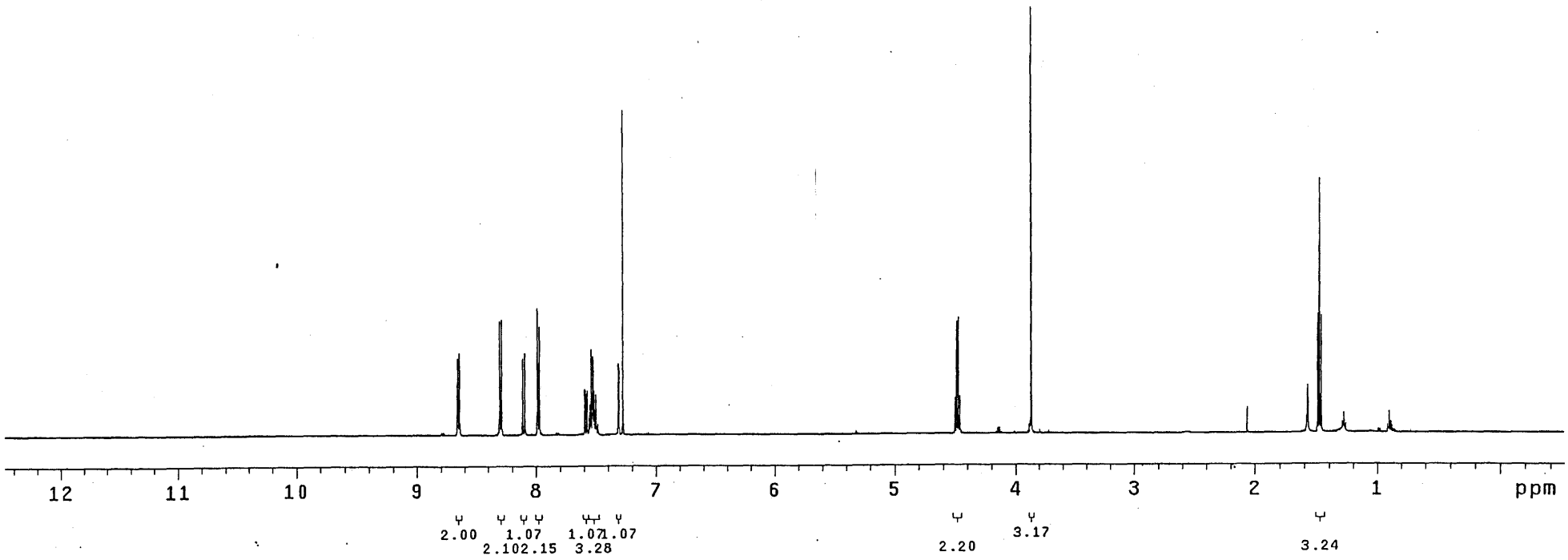

66.5
66
65
64
63
62
61
60
59
58
57
56
55.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3006.28
2956.57
2838.52
1563.73
1607.63
1533.80
1498.84
1449.24
1404.08
1346.54
1299.24
1258.83
1220.51
1173.80
1112.20
1031.38
919.47
834.50
776.04
736.80
710.75
693.30
OMe
OMe
N
N
S3k
c:\pel_data\spectra\mhv17.001 - mh-V-17

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
10 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec

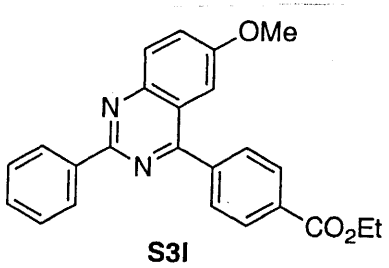


S3l

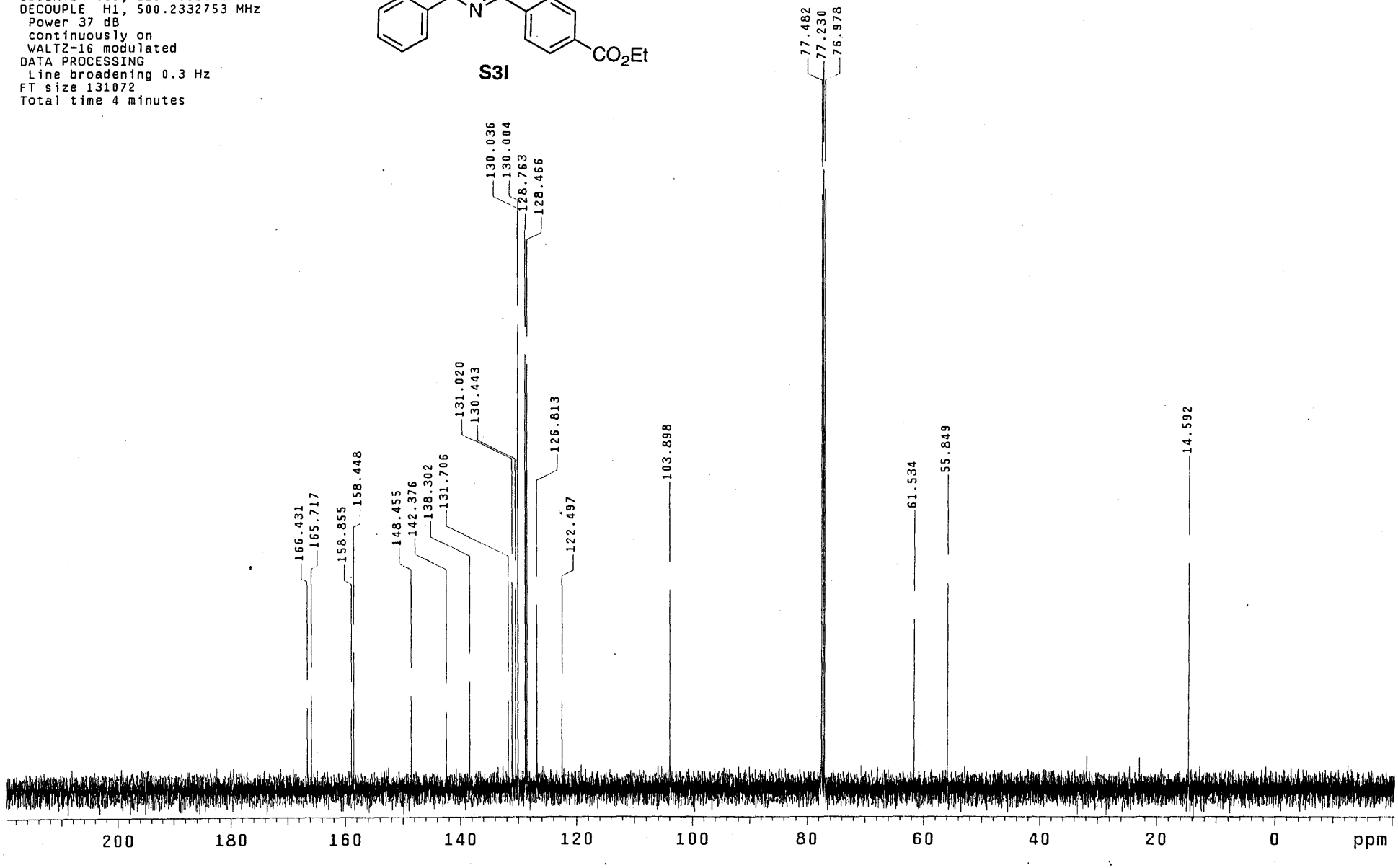


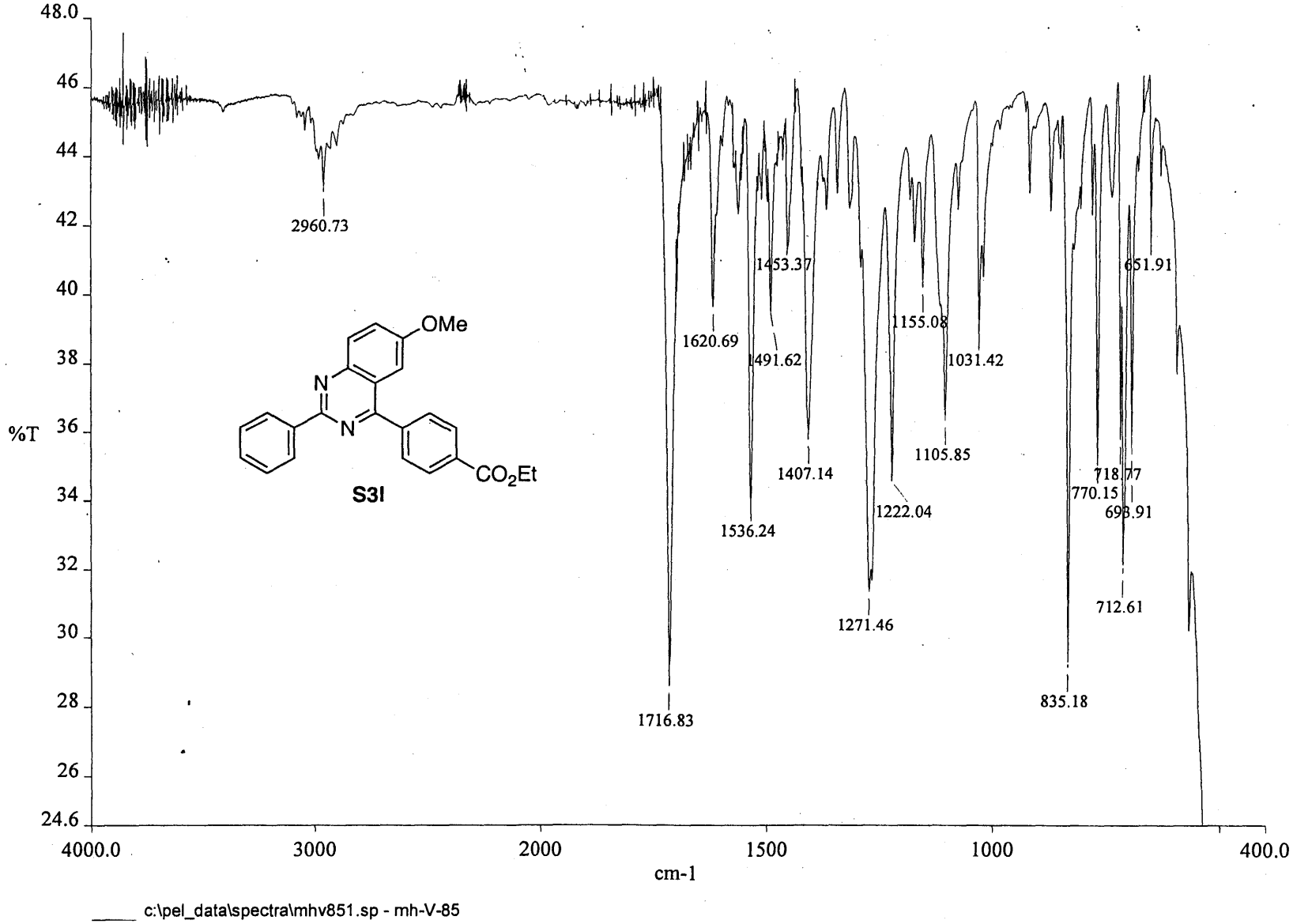
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
120 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes



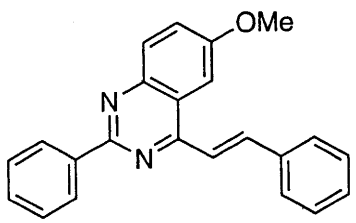
S3l




48.0
46
44
42
40
38
36
34
32
30
28
26
24.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2960.73
1716.83
1620.69
1536.24
1491.62
1453.37
1407.14
1271.46
1222.04
1155.08
1105.85
1031.42
835.18
718.77
770.15
698.91
712.61
651.91
OMe
N
N
CO2Et
S3l
c:\pel_data\spectra\mhv851.sp - mh-V-85

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

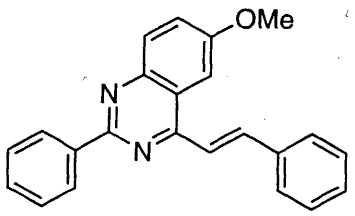
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



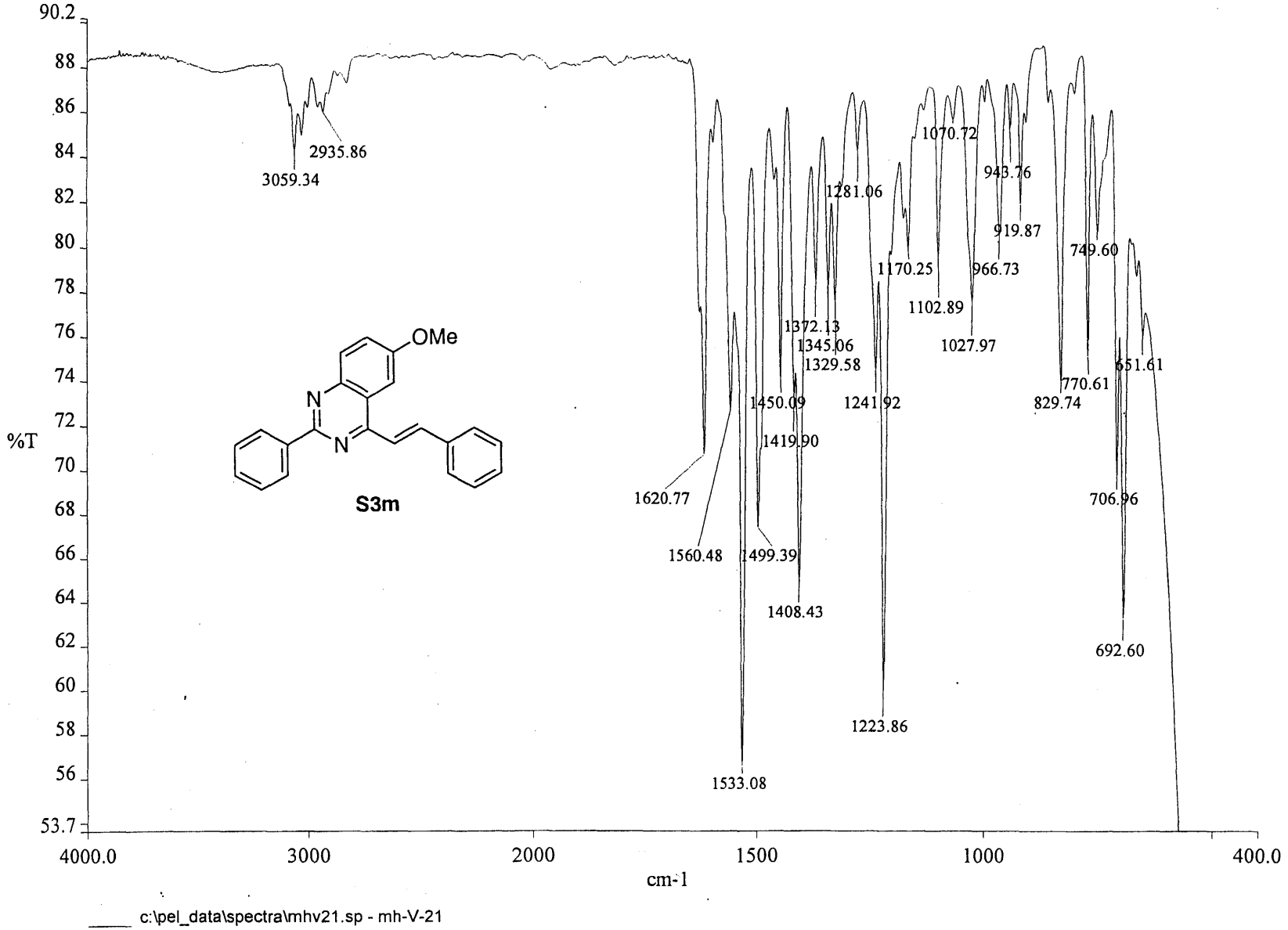
S3m

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

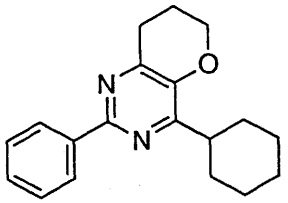
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
120 repetitions
OBSERVE C13, 125.7832309 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes



S3m


90.2
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
53.7
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3059.34
2935.86
1620.77
1560.48
1533.08
1499.39
1450.09
1419.90
1408.43
1372.13
1345.06
1329.58
1281.06
1241.92
1223.86
1170.25
1102.89
1070.72
1027.97
966.73
943.76
919.87
829.74
770.61
749.60
706.96
692.60
651.61
OMe
N
N
S3m
c:\pel_data\spectra\mhv21.sp - mh-V-21

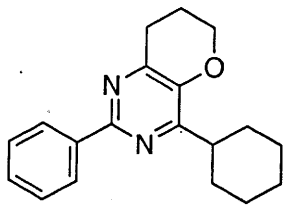
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-V-14
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



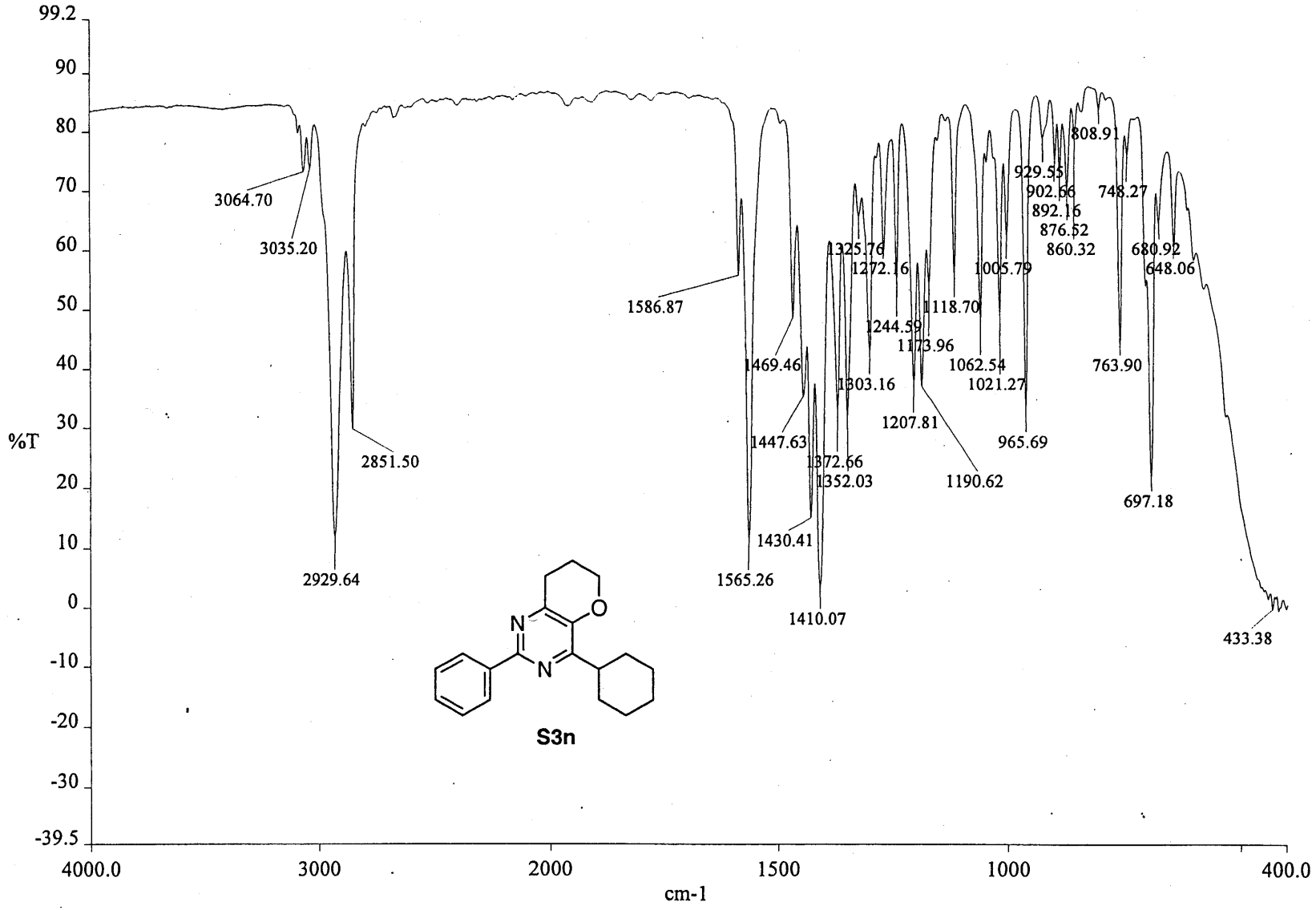
S3n

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
112 repetitions
OBSERVE C13, 125.7832349 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes

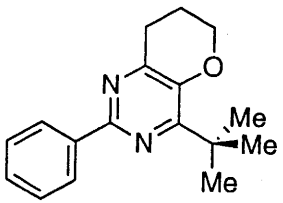


S3n


99.2
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-39.5
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3064.70
3035.20
2929.64
2851.50
1586.87
1565.26
1469.46
1447.63
1430.41
1410.07
1372.66
1352.03
1325.76
1303.16
1272.16
1244.59
1207.81
1190.62
1173.96
1118.70
1062.54
1021.27
1005.79
965.69
929.55
902.66
892.16
876.52
860.32
808.91
763.90
748.27
697.18
680.92
648.06
433.38
N
N
O
S3n
c:\pel_data\spectra\mhv14.sp - mh-V-14

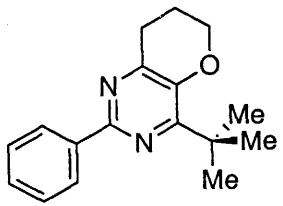
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec

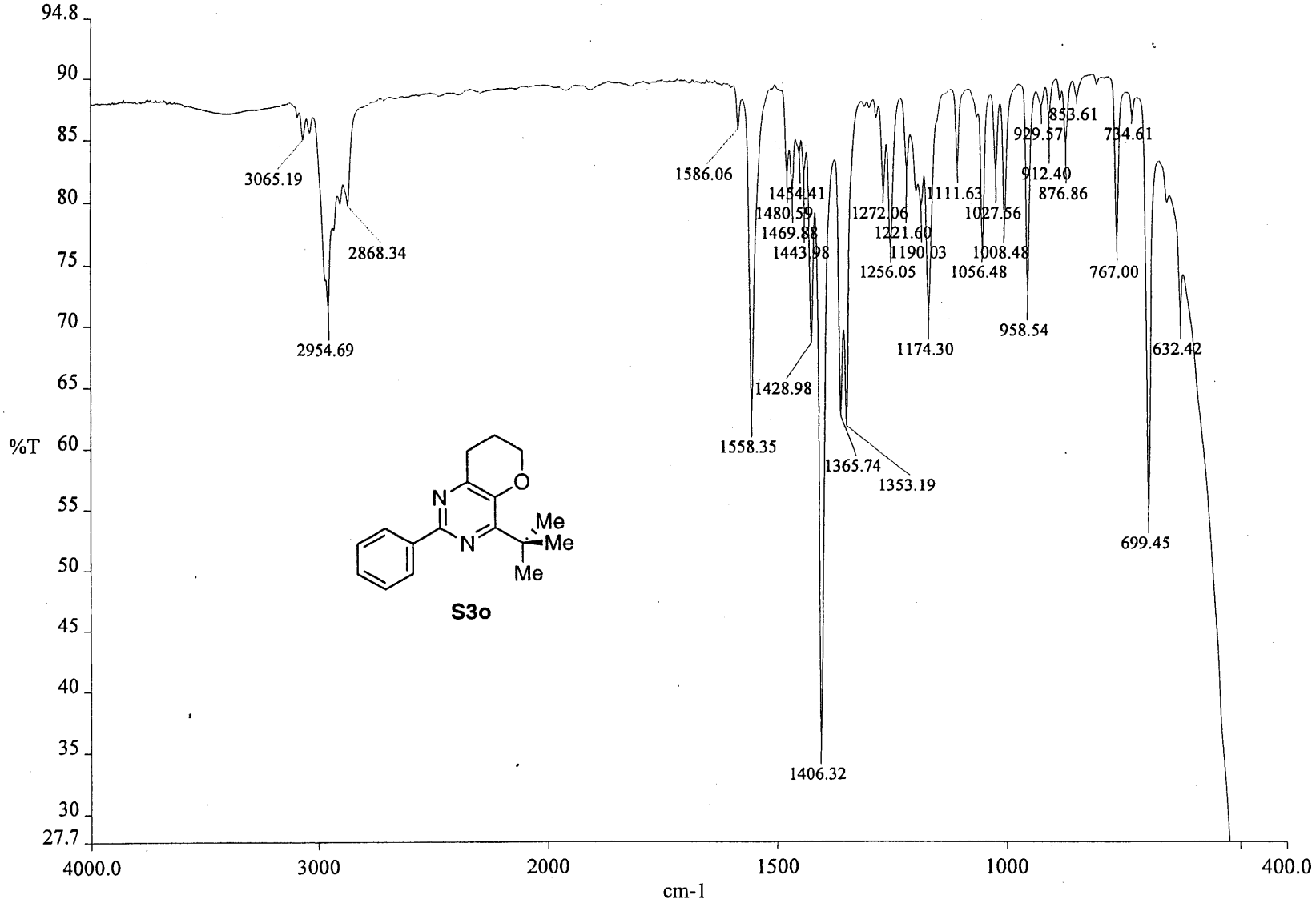


S3o

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: mh-V-52carbon
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
256 repetitions
OBSERVE C13, 125.7832309 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 9 min, 36 sec

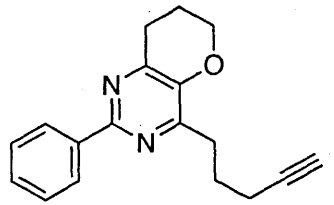


S3o

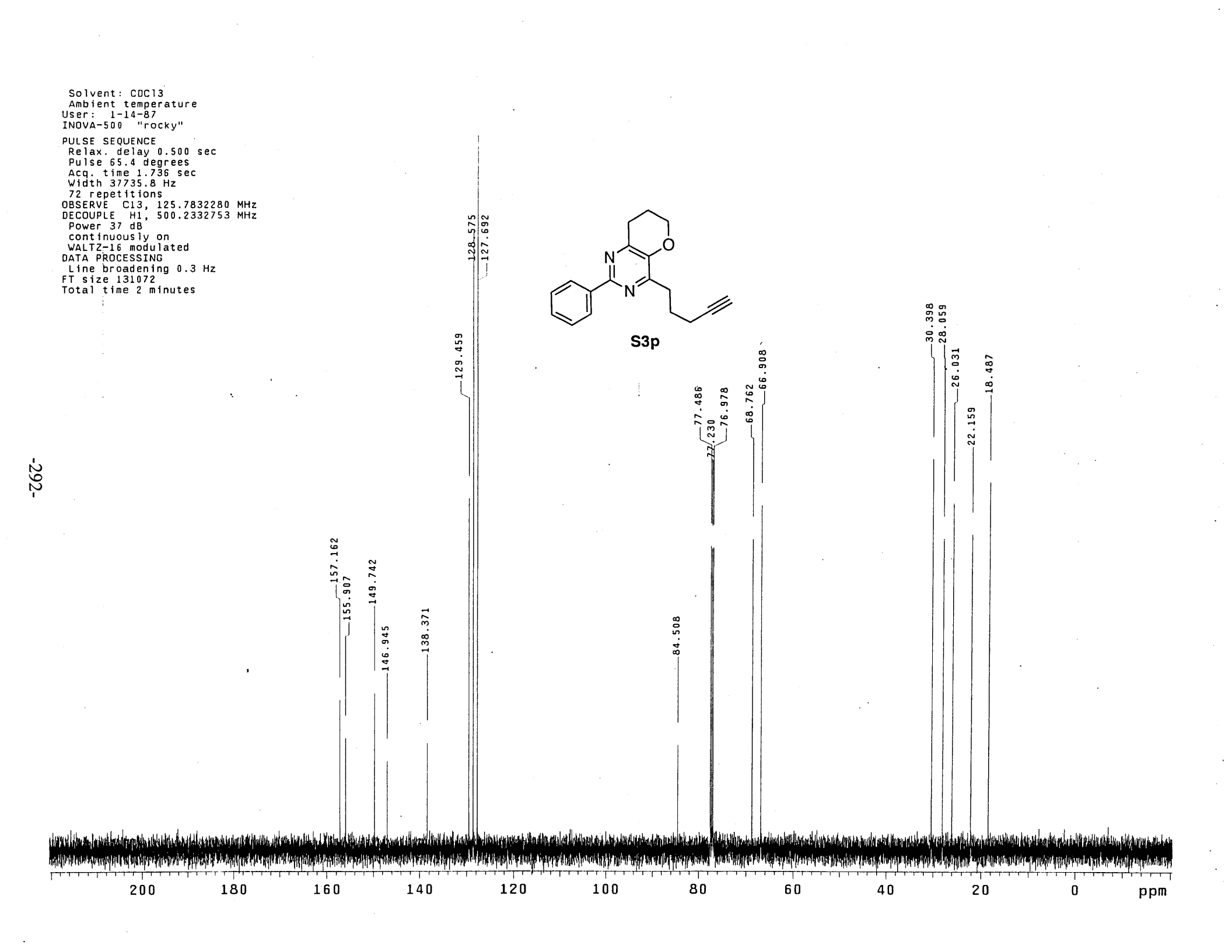

94.8
90
85
80
75
70
65
60
55
50
45
40
35
30
27.7
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3065.19
2868.34
2954.69
1586.06
1454.41
1480.59
1469.88
1443.98
1428.98
1558.35
1406.32
1365.74
1353.19
1272.06
1221.60
1190.03
1256.05
1174.30
1111.63
1027.56
1008.48
1056.48
958.54
912.40
876.86
853.61
929.57
734.61
767.00
632.42
699.45
N
O
N
Me
Me
Me
S3o
c:\pel_data\spectra\mhv52.sp - mh-V-52

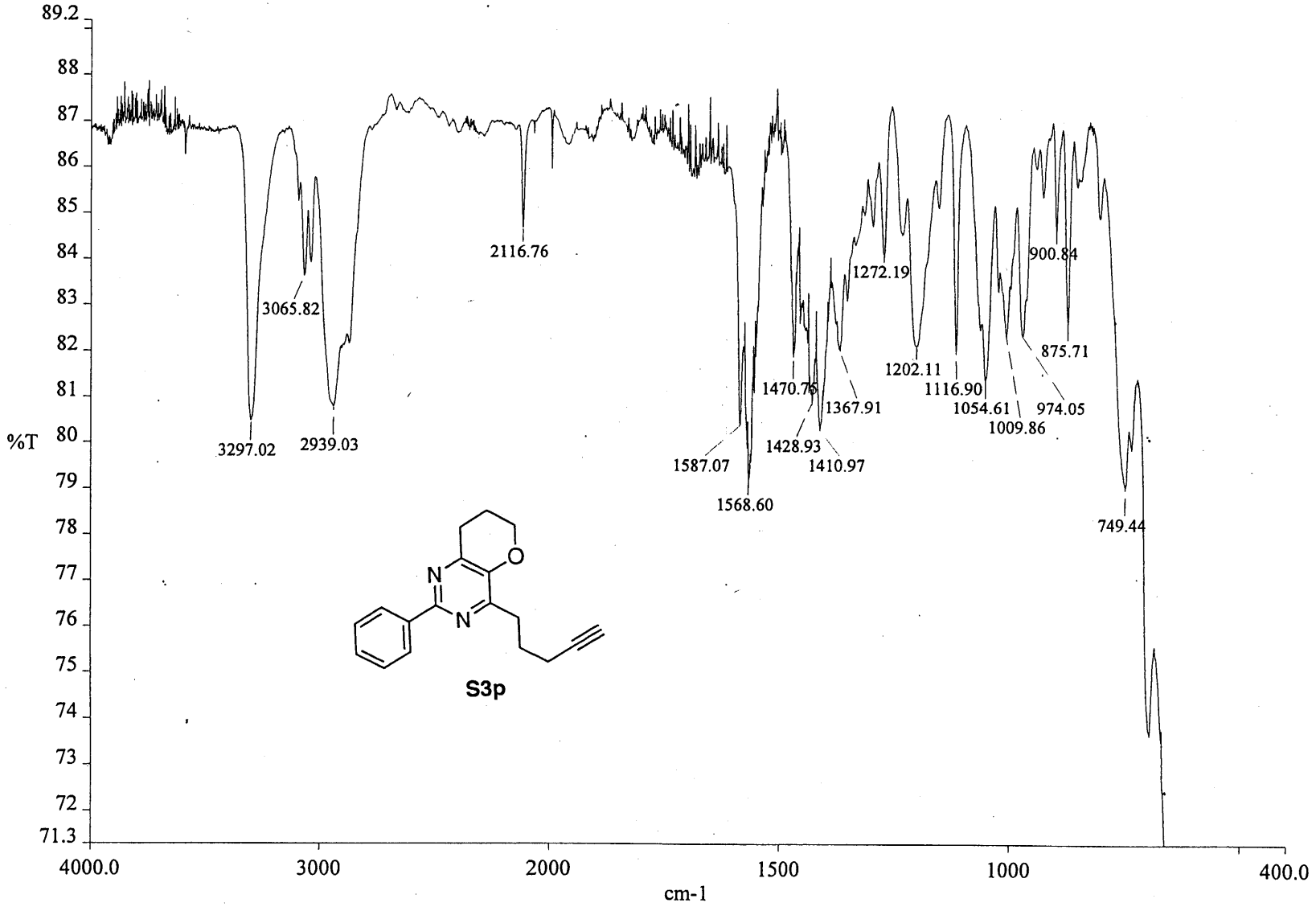
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



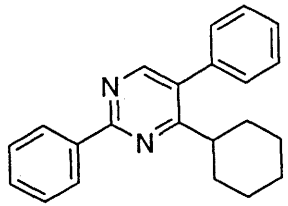
S3p


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
72 repetitions
OBSERVE C13, 125.7832280 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2 minutes
S3p
157.162
155.907
149.742
146.945
138.371
129.459
128.575
127.692
84.508
77.486
77.230
76.978
68.762
66.908
30.398
28.059
26.031
22.159
18.487
200
180
160
140
120
100
80
60
40
20
0
ppm


89.2
88
87
86
85
84
83
82
81
80
79
78
77
76
75
74
73
72
71.3
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3297.02
2939.03
3065.82
2116.76
1587.07
1568.60
1470.76
1428.93
1410.97
1367.91
1272.19
1202.11
1116.90
1054.61
1009.86
974.05
900.84
875.71
749.44
N
N
O
S3p
c:\pel_data\spectra\mhv781.sp - mh-V-78

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

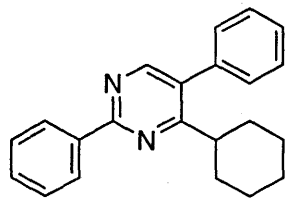
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



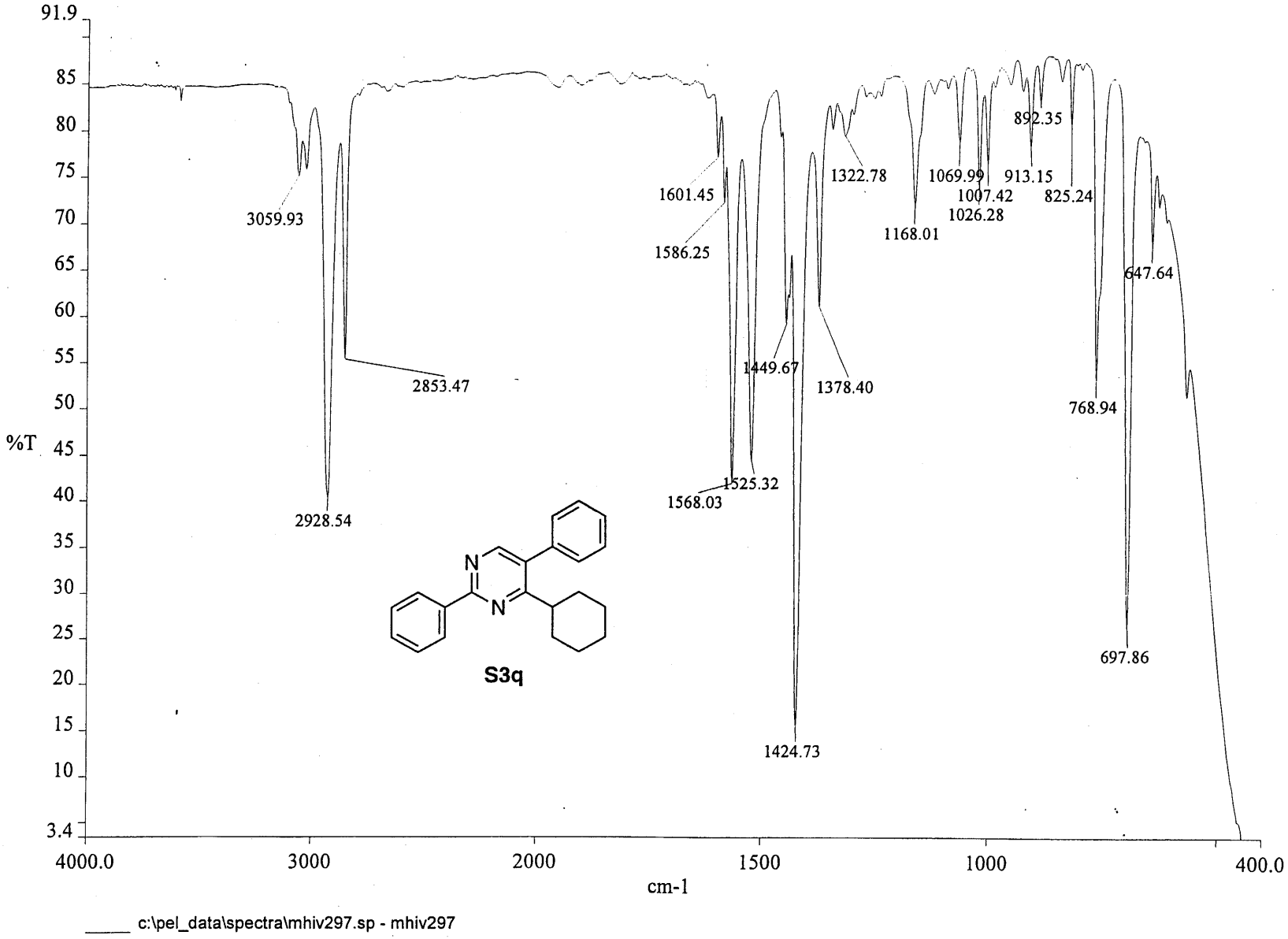
S3q

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

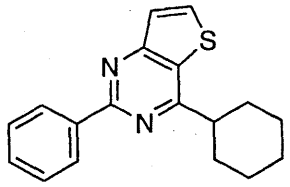
PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
40 repetitions
OBSERVE C13, 125.7832314 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes



S3q


91.9
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
3.4
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3059.93
2928.54
2853.47
1601.45
1586.25
1568.03
1525.32
1449.67
1424.73
1378.40
1322.78
1168.01
1069.99
1026.28
1007.42
913.15
892.35
825.24
768.94
697.86
647.64
N
N
S3q
c:\pel_data\spectra\mhiv297.sp - mhiv297

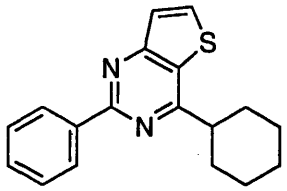
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-IV-285
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
3 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



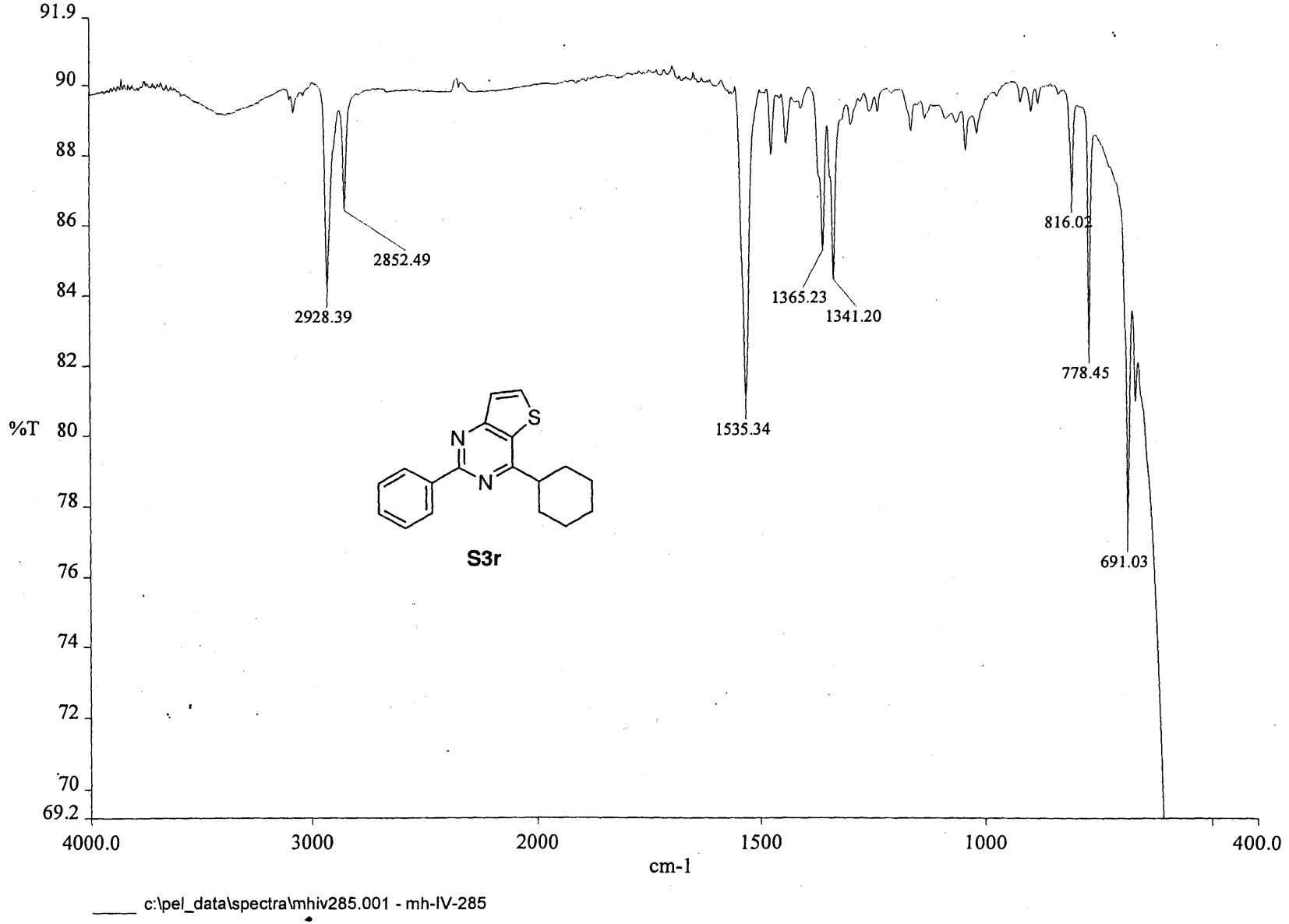
S3r

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
112 repetitions
OBSERVE C13, 125.7832286 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes



S3r

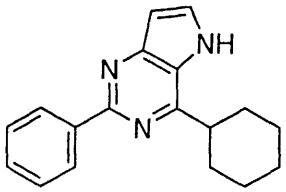

91.9
90
88
86
84
82
%T 80
78
76
74
72
70
69.2
2928.39
2852.49
1535.34
1365.23
1341.20
816.02
778.45
691.03
4000.0
3000
2000
1500
1000
400.0
cm-1
c:\pel_data\spectra\mhiv285.001 - mh-IV-285

N
S
N

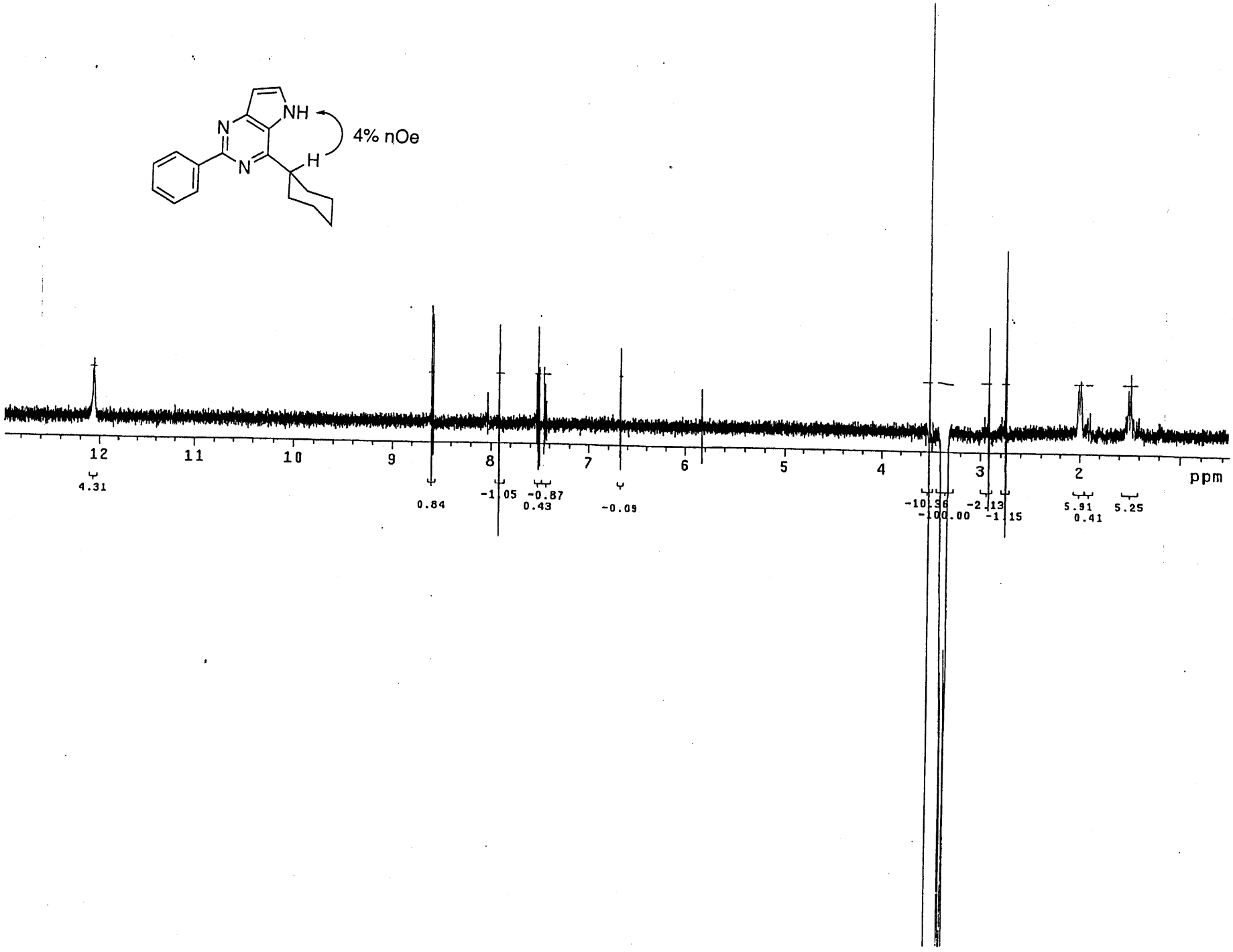
S3r

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec

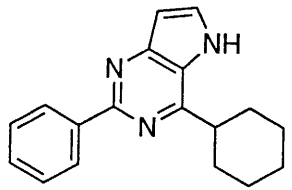


S3s

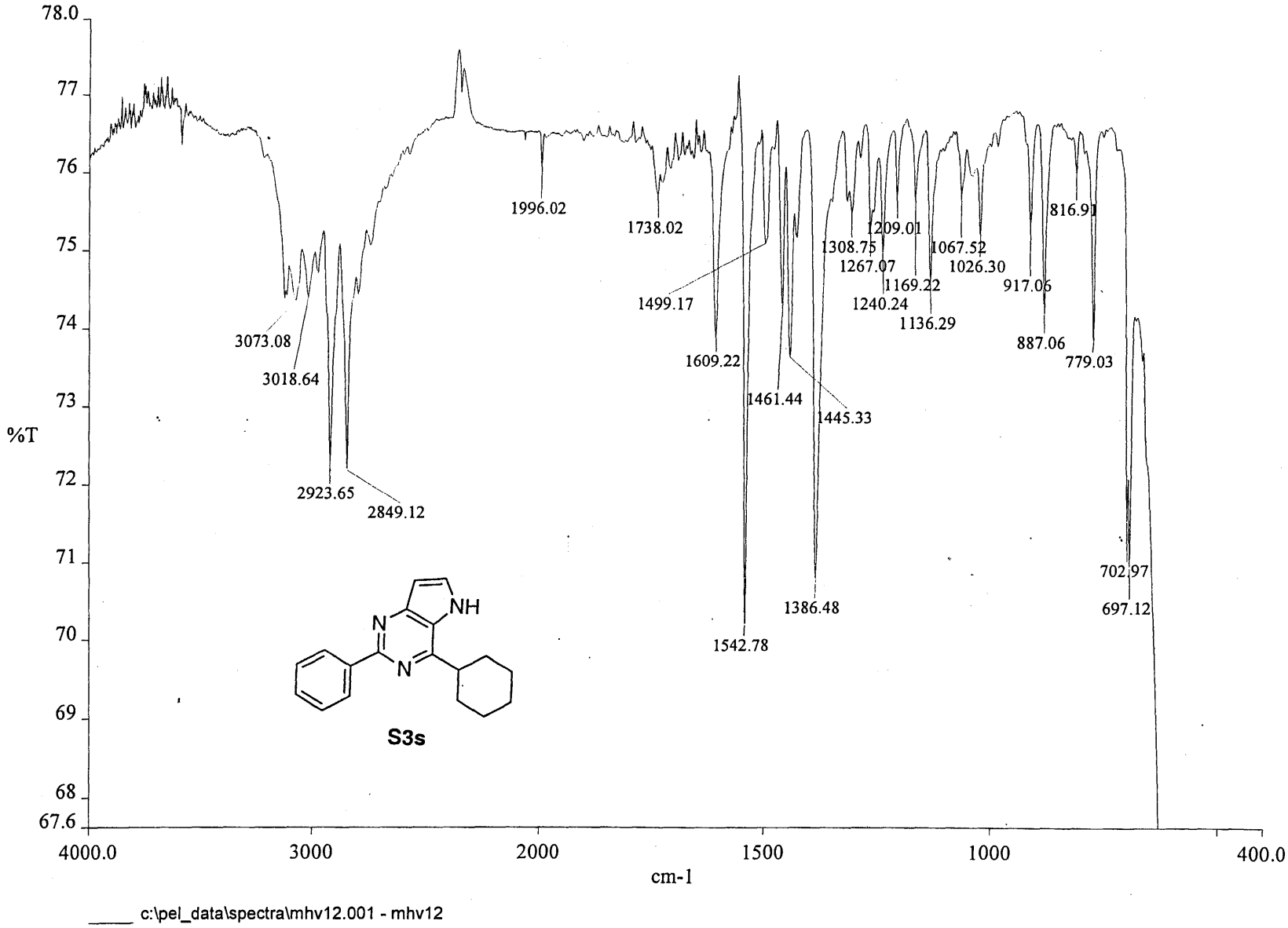

NH
N
N
H
4% nOe
12
11
10
9
8
7
6
5
4
3
2
ppm
4.31
0.84
-1.05
-0.87
0.43
-0.09
-10.36
-100.00
-2.13
-1.15
5.91
0.41
5.25

Solvent: DMF
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
168 repetitions
OBSERVE C13, 125.7836630 MHz
DECOUPLE H1, 500.2354363 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6 minutes

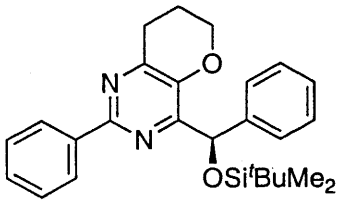


S3s


78.0
77
76
75
74
73
72
71
70
69
68
67.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3073.08
3018.64
2923.65
2849.12
1996.02
1738.02
1499.17
1609.22
1542.78
1461.44
1445.33
1386.48
1308.75
1267.07
1240.24
1209.01
1169.22
1136.29
1067.52
1026.30
917.06
887.06
816.91
779.03
702.97
697.12
NH
N
N
S3s
c:\pel_data\spectra\mhv12.001 - mhv12

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

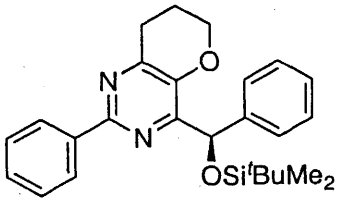
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
11 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



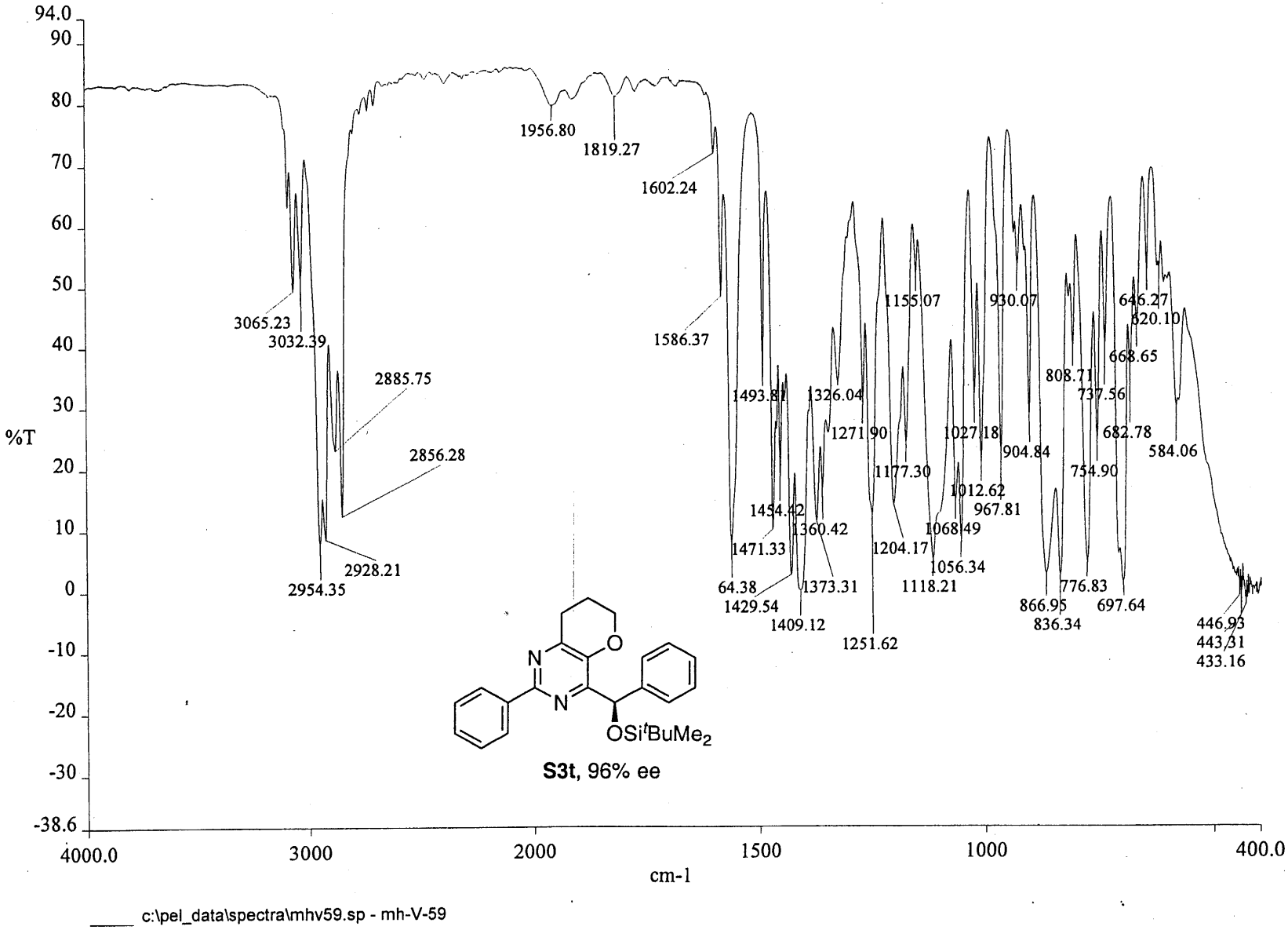
S3t, 96% ee

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
488 repetitions
OBSERVE C13, 125.7832280 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 18 minutes

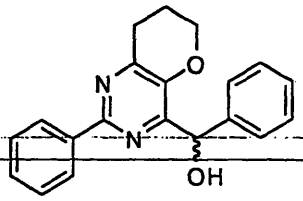


S3t, 96% ee


94.0
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-38.6
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3065.23
3032.39
2885.75
2856.28
2928.21
2954.35
1956.80
1819.27
1602.24
1586.37
1493.81
1326.04
1271.90
1155.07
1177.30
1454.42
1471.33
1360.42
1204.17
1373.31
1409.12
1251.62
1429.54
64.38
1118.21
1056.34
1068.49
1027.18
1012.62
967.81
930.07
904.84
866.95
836.34
808.71
776.83
754.90
737.56
697.64
682.78
668.65
646.27
620.10
584.06
446.93
443.31
433.16
N
N
O
OSi^{t}BuMe$_2$
c:\pel_data\spectra\mhv59.sp - mh-V-59

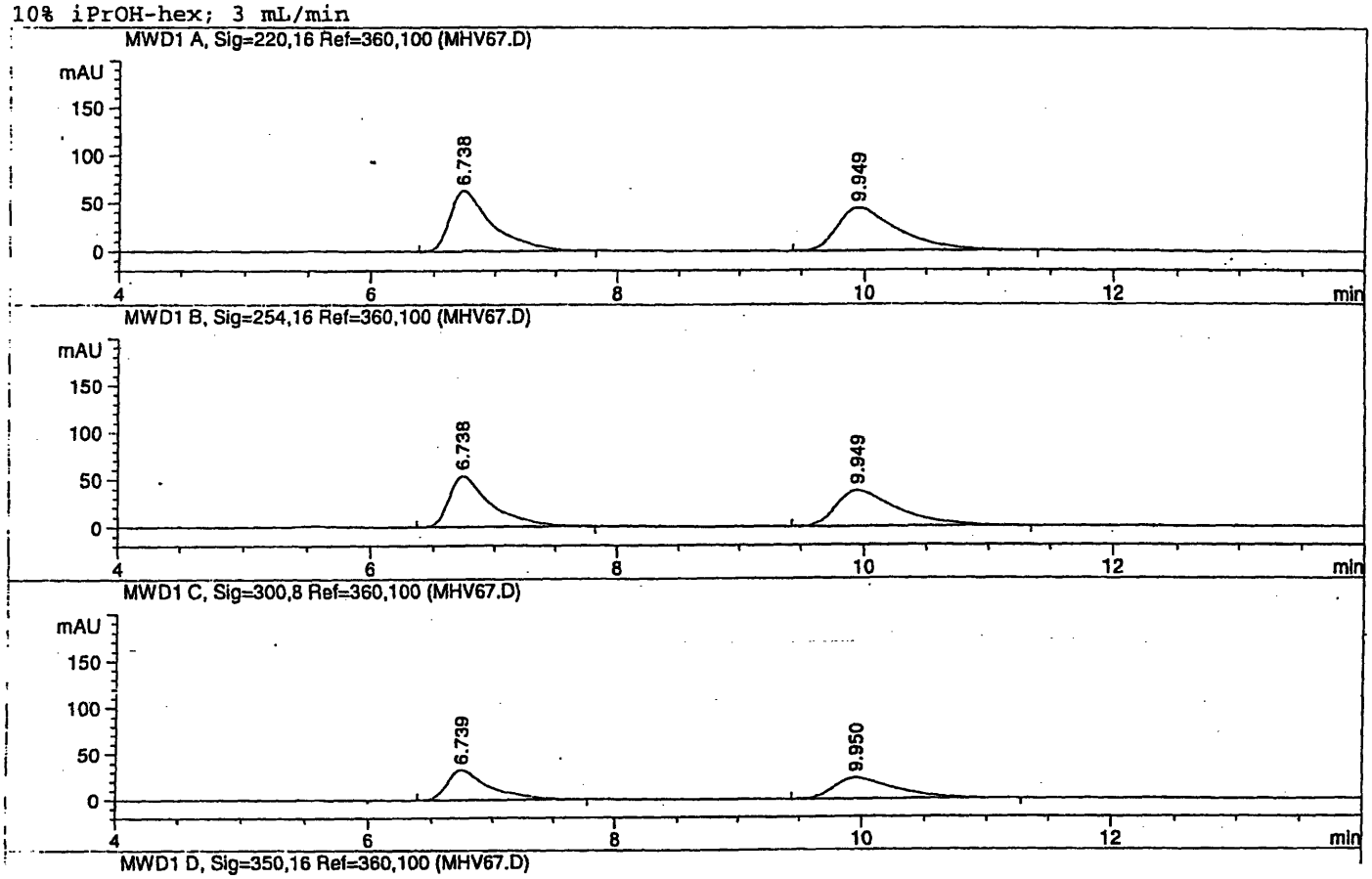
S3t, 96% ee

Injection Date : 5/17/2006 6:45:12 PM Seq. Line : 1
Sample Name : mh-V-67 Location : Vial 44
Acq. Operator : Pete Inj : 1
Inj Volume : 1 µl



Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 5/16/2006 6:11:26 PM by Pete
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed : 5/18/2006 9:55:23 AM by Pete
(modified after loading)

10% iPrOH-hex; 3 mL/min



Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.738	PB	0.3448	1484.55396	62.12878	49.9781
2	9.949	BB	0.4865	1485.85620	43.93668	50.0219
Totals :				2970.41016	106.06546	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.738	PB	0.3444	1275.83508	53.46923	49.9666
2	9.949	BB	0.4879	1277.54297	37.83992	50.0334
Totals :				2553.37805	91.30915	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.739	PB	0.3441	773.19104	32.43272	50.0029

```
Injection Date  : 5/17/2006 6:27:00 PM          Seq. Line :  1
Sample Name     : mh-V-71                      Location : Vial 45
Acq. Operator   : Pete                            Inj :  1
                                               Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\MATT.M
Last changed    : 5/16/2006 6:11:26 PM by Pete
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 5/18/2006 9:53:46 AM by Pete
                  (modified after loading)
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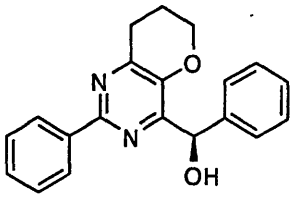
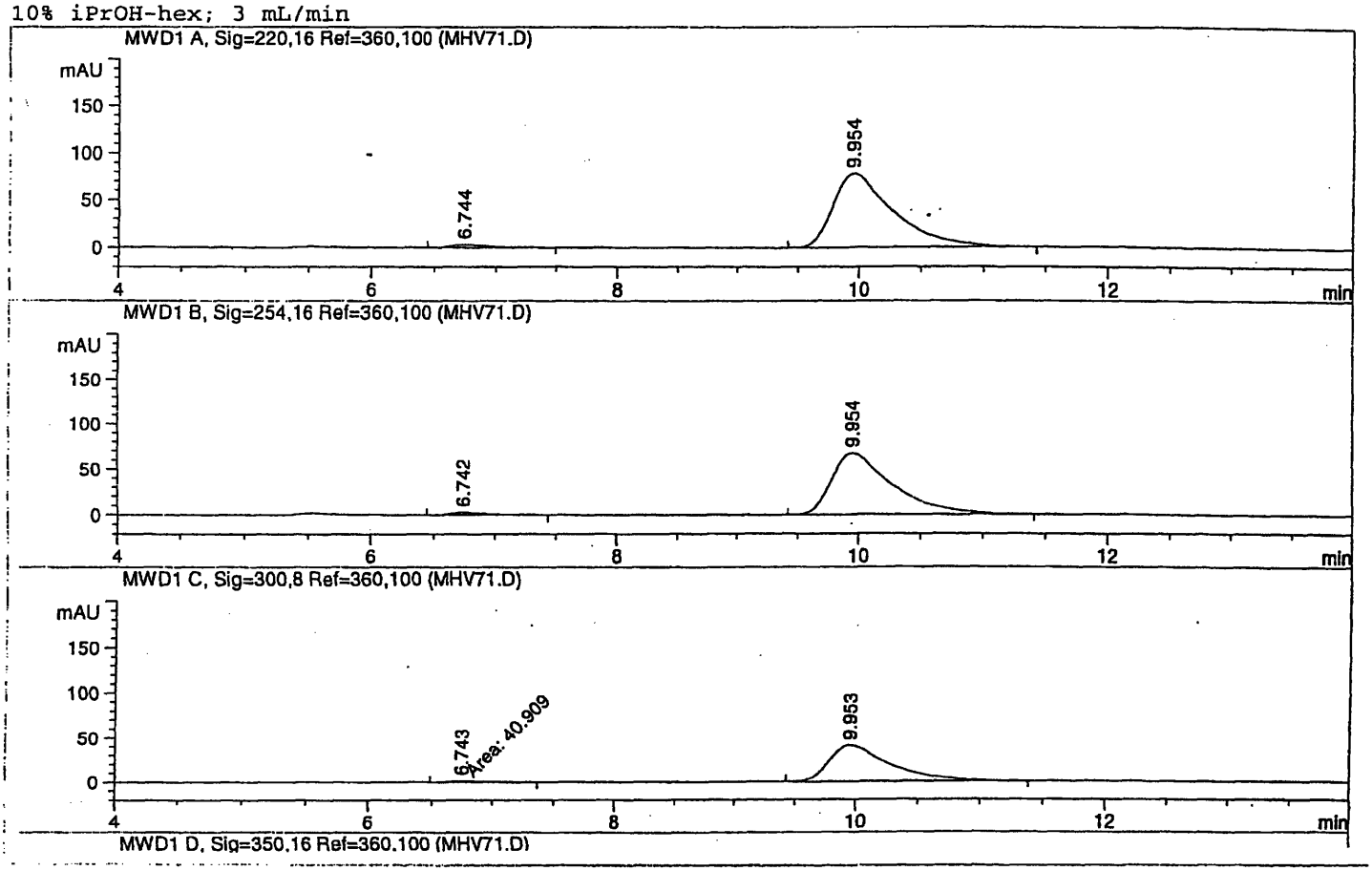


10% iPrOH-hex; 3 mL/min



Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.744	BB	0.3266	67.53790	2.97821	2.4983
2	9.954	PB	0.4889	2635.80933	77.87540	97.5017
Totals :				2703.34723	80.85362	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.742	PB	0.3238	58.46334	2.56659	2.5113
2	9.954	BB	0.4869	2269.58228	67.04366	97.4887
Totals :				2328.04562	69.61026	

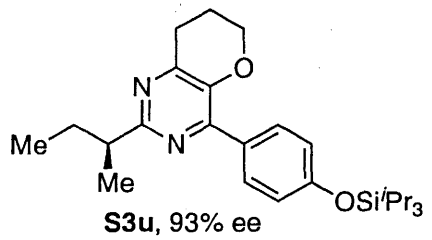
Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.743	MM	0.4127	40.90902	1.65224	2.8853
2	9.953	BB	0.4868	1376.94629	40.69079	97.1147

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

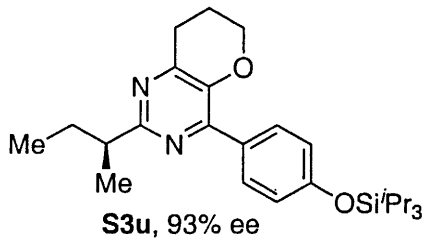
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
8 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



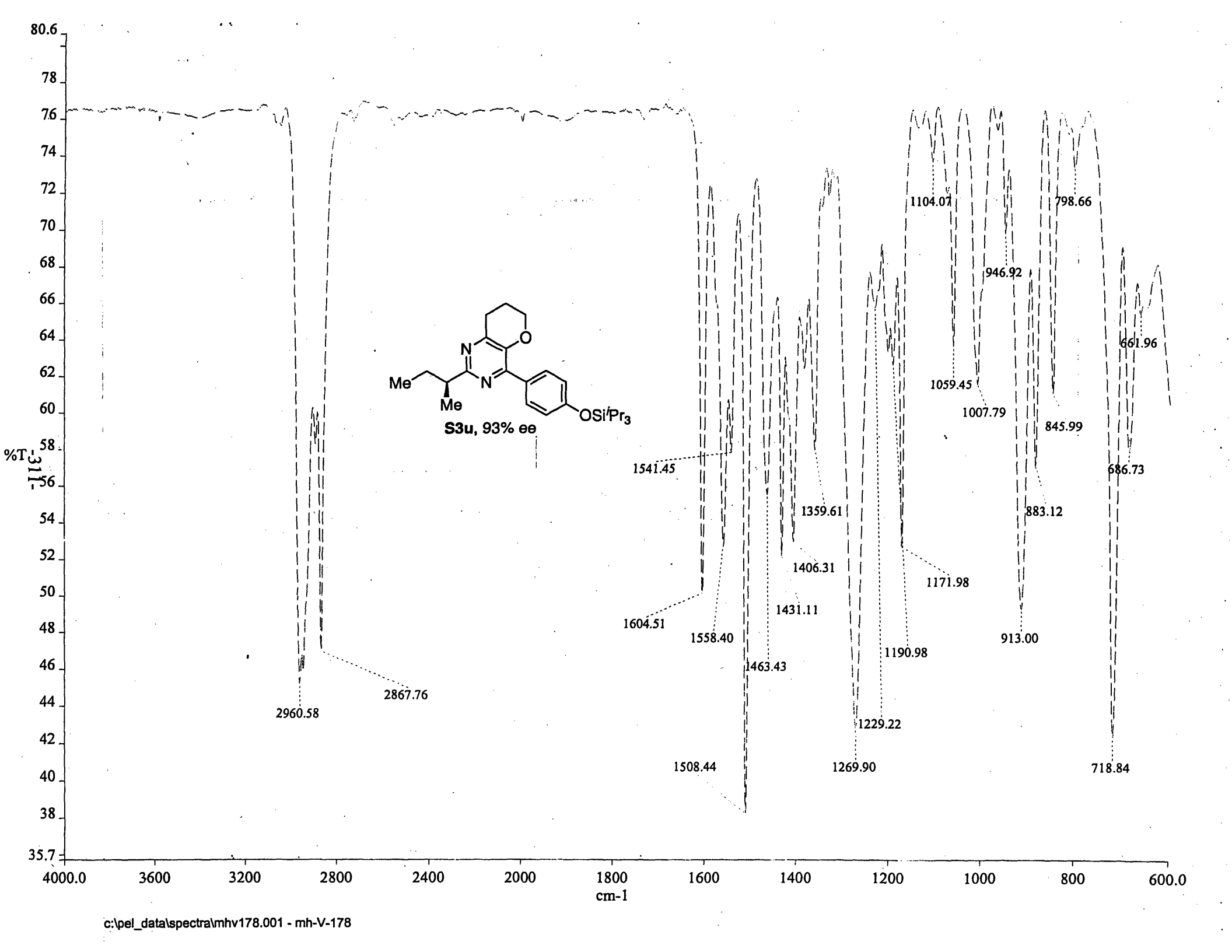
S3u, 93% ee

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

Relax. delay 0.500 sec
Pulse 36.7 degrees
Acq. time 2.001 sec
Width 31397.2 Hz
64 repetitions
OBSERVE C13, 125.6608709 MHz
DECOUPLE H1, 499.7471509 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 69713 hr, 39 min, 44 sec



S3u, 93% ee


80.6
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
35.7
%T
-311-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600.0
cm-1
Me
Me
N
N
O
OSi^{i}Pr$_3$
S3u, 93% ee
2960.58
2867.76
1541.45
1604.51
1558.40
1508.44
1463.43
1431.11
1406.31
1359.61
1269.90
1229.22
1190.98
1171.98
1104.07
1059.45
1007.79
946.92
913.00
883.12
845.99
798.66
718.84
686.73
661.96
c:\pel_data\spectra\mhv178.001 - mh-V-178

Data File C:\HPCHEM\2\DATA\MHV169.D

```
==========================================================================
Injection Date  : 9/2/2006 12:22:20 PM          Seq. Line :   1
Sample Name     : mh-V-169                      Location : Vial 31
Acq. Operator   : Mike                             Inj :   1
                                              Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\MATT.M
Last changed    : 9/2/2006 12:21:32 PM by Mike
Analysis Method : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 4/22/2008 7:21:35 PM
                  (modified after loading)
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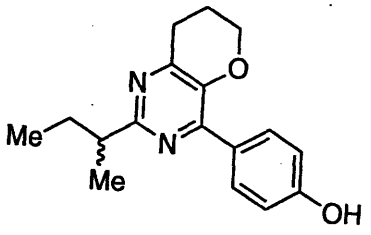
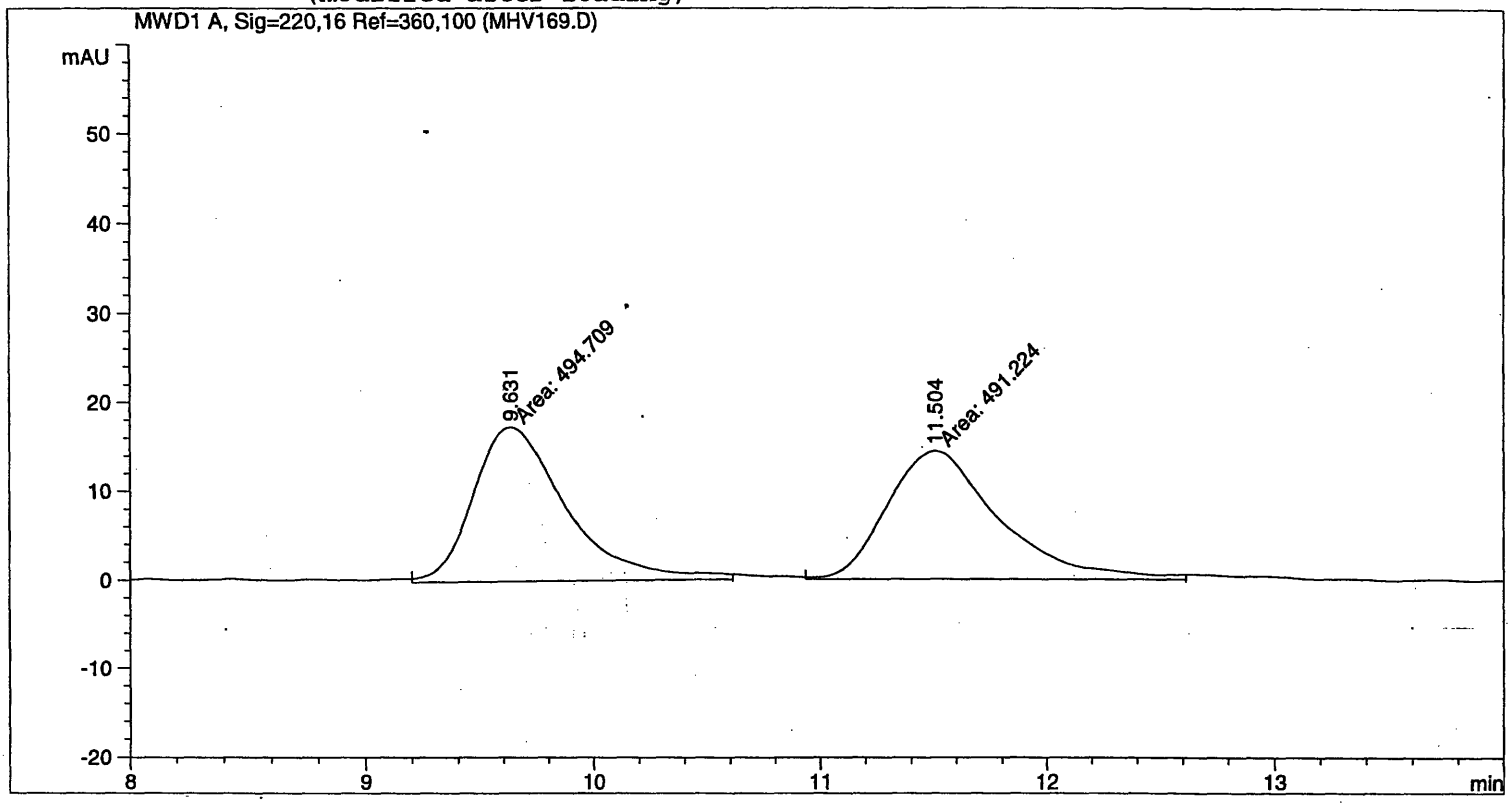


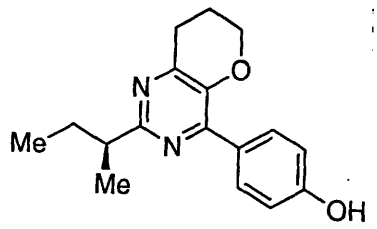


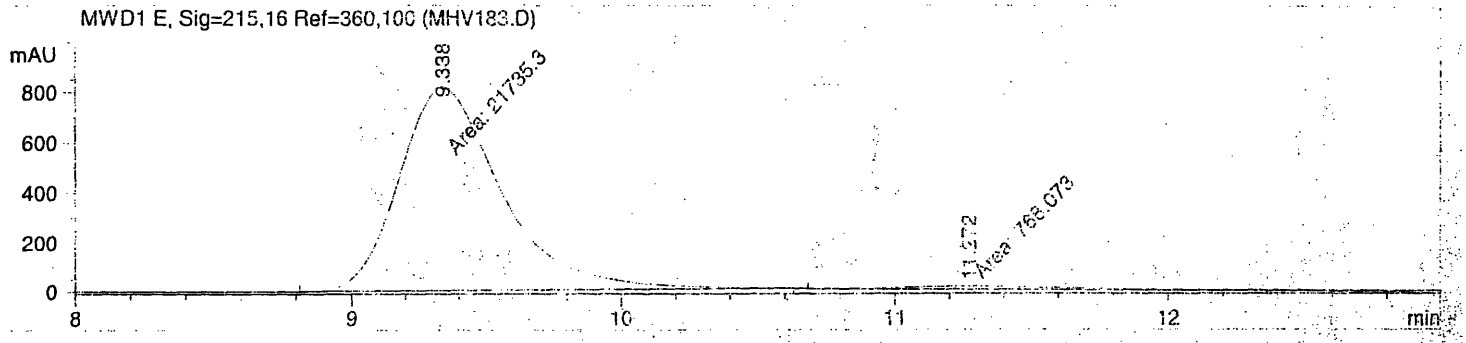

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.631 MM    0.4759  494.70941   17.32536  50.1768
   2  11.504 MM    0.5678  491.22406   14.41904  49.8232

Totals :                   985.93347   31.74440

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Data File C:\HPCHEM\2\DATA\MHV183.D Sample Name: mh-V-183

Injection Date : 8/26/2006 10:53:00 AM Seq. Line : 1
Sample Name : mh-V-183 Location : Vial 81
Acq. Operator : Mike Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\2\METHODS\MATT.M
Last changed : 8/26/2006 10:53:06 AM by Mike
(modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\D3087.M
Last changed : 8/26/2006 12:29:41 PM by Mike
(modified after loading)
Chiralcel OD 99% hex 1% ipa @ 0.5 ml/min





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.338	MM	0.4492	1.89426e4	702.87756	96.6300
2	11.265	MM	0.8626	660.62506	12.76349	3.3700
Totals :				1.96032e4	715.64105	

Results obtained with enhanced integrator!

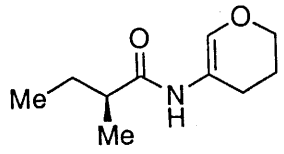
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.338	MM	0.4525	1.48901e4	548.49164	96.4967
2	11.272	MM	0.9096	540.58459	9.90517	3.5033
Totals :				1.54307e4	558.39680	

Results obtained with enhanced integrator!

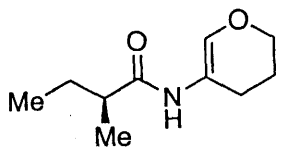
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-V-151
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
2 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



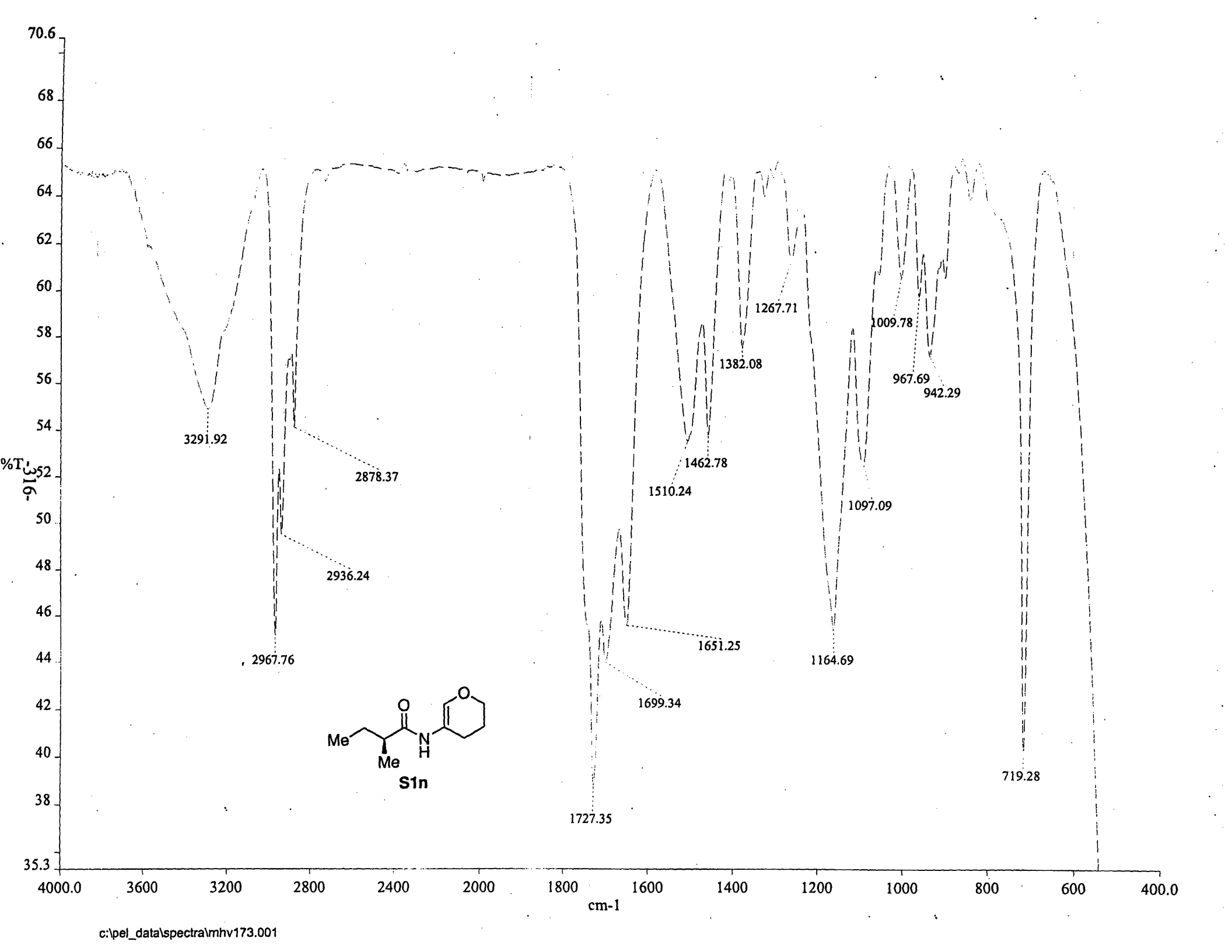
S1n

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
8 repetitions
OBSERVE C13, 125.7832337 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

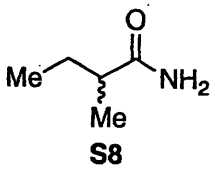


S1n


70.6
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
35.3
%T
3291.92
2967.76
2878.37
2936.24
1727.35
1699.34
1651.25
1510.24
1462.78
1382.08
1267.71
1164.69
1097.09
1009.78
967.69
942.29
719.28
Me
Me
N
H
O
O
S1n
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
c:\pel_data\spectra\mhv173.001

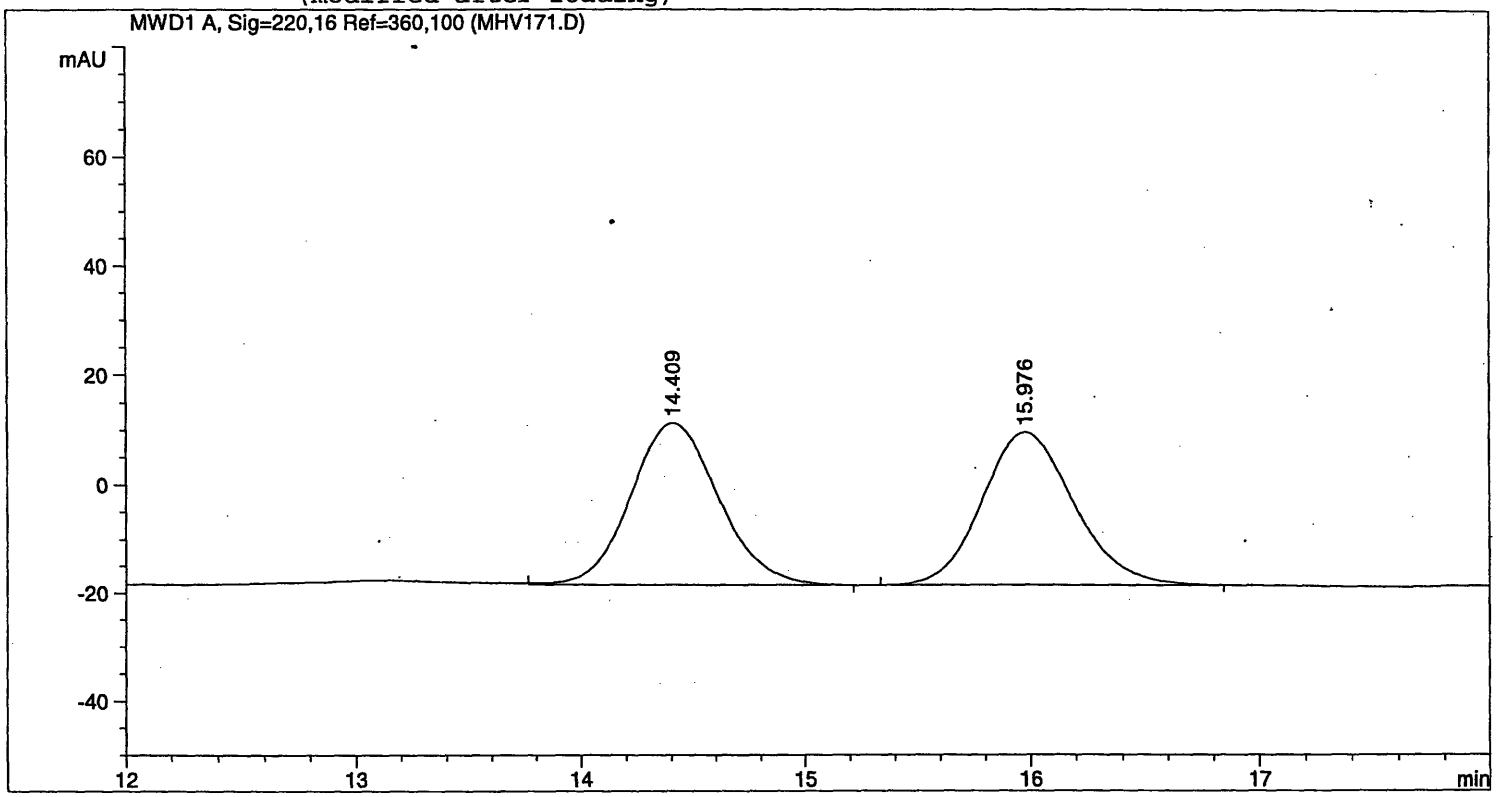
Data File C:\HPCHEM\2\DATA\MHV171.D

Racemis; Chiralcel OD 99% hex 1% IPA 0.5ml/min



S8

Injection Date	: 8/22/2006 10:50:07 AM	Seq. Line	: 1
Sample Name	: mh-v-171	Location	: Vial 52
Acq. Operator	: Mike	Inj	: 1
		Inj Volume	: 1 µl
Acq. Method	: C:\HPCHEM\2\METHODS\D3087.M		
Last changed	: 8/22/2006 10:50:23 AM by Mike (modified after loading)		
Analysis Method	: C:\HPCHEM\2\METHODS\DIAST1.M		
Last changed	: 4/22/2008 7:33:19 PM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

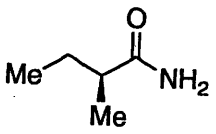
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.409	VP	0.4294	817.90497	29.87720	50.6648
2	15.976	BB	0.4386	796.44165	28.27765	49.3352
Totals :				1614.34662	58.15485	

Results obtained with enhanced integrator!

*** End of Report ***

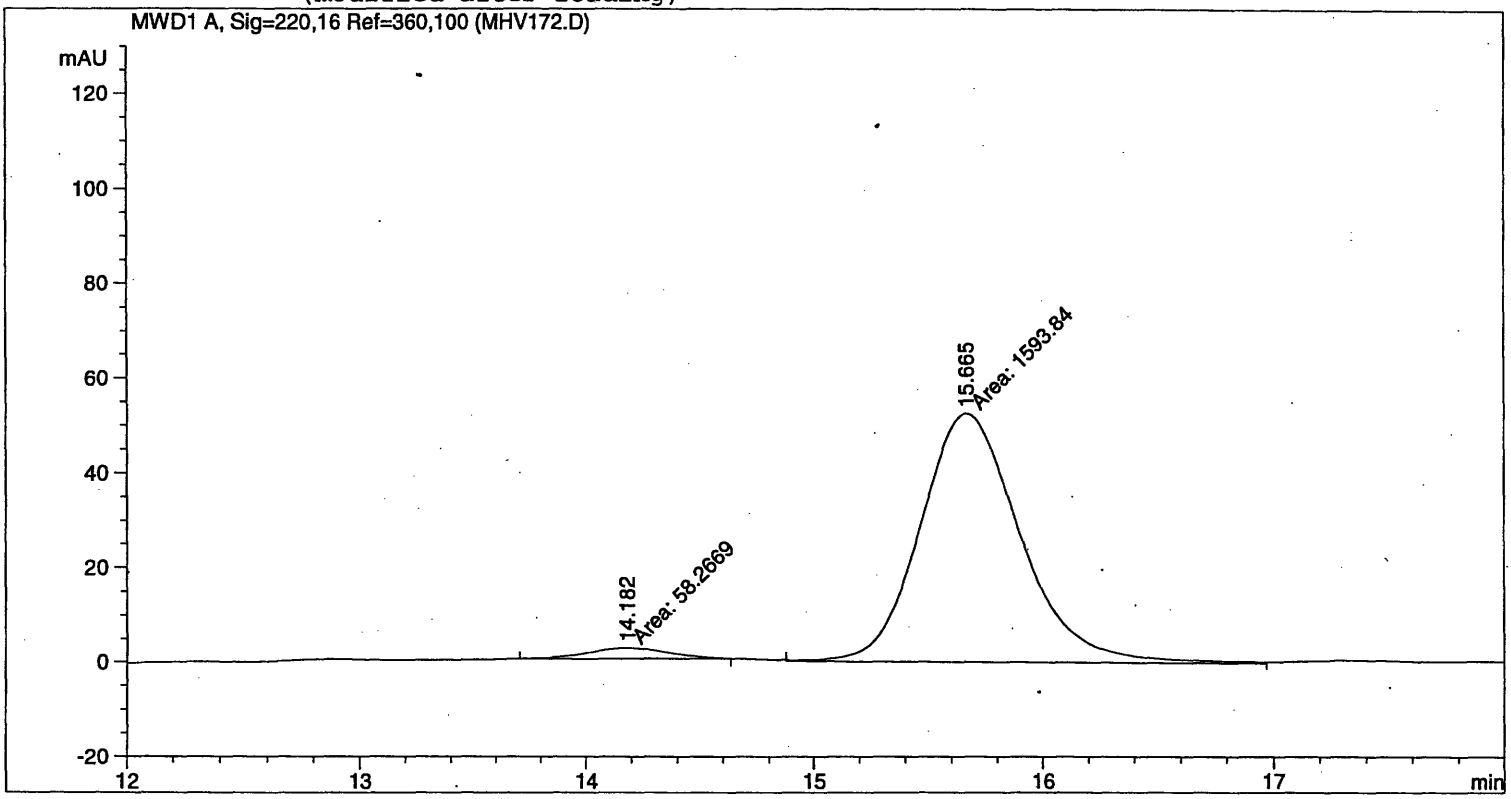
Data File C:\HPCHEM\2\DATA\MHV172.D

Racemis; Chiralcel OD 99% hex 1% IPA 0.5ml/min



S8, 93% ee

Injection Date	: 8/22/2006 11:58:22 AM	Seq. Line	: 1
Sample Name	: mh-v-172	Location	: Vial 51
Acq. Operator	: Mike	Inj	: 1
		Inj Volume	: 1 µl
Acq. Method	: C:\HPCHEM\2\METHODS\D3087.M		
Last changed	: 8/22/2006 11:57:39 AM by Mike		
Analysis Method	: C:\HPCHEM\2\METHODS\DIAST1.M		
Last changed	: 4/22/2008 7:32:05 PM (modified after loading)		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.182	MM	0.4078	58.26693	2.38120	3.5268
2	15.665	MM	0.5067	1593.83594	52.42511	96.4732
Totals :				1652.10287	54.80631	

Results obtained with enhanced integrator!

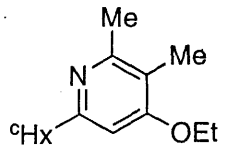
*** End of Report ***

Appendix C

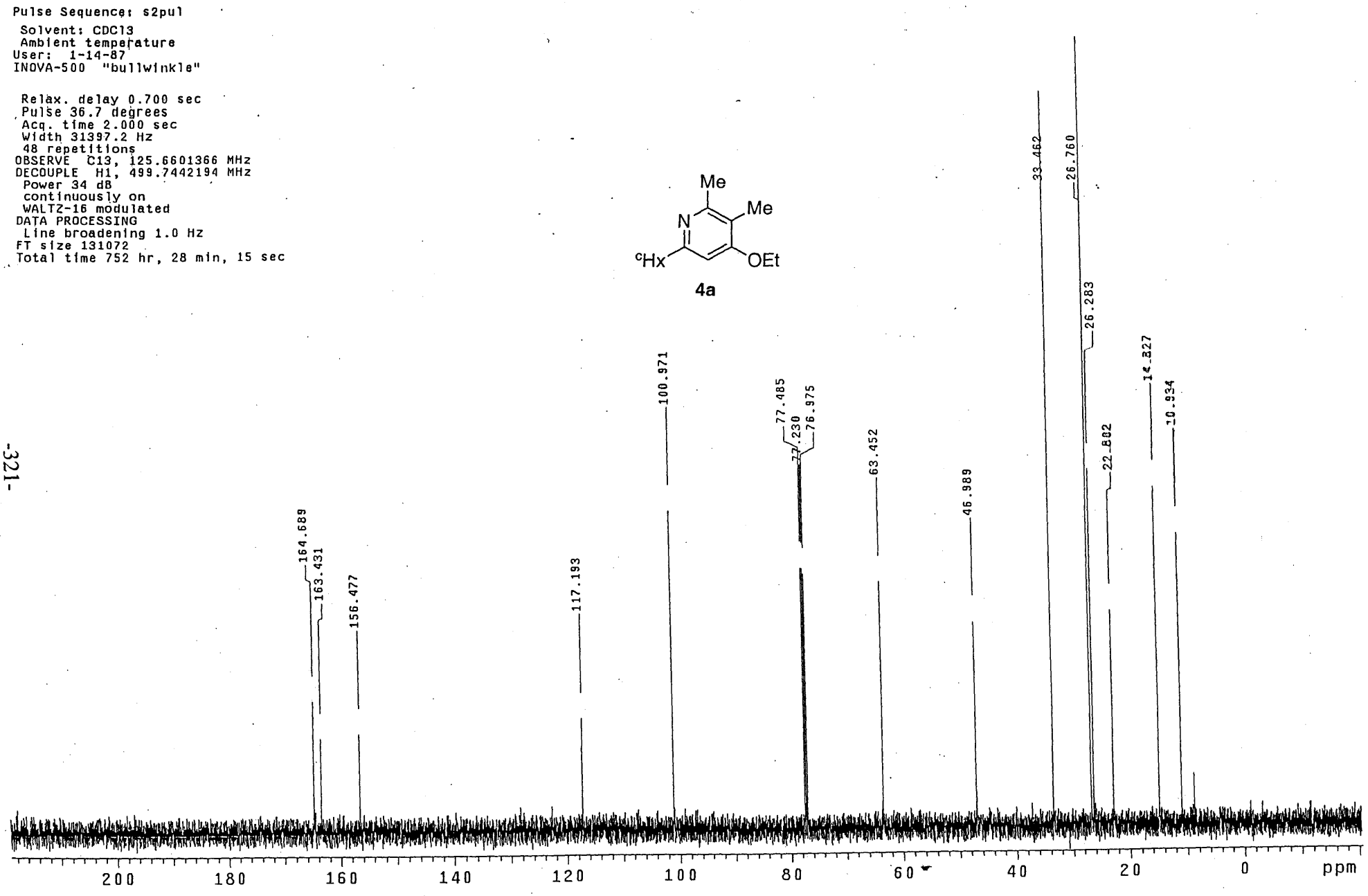
Spectra for Chapter III.

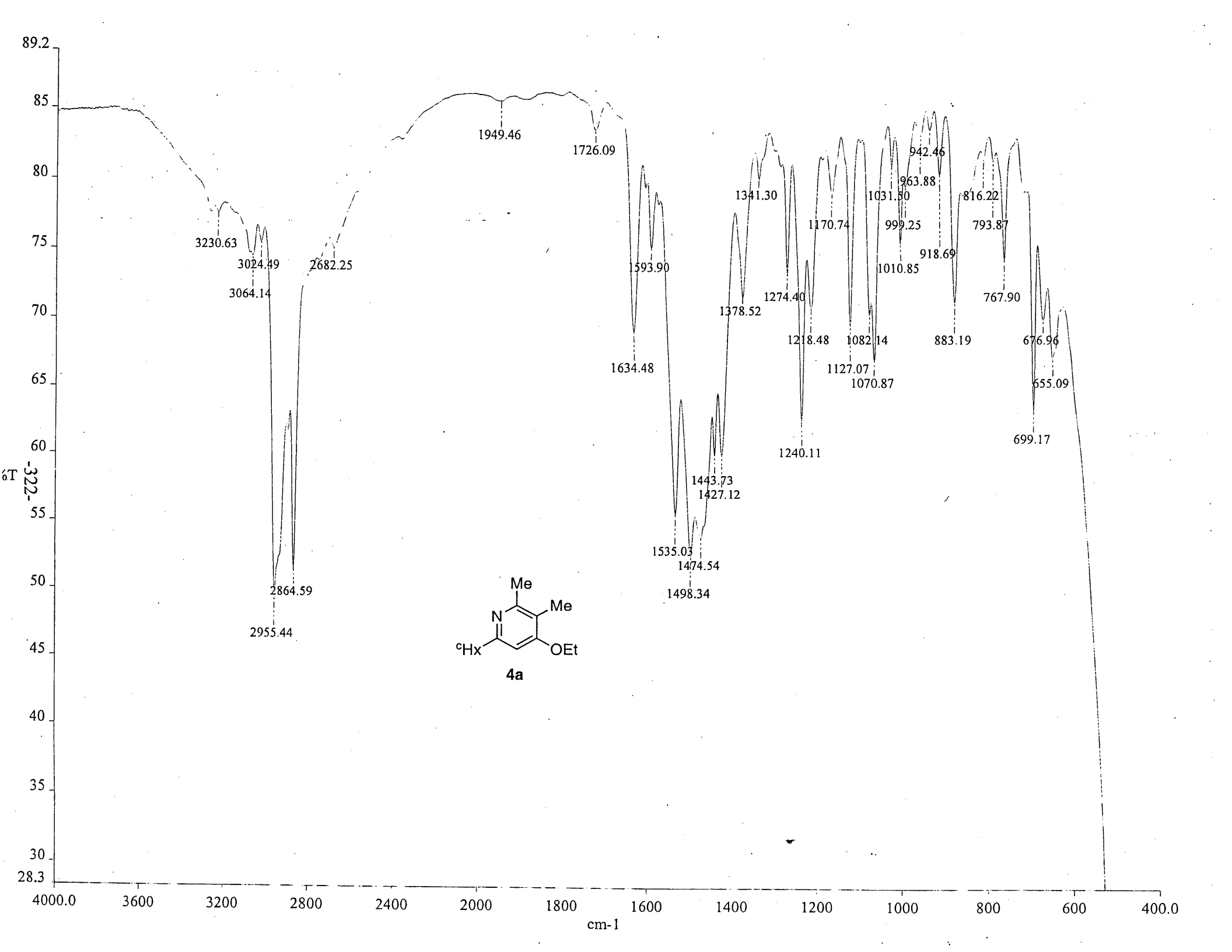
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

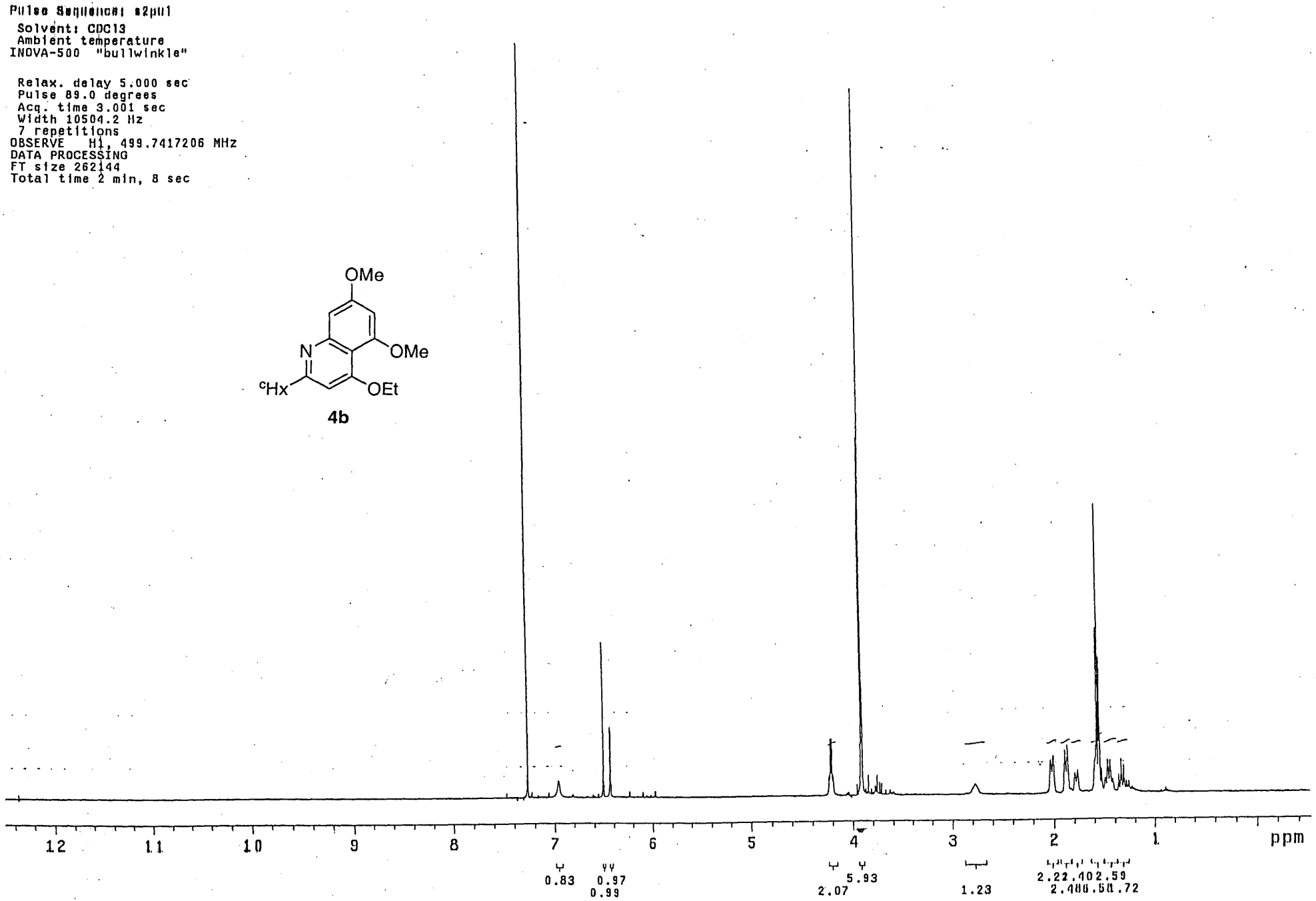
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

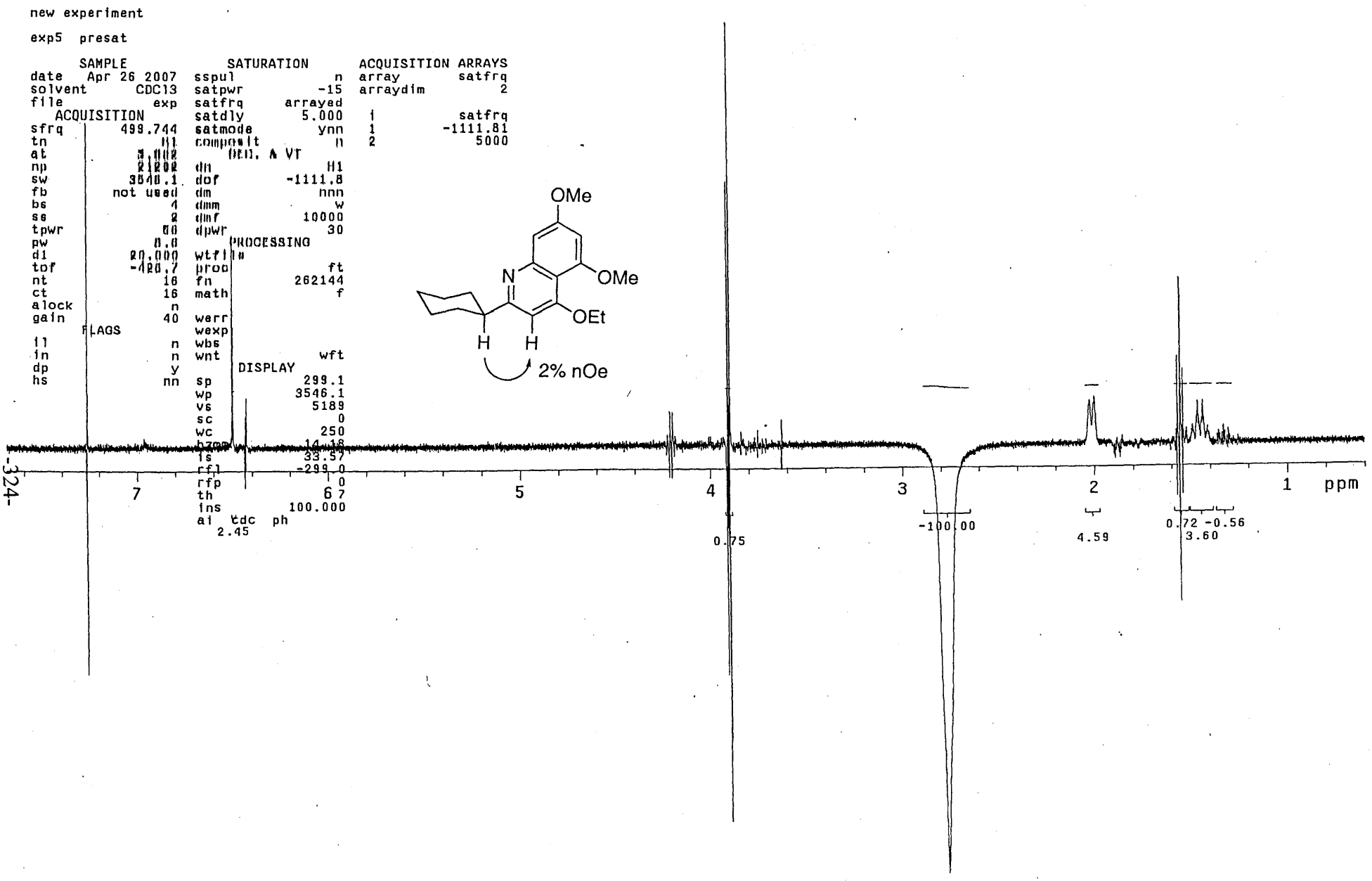


4a


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.700 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
48 repetitions
OBSERVE C13, 125.6601366 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 752 hr, 28 min, 15 sec
Me
Me
N
cHx
OEt
4a
164.689
163.431
156.477
117.193
100.971
77.485
77.230
76.975
63.452
46.989
33.462
26.760
26.283
22.882
14.827
10.934
200
180
160
140
120
100
80
60
40
20
0
ppm

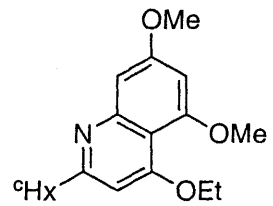

89.2
85
80
75
70
65
60
55
50
45
40
35
30
28.3
%T
-322-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
3230.63
3064.14
3024.49
2955.44
2864.59
2682.25
1949.46
1726.09
1634.48
1593.90
1535.03
1498.34
1474.54
1443.73
1427.12
1378.52
1341.30
1274.40
1240.11
1218.48
1170.74
1127.07
1082.14
1070.87
1031.50
1010.85
999.25
963.88
942.46
918.69
883.19
816.22
793.87
767.90
699.17
676.96
655.09
Me
Me
N
cHx
OEt
4a


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec
OMe
N
OMe
cHx
OEt
4b
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.83
0.97
0.99
2.07
5.93
1.23
2.22
2.40
2.59
2.48
0.50
1.72

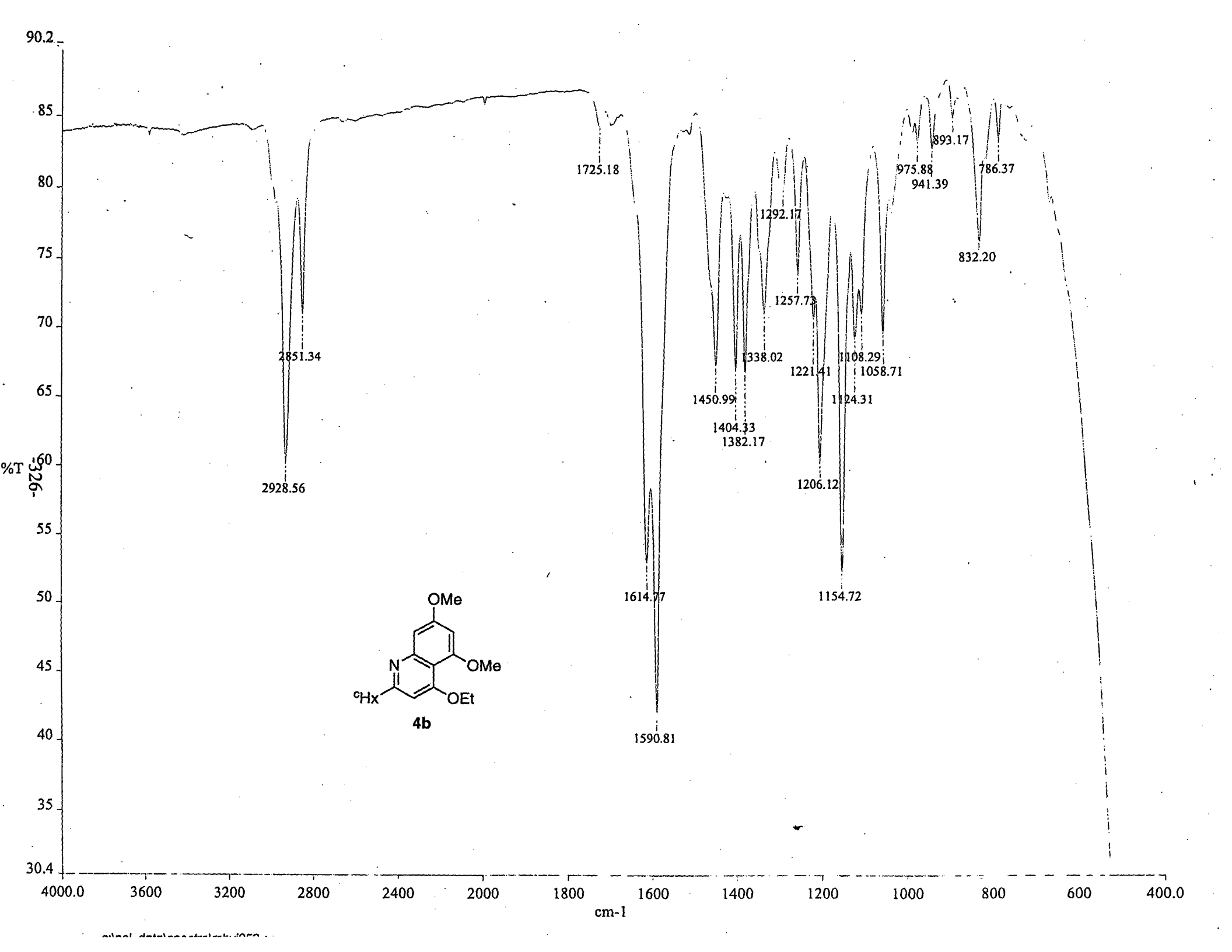

new experiment
exp5 presat
SAMPLE
date Apr 26 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 499.744
tn H1
at 3.002
np 21202
sw 3548.1
fb not used
bs 4
ss 2
tpwr 60
pw 8.0
d1 20.000
tof -420.7
nt 16
ct 16
alock n
gain 40
FLAGS
il n
in n
dp y
hs nn
SATURATION
sspul n
satpwr -15
satfrq arrayed
satdly 5.000
satmode ynn
compwit n
DEC. & VT
dn H1
dof -1111.8
dm nnn
dmm w
dmf 10000
dpwr 30
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
DISPLAY
sp 299.1
wp 3546.1
vs 5189
sc 0
wc 250
hzmm 14.18
is 33.57
rfl -299.0
rfp 0
th 67
ins 100.000
ai tdc ph
2.45
ACQUISITION ARRAYS
array satfrq
arraydim 2
i satfrq
1 -1111.81
2 5000
OMe
OMe
N
OEt
H H
2% nOe
7
6
5
4
3
2
1
ppm
0.75
-100.00
4.59
0.72 -0.56
3.60

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

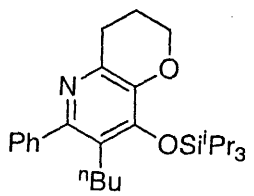
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
616 repetitions
OBSERVE C13, 125.7832297 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 69 minutes



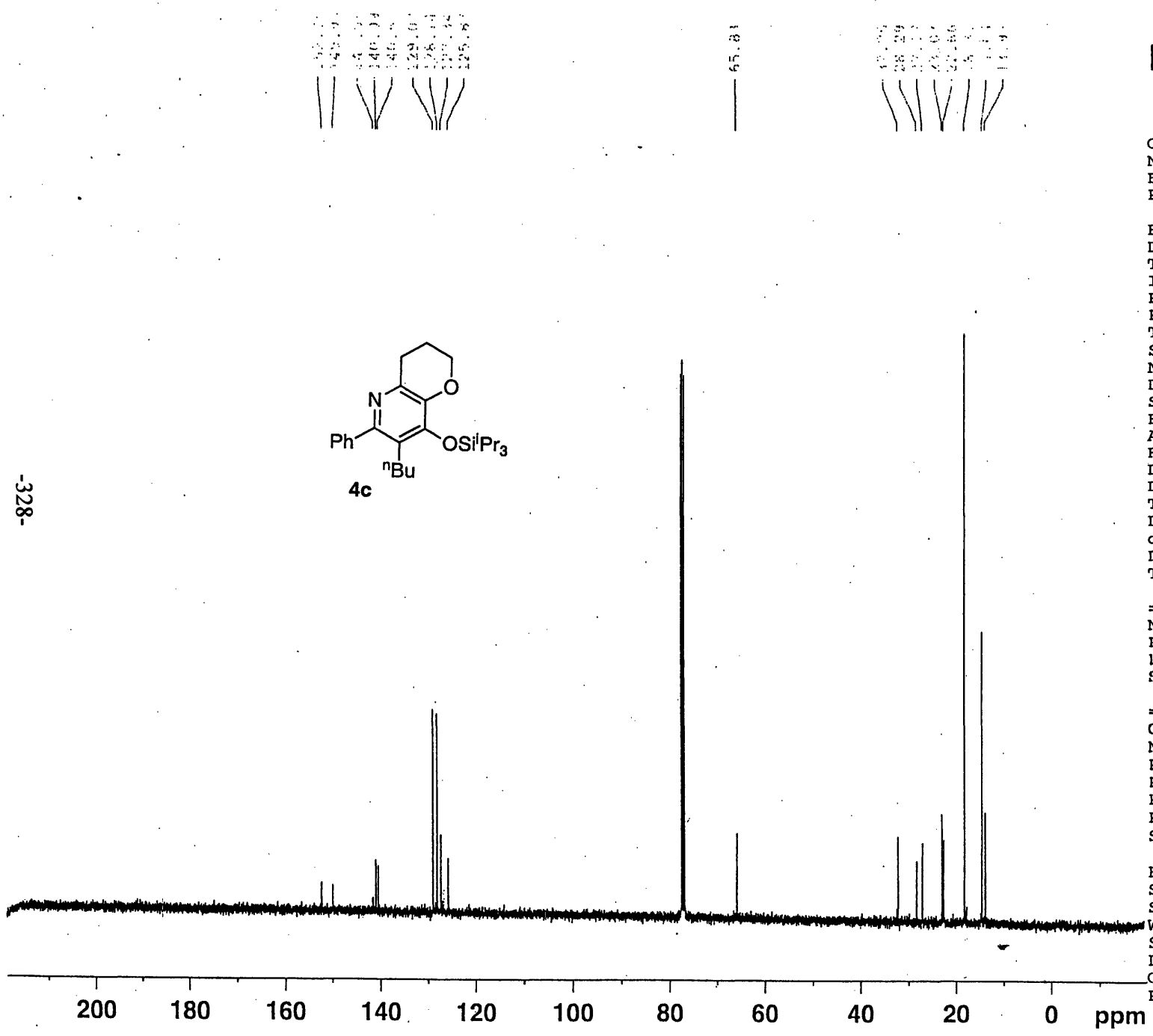
4b


90.2
85
80
75
70
65
60
55
50
45
40
35
30.4
%T
-326-
2928.56
2851.34
1725.18
1614.77
1590.81
1450.99
1404.33
1382.17
1338.02
1292.17
1257.73
1221.41
1206.12
1154.72
1124.31
1108.29
1058.71
975.88
941.39
893.17
832.20
786.37
OMe
OMe
N
cHx
OEt
4b
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-VI-212
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



4c



BRUKER

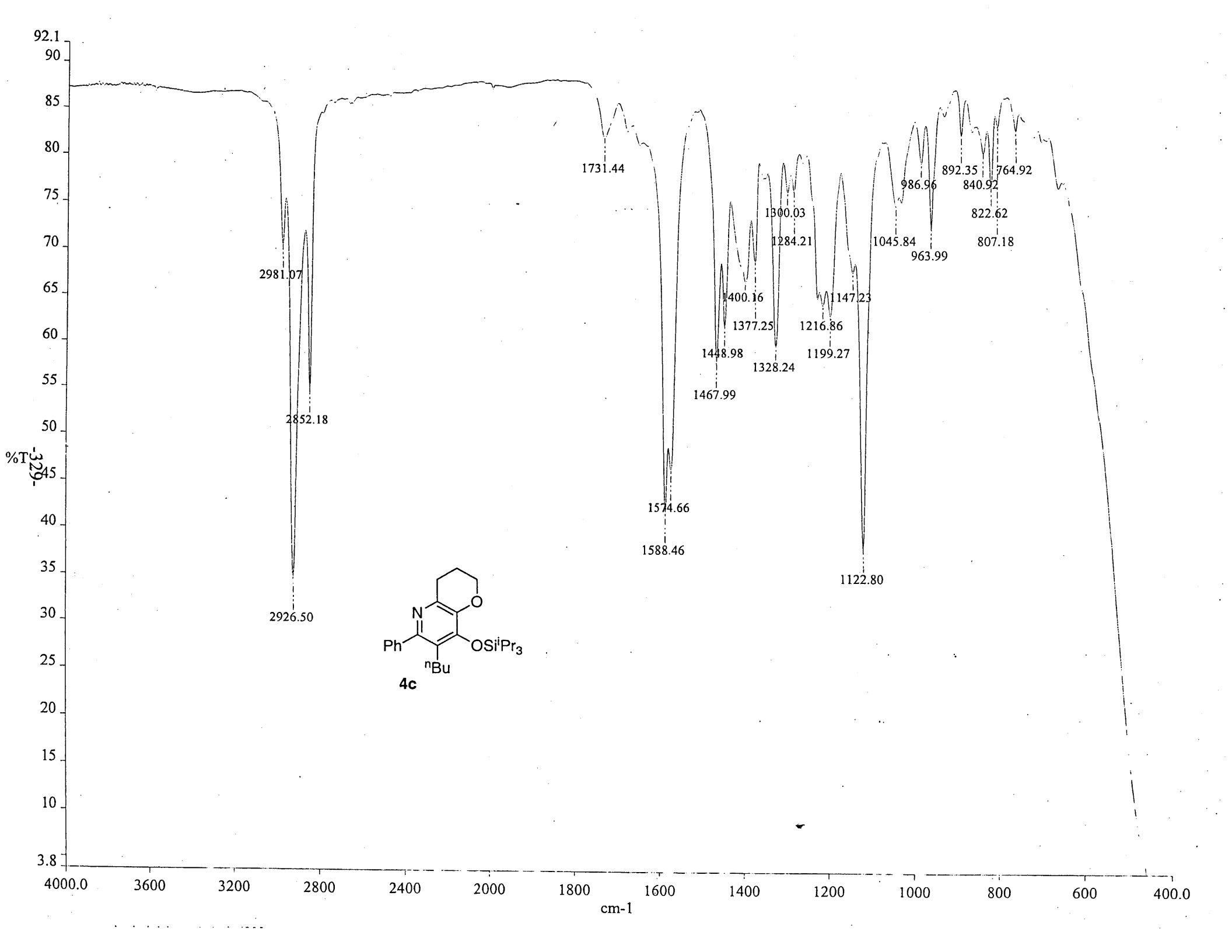
Current Data Parameters
NAME MH-VI-251
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070418
Time 18.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 667
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2580.3
DW 20.850 usec
DE 6.00 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.38 usec
PL1 0.00 dB
SFO1 100.6228298 MHz

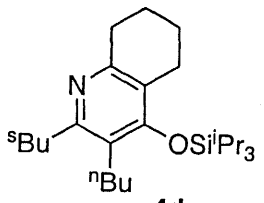
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.10 dB
PL13 19.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 100.6127535 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


92.1
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
3.8
%T
-329-
2981.07
2852.18
2926.50
1731.44
1574.66
1588.46
1467.99
1448.98
1400.16
1377.25
1328.24
1300.03
1284.21
1216.86
1199.27
1147.23
1122.80
1045.84
986.96
963.99
892.35
840.92
822.62
807.18
764.92
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
Ph
N
O
OSi^{i}Pr$_3$
^{n}Bu
4c

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

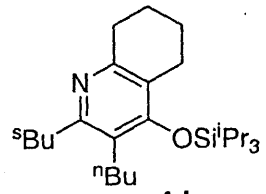
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



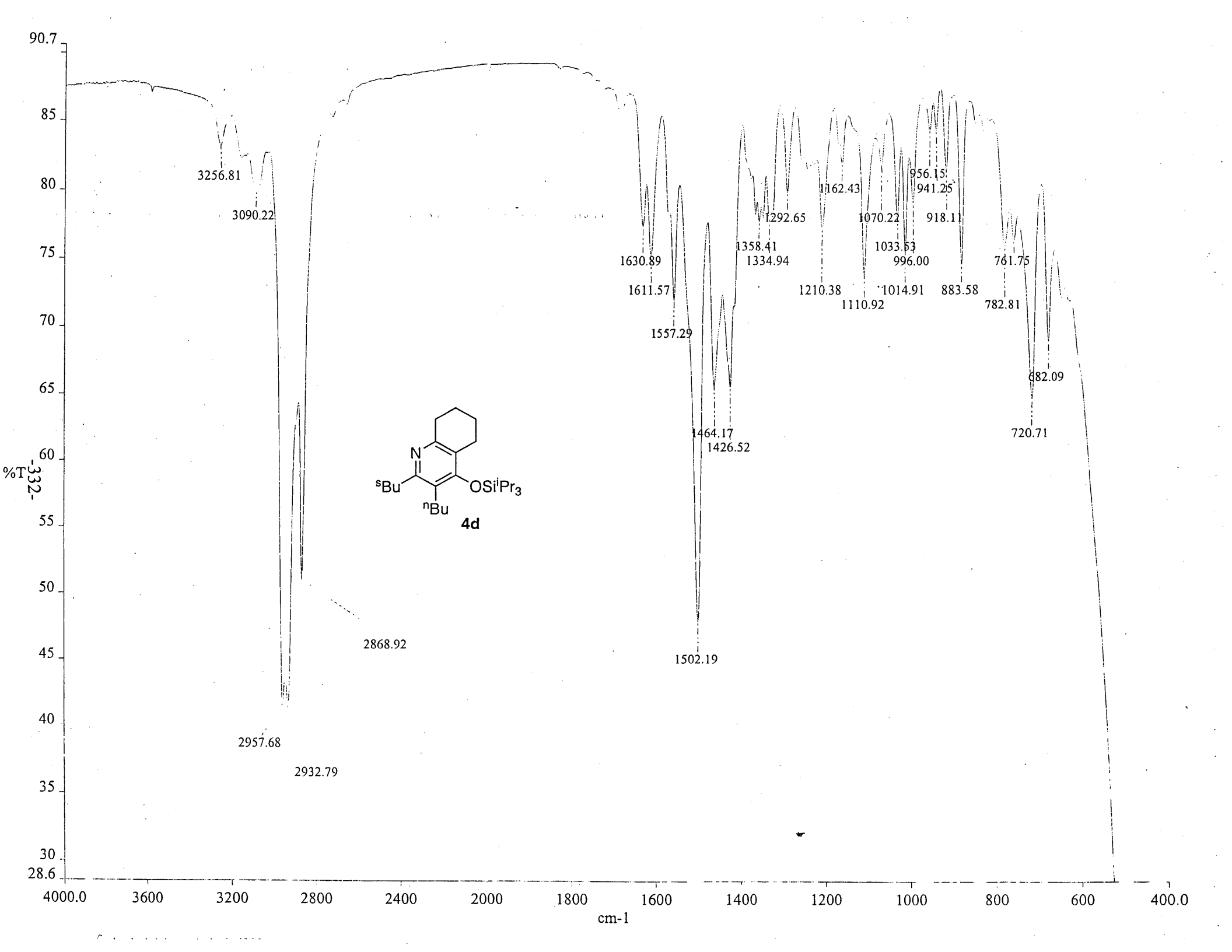
4d

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

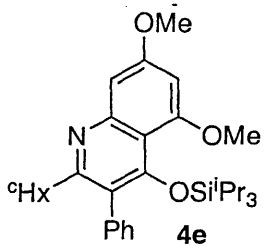
PULSE SEQUENCE
Relax. delay 0.750 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
320 repetitions
OBSERVE C13, 125.7832274 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 13 minutes



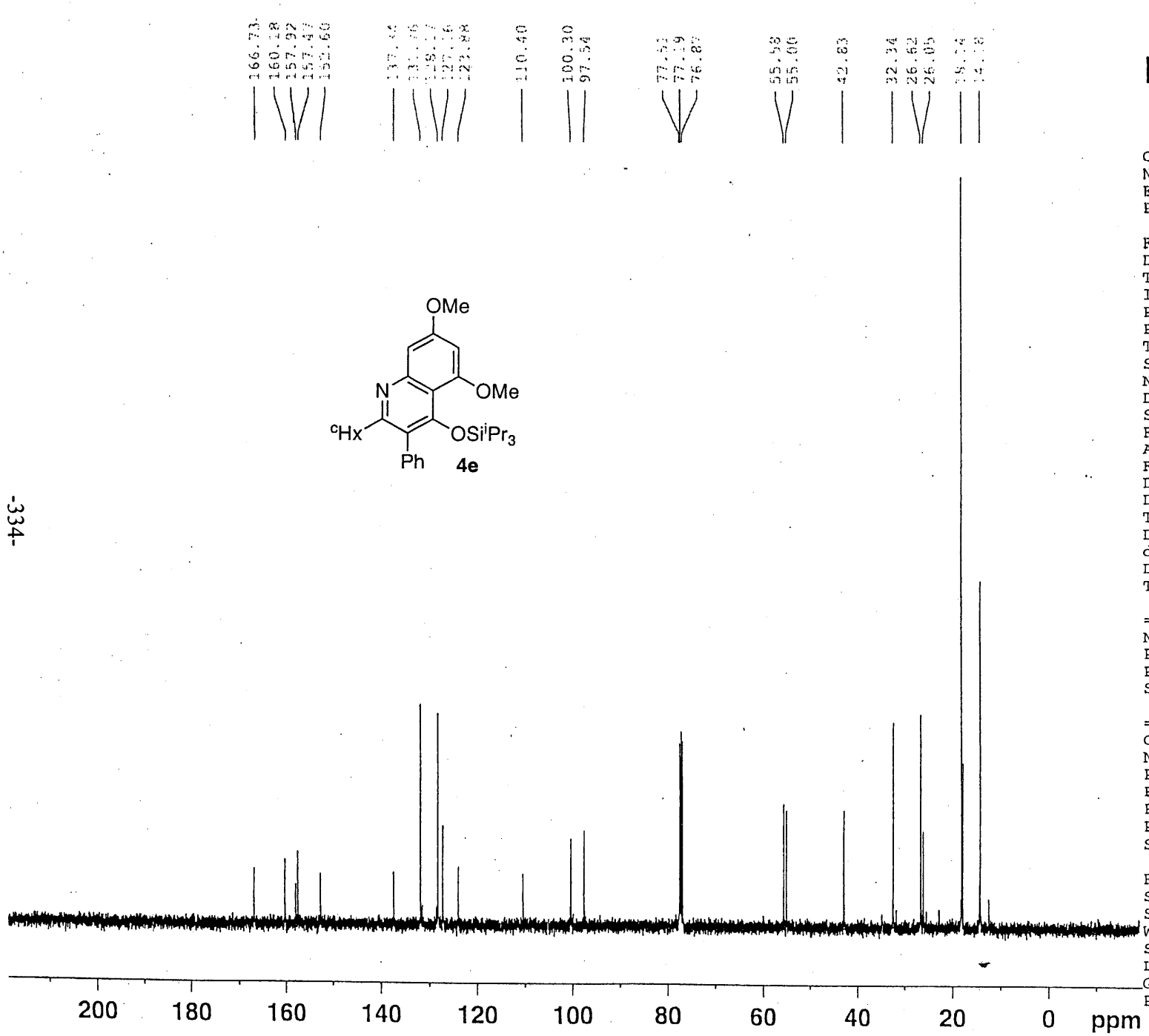
4d


90.7
85
80
75
70
65
60
55
50
45
40
35
30
28.6
%T
-332-
3256.81
3090.22
2957.68
2932.79
2868.92
1630.89
1611.57
1557.29
1502.19
1464.17
1426.52
1358.41
1334.94
1292.65
1210.38
1162.43
1110.92
1070.22
1033.53
1014.91
996.00
956.15
941.25
918.11
883.58
782.81
761.75
720.71
682.09
N
sBu
nBu
OSiiPr3
4d
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-VI-55fr7-18
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
8 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



4e



BRUKER

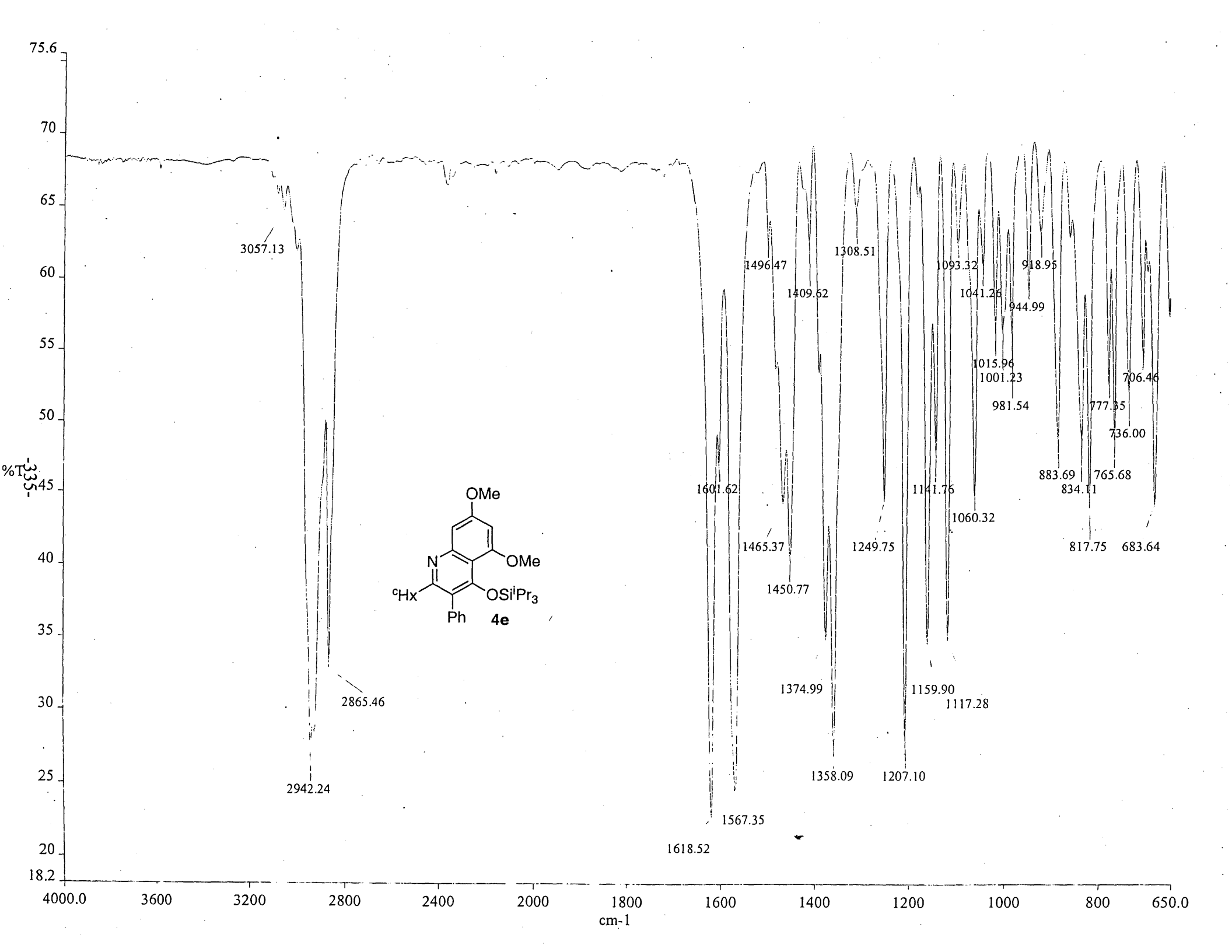
Current Data Parameters
NAME MH-VI-256
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070421
Time 17.13
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 88
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

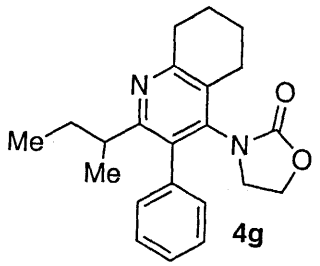
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 14.52 dB
PL13 18.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 100.6127583 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


75.6
70
65
60
55
50
45
40
35
30
25
20
18.2
%T
-335-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650.0
cm-1
3057.13
2942.24
2865.46
1618.52
1601.62
1567.35
1496.47
1465.37
1450.77
1409.62
1374.99
1358.09
1308.51
1249.75
1207.10
1159.90
1141.76
1117.28
1093.32
1060.32
1041.26
1015.96
1001.23
981.54
944.99
918.95
883.69
834.11
817.75
777.35
765.68
736.00
706.46
683.64
OMe
OMe
N
cHx
OSiiPr3
Ph
4e

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
10 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

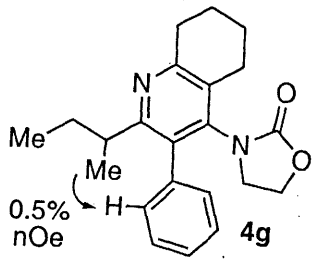


4g

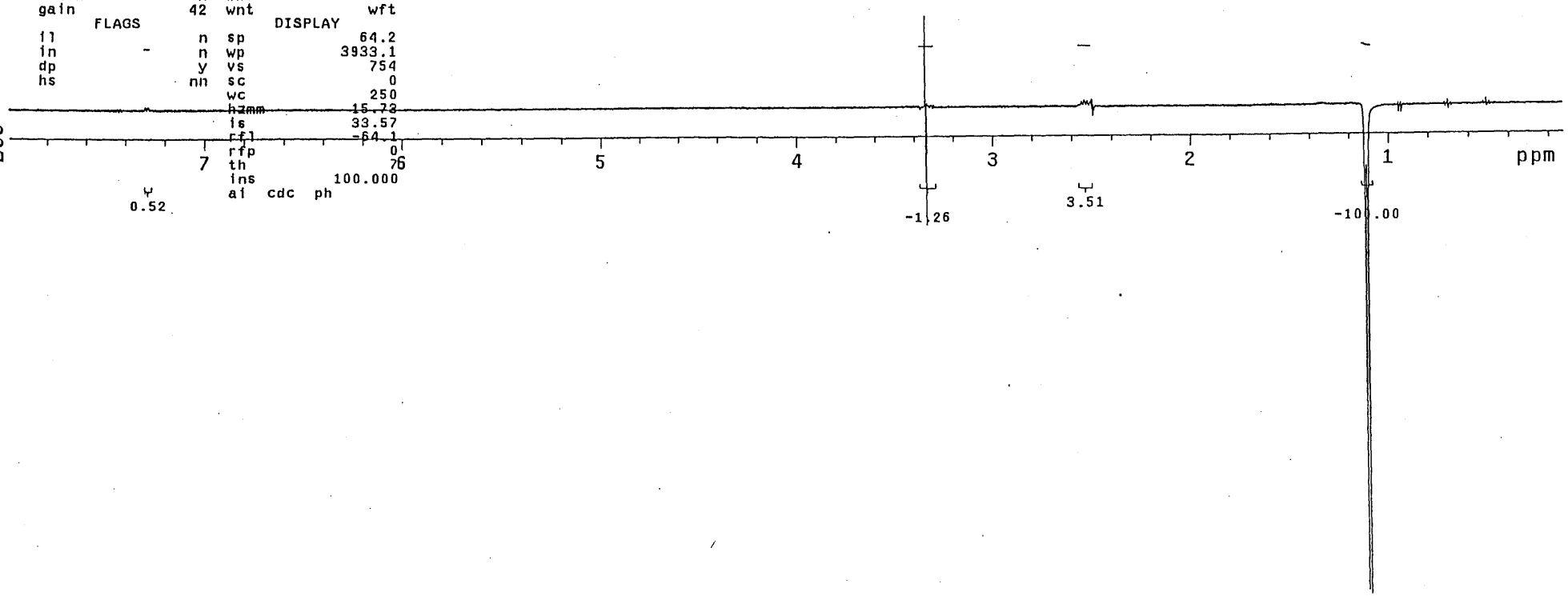
new experiment

exp5 presat

SAMPLE		SATURATION		ACQUISITION ARRAYS	
date	Apr 24 2007	sspul	n	array	satfrq
solvent	DMSO	satpwr	-16	arraydim	2
file	/data/export/~	satfrq	arrayed		
home/movassag/Mmh/~		satdly	5.000	i	satfrq
bullwinkle/mh-VI-2~		satmode	ynn	1	-1942.6
	13noe4.fid	composit	n	2	5000
ACQUISITION		DEC. & VT			
sfrq	499.746	dn	H1		
tn	H1	dof	-1942.6		
at	3.002	dm	nnn		
np	23012	dmm	w		
sw	4789.1	dmf	10000		
fb	not used	dpwr	30		
bs	4	PROCESSING			
ss	2	wtfile			
tpwr	50	proc	ft		
pw	8.8	fn	262144		
d1	20.000	math	f		
tof	-400.1				
nt	16	werr			
ct	16	wexp			
alock	n	wbs			
gain	42	wnt	wft		
FLAGS		DISPLAY			
fl	n	sp	64.2		
in	- n	wp	3933.1		
dp	y	vs	754		
hs	nn	sc	0		
		wc	250		
		hzmm	15.73		
		is	33.57		
		rfl	-64.1		
		rfp	0		
		th	76		
		ins	100.000		
		ai cdc ph			



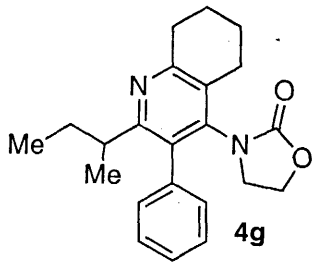
4g



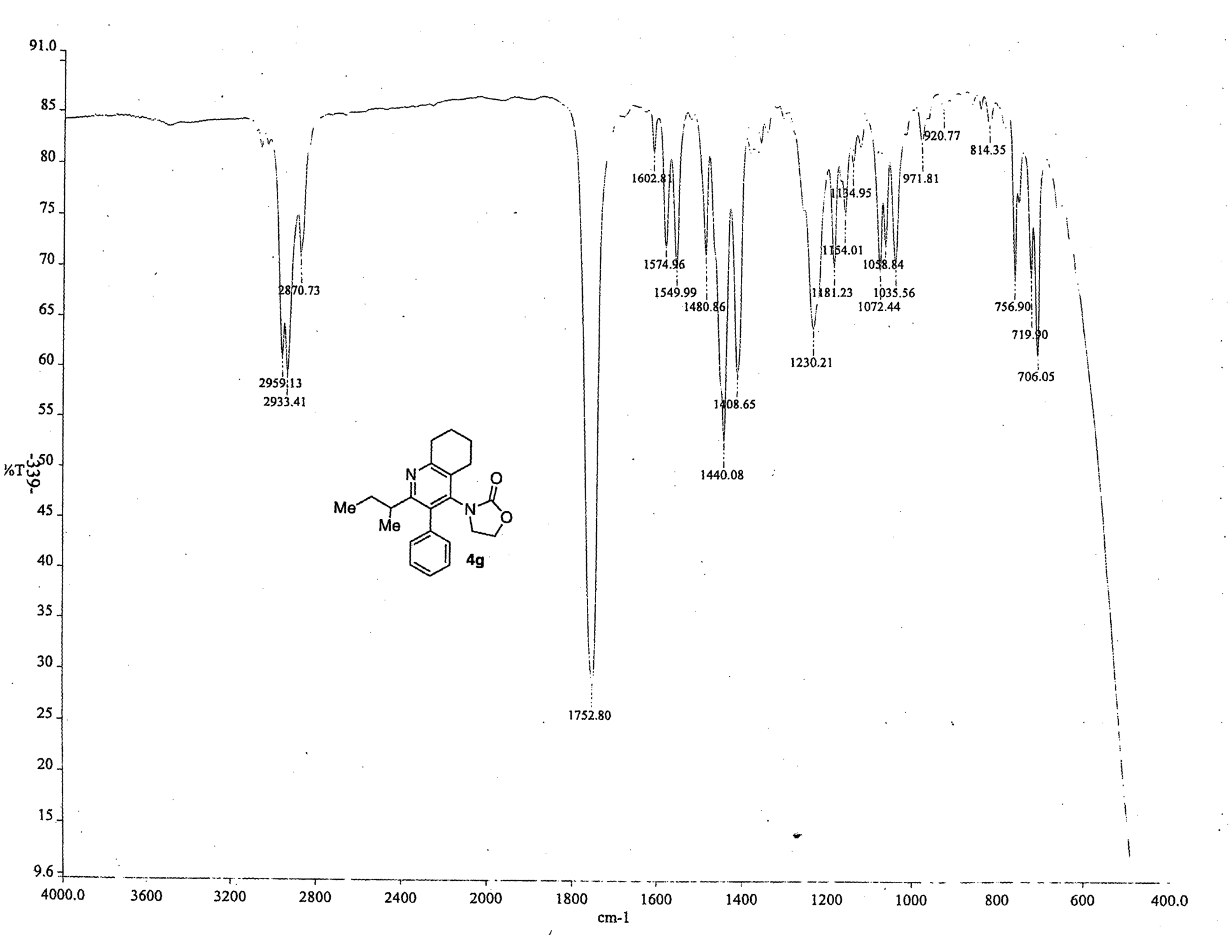
mh-VI-196

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

Relax. delay 3.000 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
96 repetitions
OBSERVE C13, 125.6601386 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 13913 hr, 35 min, 56 sec

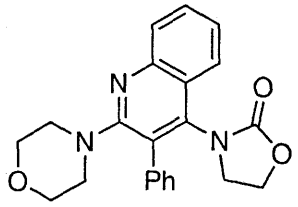


4g

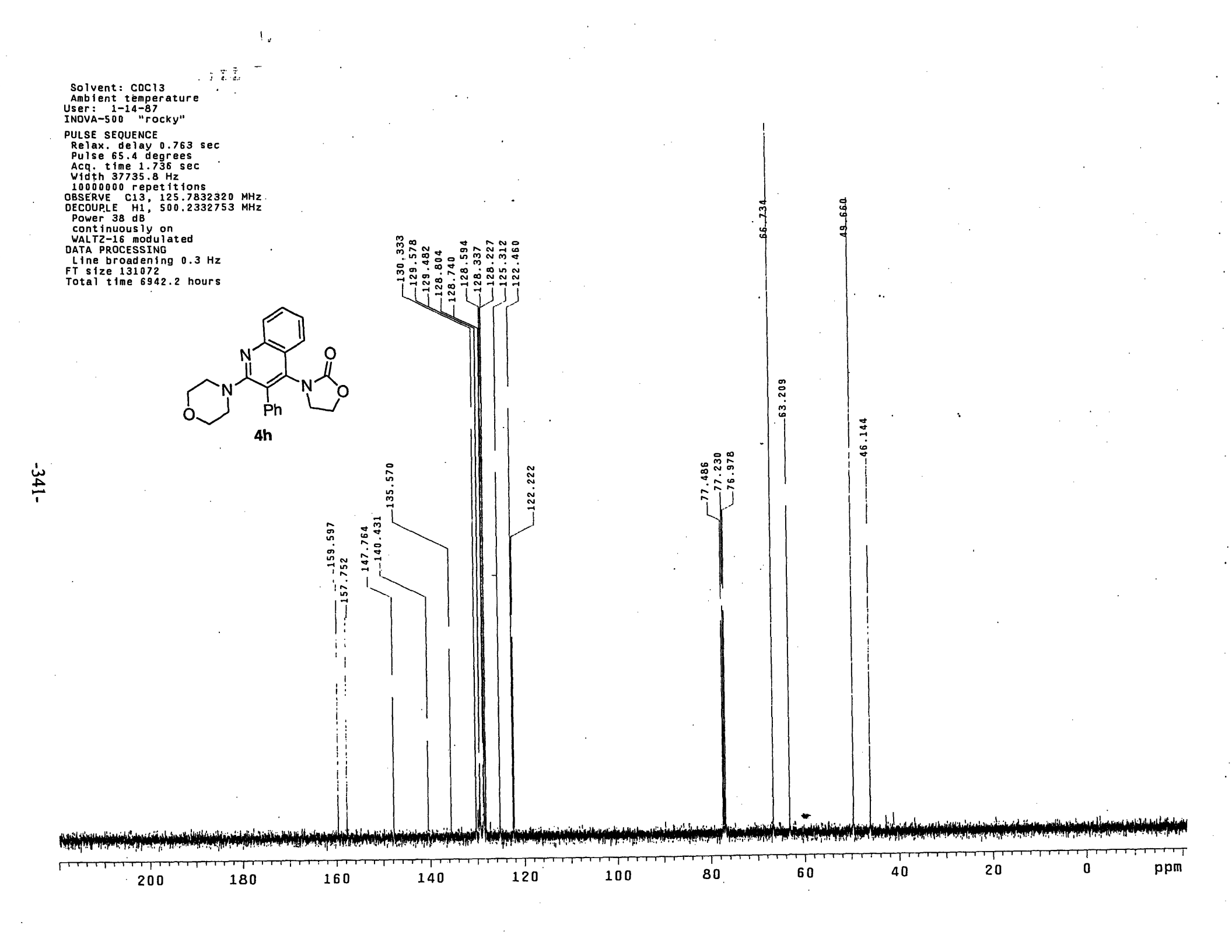

91.0
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
9.6
%T
-339-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
2959.13
2933.41
2870.73
1752.80
1602.81
1574.96
1549.99
1480.86
1440.08
1408.65
1230.21
1181.23
1154.01
1154.95
1072.44
1058.84
1035.56
971.81
920.77
814.35
756.90
719.90
706.05
Me
Me
N
O
N
O
4g

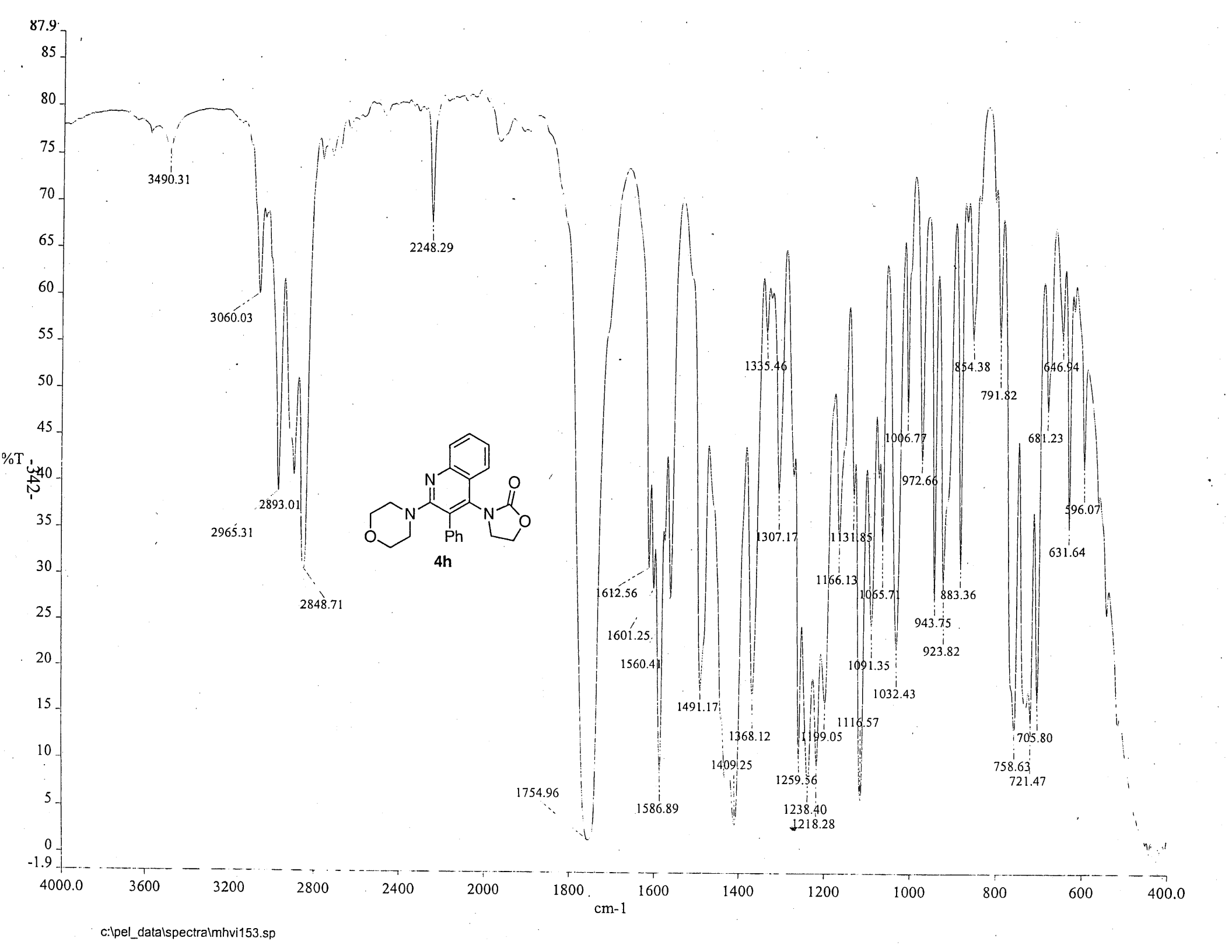
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

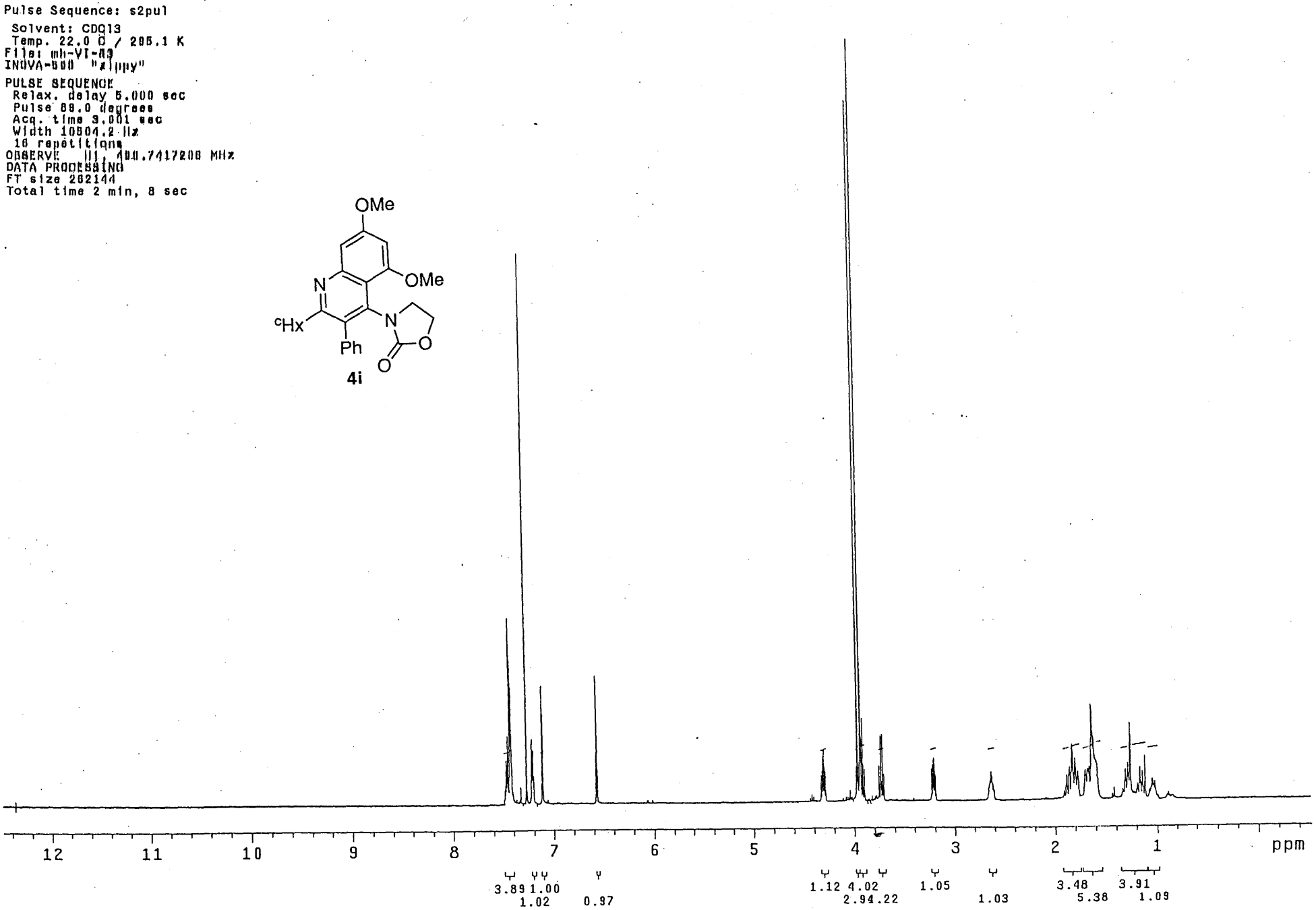
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
10 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec

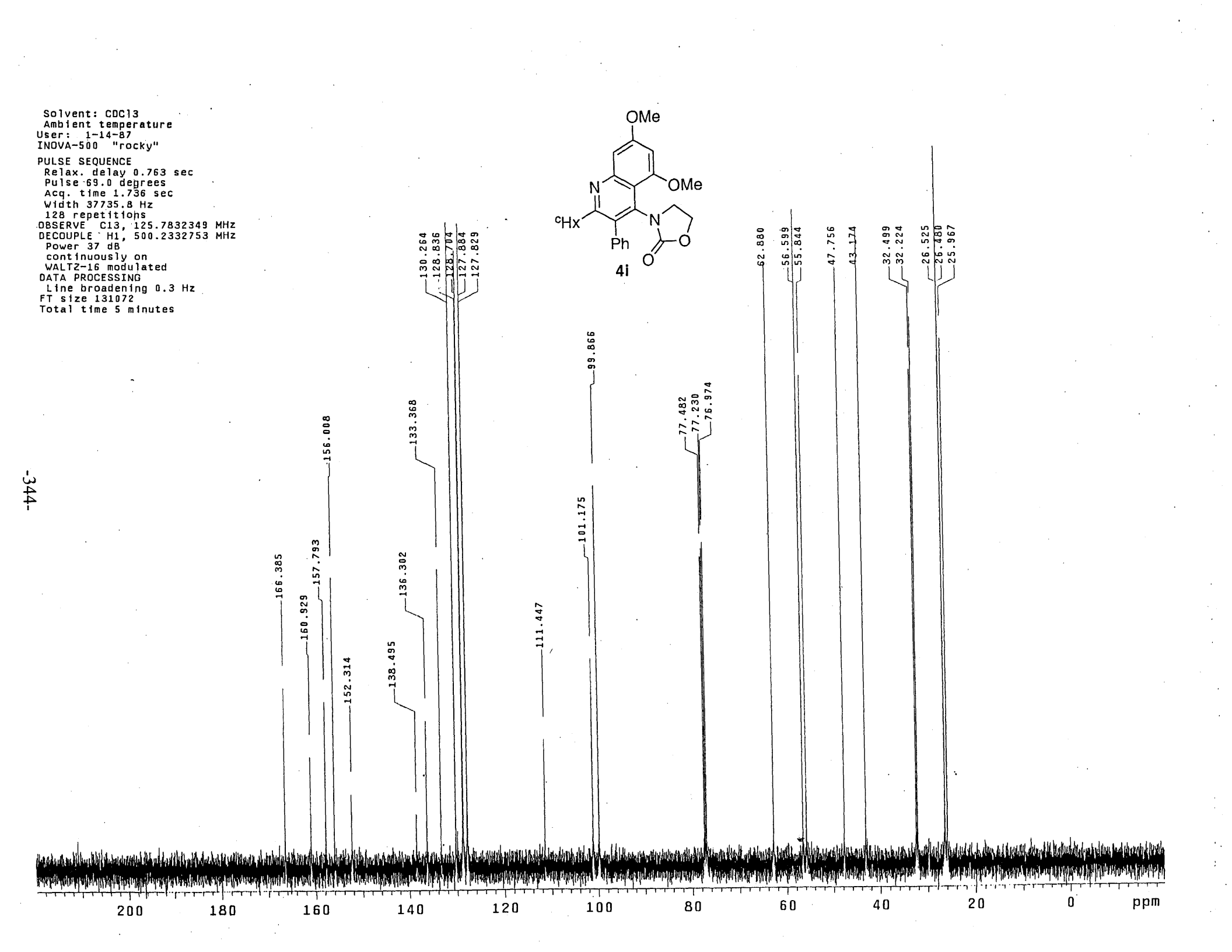


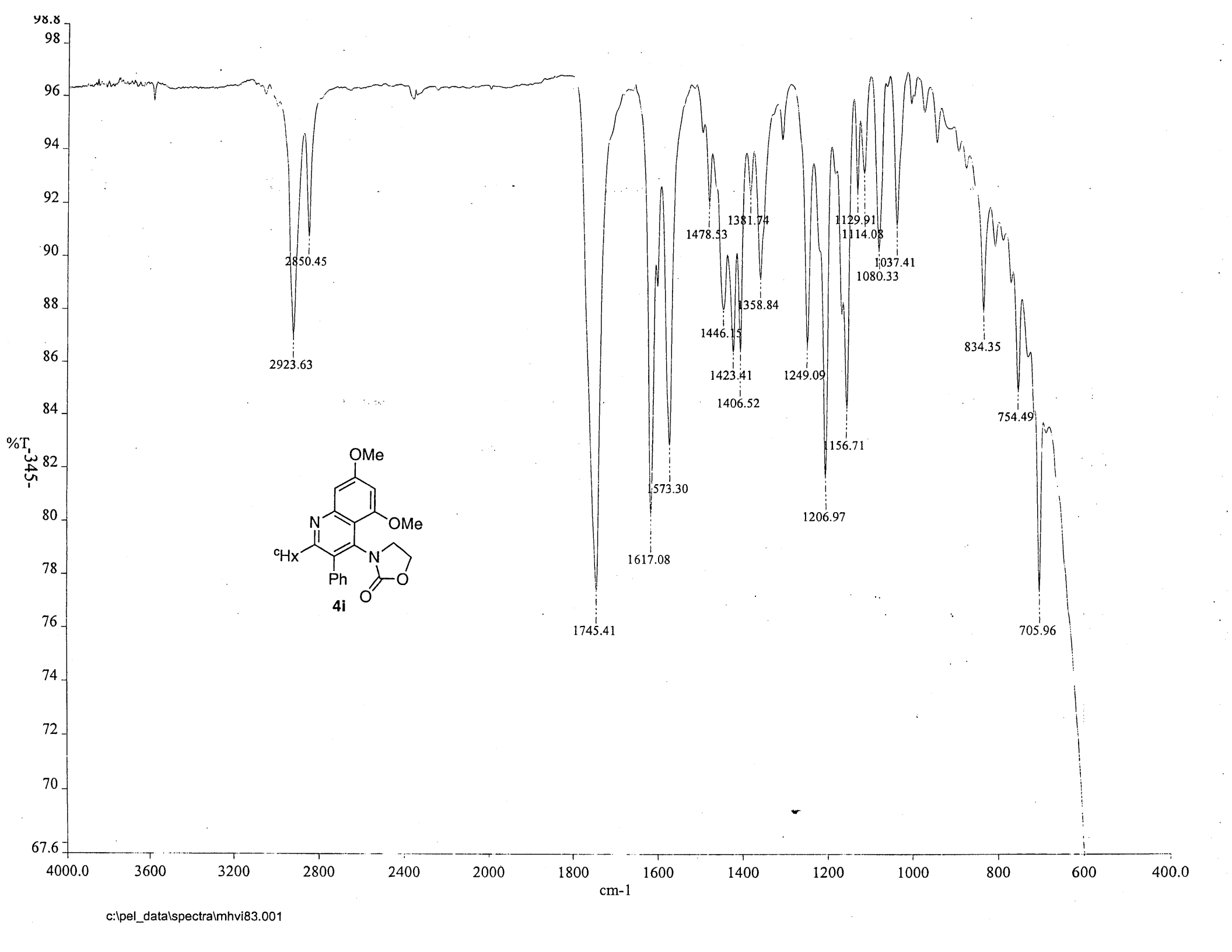
4h


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
10000000 repetitions
OBSERVE C13, 125.7832320 MHz
DECOUPLE H1, 500.2332753 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6942.2 hours
N
O
N
O
N
O
Ph
4h
130.333
129.578
129.482
128.804
128.740
128.594
128.337
128.227
125.312
122.460
122.222
159.597
157.752
147.764
140.431
135.570
77.486
77.230
76.978
66.734
63.209
49.660
46.144
200
180
160
140
120
100
80
60
40
20
0
ppm


87.9
85
80
75
70
65
60
55
50
45
%T
40
35
30
25
20
15
10
5
0
-1.9
-342-
3490.31
3060.03
2965.31
2893.01
2848.71
2248.29
1754.96
1612.56
1601.25
1586.89
1560.41
1491.17
1409.25
1368.12
1335.46
1307.17
1259.56
1238.40
1218.28
1199.05
1166.13
1131.85
1116.57
1091.35
1065.71
1032.43
1006.77
972.66
943.75
923.82
883.36
854.38
791.82
758.63
721.47
705.80
681.23
646.94
631.64
596.07
N
O
N
N
O
O
Ph
4h
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
c:\pel_data\spectra\mhvi153.sp

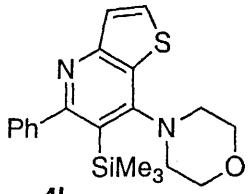

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: mh-VI-A3
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
16 repetitions
OBSERVE H1, 499.7417200 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec
OMe
OMe
N
N
cHx
Ph
O
O
4i
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.89 1.00
1.02
0.97
1.12 4.02
2.94 2.22
1.05
1.03
3.48
5.38
3.91
1.09


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
128 repetitions
OBSERVE C13, 125.7832349 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 5 minutes
OMe
OMe
N
cHx
Ph
N
O
O
4i
166.385
160.929
157.793
156.008
152.314
138.495
136.302
133.368
130.264
128.836
128.704
127.884
127.829
111.447
101.175
99.866
77.482
77.230
76.974
62.880
56.599
55.844
47.756
43.174
32.499
32.224
26.525
26.480
25.967
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
cm-1
2923.63
2850.45
1745.41
1617.08
1573.30
1478.53
1446.15
1423.41
1406.52
1381.74
1358.84
1249.09
1206.97
1156.71
1129.91
1114.08
1080.33
1037.41
834.35
754.49
705.96
OMe
OMe
N
cHx
Ph
N
O
O
4i
c:\pel_data\spectra\mhvi83.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

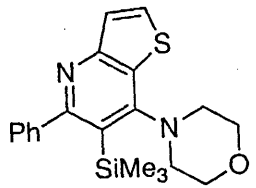
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



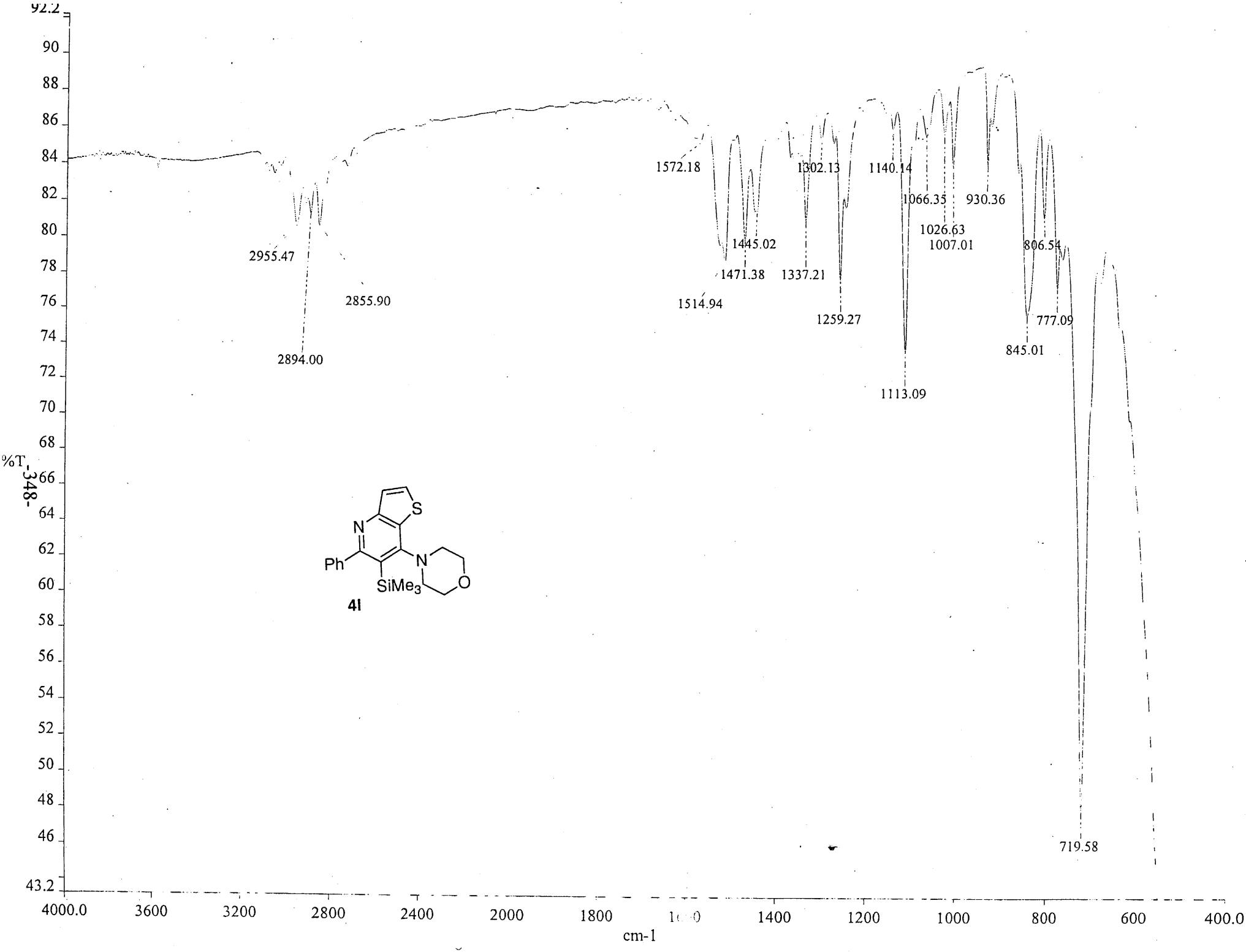
4l

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "Bullwinkle"

Relax. delay 0.750 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
104 repetitions
OBSERVE C13, 125.6601352 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 7663 hr, 35 min, 56 sec

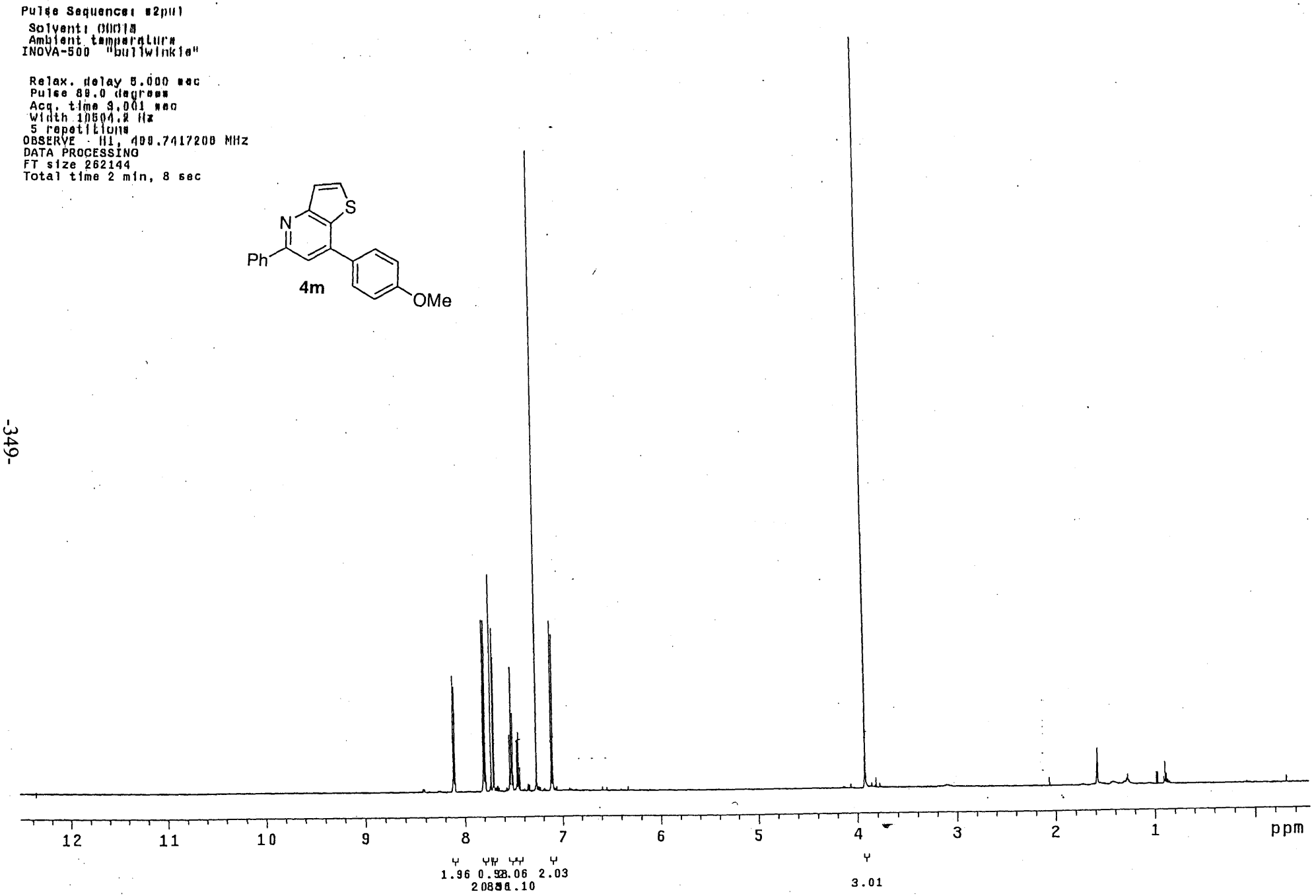


41


%T
92.2
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
43.2
2955.47
2894.00
2855.90
1572.18
1514.94
1471.38
1445.02
1337.21
1302.13
1259.27
1140.14
1113.09
1066.35
1026.63
1007.01
930.36
845.01
806.54
777.09
719.58
4000.0
3600
3200
2800
2400
2000
1800
1400
1200
1000
800
600
400.0
cm-1
c:\pel_data\spectra\mhvi152.sp

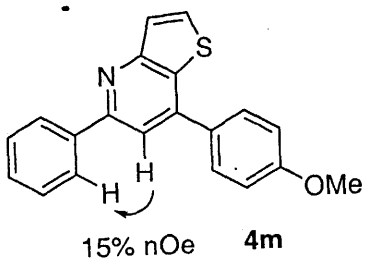
S
N
Ph
N
SiMe3
O

4l

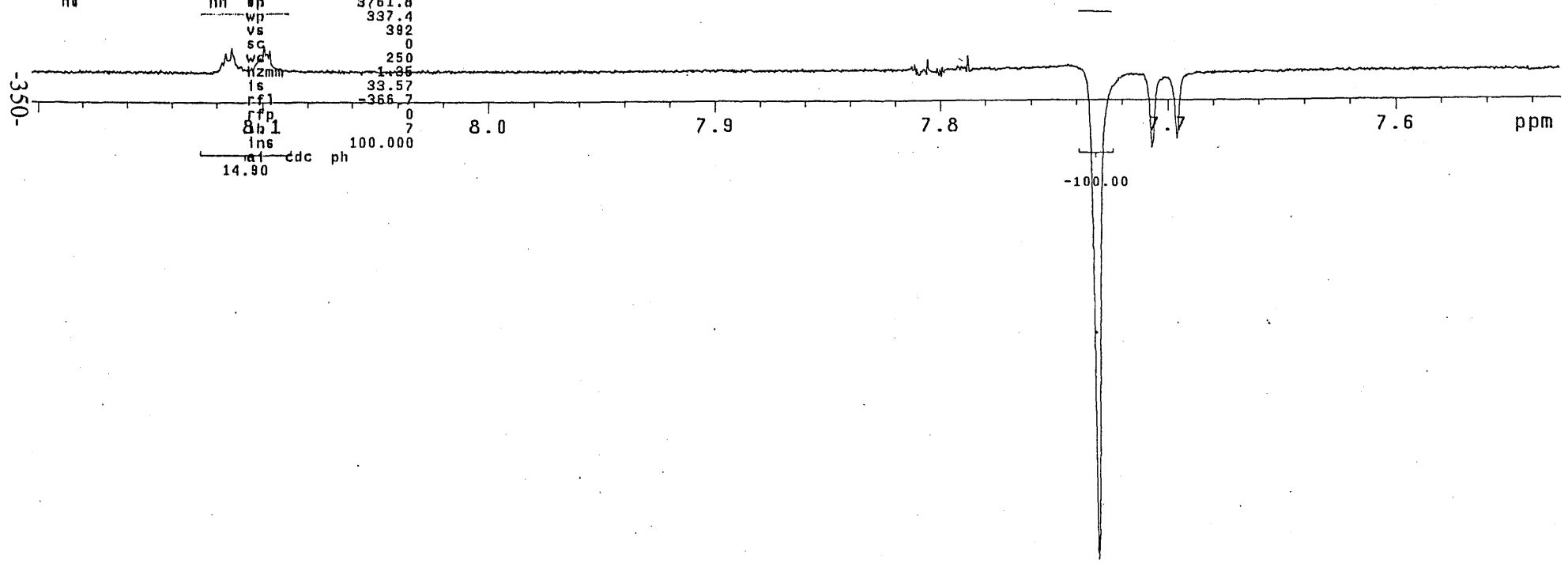

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"
Relax. delay 5.000 sec
Pulse 88.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
5 repetitions
OBSERVE H1, 499.7417208 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec
N
S
Ph
OMe
4m
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.96
0.93
3.06
2.03
3.01

exp5 presat

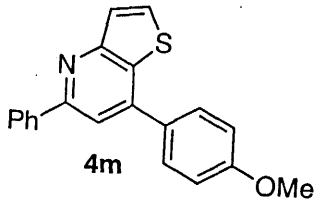
SAMPLE		SATURATION		ACQUISITION ARRAYS	
date	Apr 26 2007	sspul	n	array	satfrq
solvent	CDCl3	satpwr	-16	arraydim	2
file	exp	satfrq	arrayed		
ACQUISITION		satdly	5.000	i	satfrq
sfrq	499.744	satmode	ynn	1	1363.93
tn	H1	composit	n	2	5000
at	3.002	DEC. & VT			
np	24092	dn	H1		
sw	4012.0	dof	1363.9		
fb	not used	dm	nnn		
bs	4	dmm	w		
ss	2	dmf	10000		
tpwr	56	dpwr	30		
pw	8.6	PROCESSING			
d1	20.000	wtfile			
tof	-100.1	proc	ft		
nt	16	fn	202144		
ct	16	math	f		
alock	n				
gain	54	werr			
FLAGS		wexp			
il	n	wbs			
in	n	wnt	wft		
dp	y	DISPLAY			
hs	nn	sp	3761.8		
		wp	337.4		
		vs	392		
		sc	0		
		wc	250		
		hzmm	1.35		
		is	33.57		
		rfl	-366.7		
		rfp	0		
		th	7		
		ins	100.000		
		ai dc ph			

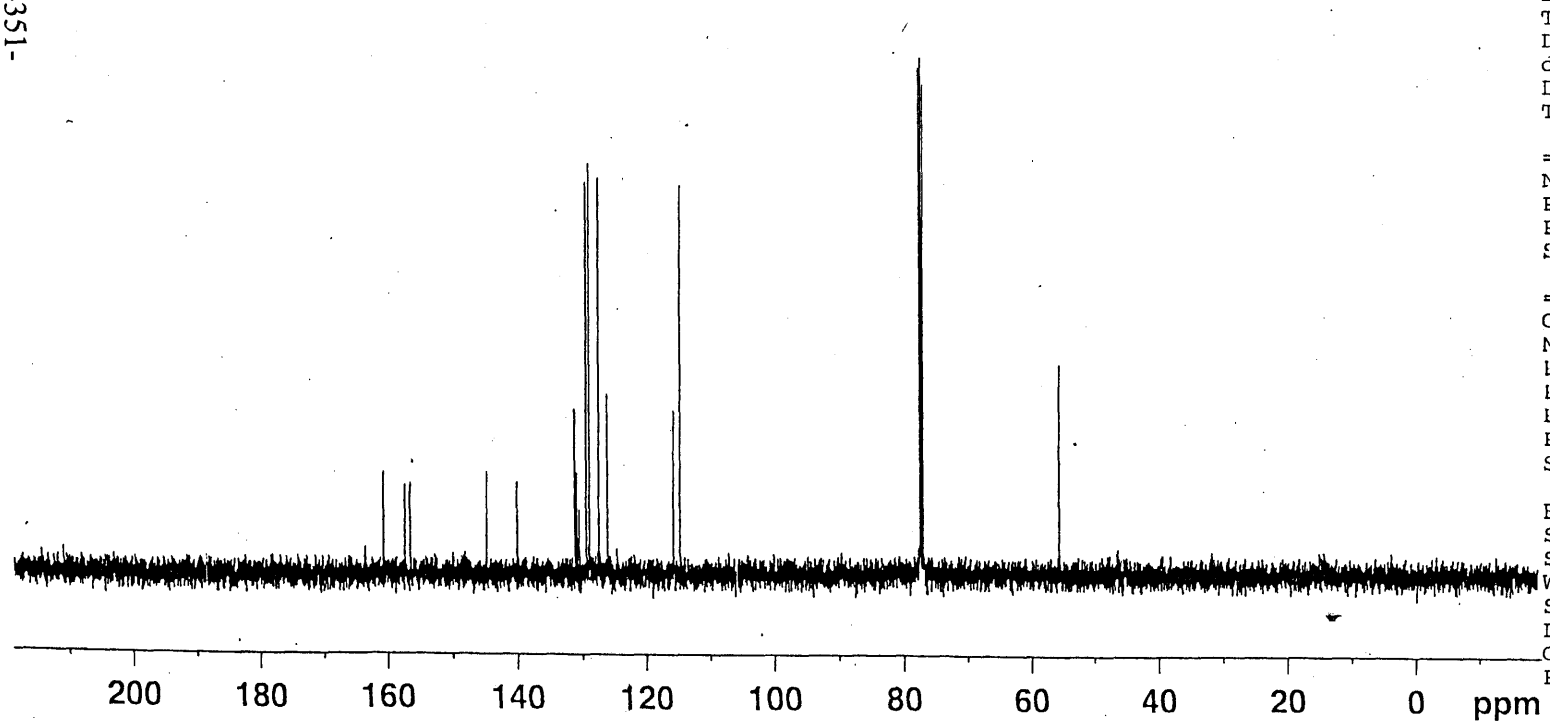


15% nOe **4m**



160.60
157.34
156.49
144.68
140.04
132.76
130.95
130.53
129.46
128.99
127.53
126.13
115.72
114.66
55.37





BRUKER

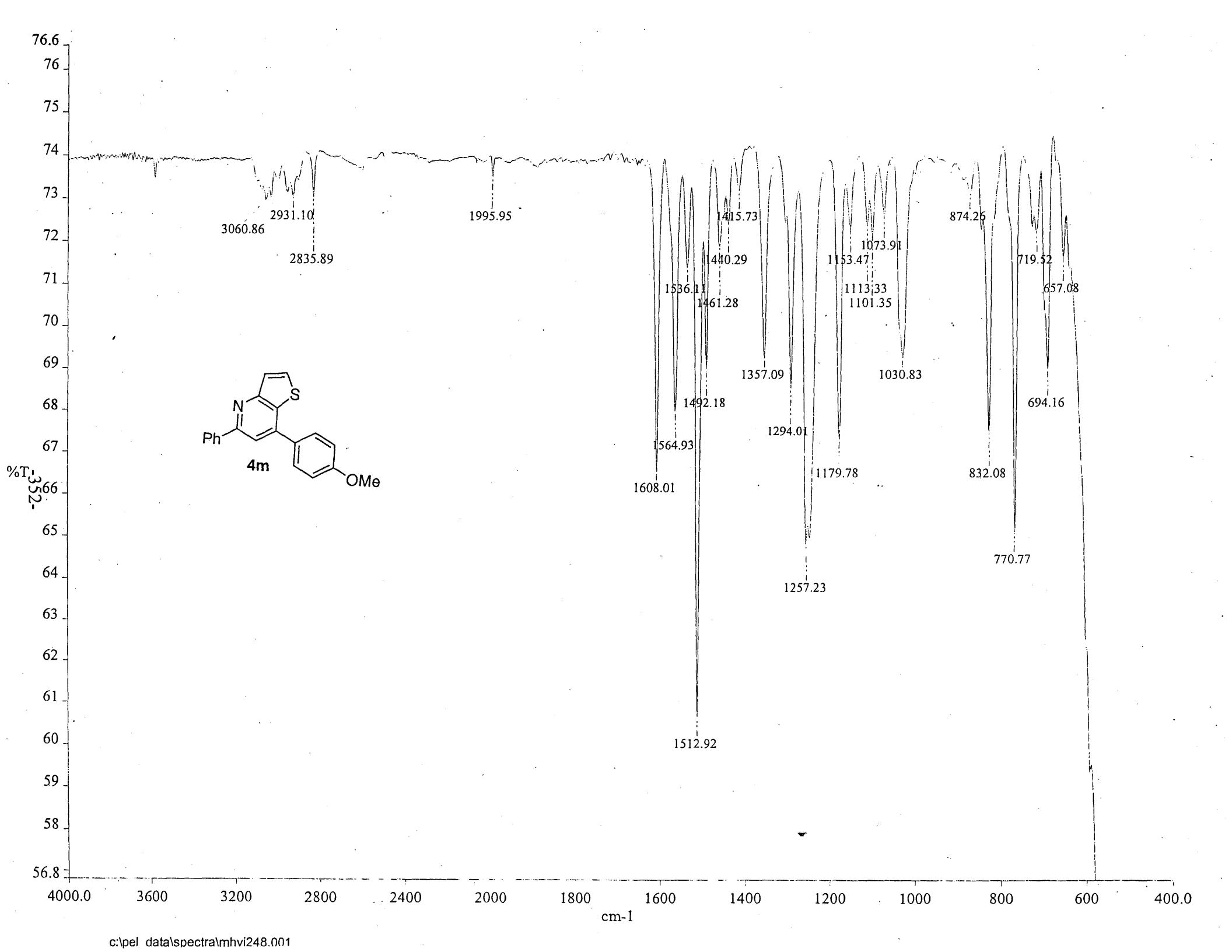
Current Data Parameters
NAME MH-VI-248
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070419
Time 18.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 48
DS 2
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 293.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

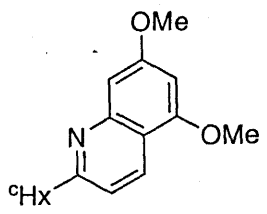
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 14.52 dB
PL13 18.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 100.6127577 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


76.6
76
75
74
73
72
71
70
69
68
67
66
65
64
63
62
61
60
59
58
56.8
%T
-352-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
3060.86
2931.10
2835.89
1995.95
1608.01
1564.93
1536.11
1512.92
1492.18
1461.28
1440.29
1415.73
1357.09
1294.01
1257.23
1179.78
1153.47
1113.33
1101.35
1073.91
1030.83
874.26
832.08
770.77
719.52
694.16
657.08
N
S
Ph
OMe
4m
c:\pel data\spectra\mhvi248.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "billiwinkle"

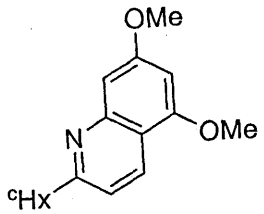
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
11 repetitions
OBSERVE H1, 499.7446521 MHz
DATA PROCESSING
FT size 131072
Total time 2 min, 8 sec



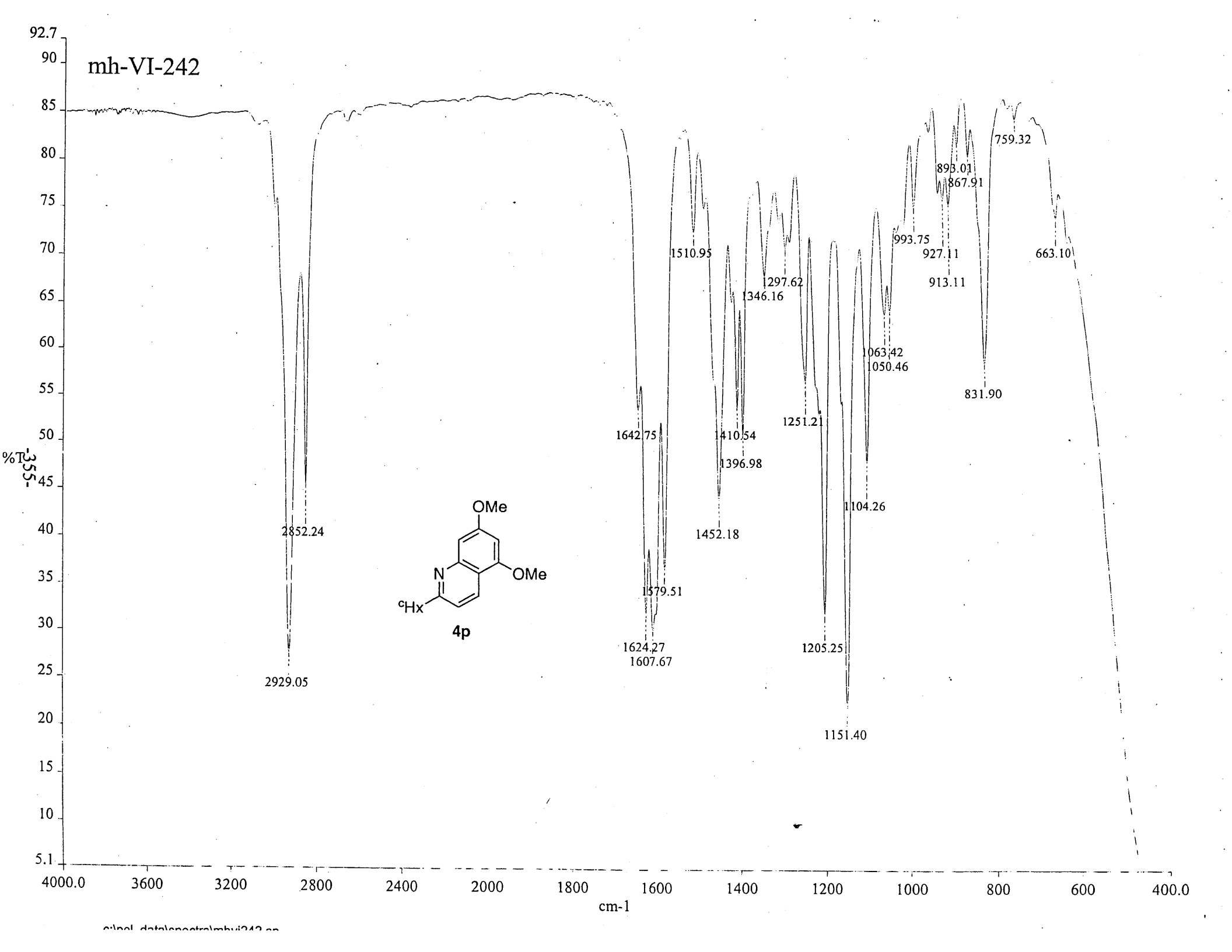
4p

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.200 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
816 repetitions
OBSERVE C13, 125.7832268 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 26 minutes

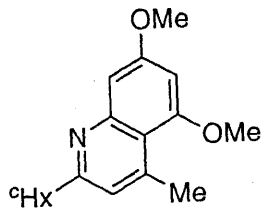


4p


mh-VI-242
92.7
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5.1
%T
-355-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
2929.05
2852.24
1642.75
1624.27
1607.67
1579.51
1510.95
1452.18
1410.54
1396.98
1346.16
1297.62
1251.21
1205.25
1151.40
1104.26
1063.42
1050.46
993.75
927.11
913.11
893.01
867.91
831.90
759.32
663.10
OMe
N
OMe
cHx
4p

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 2.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
15 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 1 min, 20 sec



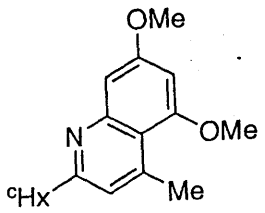
4q

STANDARD CARBON PARAMETERS

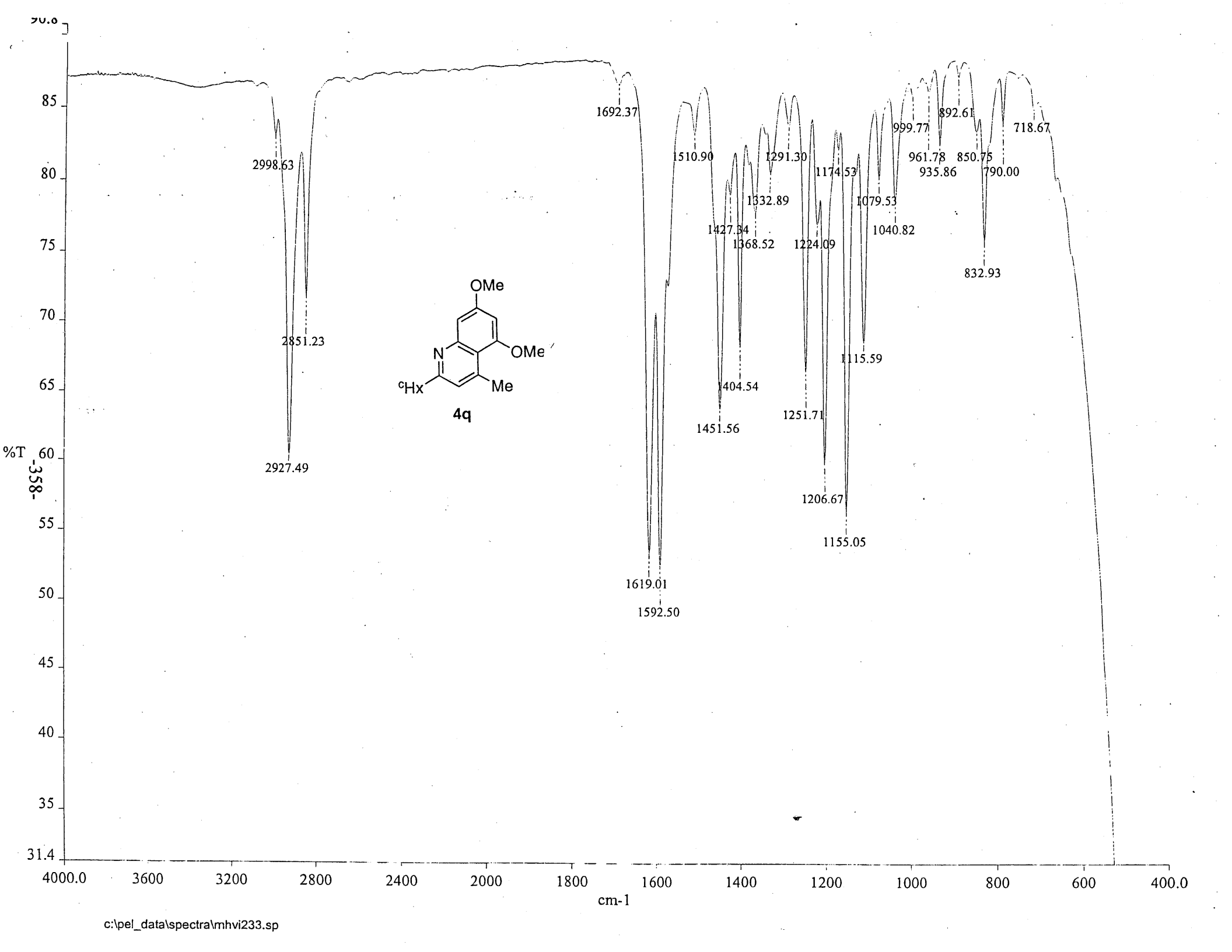
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

Relax. delay 0.000 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
192 repetitions
OBSERVE C13, 125.6001306 MHz
DECOUPLE H1, 499.7442104 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 571 hr, 54 min, 55 sec

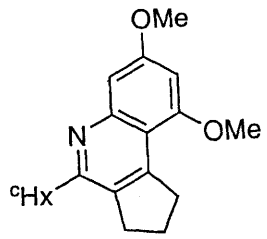


4q


2998.63
2927.49
2851.23
1692.37
1619.01
1592.50
1510.90
1451.56
1427.34
1404.54
1368.52
1332.89
1291.30
1251.71
1224.09
1206.67
1174.53
1155.05
1115.59
1079.53
1040.82
999.77
961.78
935.86
892.61
850.75
832.93
790.00
718.67
OMe
OMe
N
cHx
Me
4q
%T
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
90.8
85
80
75
70
65
60
55
50
45
40
35
31.4
c:\pel_data\spectra\mhvi233.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

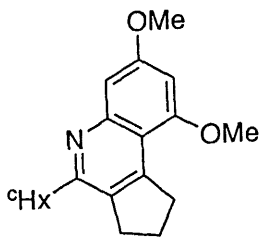
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
11 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



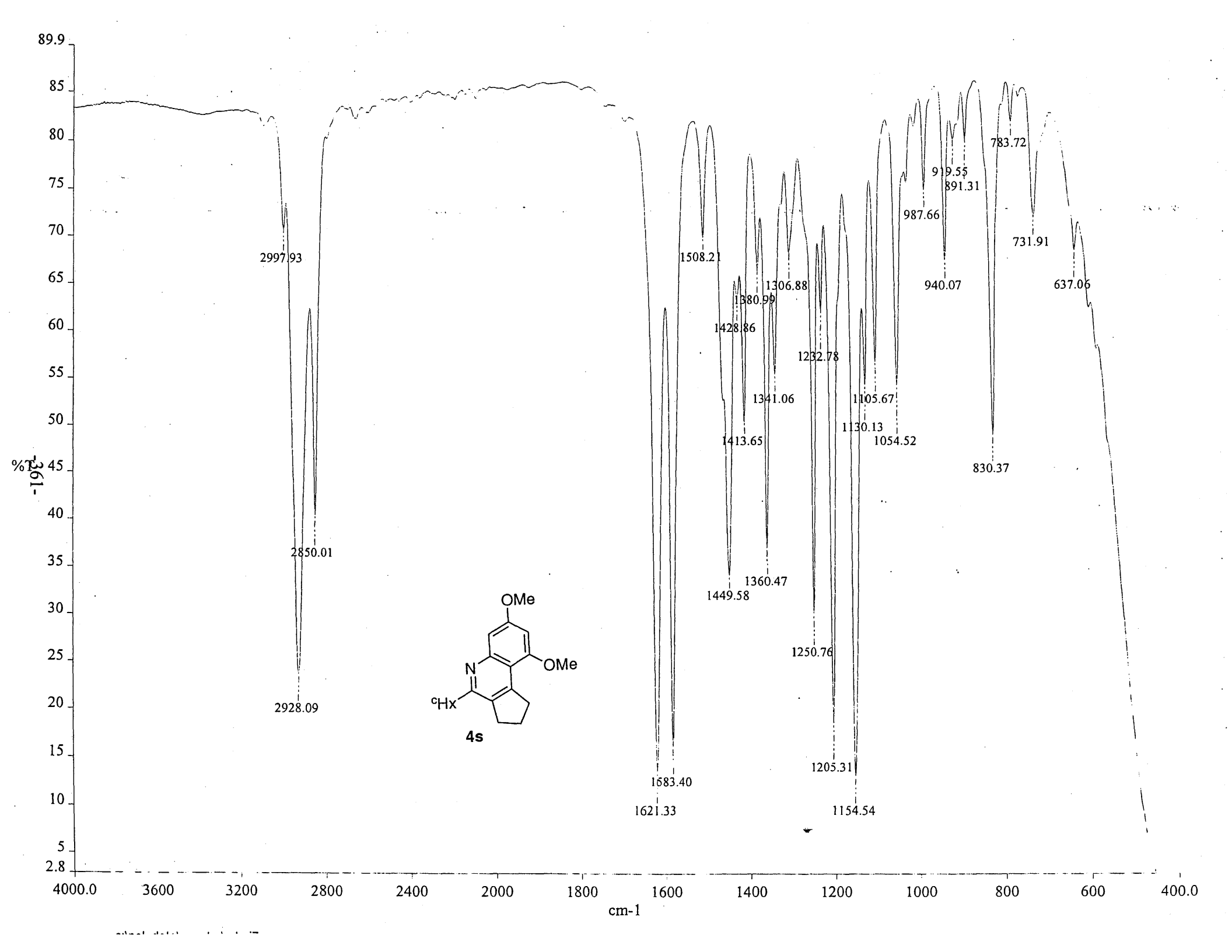
4s

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.200 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
496 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 16 minutes

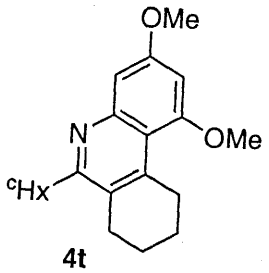


4s


89.9
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
2.8
%T
-361-
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
2997.93
2928.09
2850.01
1621.33
1583.40
1508.21
1449.58
1428.86
1413.65
1380.99
1360.47
1341.06
1306.88
1250.76
1232.78
1205.31
1154.54
1130.13
1105.67
1054.52
987.66
940.07
919.55
891.31
830.37
783.72
731.91
637.06
OMe
OMe
N
cHx
4s

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

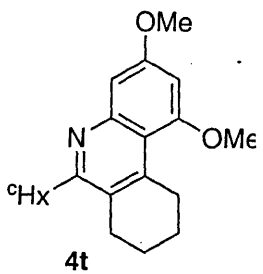
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
6 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 0 sec



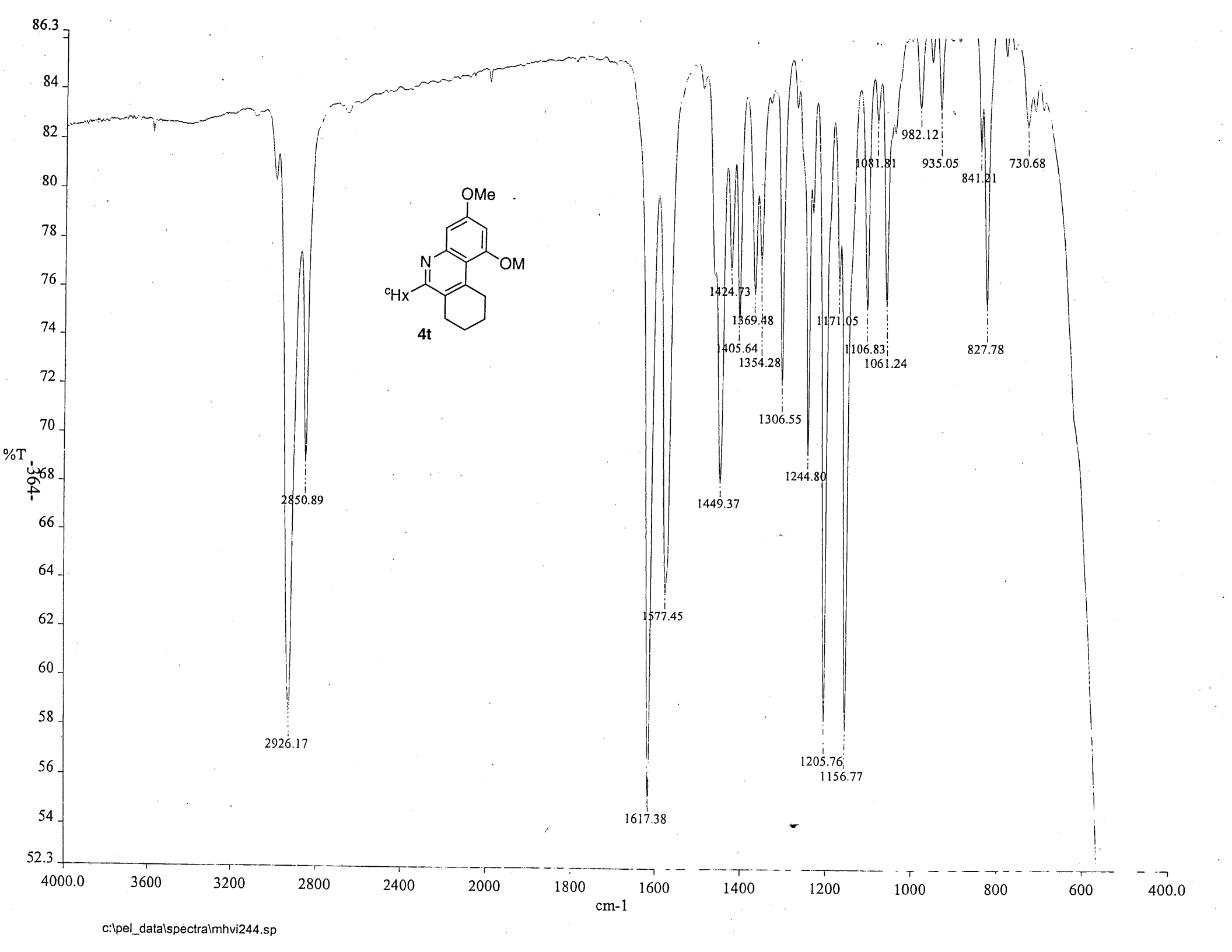
4t

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.200 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
48 repetitions
OBSERVE C13, 125.7832291 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minutes

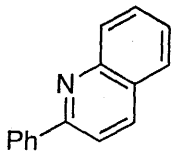


4t

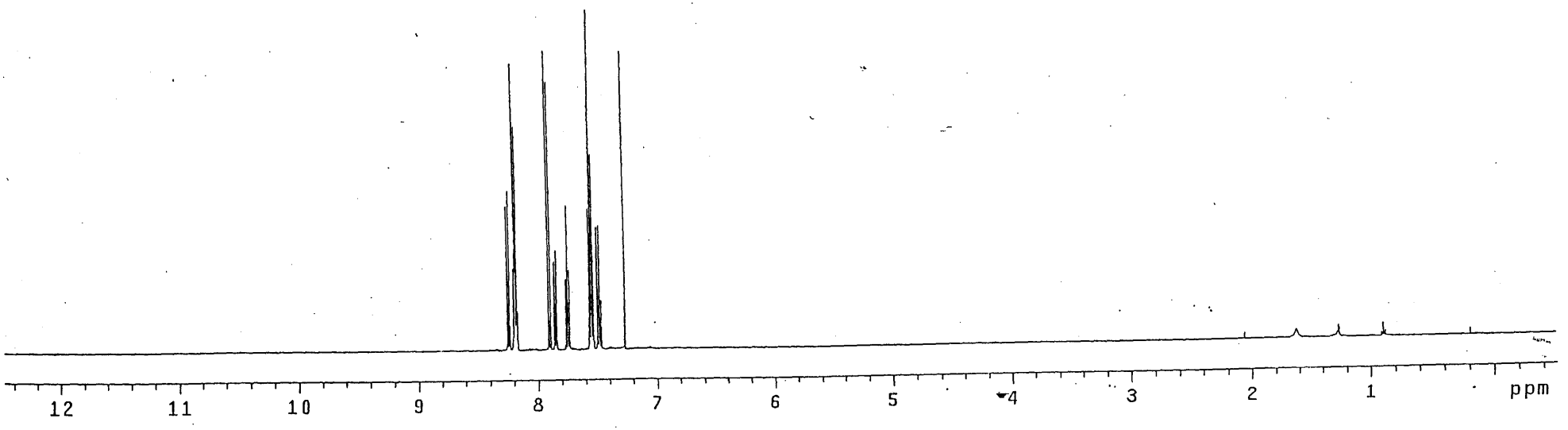

86.3
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52.3
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
OMe
N
OM
cHx
4t
2926.17
2850.89
1617.38
1577.45
1449.37
1424.73
1405.64
1369.48
1354.28
1306.55
1244.80
1205.76
1171.05
1156.77
1106.83
1081.81
1061.24
982.12
935.05
841.21
827.78
730.68
c:\pel_data\spectra\mhvi244.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

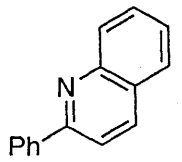
PULSE SEQUENCE
Pulse 85.8 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7537710 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 52 sec



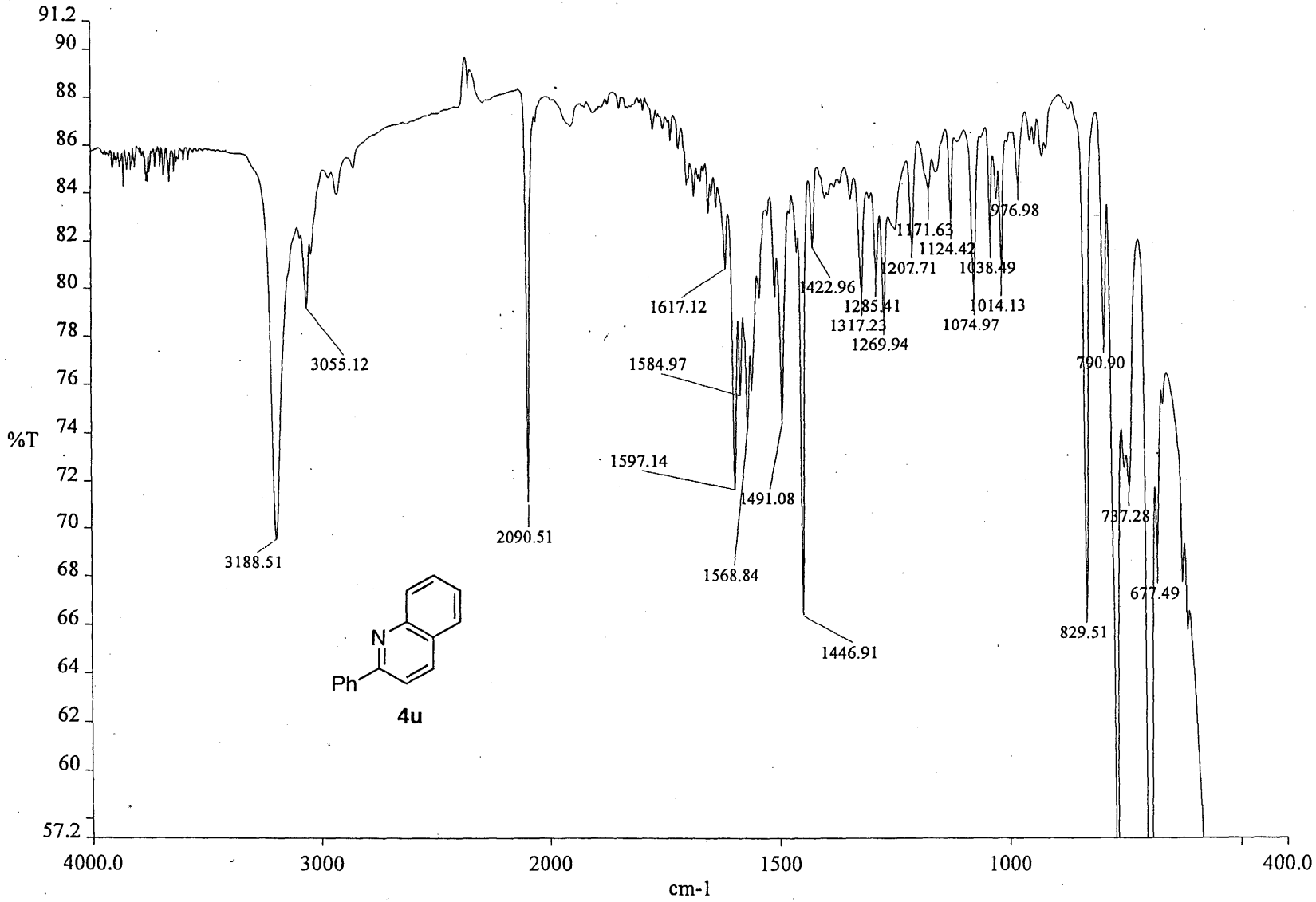
4u



Solvent: CDCl3
Temp. 20.0 C / 293.1 K
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.703 sec
Pulse 65.4 degrees
Acq. time 1.730 sec
Width 37735.8 Hz
100 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332763 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 4 minutes

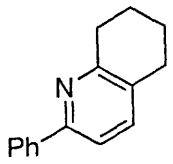


4u

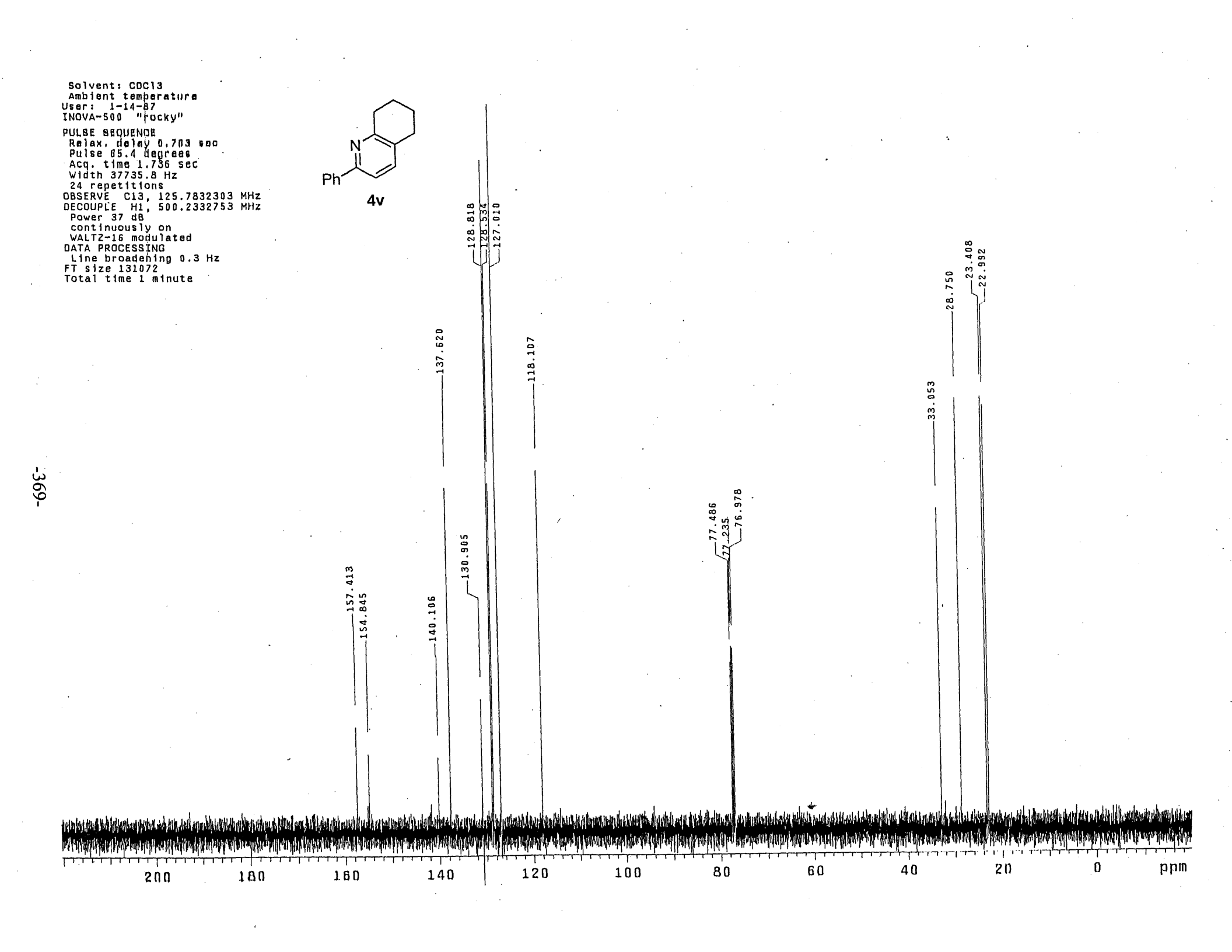

91.2
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
57.2
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3188.51
3055.12
2090.51
1617.12
1584.97
1597.14
1568.84
1491.08
1446.91
1422.96
1285.41
1317.23
1269.94
1207.71
1171.63
1124.42
1038.49
1074.97
1014.13
976.98
790.90
737.28
677.49
829.51
N
Ph
4u
c:\pel_data\spectra\mhii175.sp

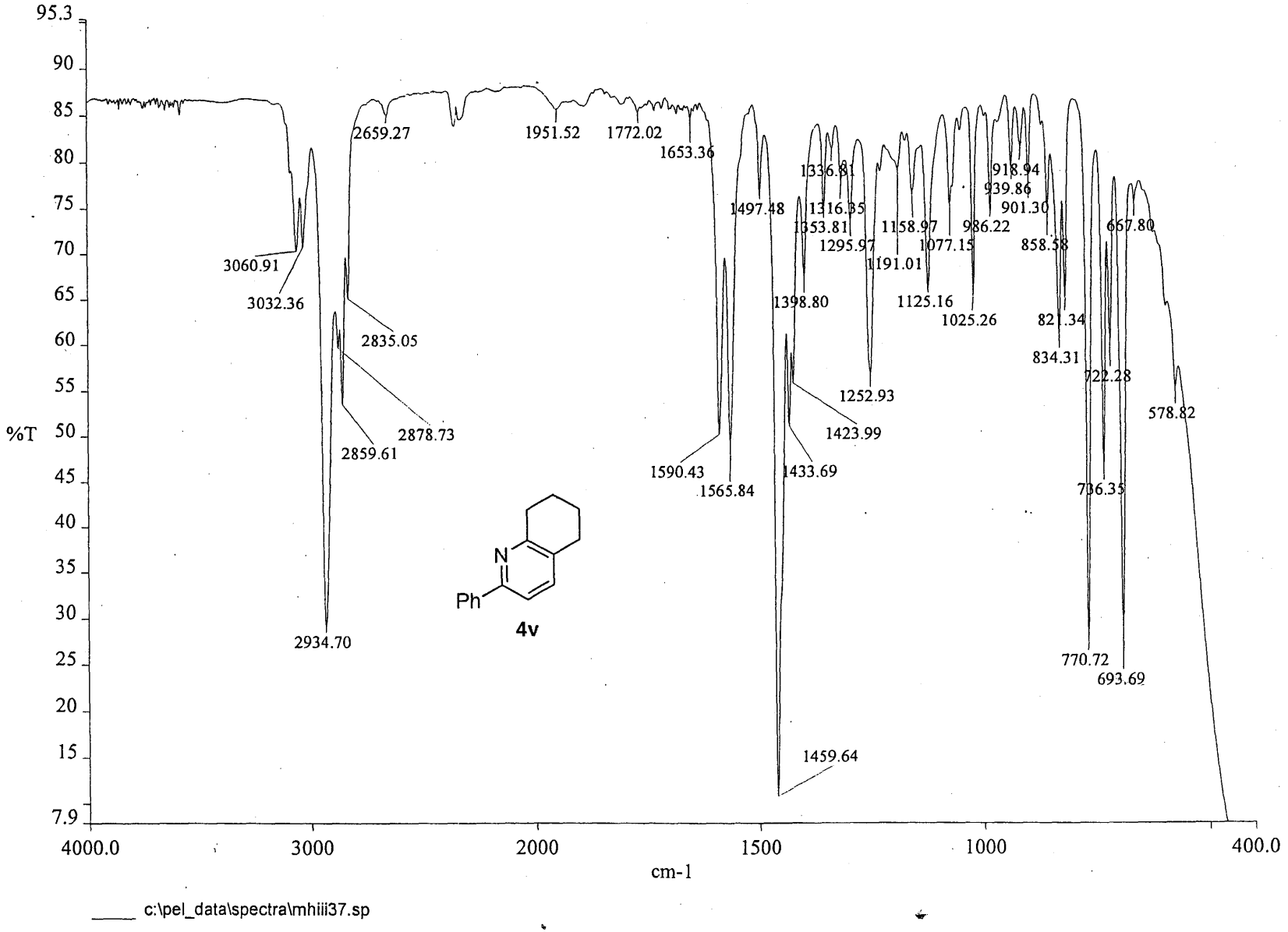
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
4 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec

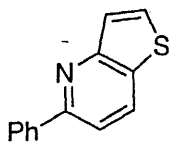


4v

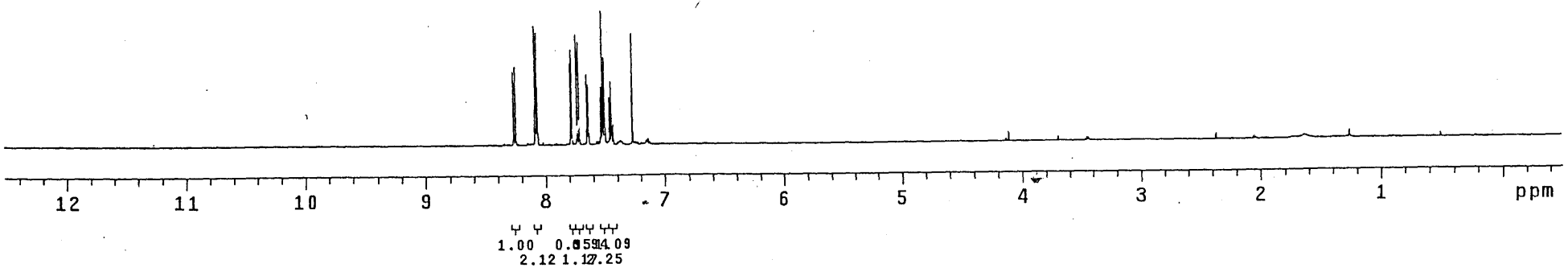

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.703 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
24 repetitions
OBSERVE C13, 125.7832303 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute
N
Ph
4v
157.413
154.845
140.106
137.620
130.905
128.818
128.534
127.010
118.107
77.486
77.235
76.978
33.053
28.750
23.408
22.992
200
180
160
140
120
100
80
60
40
20
0
ppm


95.3
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
7.9
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
3060.91
3032.36
2934.70
2659.27
2835.05
2878.73
2859.61
1951.52
1772.02
1653.36
1590.43
1565.84
1497.48
1398.80
1433.69
1459.64
1336.81
1316.35
1353.81
1295.97
1252.93
1191.01
1158.97
1125.16
1077.15
1025.26
986.22
939.86
918.94
901.30
858.58
821.34
834.31
722.28
736.35
770.72
693.69
667.80
578.82
1423.99
N
Ph
4v
c:\pel_data\spectra\mhiii37.sp

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: mh-III-113
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
16 repetitions
OBSERVE H1, 499.7446549 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 8 sec

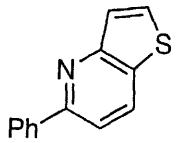


4w

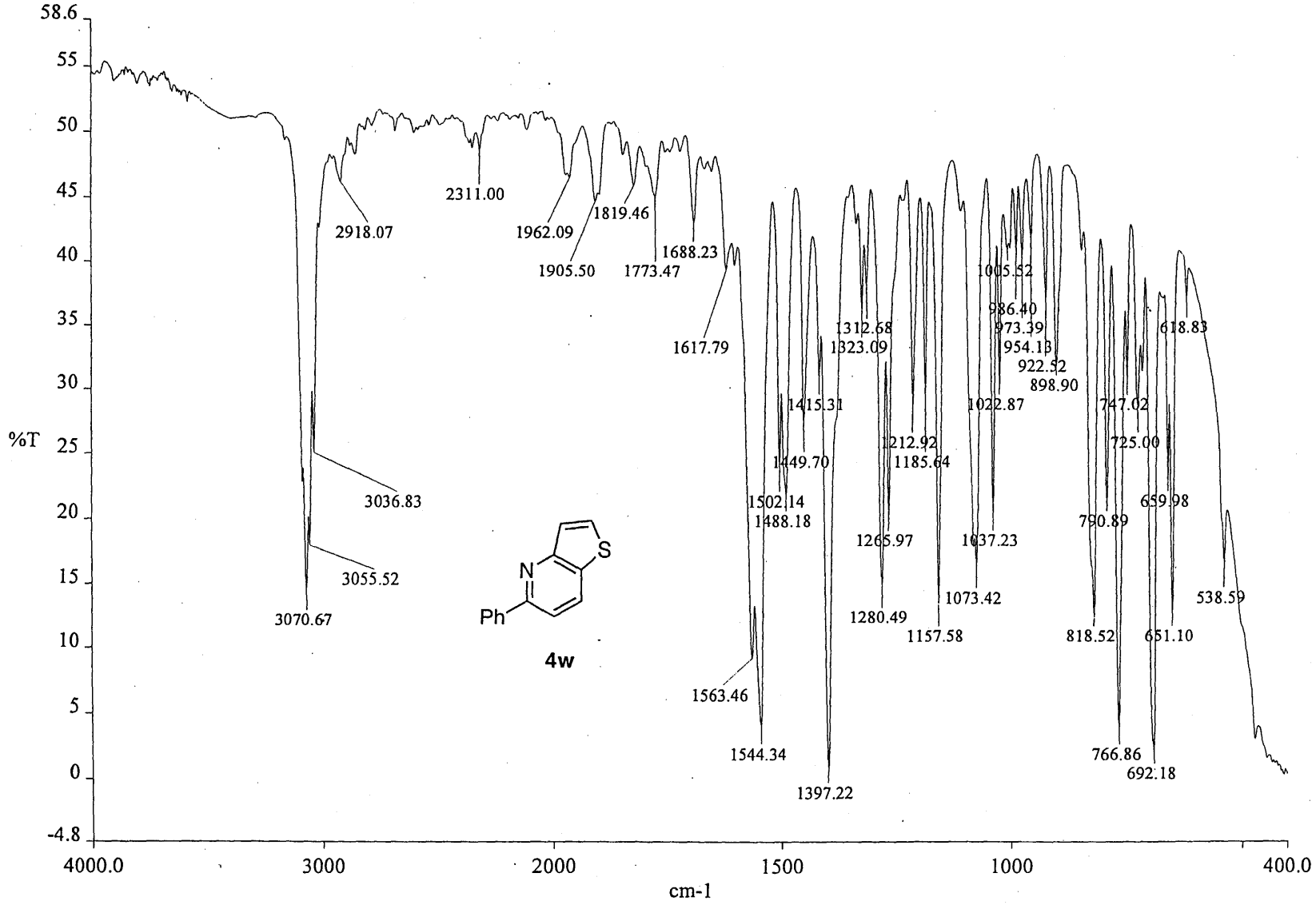


Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
16 repetitions
OBSERVE C13, 125.7832458 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 minute

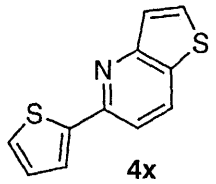


4w


58.6
55
50
45
40
35
30
25
20
15
10
5
0
-4.8
%T
4000.0
3000
2000
1500
1000
400.0
cm-1
2918.07
2311.00
1962.09
1905.50
1819.46
1773.47
1688.23
1617.79
1312.68
1323.09
1005.52
986.40
973.39
954.13
922.52
898.90
1415.31
1022.87
747.02
725.00
618.83
1212.92
1185.64
1449.70
3036.83
1502.14
1488.18
659.98
790.89
1265.97
1037.23
3055.52
1073.42
538.59
3070.67
1280.49
1157.58
818.52
651.10
1563.46
1544.34
766.86
692.18
1397.22
N
S
Ph
4w
c:\pel_data\spectra\mhiii114.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

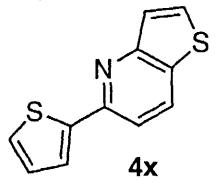
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
4 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



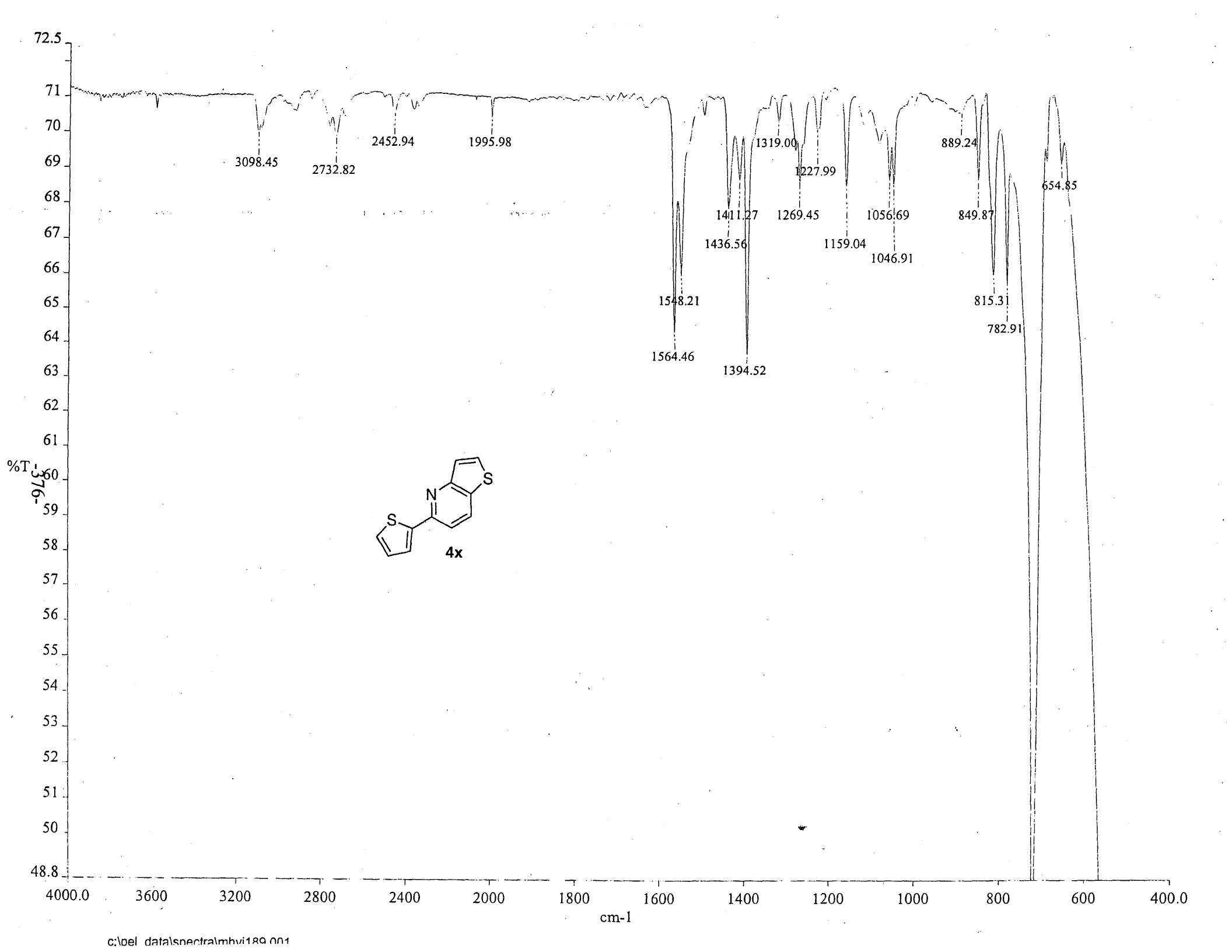
4x

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
56 repetitions
OBSERVE C13, 125.7832332 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 2 minutes

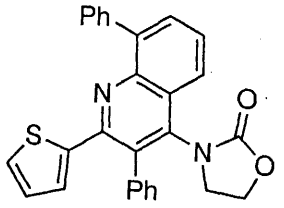


4x


72.5
71
70
69
68
67
66
65
64
63
62
61
60
59
58
57
56
55
54
53
52
51
50
48.8
%T
3098.45
2732.82
2452.94
1995.98
1548.21
1564.46
1436.56
1411.27
1394.52
1319.00
1269.45
1227.99
1159.04
1056.69
1046.91
889.24
849.87
815.31
782.91
654.85
S
N
S
4x
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
c:\bel_data\spectra\mbvi189.001

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

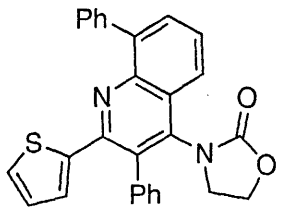
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
2 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



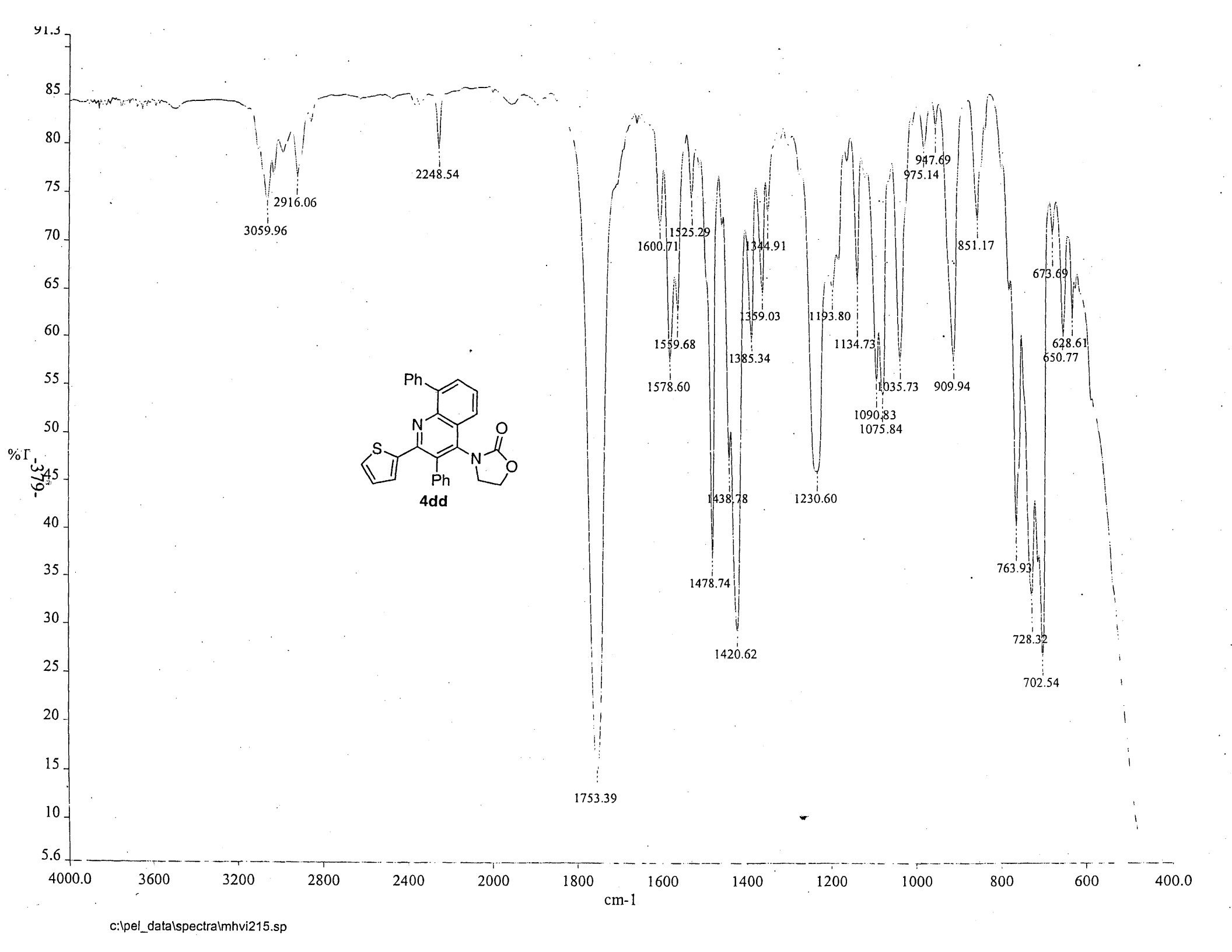
4dd

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

PULSE SEQUENCE
Relax. delay 0.050 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
208 repetitions
OBSERVE C13, 125.7832314 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 6 minutes

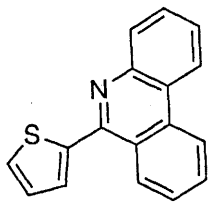


4dd

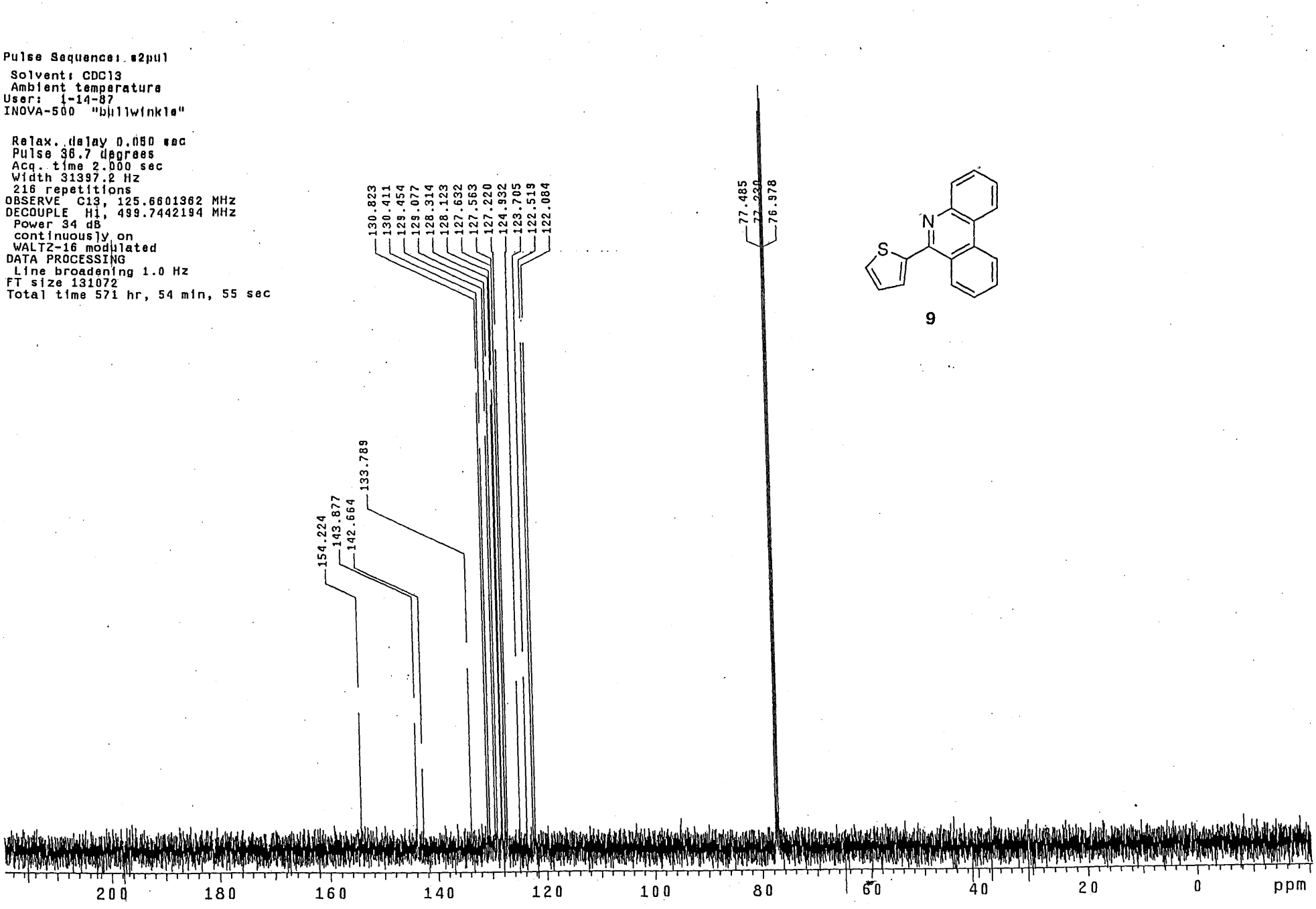

3059.96
2916.06
2248.54
1600.71
1559.68
1578.60
1525.29
1344.91
1359.03
1385.34
1438.78
1478.74
1420.62
1753.39
1193.80
1230.60
1134.73
1090.83
1075.84
1035.73
947.69
975.14
909.94
851.17
763.93
728.32
702.54
673.69
650.77
628.61
Ph
N
O
S
N
O
Ph
4dd
%T
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
c:\pel_data\spectra\mhvi215.sp

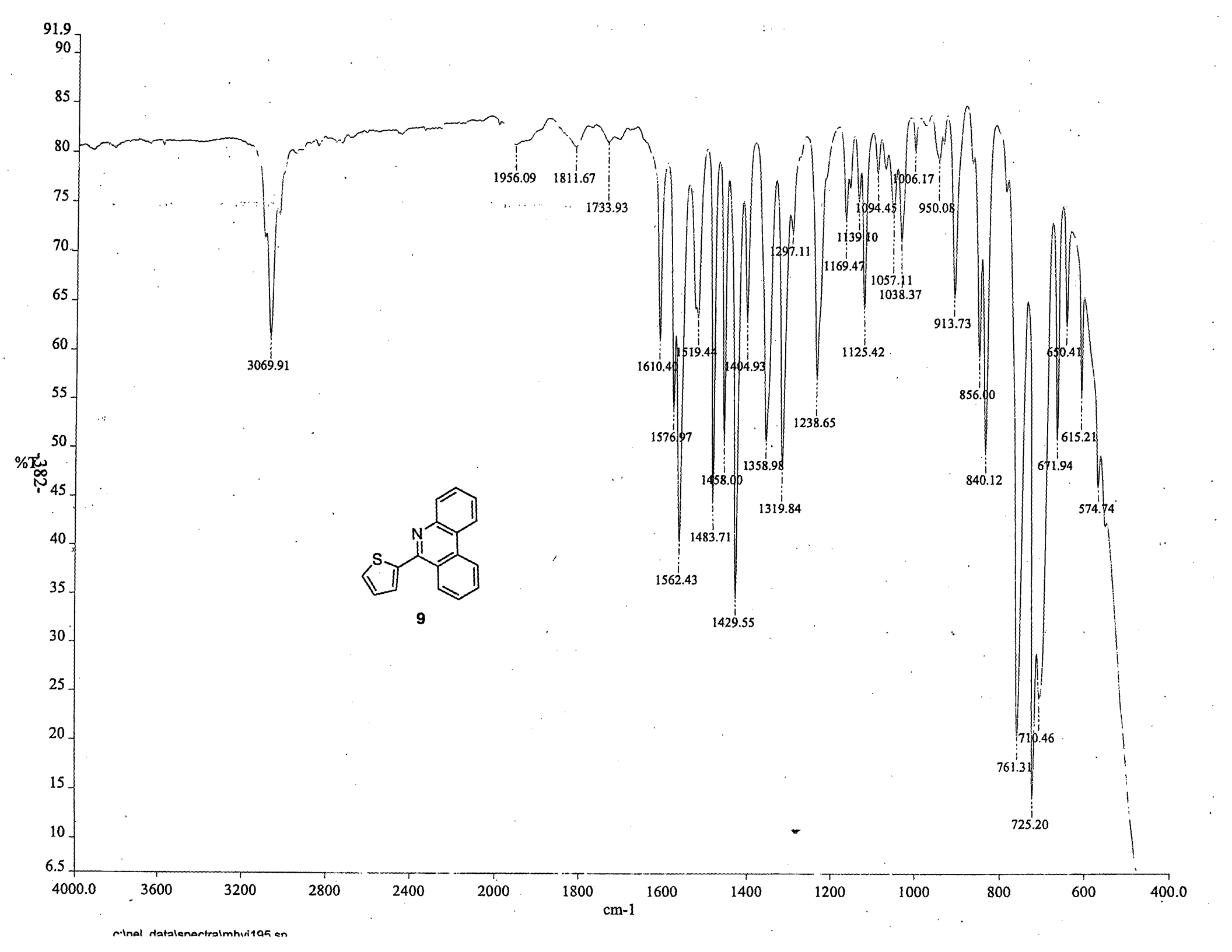
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
7 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



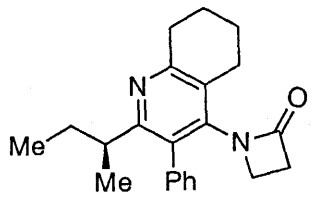
9


Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
Relax. delay 0.050 sec
Pulse 36.7 degrees
Acq. time 2.000 sec
Width 31397.2 Hz
216 repetitions
OBSERVE C13, 125.6601362 MHz
DECOUPLE H1, 499.7442194 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 571 hr, 54 min, 55 sec
130.823
130.411
129.454
129.077
128.314
128.123
127.632
127.563
127.220
124.932
123.705
122.519
122.084
154.224
143.877
142.664
133.789
77.485
77.220
76.978
S
N
9
200
180
160
140
120
100
80
60
40
20
0
ppm

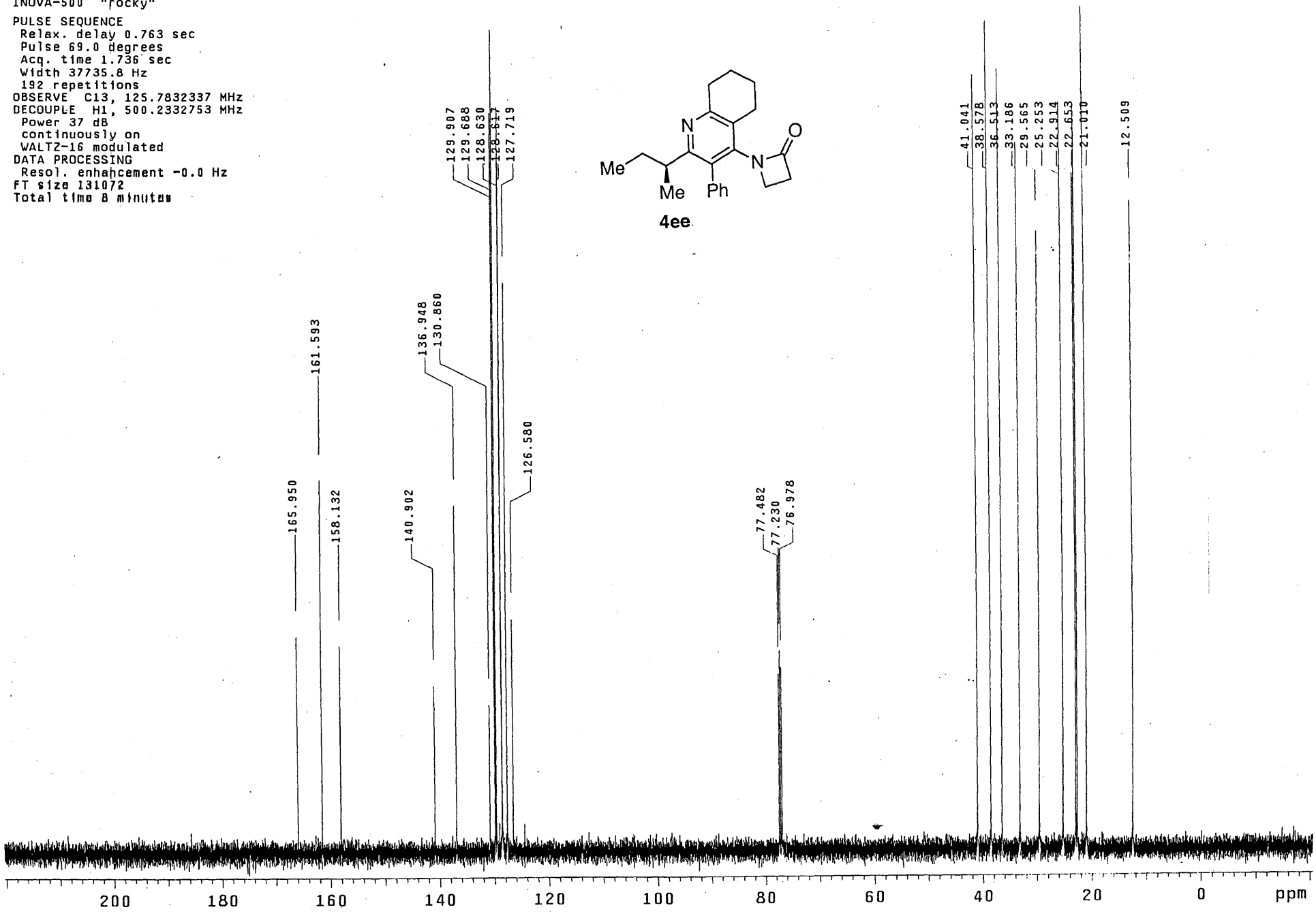

%T
cm-1
3069.91
1956.09
1811.67
1733.93
1610.40
1576.97
1562.43
1519.44
1483.71
1458.00
1429.55
1404.93
1358.98
1319.84
1297.11
1238.65
1169.47
1139.10
1125.42
1094.45
1057.11
1038.37
1006.17
950.08
913.73
856.00
840.12
761.31
725.20
710.46
671.94
650.41
615.21
574.74
N
S
9

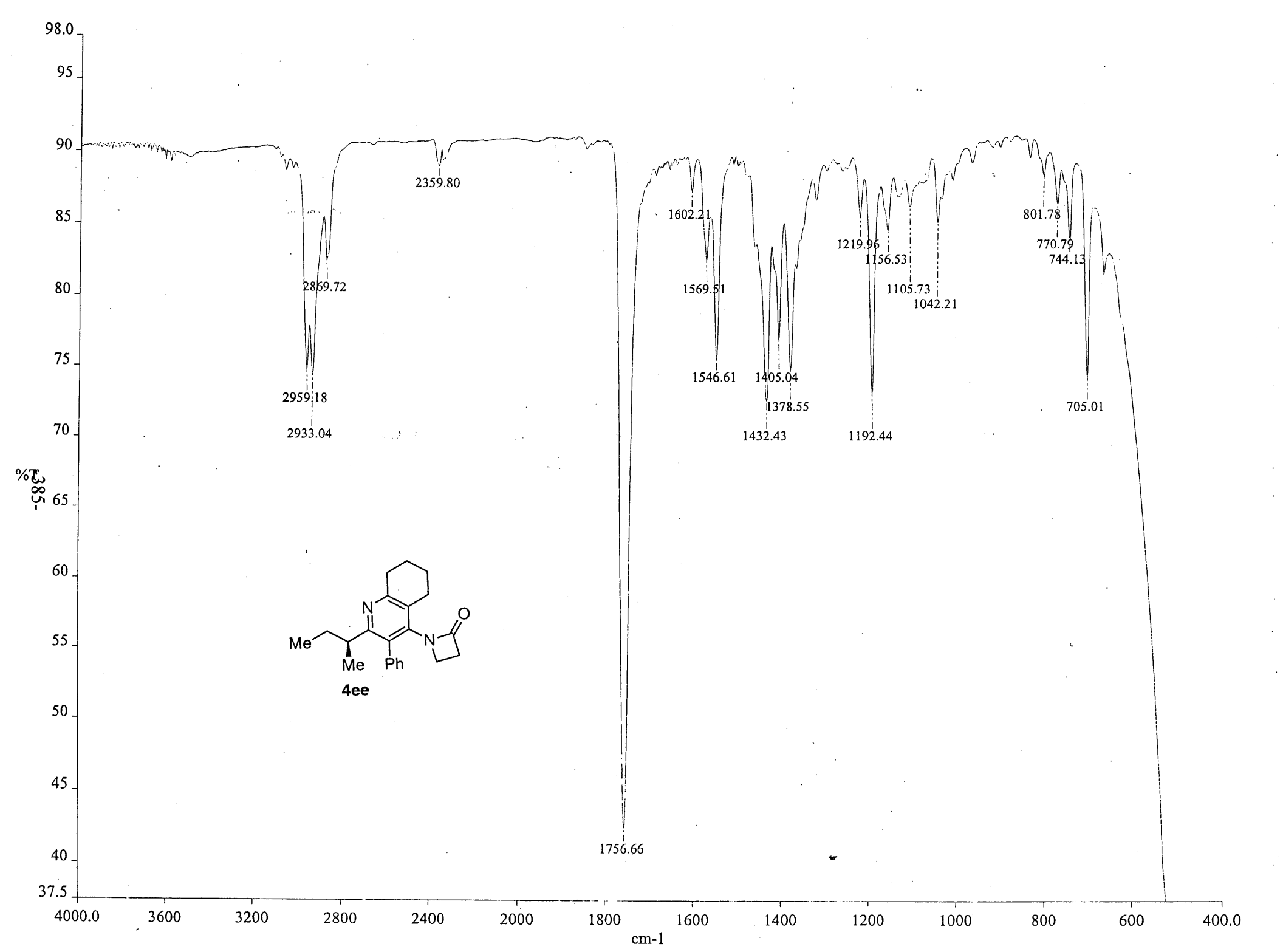
mh-VII-12

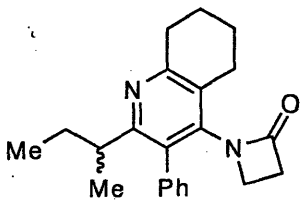
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: mh-VII-12
INOVA-500 "zippy"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 89.0 degrees
Acq. time 3.001 sec
Width 10504.2 Hz
8 repetitions
OBSERVE H1, 499.7417206 MHz
DATA PROCESSING
FT size 262144
Total time 2 min, 8 sec



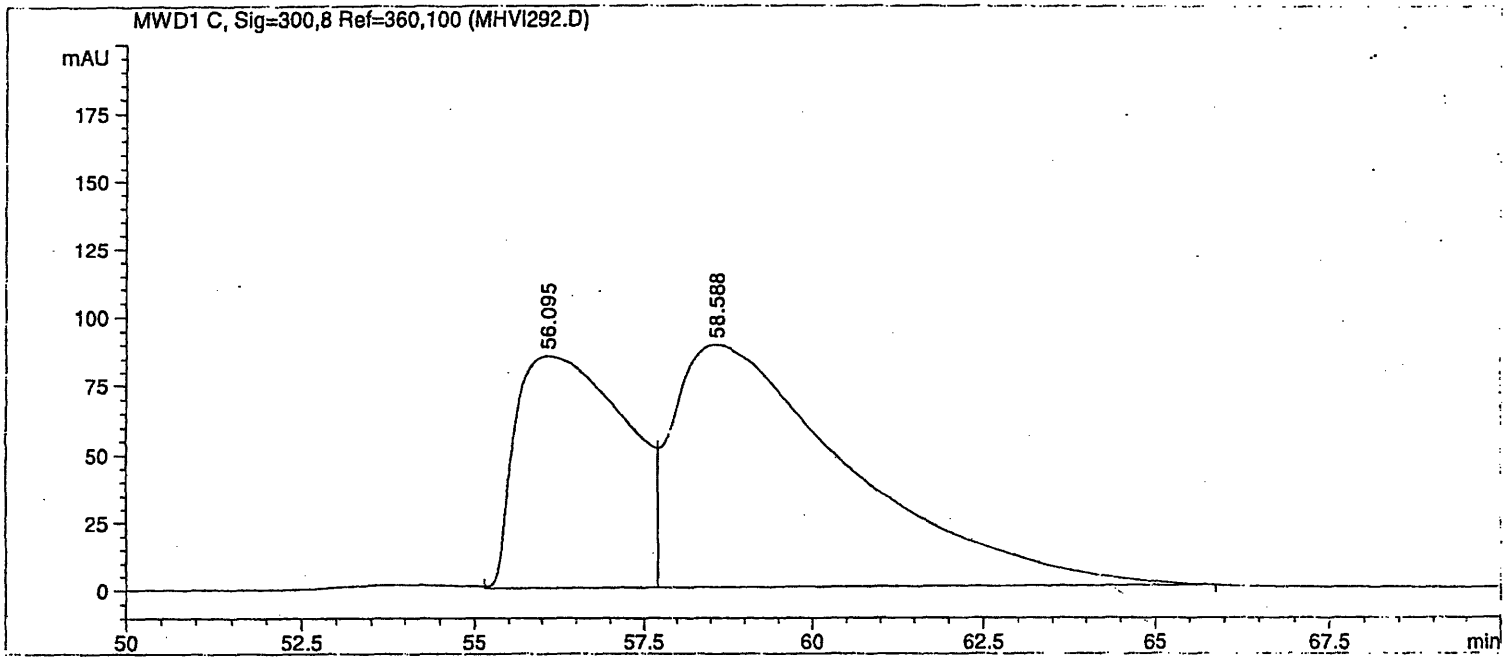
4ee


mh-VII-12
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 0.763 sec
Pulse 69.0 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
192 repetitions
OBSERVE C13, 125.7832337 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 131072
Total time 8 minutes
Me
Me
Ph
N
N
O
4ee
165.950
161.593
158.132
140.902
136.948
130.860
129.907
129.688
128.630
128.617
127.719
126.580
77.482
77.230
76.978
41.041
38.578
36.513
33.186
29.565
25.253
22.914
22.653
21.010
12.509
200
180
160
140
120
100
80
60
40
20
0
ppm


98.0
95
90
85
80
75
70
65
60
55
50
45
40
37.5
%T
2359.80
2869.72
2959.18
2933.04
1602.21
1569.51
1546.61
1405.04
1378.55
1432.43
1219.96
1156.53
1105.73
1042.21
1192.44
801.78
770.79
744.13
705.01
1756.66
N
O
N
Me
Me
Ph
4ee
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
c:\pel_data\spectra\mhvi292.sp



4ee



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.095	VV	1.5770	9719.56055	85.58348	37.3632
2	58.588	VB	2.3944	1.62942e4	89.23138	62.6368

Totals : 2.60138e4 174.81486

Results obtained with enhanced integrator!

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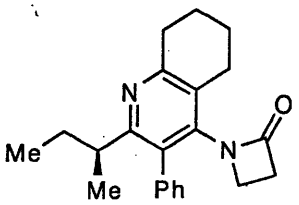
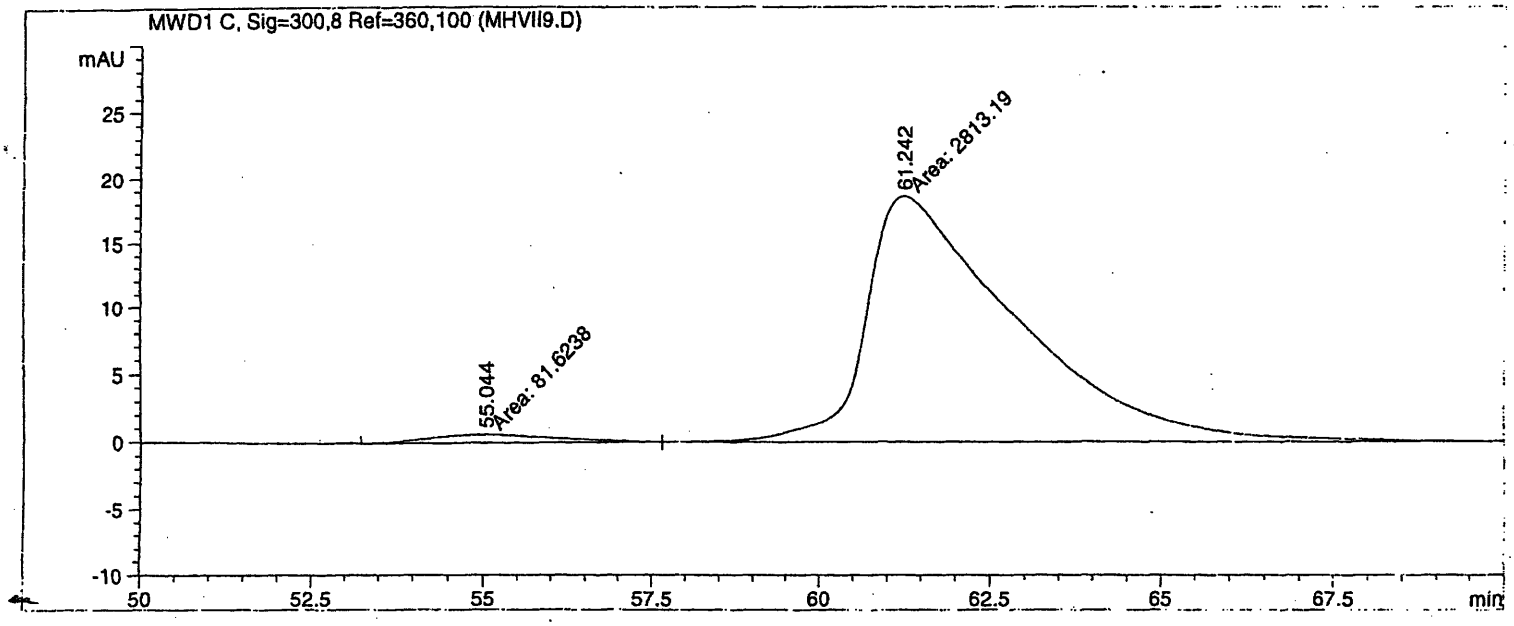
*** End of Report ***



4ee



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

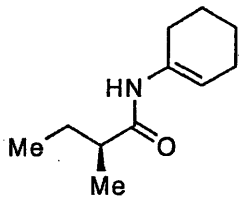
Signal 1: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.044	MM	2.1536	81.62379	6.31687e-1	2.8197
2	61.242	MM	2.5261	2813.19092	18.56096	97.1803

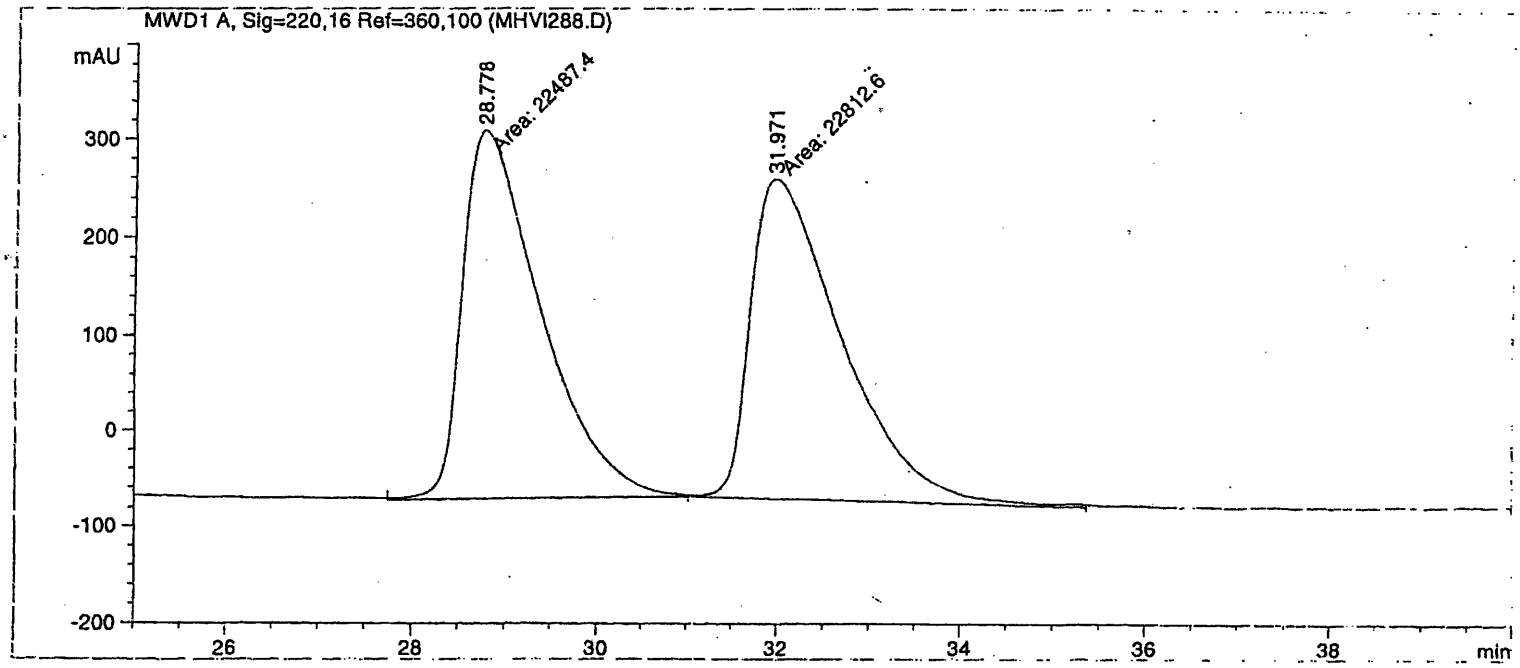
Totals : 2894.81470 19.19264

Results obtained with enhanced integrator!

*** End of Report ***



1n



Area Percent Report

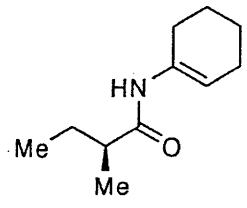
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=220,16 Ref=360,100

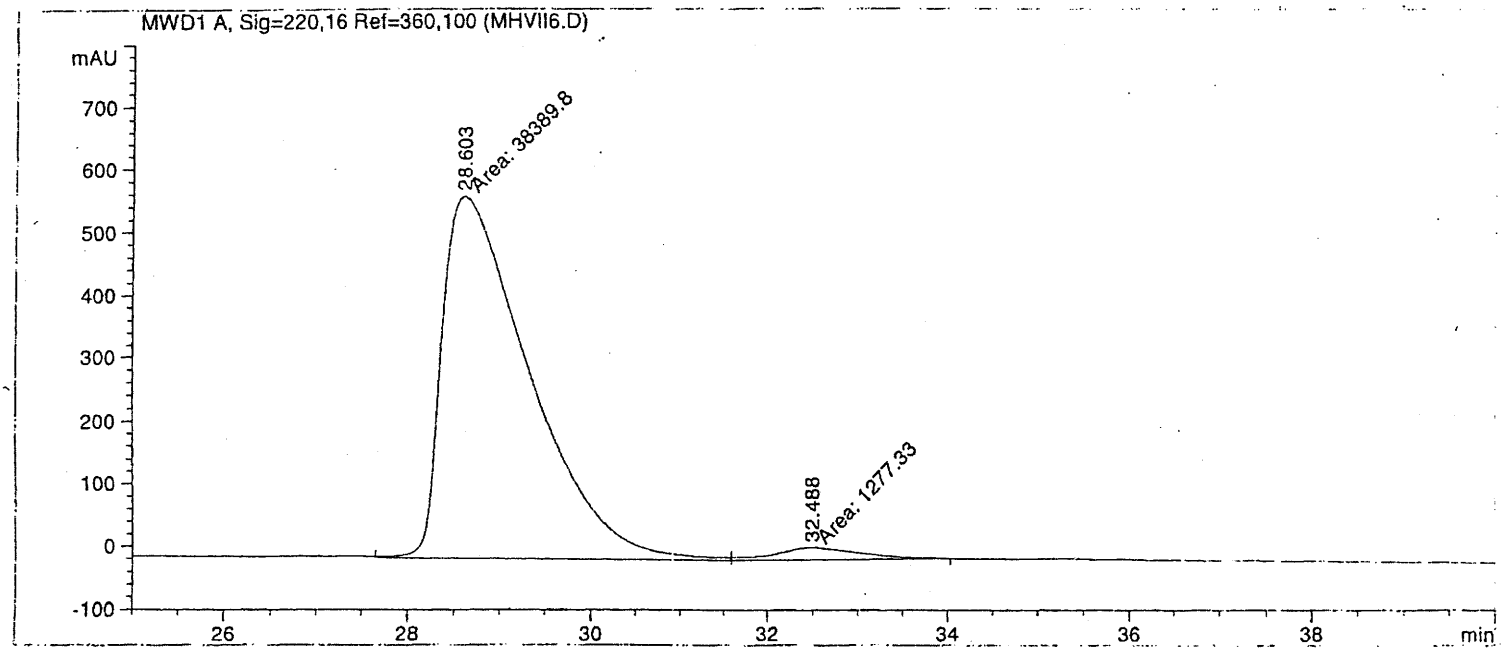
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.778	MM	0.9852	2.24874e4	380.43207	49.6411
2	31.971	MM	1.1508	2.28126e4	330.39188	50.3589
Totals :				4.53000e4	710.82394	

Results obtained with enhanced integrator!

*** End of Report ***



1n




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.603 MM    1.1097 3.83898e4   576.55585  96.7799
   2  32.488 MM    1.1118 1277.32971   19.14890   3.2201

Totals :                  3.96672e4   595.70474

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

Matthew Dennis Hill

Curriculum Vitae

Education

Massachusetts Institute of Technology, Cambridge, MA.
Ph.D. Organic Chemistry (expected 2008)
Thesis title: "Direct Synthesis of Pyridine and Pyrimidine Derivatives."

Ohio University, Athens, OH.
B.S. Biochemistry; Molecular Biology; B.S.C. Legal Communication

Research Experience

2003-present — Graduate Research Associate, Massachusetts Institute of Technology
Professor Mohammad Movassaghi, Advisor.
- Development of efficient methodology for azaheterocycle synthesis.

2003 — Undergraduate Researcher, Massachusetts Institute of Technology
Professor Alice Ting, Advisor.
- Investigation toward incorporation of biotin analogues into biotin transferase.

2001-2003 — Undergraduate Researcher, Ohio University
Professor Mark McMills, Advisor.
- Development of new synthetic methodologies for Phorbol analog synthesis.

2002 — NSF REU Undergraduate Researcher, Columbia University
Professor Koji Nakanishi, Advisor.
- Investigation of causes for age-related macular degeneration.

Teaching Experience

2003-2007 — Three semesters teaching assistantship (MIT): two organic chemistry courses (head TA for Professors M. Movassaghi/S. Buchwald) and one laboratory course.

2001-2003 — Five quarters peer mentorship (Ohio University): three organic chemistry courses (Professors M. McMills/J. Butcher).

Academic Honors and Awards

2007 — MIT Wyeth Scholar, Amgen Summer Fellowship (MIT), Morse Travel Grant (MIT)

2003 — Rhodes Scholarship State Finalist (Tennessee), Upper Ohio Valley of the American Chemical Society La Vallee Award.

2002 — Barry M. Goldwater Scholarship, NSF REU Fellowship at Columbia University, Jeanette Grasselli-Brown Research Fellowship (Ohio University), Omicron Delta Kappa Torch Scholarship (Ohio University), Lela Ewers Science Scholarship (Ohio University), Chemistry Scholarship (Ohio University), Three-time recipient of the Deans Scholarship (Ohio University), Two-time recipient of the Hiram Roy Wilson Scholarship (Ohio University), Two-time recipient of the Jesse Day Undergraduate Chemistry Award (Ohio University).

2001	Lubrizol Foundation Chemistry Scholarship (Ohio University), Sandra Lou McKay Memorial Scholarship (Ohio University), Paul C. and Beth K. Stocker Scholarship (Ohio University), Upper Ohio Valley Section of the American Chemical Society Sophomore Award.
2000	Ohio University Foundation Scholarship, CRC Handbook Award for General Chemistry (Ohio University), Provost Scholarship (Ohio University).

Professional Activities

2007-present	American Chemical Society: member of the Organic Division
2006-present	MIT Chemistry Outreach affiliate (program to stimulate interest in chemistry).
2001-2003	Alpha Chi Sigma: vice president (professional chemistry organization).

Publications

"Observations On the Use of Microwave Irradiation in Azaheterocycle Synthesis," Hill, M. D.; Movassaghi, M. *Tetrahedron Lett.* **2008**, *in press*.

"New Strategies for Synthesis of Pyrimidine Derivatives," Hill, M. D.; Movassaghi, M. *Chem. Eur. J.* **2008**, *in press*.

"Synthesis of Substituted Pyrimidines and Quinazolines," Hill, M. D.; Movassaghi, M. *Synthesis* **2008**, 823–827.

"Single-Step Synthesis of Alkynyl Imines from *N*-Vinyl and *N*-Aryl Amides. Synthesis of *N*-Phenyl-2-phenyl-4-trimethylsilyl-1-azabut-1-en-3-yne," Movassaghi, M.; Hill, M. D. *Org. Synth.* **2008**, *85*, 88–95.

"Direct Synthesis of Pyridine Derivatives," Movassaghi, M.; Hill, M. D.; Ahmad, O. K. *J. Am. Chem. Soc.* **2007**, *129*, 10096–10097.

"Single-Step Synthesis of Pyrimidines by Direct Condensation of Amides and Nitriles," Movassaghi, M.; Hill, M. D. *Nat. Protoc.* **2007**, *2*, 2018–2023.

"Synthesis of Substituted Pyridines and Quinolines," Hill, M. D.; Movassaghi, M. *Synthesis* **2007**, 1115–1119.

"Single-step Synthesis of Pyrimidine Derivatives," Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 14254–14255.

"Synthesis of Substituted Pyridine Derivatives via the Ruthenium-Catalyzed Cycloisomerization of 3-Azadienynes," Movassaghi, M.; Hill, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 4592–4593.

Presentations

"New Methodologies for the Synthesis of Azaheterocycles."
- Oral presentation: American Chemical Society National Meeting (Boston, MA, August 2007).
- Poster: Gordon Research Conference: Heterocyclic Compounds (Newport, RI, June2007).
- Oral presentation: Graduate Research Symposium: MIT (Cambridge, MA, January 2007).

"Spectroscopic Determination of Changes in Vesicle Permeability Due to A2E." Oral presentation: REU Summer Seminar: Columbia University (New York, NY, August 2002).