Asymmetric Nickel-Catalyzed Three-Component Assembly of Allylic Amines from Alkynes, Imines and Organoboron Reagents

by

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B. S., Chemistry and Biology
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Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
IN ORGANIC CHEMISTRY

at the

Massachusetts Institute of Technology
May 2004 [June 2004]

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Chairman, Departmental Committee of Graduate Students

V. 1

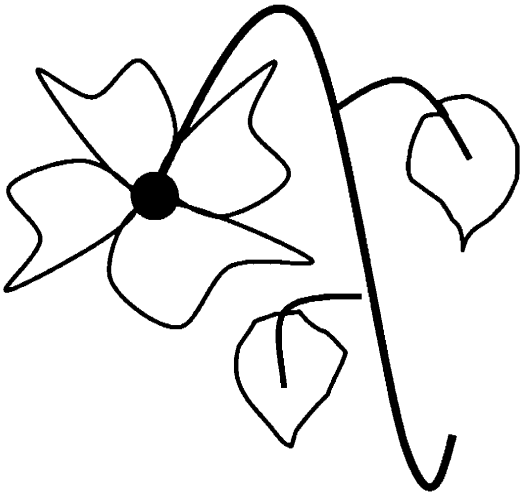
This doctoral thesis has been examined by a committee of the Department of Chemistry as follows:

Professor Gregory C. Fu _____ Chairman

Professor Timothy F. Jamison _____ Thesis Supervisor

Professor Timothy M. Swager _____

To My Family and Friends



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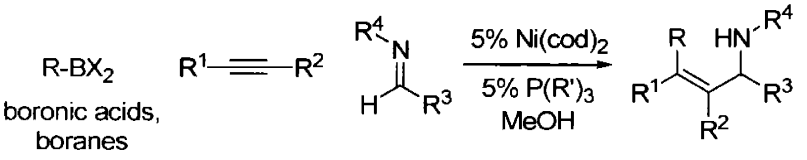
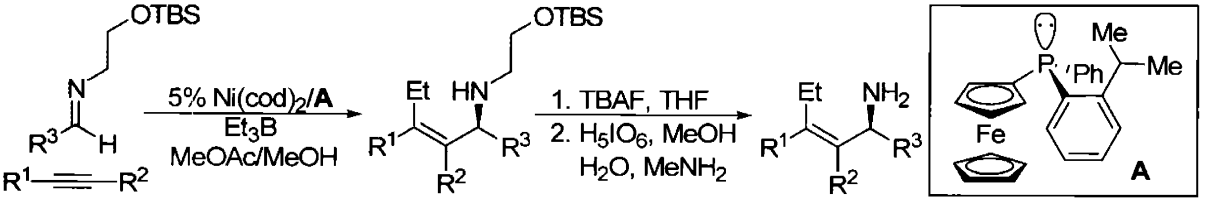
ABSTRACT



exclusive cis addition across alkyne (>97:3)
compatible with ketones, esters, and hydroxylic solvents

Allylic amines are assembled in one step from alkynes, imines, and organoboron reagents (boronic acids or boranes) using a catalyst derived from $Ni(cod)_2$ and $(c\text{-}C_5H_9)_3P$ or $(o\text{-anisyl})_3P$. This catalytic, three-component process is tolerant of ketones, esters, and free hydroxyl groups; a degree of functional group compatibility unusual for imine addition reactions. The mode of addition across the alkyne is exclusively *cis* (>97:3), thereby establishing the alkene geometry of the product in the course of two carbon-carbon bond forming events. Even though nickel-catalyzed multi-component coupling reactions involving additions to carbonyl compounds have been reported, the process described herein is the first such example involving imines and also the first that utilizes boronic acids.



An enantioselective catalytic version of the above reaction is developed to provide enantiomerically enriched, tetrasubstituted allylic amines in a single operation. Using the complex derived from $Ni(cod)_2$ and a *P*-chiral ferrocenyl phosphine **A**, both aliphatic and aromatic alkynes and imines undergo coupling reactions in high yields (up to 95%) and enantioselectivities (up to 89%). A (*tert*-butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2$–) group on the imine nitrogen not only maximizes reactivity and selectivity in these transformations, but is

also easily removed after the coupling reaction providing direct access to versatile primary allylic amines that can be recrystallized to optical purity.

Thesis Supervisor: Timothy F. Jamison

Title: Paul M. Cook Career Development Assistant Professor of Chemistry

Preface

Portions of this thesis have appeared in the following articles that were co-written by the author:

Catalytic Three-Component Coupling of Alkynes, Imines, and Organoboron Reagents
Angew. Chem. Int. Ed. **2003**, *42*, 1364-1367.
Patel, S. J.; Jamison, T. F.

Asymmetric Catalytic Coupling of Organoboranes, Alkynes, and Imines Possessing A Removable (Trialkylsilyloxy)ethyl Group — Direct Access to Enantiomerically Pure Primary Allylic Amines
Angew. Chem. Int. Ed. **2004**, *43*, *in press*.
Patel, S. J.; Jamison, T. F.

Acknowledgements

First, I would like to thank Professor Timothy F. Jamison for providing me with the opportunity to pursue research in his laboratory. I have learned an enormous amount of chemistry during my time in his group, and from him personally.

Along with Professor Jamison, Professor Gregory C. Fu, Professor Timothy M. Swager, Professor Peter Seeberger are gratefully acknowledged for being an integral part of my thesis committee. I really enjoyed the opportunity to discuss my research and chemistry with them. I would also like to thank Professor Barbara Imperiali for her support during my job search.

I am indebted to all the past and present members of the Jamison group for making the lab a great place to work and learn. Dr. Wei-Sheng Huang and Dr. Carmela Molinaro are greatly acknowledged for their distinguished mentoring, support and enthusiasm. I would like to thank Johann Chan, Elizabeth Colby and Karen Miller for their assistance with the preparation of phosphine ligands. I want to thank my desk, gym and birthday buddy Timothy Heffron for those unforgettable moments and for teaching me how to play cards. Thank you very much Chudi Ndubaku for walks home, you are one of the nicest people I know. Special thanks to David Goeddel and Andrew Knox for keeping the lab constantly lively. I would like to thank Aaron Skaggs for just listening on venting coffee breaks. Despite our rough moments during synthesis meetings, it was wonderful to have met Robert Jackson, and I know one day you will make a great lawyer. Lastly, I want to thank Dr. Graham Simpson, Ryan Moslin, Jim Trenkle, Cici Ng, Victor Gehling, and Brandon Conley, Valer Jeso, Justin Cohen, Andrew Wong, Eleanor Lin, Darlene Staines, Ryan Zeidan, Torsak Luanphaisarnnont, Anna Hirsch, KC O'Brien, Jianlong Tang and Joel Yuen for smiley greetings in the lab.

I would like to thank Chugster, Moli, Monodeuterated Benzene. Johann, Graham and Heffron for all their useful suggestions and corrections through the early drafts of my thesis. I know it was not easy proof reading 'sejalese' and I truly appreciated all your help in smoothing out rough thesis.

I want to thank members of the Buchwald and Fu group for their generous help with instruments, experimental details, and lending chemicals and glassware. I want to thank Dr. Jeff Simpson, Dr. Mark Wall and Dr. David Bray with NMR assistance, Li Li for conducting HR-MS, and Bill Davis for X-ray structural analysis. I want to thank everyone from Chemistry Education Office and Chemistry Headquarters during my time here especially Susan Brighton for always knowing the answer to every question. I also want to thank Marcia and Kevin for their invaluable administrative assistance.

I want to acknowledge my undergraduate supervisor Prof. Allen Gibbs and Prof. Christopher Grayce for providing me an opportunity to work in their labs and introducing me to research. I was never able to get grasshoppers to mate on my first research project, but without that experience, I would have never considered going to graduate school.

From the first week that I started at MIT, till the last week I will be in Boston, THDA members have always been available to drink, laugh and chill out on a moments notice. Many thanks to Linda for visits to the Cape and slightly hazardous activities, Lara for relaxing lunches, Miranda and Oliver for curry dinners and allowing me to look after Ophie, Conor, Jay and Corey for Frankenstein, Trivial Pursuit and poker games, Susan for afternoon Teas, Gary for poutin and fried items, Tom, Kevin, Katie, Peter and Wojciech for good memorable moments. I am especially grateful to Linda and Lara for all their support in good and bad times.

I want to thank Mey and Cara for dancing nights, Sanjay for being my personal shrink, Arindam for intense conversations, Emily for the best times and good laughs, Ksenia for an excellent Russian food, Vandana and Ayesha for going to Garba and watching Bollywood movies, Luisa and Antonio for their generous hospitality during my trip to Italy. I am truly grateful to Luisa for her priceless friendship and would like to thank her for her support during my swimming lessons, breakfast at 1369 Coffee House, fabulous dinners and offering me a ride to whenever and wherever.

I would like to acknowledge my undergraduate mates Pavana, Mike, Jigna, Vy and Uyen for their support and friendship through graduate school. Special thanks to Yong, Hong, Maria, Alice and Isaac from Kosan Biosciences for their wise advice and encouragement. I also want to thank all my current and former housemates for making 36 Adrian St Home. Linda, Susan, Lara, Stephanie, Robert, Maurice, Oyvind, David, Andres, Mey, Luisa, Emma, Joby, Rocco and Jen, it was a pleasure watching television, and having dinner together.

I want to thank members of Women in Chemistry for their friendship and assistance. It has also been my great pleasure participating and planning activities offered by Graduate Student Council, Indian Business Club and SAAS cultural show at MIT.

I would like to thank each and every member of my 'Patel' family for their constant love, care, enthusiasm and encouragement. I am indebted to my family, especially, my aunt Rekha for always showing me positive side of the worst situations. I also like to thank my cousin Mona for allowing me to visit her in NY whenever I was homesick and needed home cooked Indian food.

Last but not least, I thank my parents for their continual support and encouragement in my education and life. Words are not enough to express my sincere gratitude.

-Creative Cat, 2004

Table of Contents

Abbreviations

9-BBN	9-borabicyclo[3.3.1]nonane
AC	alkylative coupling
Alk	Alkyl
Ar	Aryl
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binapthyl
Bn	benzyl
Cy	cyclohexyl
Cyp	cyclopentyl
δ	chemical shift in parts per million
dppe	1,2-Bis(diphenylphosphino)ethane
dppb	1,4-Bis(diphenylphosphino)butane
dppf	1,1'-Bis(diphenylphosphino)ferrocene
DuPhos	(-)-1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene
ee	enantiomeric excess
eq	equation
EtOAc	ethyl acetate
EtOH	ethanol
Fc	ferrocenyl
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectroscopy
Hz	hertz
IPA	isopropanol
IR	infrared
m	meta
M	molar
Me-BPE	(+)-1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)ethane
MeOAc	methyl acetate
(*R*)-MOP	(*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl
MHz	megahertz
mmol	millimole
μL	microliter
mL	milliliter
MS	mass spectroscopy
NMDPP	(neomenthyl)diphenylphosphine
NMR	nuclear magnetic resonance
o	ortho
p	para
SiO_2	silica gel
RC	reductive coupling
RT	room temperature
t_R	retention time
TLC	thin layer chromatography
Tos	tosyl
TBAF	tetrabutylammonium fluoride
TBS	*tert*-butyldimethylsilyloxy

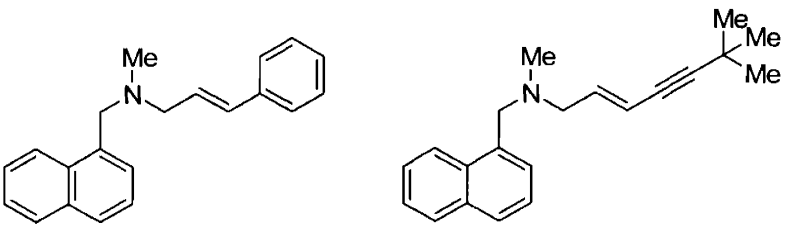
Chapter 1

Nickel-catalyzed Three-component Assembly of Alkynes, Imines and Organoboron Reagents

A. Introduction

Allylic amines are key structural features found in several marine natural products such as microcystins, nodularin, motuporin, cyclotheonamides, and criamides.[1] They are also powerful specific inhibitors of fungal squalene epoxidase, a key enzyme in sterol biosynthesis (Figure 1.1).[2] For example, SF 86-237 (Lamisil®) is highly active *in vitro* against wide range of fungi, and is the most prescribed medicine (US $ 873 million in sales 2003) against nail fungal infections.

Figure 1.1. Antifungal agents containing allylic amine functionality.



Naftifine (Exoderil®) SF-86-237 (Lamisil®)

Furthermore, allylic amines have found use in the synthesis of α– and ß– amino acids and other widely used compounds by way of a variety of functional group manipulations.[3] Due to the great utility of allylic amines, their synthesis has attracted attention from several groups.

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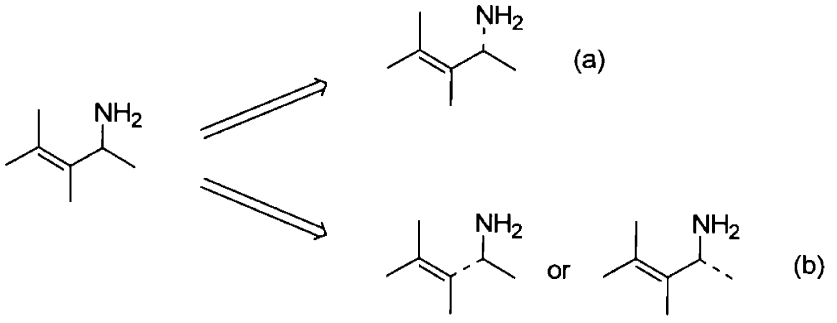
(1) (a) Microcystins and nodularin: Reinhart, K. L.; Harada, K.-i.; Namikoshi, M.; Chen, C.; Harvis, C. A.; Munro, M. H. G.; Blunt, J. W.; Mulligan, P. E.; Beasley, V. R.; Dahlem, A. M.; Carmichael, W. W. *J. Am. Chem. Soc.* **1988**, *110*, 8557. (b) Motuporin: de Silva, E. D.; Williams, D. E.; Anderson, R. J.; Klix, H.; Holmes, C. F. B.; Allen, T. M. *Tetrahedron Lett.* **1992**, *33*, 1561. (c) Cyclotheonamides: Fusetani, N.; Matsunaga, S.; Matsumoto, H.; Takebayashi, Y. *J. Am. Chem. Soc.* **1990**, *112*, 7053. (d) Criamides: Coleman, J. E.; de Silva, E. D.; Kong, F.; Andersen, R. J.; Allen, T. M. *Tetrahedron* **1995**, *51*, 10653. (e) Leucascandrolide A: D'Ambrosio, M.; Guerriero, A.; Debitus, C.; Pietra, F. *Helv. Chim. Acta* **1996**, *79*, 51.

(2) Petranyi, G.; Ryder, N. S.; Stütz, A. *Science* **1984**, *224*, 1239.

(3) Examples: (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1027. (b) Hagihara, M.; Anthony, N. J.; Stout, T. J.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 6568. (c) Vedejs, E.; Gringras, M. *J. Am. Chem. Soc.* **1994**, *116*, 579. (d) Johnson, T. A.; Curtis, M. D.; Beak, P. *J. Am. Chem. Soc.* **2001**, *123*, 1004. (e) Takasago process: Noyori, R. *Asymmetric Catalysis in Organic Synthesis*, Wiley: New York, 1994.

Methods to make allylic amines can be categorized into two main groups: (a) C-N bond formation and (b) C-C bond formation (Scheme 1.1).

Scheme 1.1. Possible approaches for allylic amine synthesis:
a) C-N or b) C-C bond forming reactions.



Nucleophilic allylic amination of an already functionalized allylic C-X (X = heteroatom, halide) is one of the simplest and direct ways of synthesizing allylic amines. Electrophilic amination of an unfunctionalized double bond by C-H activation is also an attractive strategy.[4] In contrast, addition of organometallic reagents to α, β-unsaturated imines and alkenylmetal reagents to imines are commonly used methods that feature carbon-carbon bond formation and the creation of a new stereogenic center.[5]

Petasis and coworkers have reported a one-step, multi-component process involving the condensation of alkenyl, or aryl boronic acids with amines and certain carbonyl compounds, such as α-keto acids and α-hydroxy aldehydes, leading to allylamines (Scheme 1.2).[6]

---

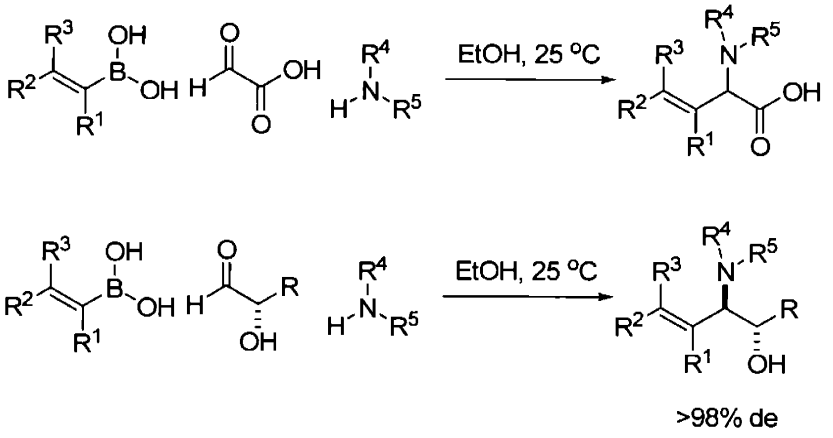
(4) For recent review on allylic amination: (a) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689. For hydroamination of 1,3 dienes: (b) Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669.

(5) Asymmetric addition to imines to synthesize enantiomerically-enriched allylic amines will be discussed in Chapter 2, Background.

(6) (a) Petasis, N. A.; Akritopoulou, I. *Tetrahedron Lett.* **1993**, *34*, 583-586. (b) Petasis, N. A.; Zavialov, I. A. *J. Am. Chem. Soc.* **1997**, *119*, 445. (c) Petasis, N. A.; Zavialov, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 11798.

Vinylboronic acid is unreactive with an isolated iminium salt, suggesting that the formation of a vinylboronate adduct with a pendant heteroatom on the electrophile is required.[7]

Scheme 1.2. Synthesis of allylic amines from alkenyl boronic acids.



Wipf and coworkers have reported in situ hydrozirconation of terminal alkynes, followed by transmetalation to zinc and addition to *N*-diphenylphosphinoylimines to give allylic amines (Scheme 1.3, eq 1).[8] No addition to the imine occurs in the absence of the dialkylzinc additive and stoichiometric dimethylzinc is necessary for efficient reactivity. Recently, Rh(I) catalyzed addition of alkenylzirconocene chlorides to *N*-Tos aldimines have been reported (Scheme 1.3, eq 2).[9]

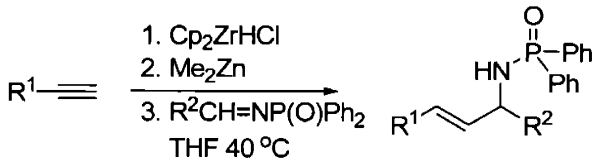
---

(7) (a) Petasis, N. A.; Patel, Z. D. *Tetrahedron Lett.* **2000**, *41*, 9607. (b) Schlienger, N.; Bryce, M. R.; Hansen, T. K. *Tetrahedron Lett.* **2000**, *41*, 1303. (c) Wang, Q.; Finn, M. G. *Org. Lett.* **2000**, *2*, 4063. (d) Petasis, N. A.; Boral, S. *Tetrahedron Lett.* **2001**, *42*, 539. For related reaction involving N-acyliminium ions, see (e) Batey, R. A.; MacKay, D. B.; Santhakumar, V. *J. Am. Chem. Soc.* **1999**, *121*, 5075.

(8) (a) Wipf, P.; Kendall, C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2001**, *123*, 5122. (b) Wipf, P.; Kendall, C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2003**, *125*, 761.

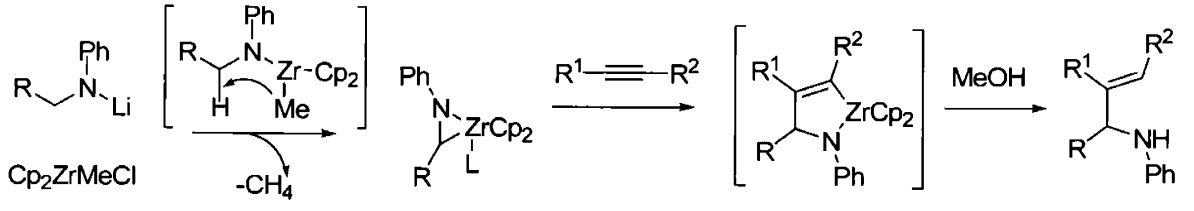
(9) (a) Kakuuchi, A.; Taguchi, T.; Hanzawa, Y. *Tett. Lett.* **2003**, *44*, 923. (b) For a single report of Rh(I) catalyzed addition of vinyl tin to aldimine, see: Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tetrahedron Lett.* **1999**, *40*, 9259.

Scheme 1.3. Dimethylzinc-mediated and Rh(I) catalyzed additions of alkenylzirconocenes to aldimines.



Alternatively, Buchwald and coworkers have reported imine zirconocene complexes that react with alkynes to afford geometrically pure allylic amines after protonation.[10] As shown in Scheme 1.4, treatment of zirconocene(methyl) chloride with secondary amide forms a zirconocene-imine complex as an intermediate *via* a formal β-H elimination followed by reductive elimination of methane. Excellent substrate scope and good reaction yields are observed. However, the requirement of a stoichiometric amount of transition metal complex is a drawback for practical use. Related examples involving titanium and tantalum complexes of alkynes that react with imine electrophiles have also been reported to yield allylic amines.[11]

Scheme 1.4. Reactions of alkynes with imine zirconocene complexes.



(10) (a) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. Related example involving reductive cocyclization of alkynes and unsaturated hydrazones mediated by zirconocene complexes, see (b) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495.

(11) (a) Takai, K.; Miwatashi, S.; Kataoka, Y.; Utimoto, K. *Chem. Lett.* **1992**, 99. (b) Gao, Y.; Harada, K.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 5913.

Each of the above mentioned methods for synthesizing allylic amines *via* carbon-carbon bond forming reactions are stoichiometric in transition metals, and/or require directing groups on the electrophiles. At the onset of our studies there were no general, direct, and practical methods of synthesizing allylic amines in a catalytic fashion from alkynes and imines. If this were feasible, these widely used organic functional groups could be joined in a single catalytic operation and also be amenable to enantioselective synthesis to provide enantiomerically enriched, chiral allylic amines.

Transition metal-catalyzed coupling reactions enable convergent synthesis and are among the most efficient methods of assembling complex organic molecules from simpler fragments.[12] Our group reported the first highly selective, nickel-catalyzed intermolecular *reductive coupling* of alkynes and aldehydes (Scheme 1.5).[13] Exclusive *cis* addition across the alkyne is observed; both internal and terminal alkynes, and aliphatic and aromatic aldehydes undergo reductive coupling in good to excellent yields and regioselectivity. In most cases, 100 mol% of the alkyne and 100 mol% of the aldehyde are sufficient for high yields. A related nickel-catalyzed, intermolecular *alkylative coupling* of terminal alkynes, aldehydes and dialkylzinc reagents has been reported by Montgomery and co-workers to prepare trisubstituted allylic alcohols (Scheme 1.6).[14]

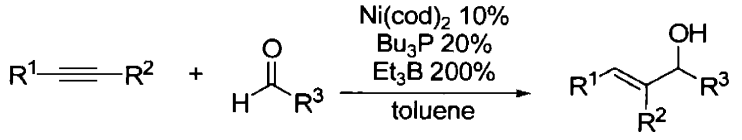
---

(12) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley: New York, 1997.

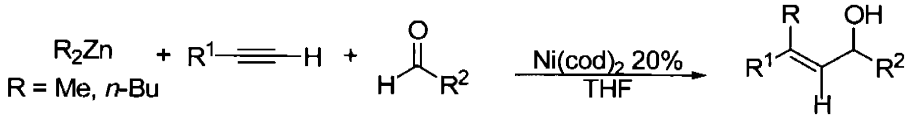
(13) (a) Huang, W. S.; Chan, J.; Jamison, T. F. *Org. Lett.* **2000**, *2*, 4221. (b) For alkene-directed, nickel-catalyzed coupling reactions of alkynes: Miller, K. M.; Luanphaisarnnont, T.; Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 4130. (c) For recent report on intermolecular coupling of alkyne and aldehydes using $Ni(cod)_2$ and imidazolium carbene ligands: Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698.

(14) (a) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065. (b) Ni, Y.; Amarasinghe, K. K. D.; Montgomery, J. *Org. Lett.* **2002**, *4*, 1743. For reductive cyclizations of alkynals, see: (d) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 6098. (e) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **2000**, *122*, 6950.

Scheme 1.5. Nickel-catalyzed, intermolecular reductive coupling of alkynes, and aldehydes.



Scheme 1.6. Nickel-catalyzed, intermolecular alkylative coupling of alkynes, and aldehydes.



Even though there are several examples of nickel-catalyzed, multi-component coupling reactions involving additions to carbonyl compounds,[13-15] to the best of our knowledge there are no such examples (either intermolecular/intramolecular or alkylative/reductive coupling) involving addition to imines.

One of the challenges in developing this catalytic reaction is the requirement for a stoichiometric reducing agent. The starting materials and products are all subject to reduction, and undesired oligomerization of the alkynes and imines can be problematic.[16] Furthermore, imines and related C=N functionalities have some unusual chemical properties that make their selective, catalytic addition more complex than that of the carbonyl compounds. First, even though imine preparation starting from the corresponding amine derivative and carbonyl compound is relatively simple, complete conversion is not always possible and formation of

(15) Reaction involving 1,3 dienes: (a) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (b) Kimura, M.; Ezoe, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033. Reviews on nickel-catalyzed multi-component reactions: (c) Montgomery, J. *Acc. Chem. Res.* **2000**, *33*, 467. (d) Ikeda, S. *Acc. Chem. Res.* **2000**, *33*, 511. (e) Ikeda, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 5120.

(16) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, Chapter 7.3.

trimers and oligomers can occur.[17] Second, nucleophilic addition to aldimines is not nearly as developed, partly due to the diminished electrophilicity and the softer Lewis basic character of imines compared to carbonyl groups.[18] Imines are often sensitive to hydrolysis and imine/enamine isomerization, and *syn/anti* isomers of imines can be problematic.[19]

The focus of this chapter is the development of a selective, catalytic assembly of allylic amines from alkynes and imines. Possible mechanisms for this novel transformation and development of removable (*tert*-butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2$–) group on the imine nitrogen is also discussed.

B. Initial Experiments and Optimization Studies

The markedly diminished electrophilicity of imines relative to aldehydes presented significant challenges in our initial experiments. Several different imine electrophiles (Figure 1.2) and reducing agents (Et_3SiH, PMHS, BH_3, Et_3B, Et_3Al, Et_2Zn) were examined for the selective, nickel-catalyzed coupling reaction of alkynes and imines. Under all the conditions examined, however, either no reaction was observed or only undesired side reactions (alkyne polymerization, simple reduction and addition of ethyl group to alkyne and/or imines) took place. In the case of more electrophilic imines such as tosyl imines or phosphonimides, only starting material was isolated, and no polymerization of the starting alkyne was observed. These results suggest that tosyl imines and phosphonimides might act as irreversibly binding ligands for low-valent nickel, making the catalyst inactive.

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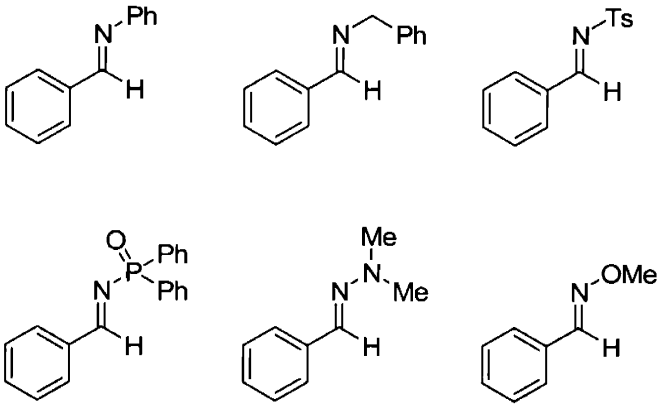
(17) Blaser, H-U.; Spindler, F. Hydrogenation of Imino groups. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Germany, 1999; vol. 1, pp 247-265.

(18) (a) Bloch, R. *Chem. ReV.* **1998**, *98*, 1407. (b) Enders, D.; Reinhold: U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895. (c) Denmark, S. E.; Nicaise, O. J.-C. J. Chem. Soc., *Chem. Commun.* **1996**, 999.

(19) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069.

Figure 1.2. Imines evaluated for nickel-catalyzed couplings of alkynes and imines.



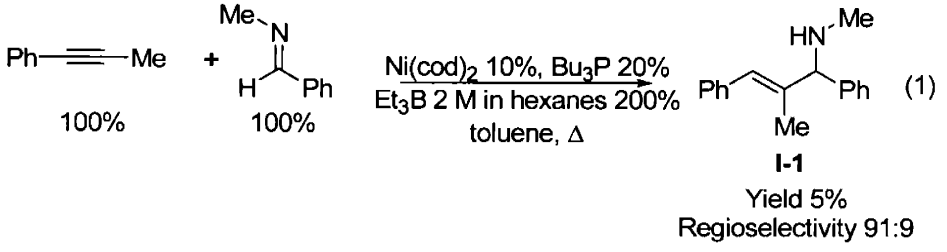
When the imines derived from benzaldehyde and methyl amine, and 1-phenyl-1-propyne were exposed to $Ni(cod)_2$, tributylphosphine, and triethylborane in refluxing toluene, reductive coupling product **I-1** was observed in low yield but with high regioselectivity (eq. 1). Exclusive *cis* addition across the alkyne was observed and carbon-carbon bond formation occurred distal to the aromatic group affording the trisubstituted allylic amine in a single step.[20] Further optimization of reaction conditions by changing the catalyst loading [$Ni(cod)_2$, Bu_3P] to 5 mol%, Et_3B 3M in hexanes (300%) and slow addition of alkyne (200%) afforded a slight increase in reaction yield to 15% when the reaction was run at 50 °C (eq. 2). Even though 15% yield was not synthetically useful, it was the first time catalysis was observed and provided a good starting point for further development.

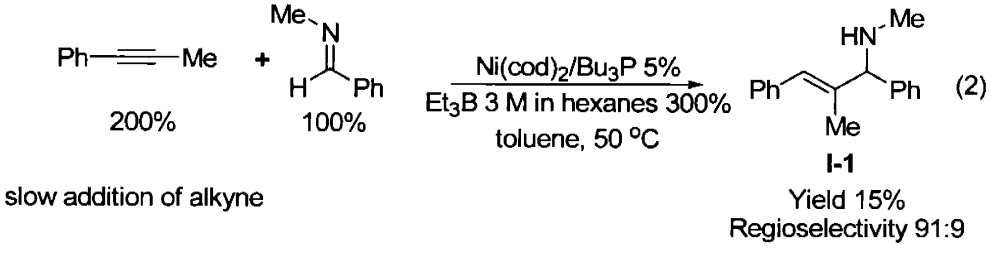
Polymerization of the alkyne was the major competing side reaction, consuming the starting material alkyne. However, no significant increase in reaction yield was observed with dilute reaction conditions or with slow addition of alkyne (>10 hr). The presence of Et_3B at the

(20) Determined using ^1H NMR and NOE measurements.

beginning of the reaction was necessary, and up to 22% yield of **I-1** was obtained with portion-wise addition of Et_3B and alkyne over four hours (see Experimental Section).

Several groups have reported coordination of a Lewis acid with the nitrogen lone pair to enhance electrophilicity of the azomethine carbon of imines.[21] However, no enhancement in reaction yield was observed when several different Lewis acids were employed in the nickel-catalyzed coupling reaction of alkynes and imines.[22]





The coordination of a negatively charged base to the boron atom has been recognized as an efficient method of increasing its nucleophilicity, thereby facilitating the transfer of the organic group on boron to the adjacent positive center (1,2-migration reaction or σ-bond

(21) (a) Wada, M.; Sakurai, Y.; Akiba, K. *Tetrahedron Lett.* **1984**, *25*, 1079. (b) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407.

(22) 100 mol% Lewis acid was used for the reaction as shown in eq. 2. Lewis acids tested: LiCl, $BF_3{\cdot}Et_2O$, CsF, $Ti(i\text{-}OPr)_4$, $AlCl_3$, Et_3Al, Me_3Al, and TMSCl.

metathesis).[23] For example, in Suzuki cross coupling reactions, it is generally believed that Lewis-base additives facilitate the transfer of the organic group to the metal by binding to the organoboron reagent and forming a more reactive four-coordinate "ate" complex.[24] Nevertheless, when a variety of Lewis bases[25] were utilized in our reductive coupling of alkynes and imines, the yield of the desired allylic amine product did not improve.

Triethylborane was the best reducing agent in our hands and the reaction without triethylborane only afforded alkyne polymerization. Other reducing agents such as Et_2Zn, Et_3Al, Et_3SiH, PMHS, BH_3·THF, H_2(g), and 3-pentanol gave either no reaction or complex reaction products that included direct addition of hydride or ethyl group to imines and/or alkynes. In contrast, direct addition of ethyl or hydride from triethylborane to imine was not observed.

The ratio of $Ni(cod)_2$:phosphine was found to be an important parameter. A 1:1 ratio furnished an active catalyst, while 2:1 ratio afforded <5% allylic amine products. Several different classes of phosphine ligands were tested. Monodentate electronically-rich phosphines such as Bu_3P and Et_3P proved to be the best for nickel-catalyzed reductive coupling of alkynes and imines. Bisphosphines (dppe, dppf, racemic BINAP), triarylphosphines (Ph_3P, $FcPPh_2$), phosphoramidates, phosphites, or imidazolium carbene ligands were ineffective for the reductive couplings of alkynes and imines.

A surprising finding with imine coupling reactions was that the choice of solvent determined whether the allylic amine product was the result of a *reductive* coupling (transfer of H from Et_3B, **I-1**) or an *alkylative* coupling (transfer of Et from Et_3B, **I-2**). As shown in

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(23) (a) Onak, T. *Organoborane Chemistry;* Academic: New York, **1975**. (b) Mikhailov, B. M.; Bubnov, Yu. N. *Organoboron Compounds in Organic Synthesis;* Hanvood Academic Pub.: Amsterdam, **1983**. (c) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents;* Academic: New York, **1988**.

(24) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(25) 100 mol% Lewis base was used for the reaction as shown in eq. 2. Lewis bases tested: LiOH, $NaHCO_3$, Na_2CO_3, $KHCO_3$, K_2CO_3, $KHSO_4$, KH_2SO_4, K_2HPO_4, K_3PO_4, and Cs_2CO_3, 4-dimethylaminopyridine.

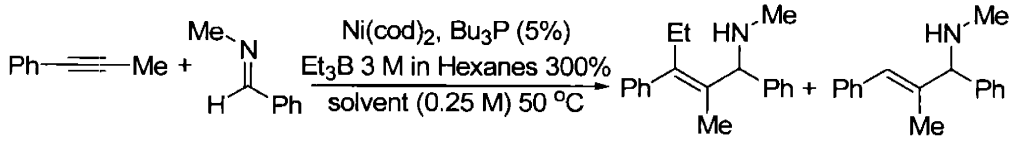
Table 1.1, toluene, THF, and DMF as solvents favored the reductive coupling product (**I-1**), while hydroxylic solvents (MeOH, EtOH, *i*PrOH) favored the alkylative coupling product (**I-2**). Other solvents such as hexanes, acetonitrile, MeOAc and EtOAc were not selective and gave ~1:1 ratio of alkylative and reductive coupling products. Methanol in particular provided substantial increases in reaction yield and selectivity for alkylative coupling product **I-2** (Table 1.1, entry 6) affording geometrically pure tetrasubstituted allylic amines.[26] Methanol increased the yields of the desired coupling reaction while slowing down alkyne polymerization.[27] This solvent dependence on the ratio of alkylative to reductive products offers another level of flexibility to reactions involving imines.[28]

(26) This phenomenon probably does not result from water, as substoichiometric, stoichiometric, or excess amounts depreciate yield. EtOH and iPrOH gave significantly lower yields.

(27) Qualitative GC/MS data. Less polymerization of alkyne was observed when reaction was performed in MeOH.

(28) However, greater than 25% yield of the reductive coupling product **I-1** has not been achieved thus far.

Table 1.1. Solvent dependence on reaction yields and selectivity in nickel-catalyzed coupling reactions of alkynes and imines.[a]



I-2 **I-1**

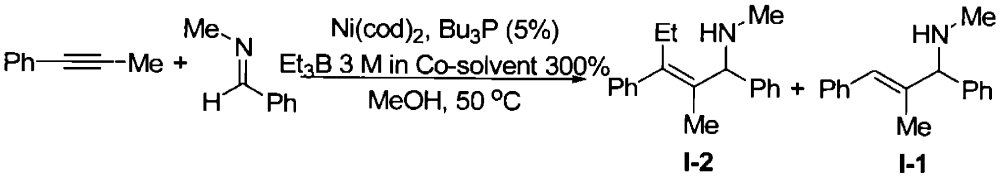
Entry	Solvent	Yield %	**I-2**:**I-1**[b]
1	Toluene	15	< 5:95
2	THF	7	27:73
3	TBME	<5	55:45
4	Hexanes	9	42:58
5	DMF	<5	20:80
6	MeOH	60	94:6
7	EtOH	8	90:10
8	*i*-PrOH	5	71:29
9	CH_3CN	6	50:50
10	EtOAc	6	41:59
11	MeOAc	<5	40:60

[a] Reaction performed on 1 mmol scale, 200% alkyne and 100% imine used. [b] Ratios determined by ^1H NMR.

Further optimizations were initiated for the nickel-catalyzed *alkylative* coupling reaction to synthesize tetrasubstituted allylic amines. Each individual reaction component was varied to identify the optimal reaction conditions. Very small changes in regioselectivity and alkylative coupling to reductive coupling ratios were observed with different Et_3B solutions (Table 1.2, entry 1-5). However, Et_3B solutions in MeOH and MeOAc provided slightly higher reaction yields. We chose to proceed with 3M Et_3B solutions in MeOAc for further optimization because

it provided comparable results and prevented the decomposition of Et_3B to Et_2BOMe and $EtB(OMe)_2$ upon storage.[29]

Table 1.2. Optimization of catalytic three-component coupling reaction with respect to Et_3B solutions and reaction concentration.[a]



Entry	Co-solvent	MeOH	Yield%	**I-2**:**I-1**[b]	Regioselectivity[c]
1	MeOH	0.25 M	69	94:6	95:5
2	hexanes	0.25 M	59	94:6	95:5
3	toluene	0.25 M	61	93:7	96:4
4	EtOAc	0.25 M	60	94:6	95:5
5	MeOAc	0.25 M	68	94:6	96:4
6	MeOAc	0.50 M	28	90:10	96:4
7	MeOAc	0.67 M	32	90:10	94:6
8	MeOAc	0.25 M	68	94:6	96:4
9	MeOAc	0.20 M	74	95:5	95:5
10	MeOAc	0.17 M	80	94:6	96:4
11	MeOAc	0.14 M	79	87:13	87:13
12	MeOAc	0.12 M	80	87:13	87:13

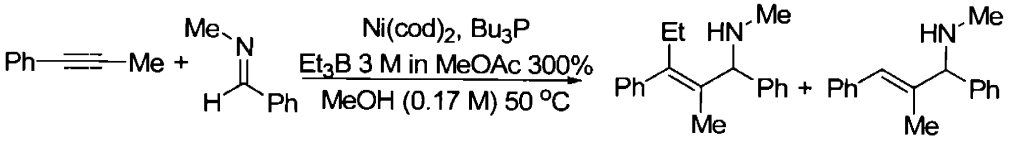
[a] Reaction performed on 1 mmol scale, 200% alkyne and 100% imine used. [b] Ratios determined by ^1H NMR. [c] Regioselectivity in **I-2** (determined by ^1H NMR).

Highest reaction yields and selectivity were observed at 0.17 M reaction concentration (Table 1.2, entry 6-12). At higher reaction concentration, significant alkyne polymerization was observed, leading to low yield of the desired three-component coupling product. Increasing the catalyst loading to 10% did not further increase the reaction yields, and the optimum ratio of

(29) (a) Narasaka, K.; Pai, F.-C. *Tetrahedron*, **1984**, *40*, 2233. (b) Chen, K.-M.; Gunderson, K. G.; Hardtmann, G. E.; Prasad, K.; Repic, O.; Shapiro, M. J. *Chem. Lett.* **1987**, 1923.

$Ni(cod)_2$ to phosphine ligand was 1:1 (Table 1.3). Among the nickel sources examined, $Ni(cod)_2$ was superior than *in situ* generated Ni(0) species.[30]

Table 1.3. Varying nickel to phosphine ratios in catalytic, three-component assembly of allylic amines.



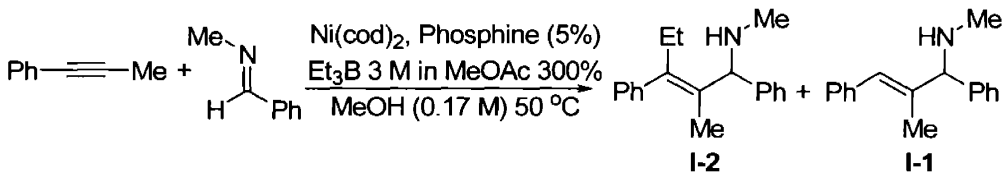
Entry	$Ni(cod)_2$ %	Bu_3P %	Yield %	**I-2**:**I-1**[b]	Regioselectivity[c]
1	5	5	80	94:6	96:4
2	5	10	57	94:6	97:3
3	10	10	78	92:8	96:4
4	10	20	40	95:5	96:4

[a] Reaction performed on 1 mmol scale, 200% alkyne and 100% imine used. [b] Ratios determined by ^1H NMR. [c] Regioselectivity in **I-2** (determined by ^1H NMR).

In order to exclusively favor the alkylative coupling product, several phosphines with varying cone angles were tested (Table 1.4). Notably, larger trialkylphosphines gave the highest yields (entries 1-2) while smaller ones exhibited the highest selectivity (entries 3-6). The electron-rich, tricyclopentylphosphine was the optimum ligand for this transformation, giving both excellent reaction yields and selectivity (entry 3). Reactions conducted using bulky tri(*t*-butyl)phosphine (entry 9), triaryl phosphines (entries 11-12) and bisphosphines (entries 13-15) provided allylic amines in low yields and selectivity.

(30) $Ni(acac)_2$ without reducing agents did not afford the desired coupling reaction. DIBAL-H was the best reducing agent in our hands, and treatment of $Ni(acac)_2$, DIBAL-H and monodentate phosphine in toluene afforded the active catalyst, but around 20% yields of the desired alkylative coupling reactions were obtained. In situ reduction of $NiCl_2$ did not lead to active catalyst.

Table 1.4. Ligand effects in catalytic, three-component assembly of allylic amines.[a]



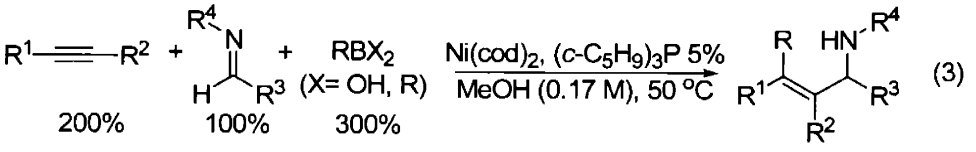
Entry	Phosphine	Yield %	**I-2**:**I-1**[b]	Regioselectivity[c]
1	$(i\text{-Pr})_3P$	90	90:10	89:11
2	Cy_3P	88	89:11	91:9
3	Cyp_3P	85	92:8	91:9
4	Bu_3P	80	94:6	96:4
5	Et_3P	74	94:6	95:5
6	Bn_3P	72	97:3	93:7
7	$(i\text{-Bu})_3P$	71	93:7	96:4
8	$(t\text{-Bu})_2PMe$	70	92:8	92:8
9	$(t\text{-Bu})_3P$	9	93:7	80:20
10	$Cy_2P(o)$-biphenyl	50	94:6	86:14
11	Ph_3P	34	95:5	91:9
12	$FcPPh_2$	16	93:7	92:8
13	dppb	10	96:4	94:6
14	dppe	7	95:5	88:12
15	BINAP	<5	95:5	95:5

[a] Reaction performed on 1 mmol scale, 200% alkyne and 100% imine used. [b] Ratios determined by ^1H NMR. [c] Regioselectivity in **I-2** (determined by ^1H NMR).

In summary, each individual component of nickel-catalyzed three-component coupling reaction was thoroughly examined to optimize the yields and selectivity of tetrasubstituted allylic amines. Best results were obtained with catalyst derived from $Ni(cod)_2$ and tricyclopentylphosphine (1:1), using Et_3B solution in MeOAc at 0.17 M reaction concentration, and portion-wise addition of Et_3B and alkyne over four hours (see Experimental Section).

C. Evaluation of Substrate Scope

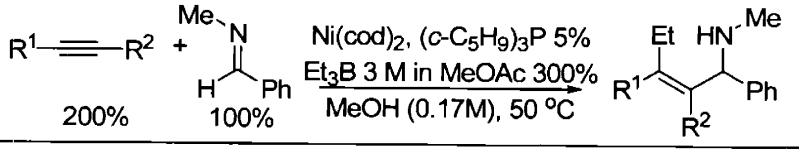
In the previous section, a nickel-catalyzed three-component coupling reaction for the synthesis of tetrasubstituted allylic amines was described. Using the optimum conditions, the reaction substrate scope was evaluated varying alkynes, imines, and organoboron reagents (eq. 3).



(3)

We discovered that a series of alkynes undergo the alkylative three-component coupling in moderate to high yields (Table 1.5). The reactions involving internal alkynes with at least one aryl substituent were high yielding and highly selective, favoring the carbon-carbon bond formation distal to the aromatic group (entry 1). Symmetric aliphatic alkynes were the highest yielding, affording allylic amines in >90% yield (entry 2). Non-symmetric aliphatic alkynes coupled in good yields but poor selectivity (entries 3 and 4). Aryl-aryl alkynes suffered from low solubility in methanol and afforded low yields of the desired coupling product (entry 5). The presence of a bulky trimethylsilyl group on the alkyne afforded protiodesilylated products after silica gel chromatography in low yield but with almost complete alkylative/reductive coupling selectivity and regioselectivity (entries 6 and 8). Terminal alkynes polymerize rapidly under the reaction condition, but both aryl and alkyl substituted terminal alkynes afforded the trisubstituted allylic amine in moderate yield and selectivity (entries 7 and 9).

Table 1.5. Alkyne scope in catalytic three-component assembly of allylic amines[a]



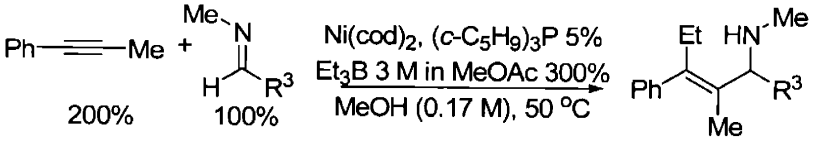
200% 100%

Entry	R^1	R^2	Yield %	Product	AC:RC[b,c]	Regioselectivity[c]
1	Ph	Me	85	**I-2**	92:8	91:9
2	*n*-Pr	*n*-Pr	91	**I-3**	94:6	--
3	*c*-C_6H_{11}	Me	70	**I-4**	85:15	60:40
4[d]	*n*-C_5H_{11}	Me	94	**I-5**	56:44	52:48
5	Ph	Ph	30	**I-6**	n.d.	--
6[e]	Ph	TMS	22	**I-7**	>95:5	>98.2
7[f]	Ph	H	33	**I-8**	93:7	>98:2
8[e]	*n*-C_4H_9	TMS	6	**I-9**	>95:5	>98:2
9	*n*-C_6H_{13}	H	37	**I-10**	68:32	90:10

[a] 1 mmol scale. See Experimental Section for detailed procedures. [b] AC = alkylative coupling and RC = reductive coupling. [c] Determined by ^{1}H NMR. [d] At 0 °C, AC:RC = 90:10, regioselectivity = 55:45, 31% yield. [e] Isolated protiodesilylated product. [f] Benzylidene-propyl-amine was used.

Several imines derived from aromatic aldehydes undergo three-component coupling reactions (Table 1.6). Aromatic imines with moderate steric hindrance (Table 1.6, entry 2), possessing either electron-withdrawing (entries 3-6) or electron-donating (entry 7) groups afforded the desired allylic amines in good to quantitative yields and in high selectivity. Notably, esters and ketones (entries 5 and 6) were compatible, and only selective addition to imines was observed.

Table 1.6. Aromatic Imines in catalytic three-component assembly of allylic amines[a]

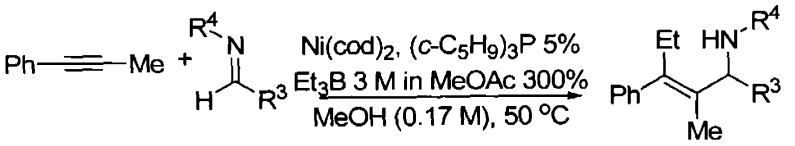


Entry	R^3	Yield %	Product	AC:RC[b,c]	Regioselectivity[c]
1	Ph	85	**I-4**	92:8	91:9
2	*o*-tolyl	85	**I-11**	94:6	90:10
3	(*p*-Cl)Ph	95	**I-12**	96:4	90:10
4	(*p*-CF_3)Ph	98	**I-13**	94:6	89:11
5	(*p*-CO_2Me)Ph	82	**I-14**	>96:4	90:10
6	(*p*-C(O)Me)Ph	78	**I-15**	>96:4	91:9
7	(*p*-OMe)Ph	64	**I-16**	86:14	91:9

[a] 1 mmol scale. See Experimental Section for detailed procedures. [b] AC = alkylative coupling and RC = reductive coupling. [c] Determined by ^{1}H NMR.

Several aliphatic imines also underwent three-component coupling reactions in moderate to good yields and selectivity (Table 1.7). Imine to enamine isomerization was the major competing pathway and side products resulting from Mannich-type reactions were identified. Moreover, allylic amine products derived from aliphatic imines were very polar, preventing their isolation using silica gel chromatography. Accordingly, changing the group on the imine nitrogen from *N*-methyl to *N*-propyl improved the isolated yields of tetrasubstituted allylic amines by twenty percent when imines derived from cyclohexylcarboxaldehyde were used (Table 1.7, entries 1 and 2). In addition, aliphatic alkynes and aliphatic imines were effective coupling partners (entry 3). Imines derived from primary and tertiary aliphatic aldehydes afforded low yields and good selectivity in allylic amine products (entries 4 and 5).

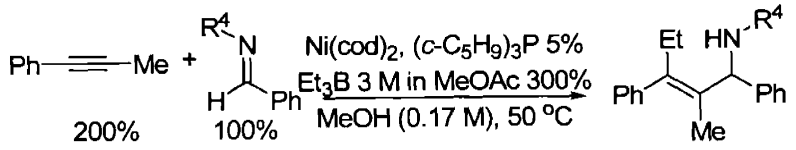
Table 1.7 Aliphatic imines in catalytic three-component assembly of allylic amines[a]

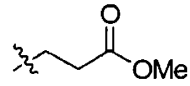


Entry	R^3	R^4	Yield %	Product	AC:RC[b,c]	Regioselectivity[c]
1	*c*-(C_6H_{11})	Me	26	**I-17**	92:8	n.d.
2	*c*-(C_6H_{11})	*n*-Pr	46	**I-18**	94:6	88:12
3[d]	*c*-(C_6H_{11})	*n*-Pr	52	**I-19**	95:5	--
4	*n*-Pr	*n*-Pr	30	**I-20**	90:10	91:9
5	*t*-Bu	Me	18	**I-21**	95:5	n.d.

[a] 1 mmol scale. See Experimental Section for detailed procedures. [b] AC = alkylative and RC = reductive coupling. [c] Determined by ^{1}H NMR. [d] 4-octyne was used.

Table 1.8 Variation of the substituents on the imine nitrogen in catalytic three-component coupling reactions.[a]

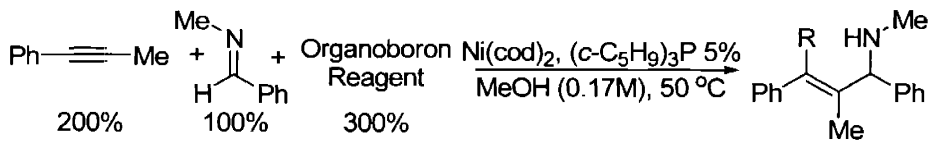


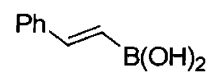
Entry	R^4	Yield %	Product	AC:RC[b,c]	Regioselectivity[c]
1	Me	85	**I-2**	92:8	91:9
2	*n*-C_3H_7	96	**I-22**	95:5	93:7
3		75	**I-23**	94:6	91:9
4	CH_2Ph	53	**I-24**	92:8	88:12

[a] 1 mmol scale. See Experimental Section for detailed procedures. [b] AC = alkylative and RC = reductive coupling. [c] Determined by ^{1}H NMR.

Besides alkyl groups, such as methyl and *n*-propyl, on the imine nitrogen, ß-amino esters and benzyl groups were tolerated in nickel-catalyzed three-component coupling reactions (Table 1.8). Moreover, the imine derived from propylamine was more reactive and selective in comparison to the imine derived from methylamine. Even under optimized conditions, electron-withdrawing groups (tosyl and phosphonyl) on the nitrogen did not undergo the desired coupling reaction.

Table 1.9 Organoboron reagents in catalytic three-component assembly of allylic amines[a]



Entry	Organoboron Reagent	Yield %	Product	AC:RC[b,c]	Regioselectivity[c]
1	Et_3B	85	**I-2**	92:8	91:9
2	$(n\text{-}Bu)_3B$	70	**I-25**	90:10	91:9
3	Ph_3B	65	**I-26**	--	93:7
4[d]	$n\text{-}C_7H_{15}$-(9-BBN)	30	**I-27**	94:6	91:9
5[d]	$PhCH_2CH_2$-(9-BBN)	28	**I-28**	92:8	90:10
6	$PhB(OH)_2$	72	**I-26**	--	92:8
7		68	**I-29**	--	92:8
8	*n*-hexB(OH)$_2$	0	–	--	--

[a] 1 mmol scale. See Experimental Section for detailed procedures.
[b] AC = alkylative and RC = reductive coupling. [c] Determined by ^1H NMR.
[d] 150% alkyl-(9-BBN) used.

In addition to triethylborane, other trialkylboranes and triarylboranes were also effective, affording a variety of tetrasubstituted allylic amines (Table 1.9, entries 1-3). In addition,

(alkyl)-9-BBN reagents derived from hydroboration of alkenes underwent coupling in moderate yields but with good selectivity (entries 4 and 5). While selective transfer of the *n*-alkyl group was observed, chiral organoborane reagents derived from α-pinene boranes were much less reactive (yields <5%), and no enantioselectivity was observed in the formation of the desired alkylative allylic amines.[31]

Of even greater significance was that both alkenylboronic and arylboronic acids were of equal or better efficacy in these reactions (Table 1.9, entries 6 and 7). Since there are no β-hydrogens in triarylboranes or in aryl and vinyl boronic acids, only alkylative coupling products were observed. Unfortunately, alkyl boronic acids did not undergo three-component coupling, likely because of the known difficulty of the transfer of an alkyl group from a boronic acid to a metal.[24] Lewis bases ($K_3HPO_4 \cdot H_2O$, KF) were added to facilitate transmetalation from alkyl boronic acid, yet no reaction was observed.

Even though several organoboranes are commercially available and their synthesis is generally straightforward *via* the hydroboration of olefins, they suffer from the drawback of not being air-stable. In contrast, boronic acids are air-stable, commercially available and are tolerant of many functional groups in comparison to organoboranes. As a consequence of these practical considerations, the ability to employ boronic acids in nickel-catalyzed coupling reactions represented a very important achievement and significantly increased the scope and utility of this method. These were the first examples that utilized boronic acids in nickel-catalyzed multi-component coupling reactions of imines. No direct addition of the organoboron reagents to imines was observed.[32]

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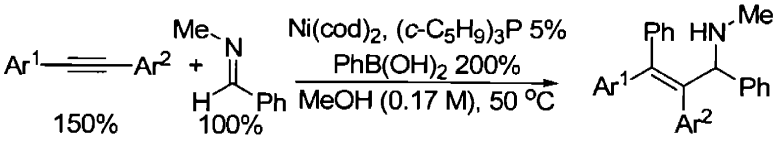
(31) See Experimental Section for reaction details.

(32) (a) Shibata, K.; Kimura, M.; Kojima, K.; Tanaka, S.; Tamaru, Y. *J. Organomet. Chem.* **2001**, *624*, 348. (b) Ueda, M.; Saito, A.; Miyura, N. *Synlett* **2000**, *11*, 1637.

Further studies aimed at the synthesis of tetrasubstituted allylic amines with three different aryl groups were undertaken. Initial experiments with differentially substituted diaryl alkynes and phenyl boronic acid resulted in both poor yields and regioselectivity (Table 1.10). Some steric bias was observed with an *o*-tolyl substituent on the diaryl alkyne (entry 4), but varying the electronic nature of the aryl groups had little effect on regioselectivity. Further studies are necessary to improve these initial observations.

Table 1.10. Phenyl boronic acid in catalytic three-component assembly of allylic amines[a]



Entry	Ar^1	Ar^2	Yield %	Product	Regioselectivity[b]
1[c]	Ph	Ph	65	**I-30**	--
2	Ph	*p*-anisyl	31	**I-31**	55:45
3	Ph	*m*-Cl(Ph)	12	**I-32**	57:43
4	Ph	*o*-tolyl	10	**I-33**	67:33

[a] 1 mmol scale. See Experimental Section for detailed procedures. [b] Determined by ^{1}H NMR. Major product unknown. [c] 20% catalyst used; 36% yield with 5% catalyst.

In summary, this nickel-catalyzed transformation (eq 3) represents a significant amplification of molecular complexity and tolerates aryl ketones, esters and even unprotected hydroxyl groups, three functional groups that are typically problematic in imine addition reactions.[33] This three-component coupling reaction is catalyzed by commercially available

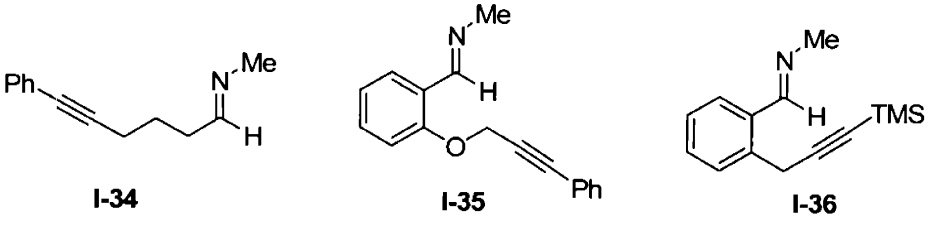
(33) The Strecker and Mannich reactions are similarly tolerant to these functional groups. Examples of imine addition reactions in the presence of aldehydes, see (a) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641. (b) Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1997**, *62*, 232.

$Ni(cod)_2$ and $(c\text{-}C_5H_9)_3P$, and exhibits wide substrate scope. Direct addition of the organoboron reagent to the imine is not observed, and the mode of addition across the alkyne is exclusively *cis* (>97:3), thereby establishing the configuration of the double bond in the course of two carbon–carbon bond-forming events. Methanol appears to be critical for catalytic turnover and alkylative/reductive selectivity. In the optimized reaction conditions, undesired side reactions of the alkynes are minimized, and high yields of the desired tetrasubstituted allylic amines are observed.

D. Catalytic Cyclizations

Catalytic alkylative cyclizations of alkyne-containing imines have the potential to provide allylic amines containing one or more rings, and toward this end several such substrates were synthesized to examine the nickel-catalyzed cyclizations of alkynes and imines (Figure 1.3).

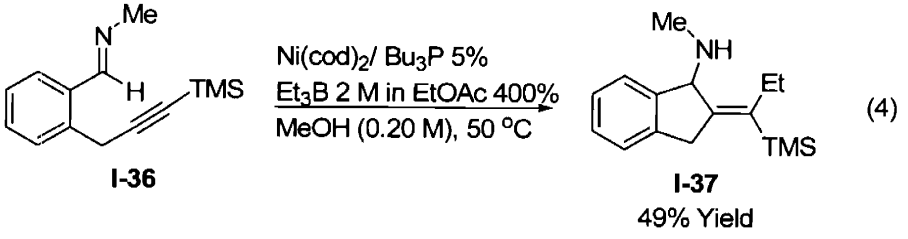
Figure 1.3. Intramolecular substrates for nickel-catalyzed cyclizations.



Starting materials **I-34**, **I-35** and **I-36** were prepared by condensation of the corresponding known aldehydes[34] and methylamine. When these substrates were subjected to the intramolecular nickel-catalyzed reaction, compound **I-34** underwent imine-enamine isomerization leading to undesired oligomerizations. Starting material **I-35** afforded products

(34) For synthesis of aldehydes corresponding to imines **I-34**, **I-35**, and **I-36**, see in order: (a) Oblinger, E; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065. (b) Boger, D. L.; Corbett, W. L. *J.Org.Chem.* **1993**, *58*, 2068. (c) Knobloch, K; Eberbach, W. *Org. Lett.* **2000**, *2*, 1117.

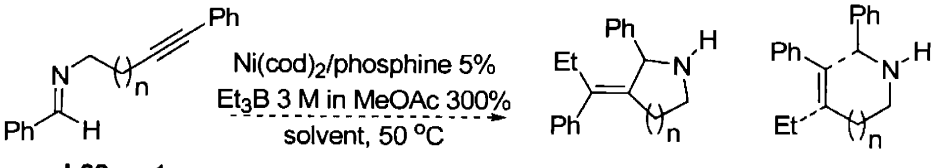
arising from aryl ether bond cleavage. Substrate **I-36**, however, underwent nickel-catalyzed alkylative cyclization in MeOH to provide exclusively tetrasubstituted allylic amine **I-37** as a single regioisomer and diastereomer in 49% yield (eq. 4).[35] A *cis-5-exo-dig* mode of cyclization was observed, despite the fact that the $SiMe_3$ group of the alkyne would normally be expected to favor the opposite sense of regioselectivity (Table 1.5, entries 6 and 8).



I-36 **I-37** 49% Yield (4)

Alkyne containing imines **I-38** and **I-39** were synthesized from condensation of known primary alkynyl amines and benzaldehyde to examine if *cis* addition would be retained or *trans* addition would be favored (Scheme 1.7). However, under a variety of reaction conditions tested these substrates did not undergo nickel-catalyzed cyclizations. If the cyclizations were to proceed *via* an azametallocyclopentene intermediate (Chapter 1, Section E), the products derived from **I-38** and **I-39** would require formation of a double bond at the bridgehead position.

Scheme 1.7. Nickel-catalyzed cyclizations of imines containing alkynes



I-38, n=1
I-39, n=2

cis-addition *trans*-addition

Phosphine = $(c\text{-}C_5H_9)_3P$, Bu_3P or (–)-NMDPP
Solvent = Toluene, THF, or MeOH

(35) Alkene geometry confirmed by 2D NOESY experiment.

E. Proposed Mechanisms

Contrasting mechanisms have been reported for Ni-catalyzed coupling reactions involving carbonyl compounds,[36] but imines have yet to be studied in this regard. Two limiting mechanistic frameworks for nickel-catalyzed three-component coupling reactions of alkynes, imines, and organoboron reagents are illustrated in this section. In these reactions, it is possible that Et_3B plays a dual role — as the reducing/alkylative agent and as a Lewis acid for imine activation.

In proposed mechanism **A**, an azametallocyclopentene is a key intermediate and is formed prior to reductive or alkylative coupling products (Scheme 1.8). Oxidative cyclization of Ni(0) with an alkyne and imine would directly afford an azametallocyclopentene. All attempts to isolate or characterize an azametallocyclopentene intermediate failed in our hands. Nevertheless, this proposed intermediate is analogous to azametallocyclopentenes of early transition metals[10, 11] and related to oxametallocyclopentenes proposed for other nickel-catalyzed couplings of alkynes and aldehydes.[36]

Transmetalation of the organoboron reagent would produce a vinyl nickel species that would either directly undergo reductive elimination to afford alkylative coupling products or β-hydride elimination followed by reductive elimination to afford reductive coupling products. Since there are no β-hydrogens when triarylboranes, aryl and vinyl boronic acids were utilized, only alkylative coupling products are observed (Table 1.9).

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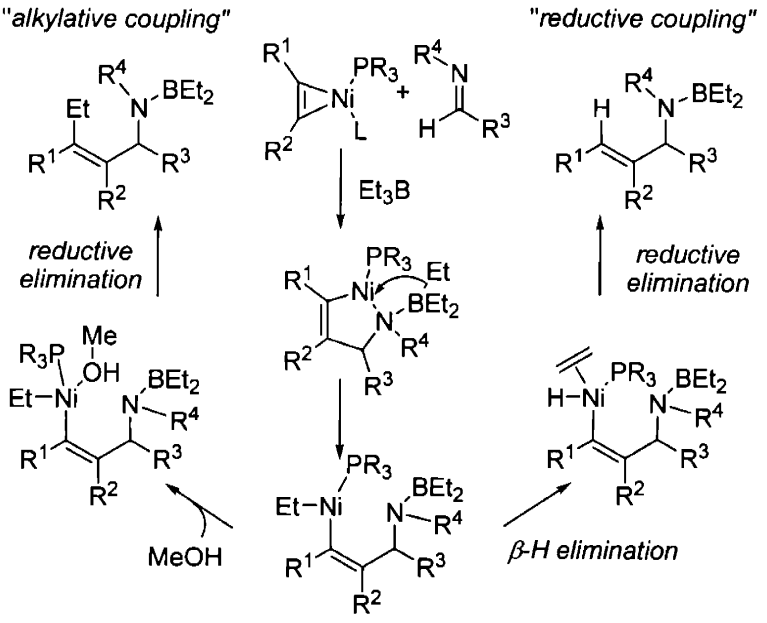
(36) (a) Tsuda, T.; Kiyoi, T.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2554. (b) Sato, Y.; Takanashi, T.; Mori, M. *Organometallics* **1999**, *18*, 4891. (c) Sato, Y.; Saito, N.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 2371. (d) Chowdhury, S. K.; Amarasinghe, K. K. D.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **2000**, *122*, 6775. (e) Amarasinghe, K. K. D.; Chowdhury, S. K.; Heeg, M. J.; Montgomery, J. *Organometallics* **2001**, *20*, 370. (f) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698.

Scheme 1.8. Proposed mechanism **A** for the nickel-catalyzed reactions of alkynes, imines and organoboron reagents (Et_3B as shown) – azametallocyclopentene as an intermediate.



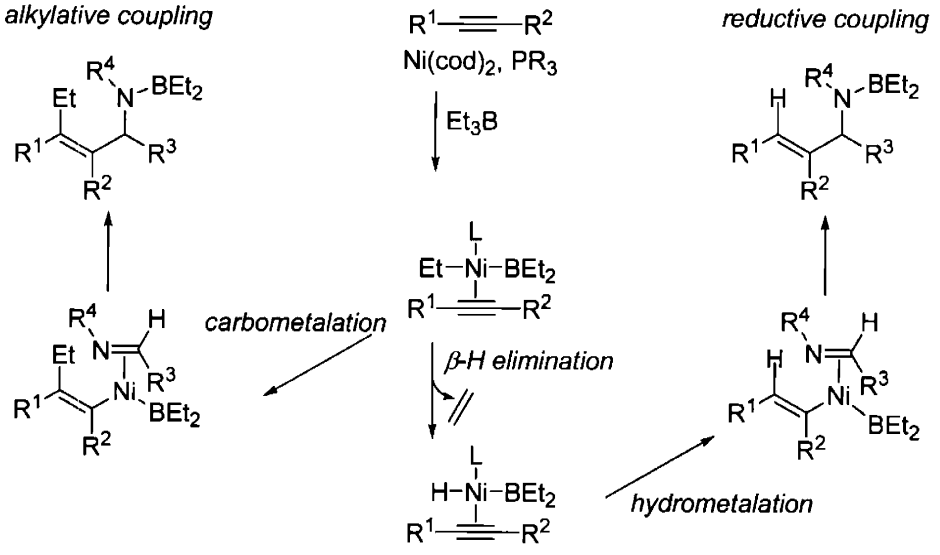
This mechanism accounts for the high selectivity for alkylative coupling imparted by MeOH (see Table 1.1), occupation of coordination sites required for a β-H elimination step that would lead to reductive coupling.[37] Alternatively, it may be necessary to consider mechanisms in which MeO-BEt_2 is the source of an Et group since Et_3B reacts rapidly with alcohols to give products of this type.[29] However, inconsistent with this possibility is that replacement of Et_3B with MeO-BEt_2 does not lead to formation of the allylic amine under otherwise identical conditions, suggesting that Et_3B is the reactive species.

In proposed mechanism **B**, a Ni-H or Ni-alkyl species hydrometalates/carbometalates the alkyne prior to imine addition (Scheme 1.9). Even though several groups have recently reported Rh-catalyzed addition of organostannanes, aryl boronic acids, or alkenyl zirconium reagents to

(37) MeOH may also promote group transfer from B to Ni, in analogy to Suzuki reaction additives, but this hypothesis does not account for alkylative/reductive selectivity.

imines (proposed mechanisms involve alkenylrhodium or arylrhodium as an intermediate), to the best of our knowledge, there are no such reports involving nickel catalysis.[38]

Scheme 1.9. Proposed mechanism **B** for the nickel-catalyzed reactions of alkynes, imines and organoboron reagents (Et_3B as shown)– hydrometalation/carbometalation of alkyne.



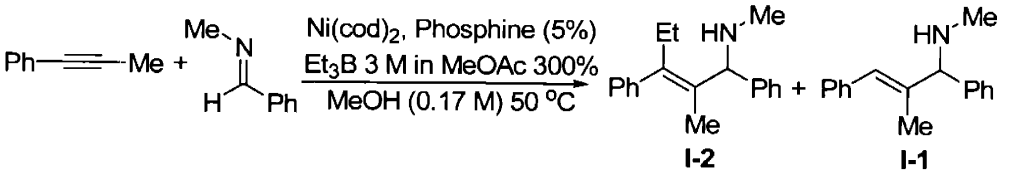
F. Role of MeOH and Discovery of (*o*-anisyl)$_3$P

As noted above, methanol as a solvent is necessary to obtain high catalyst turnover and to impart selectivity for the alkylative coupling product. We hypothesized that methanol might be occupying a coordination site on nickel required for β-H elimination step that would lead to reductive coupling product (Scheme 1.8). If the above postulate is correct, phosphines with additional groups that could coordinate to nickel should further increase the alkylative coupling

(38) (a) Kakuuchi, A.; Taguchi, T.; Hanzawa, Y. *Tett. Lett.* **2003**, *44*, 923. (b) For a single report of Rh(I) catalyzed addition of vinyl tin to aldimine, see: Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tett. Lett.* **1999**, *40*, 9259. For Rh-catalyzed arylation of imines, see: (c) Ueda, M.; Miyaura, N. *J. Organomet. Chem.* **2000**, *595*, 31. (d) Ueda, M.; Saito, A.; Miyaura, N. *Synlett.* **2000**, *11*, 1637. (d) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976. (e) Hayashi, T.; Ishigedani, M. *Tetrahedron.* **2001**, *57*, 2589.

reaction yields and selectivity. Therefore, commercially available tri-*o*-anisylphosphine was examined in the nickel-catalyzed three-component coupling reaction (Table 1.11, entry 2).

Table 1.11. Effects of triarylphosphines in catalytic three-component assembly of allylic amines.[a]



I-2 **I-1**

Entry	Phosphine	Yield %	**I-2**:**I-1**[b]	Regioselectivity[c]
1	Ph_3P	34	95:5	91:9
2	P(*o*-anisyl)$_3$	98	93:7	92:8
3[d]	P(*o*-anisyl)$_3$	60	>98:2	95:5
4	P(*p*- anisyl)$_3$	43	94:6	92:8
5	P(*o*-tolyl)$_3$	13	93:7	85:15
6	P(*p*-tolyl)$_3$	23	95:5	90:10
7	P(2,4,6-trimethoxy)Ph_3	63	82:18	83:17
8	P(*p*-Cl)Ph_3	25	96:4	90:10
9	P(CH_2CH_2CN)$_3$	7	96:4	92:8
10	P(CH_2OH)$_3$	50	95:5	90:10

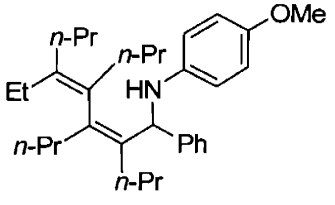
[a] Reaction performed on 1 mmol scale, 200% alkyne and 100% imine used.
[b] Ratios determined by ^{1}H NMR. [c] Regioselectivity in **I-2** (determined by ^{1}H NMR).
[d] Reaction at room temperature.

This modification of adding a methoxy group at the *ortho* position of the phenyl group significantly enhanced reaction yield (Table 1.11, entries 1-2). Tri-*o*-anisylphosphine afforded a nearly quantitative yield for the reaction, and was the first case of a ligand that was effective at room temperature (entries 2 and 3). *p*-Anisyl or *o*-tolyl substituents on the phenyl rings did not provide similar enhancement (entries 4 and 5), indicating that an ortho methoxy group might be coordinating to nickel, resulting an increase in reactivity and selectivity. The bulkier 2,4,6-

trimethoxyphenyl substituted phosphine provided moderate yields but attenuated both the alkylative/reductive coupling selectivity and regioselectivity (entry 7). Furthermore, other aryl substituted and alkyl coordinating phosphines afforded inferior results (entries 8-10).

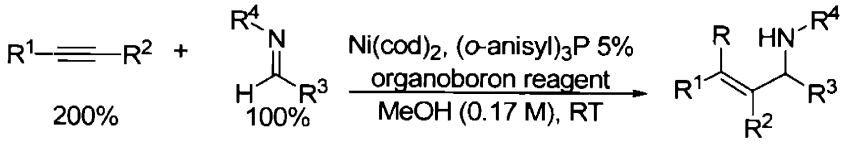
Additional experiments using (*o*-anisyl)$_3$P in different solvents (THF, toluene) showed enhanced selectivity for alkylative coupling product. Methanol was still necessary as a solvent in order to obtain high reaction yields. These results suggest that aside from providing high selectivity for alkylative coupling product, methanol assists in accelerating the desired three-component coupling reaction relative to competing side reactions.

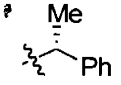
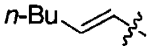
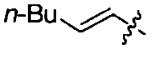
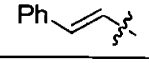
The substrate scope using (*o*-anisyl)$_3$P in nickel-catalyzed alkylative coupling reaction was examined, and the results are shown in Table 1.12. Most reactions were run at room temperature, and only alkylative coupling (>98%) was observed in all cases (^{1}H NMR). In contrast to our previous studies, imines containing aryl groups on the nitrogen smoothly underwent the desired coupling reaction in good yield and selectivity (entries 2-4 and 8). Surprisingly, for the first time we observed the minor coupling product **I-43** derived from reaction of two equivalents of alkyne with one equivalent of imine and Et_3B (entry 4). The presence of this side product was specific for that combination of alkyne and imine.



I-43

Table 1.12. Evaluation of the reaction substrate scope employing (*o*-anisyl)$_3$P.[a]



Entry	R^1	R^2	R^3	R^4	R	Yield %	Product	Regioselectivity[b]
1	Ph	Me	Ph	Me	Et	60	**I-2**	95:5
2[c]	Ph	Me	Ph	*p*-anisyl	Et	78	**I-40**	90:10
3[c]	Ph	Me	Ph	*o*-anisyl	Et	60	**I-41**	91:9
4[d]	*n*-C_3H_7	*n*-C_3H_7	Ph	*p*-anisyl	Et	40	**I-42**	--
5	*n*-C_3H_7	*n*-C_3H_7	Ph	CH_2Ph	Et	25	**I-44**	--
6	Ph	Me	Ph		Et	75	**I-45**	85:15 d.r. = 74:26
7	Ph	Me	*n*-C_3H_7	*n*-C_3H_7	Et	51	**I-20**	85:15
8	Ph	Me	*i*-C_3H_7	*p*-anisyl		36	**I-46**	80:20
9	Ph	Me	*i*-C_3H_7	CH_2Ph		26	**I-47**	75:25
10[c]	Ph	Me	*i*-C_3H_7	CH_2Ph		40	**I-48**	85:15

[a] 1 mmol scale, >98:2 alkylative coupling was afforded in all reactions. Entries 1-7, 300% Et_3B 3 M MeOAc used; entries 8-10, 200% correspnding alkenyl boronic acid used. [b] Determined by ^1H NMR. [c] Reaction run at 50 °C. [d] Also isolated 12% yield of alkylative product **I-43** arising from reaction of 2 alkynes + imine.

An α-substituent on the *N*-benzyl imine (Table 1.12, entry 6) was tolerated, and moderate diastereoselectivity (76:24) was observed in the three-component coupling reaction. As a result of being able to perform the reaction at room temperature, combined with the lower basicity of (*o*-anisyl)$_3$P, a primary aliphatic imine gave superior yield of the desired tetrasubstituted allylic

amine (entry 7). Alkenylboronic acids were also compatible coupling partners with aliphatic imines and gave substituted conjugated 1,3-dienes in moderate yields and regioselectivity (entries 8-10).

G. Development of Novel Removable Group on Nitrogen: Access to Primary Allylic Amines

To further extend the utility of the above described nickel-catalyzed three-component coupling reactions, we desired access to more versatile primary allylic amines. Readily removable groups on nitrogen such as *N*-phosphinoyl or *N*-tosyl imines did not undergo nickel-catalyzed coupling reactions. As discussed above, imines derived from *N*-alkyl amines are generally high yielding and afford good selectivity in nickel-catalyzed three-component coupling reactions of alkynes, imines and organoboron reagents. However, selective removal of *N*-alkyl group was not a feasible transformation.[39] Benzyl and aryl groups on the imine nitrogen are also tolerated and afford moderate yields and selectivity in nickel-catalyzed coupling reactions. Nevertheless, selective removal of *N*-benzyl protecting group is extremely challenging, since allylic amine products derived from aromatic imines are doubly benzylic. As shown in Scheme 1.10, ceric ammonium nitrate deprotection afforded the desired primary allylic amine in moderate yield.[40] Yet, this result was difficult to reproduce consistently and varied drastically with different substrates.

We then focused our attention to developing a group on the imine nitrogen that could be easily removed but also would provide the necessary reactivity in the coupling reaction. At first,

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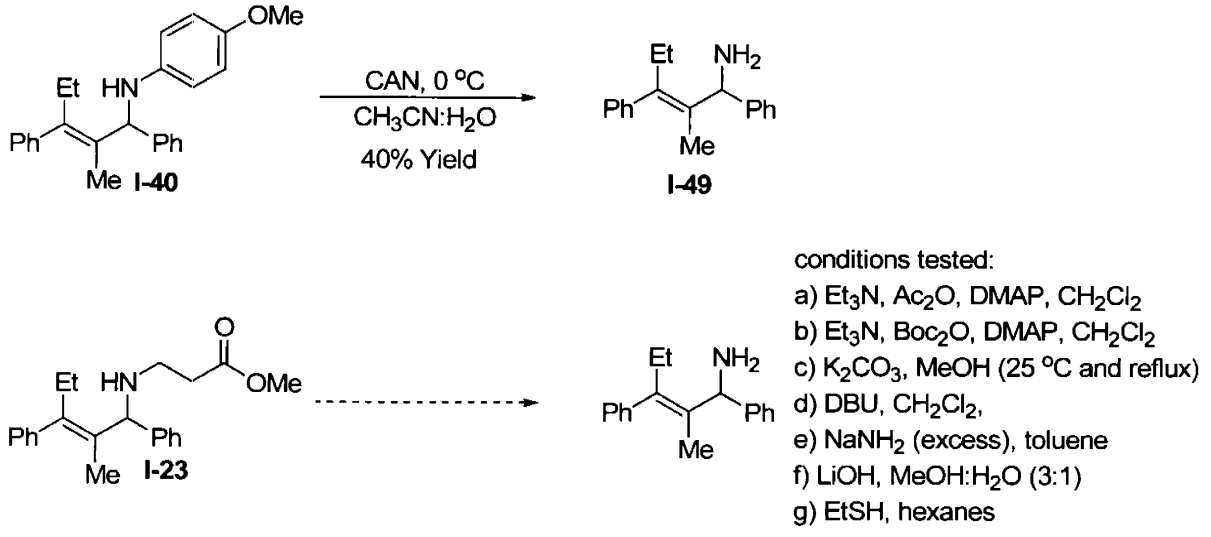
(39) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley-Interscience; 3rd edition, 1999.

(40) For literature procedures on CAN deprotection of allylic amines, see: Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J. *Org. Lett.* **2003**, *5*, 1809.

we were pleased to observe comparable yields and selectivity in nickel-catalyzed coupling reactions with imines derived from 3-amino-propionic acid methyl ester (Table 1.8, entry 1 and 3). However, several different conditions examined for E2 elimination to remove the *N*-$CH_2CH_2CO_2Me$ protecting group were unsuccessful and resulted in recovered starting material or decomposition.

Scheme 1.10. Evaluation of allylic amine products to access primary allylic amines.

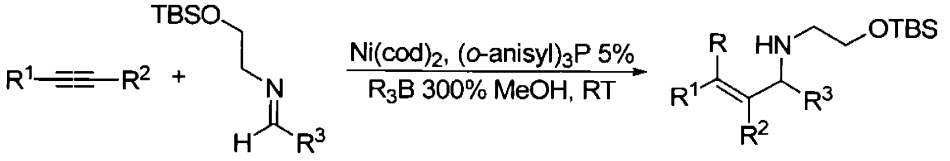


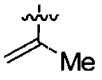
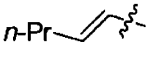
After extensive studies, *N*-(*tert*-butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2N$–) was identified as a general *N*-alkyl removable group. The corresponding imines were easily prepared by condensation of aldehydes and $TBSOCH_2CH_2NH_2$ in the presence of molecular sieves and purified by distillation or recrystallization. These imines underwent efficient nickel-catalyzed three-component coupling reactions, affording several different tetrasubstituted allylic amines in moderate to excellent yields and selectivity (Table 1.13).

Good yields and regioselectivity in the allylic amine products were obtained with internal alkynes containing at least one aryl group (Table 1.13, entries 1-3). However, the reaction yield was seriously diminished with sterically demanding Aryl-C≡C-(*i*-C_3H_7) alkynes (entry 4). A conjugated enyne was an efficient substrate in the preparation of a dienyl allylic amine, forming an exclusive carbon-carbon bond proximal to the alkyl group (entry 5).[13b] It is noteworthy that the diene products do not undergo further reaction with another molecule of imine.[15] Both symmetrical and non-symmetrical internal aliphatic alkynes provided good yields (entries 6-8), but in the case of non-symmetrical alkynes, only moderate regioselectivity (75:25) was observed favoring the regioisomer depicted (entry 8).[41] Several aliphatic imines were good participants in this procedure, providing yields of up to 90% and good selectivity (Table 1.13, entries 9-14). With different imines, 1-phenyl-1-butyne offered higher regioselection than 1-phenyl-1-propyne (entries 11-14). In addition, tributylborane efficiently incorporated a butyl substituent in the allylic amine product (entry 15). However, aryl and vinyl boronic acids afforded low yields of the allylic amines using this protocol.

(41) Ozonolysis of the major regioisomer resulted in α-amino methyl ketone.

Table 1.13. Substrate scope employing imines derived from -$NH_2CH_2CH_2OTBS$.[a]

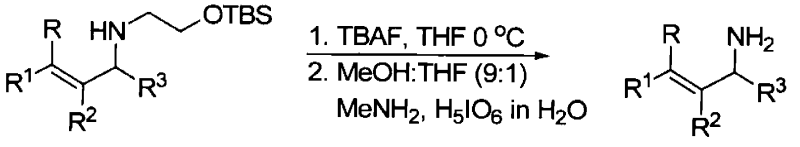


Entry	R^1	R^2	R^3	R	Yield %	Product	Regioselectivity[b]
1	Ph	Me	Ph	Et	80	**I-50**	93:7
2	Ph	Et	Ph	Et	81	**I-51**	>98:2
3	2-naphthyl	Me	Ph	Et	80	**I-52**	91:9
4	Ph	*i*-C_3H_7	Ph	Et	10	**I-53**	>98:2
5[c]		Et	Ph	Et	52	**I-54**	>98:2
6	*n*-C_3H_7	*n*-C_3H_7	Ph	Et	60	**I-55**	--
7	*n*-C_2H_5	*n*-C_2H_5	Ph	Et	76	**I-56**	--
8	*c*-C_6H_{11}	Me	Ph	Et	60	**I-57**	75:25
9	*n*-C_3H_7	*n*-C_3H_7	*c*-C_6H_{11}	Et	53	**I-58**	--
10	Ph	Me	*n*-C_3H_7	Et	40	**I-59**	87:13
11[d]	Ph	Me	*c*-C_6H_{11}	Et	90	**I-60**	90:10
12	Ph	Me	*c*-C_3H_5	Et	45	**I-61**	85:15
13	Ph	Et	*c*-C_6H_{11}	Et	85	**I-62**	95:5
14	Ph	Et	*c*-C_3H_5	Et	50	**I-63**	90:10
15	*n*-C_3H_7	*n*-C_3H_7	Ph	Bu	75	**I-64**	--
16[e]	*n*-C_3H_7	*n*-C_3H_7	Ph	Ph	15	**I-65**	--
17[e]	Ph	Me	Ph	Ph	38	**I-66**	90:10
18[f]	Ph	Me	*c*-C_6H_{11}	*n*-Pr 	27	**I-67**	80:20

[a] Reaction performed on 0.5 mmol scale, 100% imine and 200% alkyne. [b] Determined by ^1H NMR. [c] 50 °C and 5% (*c*-$C_5H_9)_3P$ was used. [d] 1 mmol scale. [e] 100% $PhB(OH)_2$. [f] 200% hexenyl boronic acid.

Several of the *N*-(*tert*-butyldimethyl)silyloxyethyl-protected allylic amine products were deprotected using a mild, two-step protocol, a TBAF deprotection of the TBS ether and oxidative cleavage of the resulting 1,2-amino alcohol.[42] Good overall yields (48% to 73%) were observed with several different allylic amines tested (Table 1.14). Several different chiral 1,2-amino alcohols (mostly derived from amino acids) have been used as auxiliaries for diastereoselective imine addition reactions,[43] but this is the first example of catalytic additions to imines derived from an *achiral* 1,2-amino alcohol.

Table 1.14. Removable (-CH_2CH_2OTBS) group on nitrogen: access to primary allylic amines



Entry	R^1	R^2	R^3	R	Yield %[a]	Product
1	Ph	Me	Ph	Et	63	**I-49**
2	*n*-C_3H_7	*n*-C_3H_7	Ph	Et	73	**I-68**
3	Ph	Me	*n*-C_3H_7	Et	72	**I-69**
4	Ph	Me	*c*-C_6H_{11}	Et	68	**I-70**
5	Ph	Me	*c*-C_3H_5	Et	60	**I-71**
6	Ph	Me	Ph	Ph	48	**I-72**

[a] Yields over two steps.

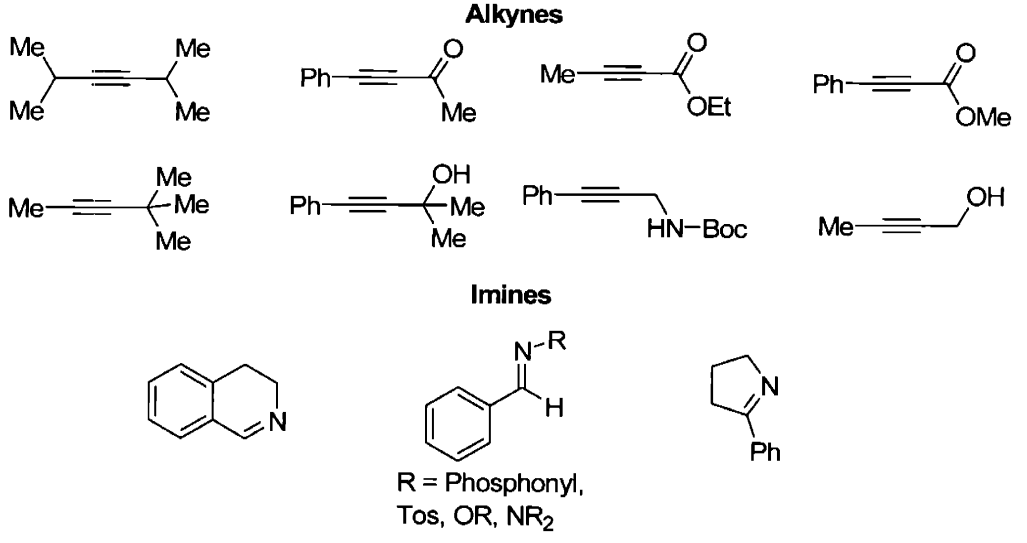
(42) (a) Spero, D. M.; Kapadia, S. R.; *J. Org. Chem.* **1997**, *62*, 5537. (b) Chang, Z.-Y.; Coates, R. M. *J. Org. Chem.* **1990**, *55*, 3475.

(43) (a) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407. (b) Enders, D.; Reinhold, U. *Tetrahedron Asymmetry* **1997**, *8*, 1895. (c) Alvaro, G.; Savoia, D. *Synlett* **2002**, *5*, 651.

H. Limitations

Several types of alkynes and imines were not compatible under the nickel-catalyzed three-component coupling reaction, and further development is necessary to overcome these limitations (Figure 1.4). Alkynes containing free propargyl hydroxyl or amino groups, or those containing electron-withdrawing esters and ketones were not tolerated. Furthermore, alkynes containing sterically demanding *t*-butyl and secondary dialkyl substituents did not couple under any of the conditions examined. Oximes, hydrazones, more electrophilic tosyl and phosphonyl imines, cyclic imines and ketamines also did not couple using the optimized protocol (eq. 3).

Figure 1.4. Substates that do not undergo three-component coupling reactions.



I. Conclusions

A novel nickel-catalyzed coupling reaction of alkynes, imines and organoboron reagents (boronic acids or boranes) was developed to access tetrasubstituted allylic amines in a single step. This catalytic, three-component process is catalyzed by commercially available $Ni(cod)_2$

and (c-C_5H_9)$_3$P or (o-anisyl)$_3$P in methanol as a solvent and is tolerant of ketones, esters, and free hydroxyl groups. The mode of addition across the alkyne is exclusively *cis* (>97:3), thereby establishing the alkene geometry of the product in the course of two carbon-carbon bond forming events. The choice of solvent determines whether the reductive coupling product or the alkylative coupling product dominates, with MeOH giving exclusively the latter.

The above reaction has a broad substrate scope. Both aliphatic or aromatic imines and alkyl or aryl alkynes afford the desired tetrasubstituted allylic amines in good to excellent yields and selectivity. Moreover, trialkylboranes and triaryl boranes, and aryl and vinyl boronic acids are compatible coupling partners. A (*tert*-butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2$–) group on the imine nitrogen was developed to access versatile primary allylic amines after deprotection.

J. Experimental Section

General Information

Unless stated otherwise, all compounds were purchased from commercial suppliers (Aldrich, Alfa Aesar, or Strem) and used without further purification. THF, Et_2O and toluene were distilled from sodium/benzophenone ketyl. All the other anhydrous grade solvents were purchased from Aldrich Chemical Co. Triethylborane, tributylborane, triphenylborane, phenyl boronic acid were obtained neat and corresponding solutions were made prior to use. *trans*-Styrylboronic acid was prepared according to the procedures from H.C. Brown and coworkers[44] and solution was made prior to use. Imines were made using known procedures from corresponding aldehydes and amines and prior to use, distilled or crystallized to >99% purity.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates precoated with a fluorescent indicator. The developed plates were analyzed with UV light and stained with 12-molybdophosphoric (PMA) stain. Flash chromatography was performed using silica gel 60 (40-63 μm) from Silicycle. All ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz or Varian 500 MHz spectrometers at ambient temperature. IR spectra were recorded as a thin film between NaCl plates on a Perkin-Elmer Model 2000 FTIR instrument. Analytical HPLC was performed on a Hewlett-Packard 1100 chromatograph equipped with a variable wavelength detector and Daicel Chiralcel OD column (0.46 cm x 25 cm).

(44) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *164*, 4370-4371.

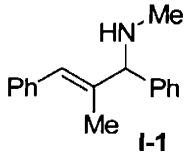
Standard Experimental Procedure A — Used during the development of intermolecular coupling of alkynes, imines and triethylborane (Table 1.1 -1.4 and Table 1.11)

For an exact amount of reagents please refer to appropriate table (Table 1.1-1.4). All reactions were performed on 1 mmol scale.

$Ni(cod)_2$, phosphine (R_3P) and teflon coated stir bar were added to an oven-dried 50mL flask in a glovebox and sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere in 50 °C oil bath. Anhydrous solvent was added followed by 200 μL of 3M solution of Et_3B. After 2 min, benzylidene-methyl-amine (1.0 mmol, 125 μL) was added followed by 1-phenyl-1-propyne (0.4 mmol, 50 μL). Reaction was stirred for an hour. Additional alkyne (1.60 mmol, 210 μL) and Et_3B solution (800 uL) were added in four equal portions over 4 h. Reaction was further stirred for 12 h at 50 °C, cooled to room temperature and opened to air. Concentrated in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines **I-1** and **I-2**. Unless otherwise stated, yields refer to combined isolated yield of all allylic amine products. Ratios of regioisomers and alkylative coupling (AC), reductive coupling (RC) were determined by ^1H NMR.

Reductive Coupling Product — Methyl-(2-methyl-1,3-diphenyl-allyl)-amine (I-1)

R_f= 0.23 (1:1 hexanes: EtOAc).



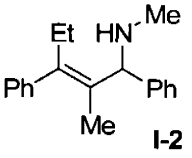
I-1

^1H NMR (500 MHz, $CDCl_3$): δ 7.45-7.20 (m, 10H), 6.78 (s, 1H), 4.20 (s, 1H), 2.46 (s, 3H), 1.74 (s, 3H), 1.61 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 139.7, 138.2, 129.2, 128.5, 128.3,

127.5, 127.3, 126.5, 126.1, 72.9, 34.9, 14.7. IR (film, CH_2Cl_2): 3332, 3024, 2948, 2788, 1490, 1449, 1029, 743 cm^{-1}. HR-MS (ESI) calcd for $C_{17}H_{20}N$ $(M+Na)^+$ 238.1590 found 238.1600.

Alkylative Coupling Product — Methyl-(2-methyl-1,3-diphenylpent-2-enyl)amine (I-2)

R_f= 0.47 (2:3 hexanes: EtOAc).



I-2

^1H NMR (500 MHz, $CDCl_3$): δ 7.50-7.00 (m, 10H), 4.89 (s, 1H), 2.64 (m, 2H), 2.52 (s, 3H), 1.27 (s, 3H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 142.8, 141.3, 131.4, 129.0, 128.4, 128.2, 127.0, 126.7, 126.3, 63.5, 34.6, 27.2, 14.1, 13.6. IR (film, CH_2Cl_2): 3333, 3024, 2969, 2931, 1600, 1575, 1491, 1441 cm^{-1}. HR-MS (ESI) calcd for $C_{19}H_{23}N$ $(M+Na)^+$ 288.1723 found 288.1734.

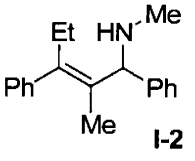
<u>Standard Experimental Procedure B</u> — Optimized procedure for the intermolecular *alkylative coupling* of alkynes, imines and organoboron reagents used in the evaluation of substrate scope (Table 1.5-1.9)

In a glovebox, $Ni(cod)_2$ (14 mg, 0.05 mmol) and tricyclopentylphosphine (Cyp_3P, 14 μL, 0.05mmol) were placed into an oven-dried 50mL flask, with teflon coated stir bar, which was then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Anhydrous MeOH (5 mL) was added followed by 200 μL of 3M MeOAc solution of RBX_2 (where X = OH, or R) and the flask was placed in 50 °C oil bath. After 2 min, imine (1.0 mmol) was added followed by alkyne (0.4 mmol). Reaction was stirred for an hour. Additional alkyne (1.60 mmol) and RBX_2 (3 M in MeOAc, 2.40 mmol, 800 μL) were added in 4

equal portions over 4 h. The reaction mixture was further stirred for 12 h at 50 °C, cooled to room temperature and opened to air. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines. Unless otherwise stated, yield refers to the combined isolated yield of all allylic amine products. Ratios of regioisomers and alkylative coupling (AC), reductive coupling (RC) were determined by ^{1}H NMR.

Methyl-(2-methyl-1,3-diphenylpent-2-enyl)amine (I-2)

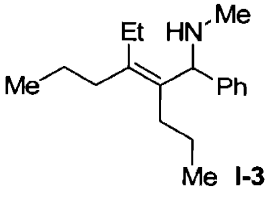
In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (225 mg, 85% yield, AC: RC = 92:8, regioselectivity 91:9). R_f= 0.47 (2:3 hexanes: EtOAc). For spectral data, see above.



I-2

(3-Ethyl-1-phenyl-2-propyl-hex-2-enyl)-methyl-amine (I-3)

In the alkylative coupling of 4-octyne (2.0 mmol, 293 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (236 mg, 91% yield, AC: RC = 94:6). R_f= 0.50 (1:3 hexanes: EtOAc).

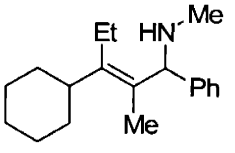


I-3

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.29 (m, 2H), 7.20 (m, 1H), 4.69 (s, 1H), 2.41 (s, 3H), 2.29 (m, 2H), 2.03 (m, 2H), 1.85 (m, 1H), 1.73 (m, 1H), 1.45 (m, 1H), 1.15 (m, 1H), 1.09 (t, J = 7.75 Hz, 3H), 0.94 (t, J = 7.25 Hz, 3H), 0.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 139.4, 134.6, 128.1, 127.2, 126.4, 64.2, 34.9, 34.1, 30.4, 24.2, 24.1, 22.2, 15.0, 14.7, 14.5. IR (film, CH_2Cl_2): 3419, 2959, 2870, 1644, 1492, 1451, 1030, 739 cm^{-1}. HR-MS (ESI) calcd for $C_{18}H_{29}N$ $(M+H)^+$ 260.2386 found 260.2382.

(3-Cyclohexyl-2-methyl-1-phenyl-pent-2-enyl)-methyl-amine (I-4)

In the alkylative coupling of prop-1-ynyl-cyclohexane (2.0 mmol, 274 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (206 mg, 70% yield, AC: RC = 85:15, regioselectivity = 60:40). R_f = 0.42 (1:3 hexanes: EtOAc).

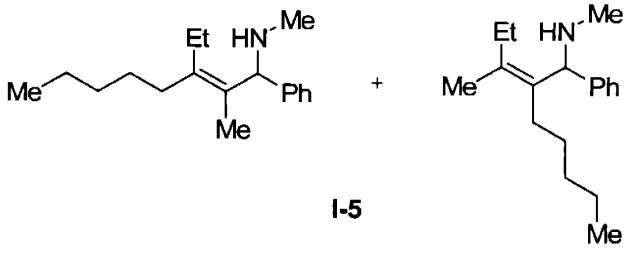


I-4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 4.68 (s, 1H), 2.49 (m, 1H), 2.42 (s, 3H), 2.25 (m, 2H), 1.75 (m, 4H), 1.59 (m, 3H), 1.41 (s, 3H), 1.34 (m, 4H), 1.09 (t, J = 7.58 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 143.1, 128.25, 128.21, 127.2, 126.5, 63.6, 42.4, 34.4, 31.6, 31.3, 27.1, 27.0, 26.5, 21.1, 16.1, 12.1. IR (film, CH_2Cl_2): 3326, 3060, 3026, 2928, 2851, 2787, 1601, 1492, 1448, 1374, 1121, 1072, 892, 745 cm^{-1}. HR-MS (ESI) calcd for $C_{19}H_{29}N$ $(M+Na)^+$ 294.2192 found 294.2200.

(3-Ethyl-2-methyl-1-phenyl-oct-2-enyl)-methyl-amine and (2-sec-butylidene-1-phenyl-heptyl)-methyl-amine (I-5)

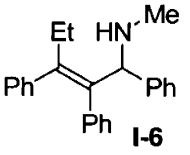
In the alkylative coupling of 2-octyne (2.0 mmol, 300 μL), benzylidene-methyl-amine(1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (244 mg, 94% yield, AC: RC = 56:44, regioselectivity = 52:48). R_f= 0.37 (1:3 hexanes: EtOAc).



I-5

Methyl-(1,2,3-triphenyl-pent-2-enyl)-amine (I-6)

In the alkylative coupling of diphenylacetylene (2.0 mmol, 356 mg), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (98 mg, 30% yield, AC: RC = not determined). R_f= 0.24 (1:1 hexanes: EtOAc).



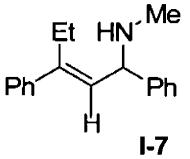
I-6

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (m, 5H), 7.07 (m, 2H), 6.95 (m, 6H), 6.53 (m, 2H), 5.12 (s, 1H), 2.84 (m, 2H), 2.58 (s, 3H), 1.61 (bs, 1H), 1.12 (t, J = 7.57 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 142.9, 142.3, 138.7, 138.5, 131.1, 129.6, 128.2, 127.5, 127.4, 127.0, 126.8, 126.1, 125.9, 63.7, 34.6, 27.4, 13.7. IR (film, CH_2Cl_2): 3328, 3056, 3024, 2965, 2929, 1490,

1440, 1103, 1072, 10129, 764, 741, 667 cm^{-1}. HR-MS (ESI) calcd for $C_{24}H_{25}N$ $(M+H)^+$ 328.2060 found 328.2072.

(1,3-Diphenylpent-2-enyl)-methylamine (I-7)

In the alkylative coupling of trimethyl-phenylethynyl-silane (2.0 mmol, 346 mg), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** used. Silica gel chromatography afforded the protiodesilylated allylic amine (56 mg, 22% yield, AC: RC > 95:5, regioselectivity > 98:2). R_f = 0.12 (1:4 hexanes: EtOAc).

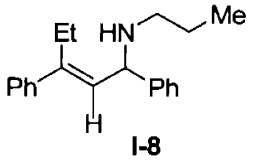


I-7

^1H NMR (400 MHz, $CDCl_3$): δ 7.5-7.2 (m, 10H), 5.79 (d, J = 9.2 Hz, 1H), 4.52 (d, J = 9.2 Hz, 1H), 2.68 (q, J = 7.5 Hz, 2H), 2.46 (s, 3H), 1.59 (bs, 1H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.1, 142.4, 130.9, 128.7, 128.4, 127.4, 127.3, 127.2, 126.7, 62.9, 34.7, 23.6, 13.8. IR (film, CH_2Cl_2): 3322, 3025, 2968, 2871, 1599, 1491, 1451, 1029, 760 cm^{-1}. HR-MS (ESI) calcd for $C_{18}H_{21}N$ $(M+H)^+$ 252.1747 found 252.1740.

(1,3-Diphenyl-pent-2-enyl)-propyl-amine (I-8)

In the alkylative coupling of phenylacetylene (2.0 mmol, 220 μL), benzylidene-propyl-amine (1.0 mmol, 147 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (92 mg, 33% yield, AC: RC = 93:7, regioselectivity > 98:2). R_f= 0.37 (1:3 hexanes: EtOAc).

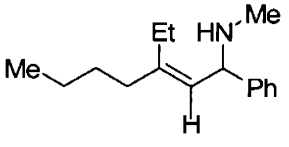


I-8

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.40-7.23 (m, 8H), 5.83 (d, J = 9.1 Hz , 1H), 4.64 (d, J = 9.1 Hz, 1H), 2.65 (m, 3H), 2.53 (m, 1H), 1.57 (m, 4H), 0.99 (t, J = 7.5 Hz , 3H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 142.6, 142.4, 131.3, 128.7, 128.4, 127.4, 127.17, 127.14, 126.7, 61.0, 49.9, 23.6, 13.8, 12.1. IR (film, CH_2Cl_2): 3312, 3058, 2962, 2872, 1599, 1492, 1452, 1377, 1029, 760 cm^{-1}. HR-MS (ESI) calcd for $C_{20}H_{25}N$ $(M+H)^+$ 280.2060 found 280.2060.

(3-ethyl-1-phenyl-hept-2-enyl]-methylamine (I-9)

In the alkylative coupling of hex-1-ynyl-trimethyl-silane (2.0 mmol, 308mg), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the protiodesilylated allylic amines as colorless oil (14 mg, 6% yield, AC: RC > 95:5, regioselectivity > 98:2). R_f = 0.28 (1:6 hexanes: EtOAc).

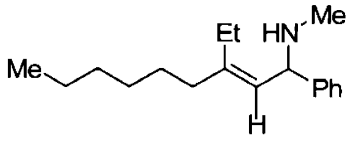


I-9

(3-ethyl-1-phenyl-non-2-enyl]-methylamine (I-10)

In the alkylative coupling of 1-octyne (2.0 mmol, 295 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure

B was used. Silica gel chromatography afforded the allylic amines as colorless oil (96 mg, 37% yield, AC: RC = 68:32, regioselectivity = 90:10). R_f= 0.28 (1:6 hexanes: EtOAc).

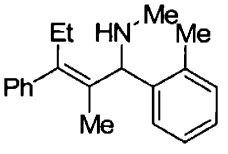


I-10

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.3 Hz, 2H), 7.30 (m, 1H), 5.50 (d, J = 9.6 Hz, 1H), 4.61 (d, J= 9.6, 1H), 2.36 (s, 3H), 2.16 (m, 2H), 2.05 (m, 2H), 1.39 (m, 2H), 1.27 (m, 6H), 0.96 (t, J = 7.5 Hz, 3H), 0.86 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.4, 128.6, 127.3, 127.2, 126.9, 62.3, 36.5, 34.6, 31.9, 29.3, 28.2, 23.7, 22.8, 14.3, 13.5. IR (film, CH_2Cl_2): 3026, 2928, 2858, 2361, 2338, 1492, 1455, 1260, 1250, 823 cm^{-1}. HR-MS (ESI) calcd for $C_{18}H_{29}N$ $(M+H)^+$ 260.2373 found 260.2384.

Methyl-(2-methyl-3-phenyl-1-*o*-tolyl-pent-2-enyl)-amine (I-11)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), methyl-(2-methyl-benzylidene)-amine (1.0 mmol, 133 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (238 mg, 85% yield, AC: RC = 94:6, regioselectivity 90:10). R_f= 0.72 (3:2 hexanes: EtOAc).



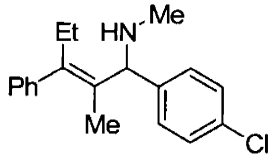
I-11

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 7.56 Hz, 1H), 7.40-7.00 (m, 8H), 4.89 (s, 1H), 2.68 (m, 2H), 2.53 (s, 3H), 2.40 (s, 3H), 1.21 (s, 3H), 0.97 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 143.4, 141.1, 140.5, 136.2, 130.49, 130.46, 128.9, 128.2, 127.1, 126.5, 126.3, 125.9, 61.7, 35.1, 26.9, 19.8, 15.9, 13.1. IR (film, CH_2Cl_2): 3327, 3020, 2970, 2871, 1599, 1576, 1462, 1440, 754 cm^{-1}. HR-MS (ESI) calcd for $C_{20}H_{25}N$ $(M+H)^+$ 280.2060 found 280.2069.

[1-(4-Chloro-phenyl)-2-methyl-3-phenyl-pent-2-enyl]-methyl-amine (I-12)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), (4-chloro-benzylidene)-methyl-amine (1.0 mmol, 154 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (284 mg, 95% yield, AC: RC = 96:4, regioselectivity 90:10). R_f= 0.53 (3:1 hexanes: EtOAc).



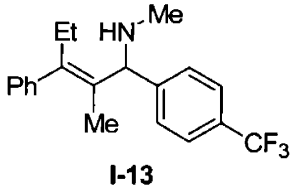
I-12

^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.00 (m, 9H), 4.79 (s, 1H), 2.55 (q, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.18 (s, 3H), 0.95 (t, J =7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 141.8, 141.2, 132.4, 130.8, 128.9, 128.5, 128.4, 128.2, 126.4, 62.9, 34.4, 27.2, 14.0, 13.6. IR (film, CH_2Cl_2): 3333, 3021, 2969, 2870, 1598, 1575, 1488, 1091, 1014, 766 cm^{-1}. HR-MS (ESI) calcd for $C_{19}H_{22}ClN$ $(M+H)^+$ 300.1514 found 300.1512.

Methyl-[2-methyl-3-phenyl-1-(4-trifluoromethyl-phenyl)-pent-2-enyl]-amine (I-13)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), methyl-(4-trifluoromethyl-benzylidene)-amine (1.0 mmol, 187 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic

amines as colorless oil (326 mg, 98% yield, AC: RC = 94:6, regioselectivity 89:11). R_f = 0.58 (1:2 hexanes: EtOAc).

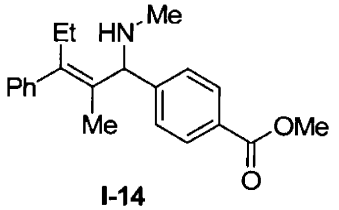


I-13

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.06 (m, 9H), 4.91 (s, 1H), 2.62 (q, J = 7.5 Hz, 2H), 2.51 (s, 3H), 1.52 (bs, 1H), 1.24 (s, 3H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.4, 142.1, 130.7, 129.2, 128.9, 128.3, 127.4, 126.5, 125.4 (q, J=15) 123.2, 63.3, 34.6, 27.3, 14.1, 13.7. IR (film, CH_2Cl_2): 3332, 2971, 2872, 1618, 1599, 1411, 1325, 1163, 1124, 1067, 1017 cm^{-1}. HR-MS (EI) calcd for $C_{20}H_{22}F_3N$ $(M)^+$ 333.1699 found 333.1696.

4-(2-Methyl-1-methylamino-3-phenyl-pent-2-enyl)benzoic acid methyl ester (I-14)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), methyl 4-methyliminomethyl-benzoic acid methyl ester (1.0 mmol, 177 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (284 mg, 82% yield, AC: RC = >96:4, regioselectivity 90:10). R_f = 0.42 (2:1 hexanes: EtOAc).



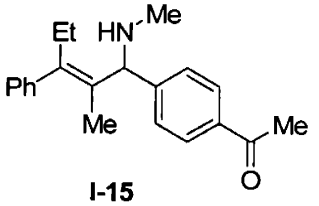
I-14

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.55 (m, 2H), 7.40-7.10 (m, 5H), 4.93 (s, 1H), 3.93 (s, 3H), 2.65 (q, J = 7.5 Hz, 2H), 2.53 (s, 3H), 1.25 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 148.3, 143.3, 141.9, 130.7, 129.7, 128.9, 128.6, 128.2, 127.0, 126.4,

63.5, 52.2, 34.5, 27.3, 14.1, 13.6. IR (film, CH_2Cl_2): 3336, 2969, 2871, 1722, 1609, 1436, 1279, 1109, 764 cm^{-1}. HR-MS (ESI) calcd for $C_{21}H_{25}NO_2$ $(M+Na)^+$ 346.1778 found 346.1775.

1-[4-(2-Methyl-1-methylamino-3-phenyl-pent-2-enyl)-phenyl)-ethanone(I-15)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), 1-(4-methyliminomethyl-phenyl)-ethanone (1.0 mmol, 161 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (257 mg, 78% yield, AC: RC = >96.4, regioselectivity 91:9). R_f= 0.28 (2:1 hexanes: EtOAc).



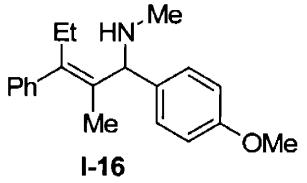
I-15

^1H NMR (400 MHz, $CDCl_3$): δ 8.00-7.90(m, 2H), 7.58 (m, 2H), 7.40-7.00 (m, 5H), 4.94 (s, 1H), 2.65 (m, 5H), 2.53 (s, 3H), 1.25 (s, 3H), 1.02 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 148.6, 143.4, 142.1, 135.8, 130.7, 128.9, 128.6, 128.3, 127.3, 126.5, 63.6, 34.6, 27.3, 26.8, 14.2, 13.7. IR (film, CH_2Cl_2): 3335, 2969, 2932, 2870, 1682, 1605, 1571, 1268, 767 cm^{-1}. HR-MS (ESI) calcd for $C_{21}H_{25}NO$ $(M+Na)^+$ 330.1828 found 330.1817.

[1-(4-Methoxy-phenyl)-2-methyl-3-phenyl-pent-2-enyl]-methyl-amine (I-16)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), (4-methoxy-benzylidene)-methyl-amine (1.0 mmol, 149 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as

colorless oil (203 mg, 64% yield, AC: RC = 86:14, regioselectivity 91:9). R_f= 0.78 (1:3 hexanes: EtOAc).

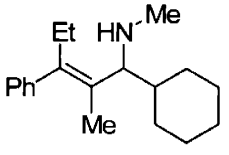


I-16

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.10 (m, 7H), 6.92 (m, 2H), 4.85 (s, 1H), 3.84 (S, 3H), 2.62 (m, 2H), 2.52 (s, 3H), 1.61 (bs, 1H), 1.28 (s, 3H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 143.8, 141.2, 134.8, 131.5, 129.0, 128.2, 128.0, 126.3, 113.7, 62.9, 55.4, 34.5, 27.2, 14.1, 13.7. IR (film, CH_2Cl_2): 3327, 3020, 2970, 2871, 1599, 1576, 1462, 1440, 754 cm^{-1}. HR-MS (ESI) calcd for $C_{20}H_{25}NO$ $(M+Na)^+$ 318.1828 found 318.1821.

(1-Cyclohexyl-2-methyl-3-phenyl-pent-2-enyl)-methyl-amine (I-17)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 125 μL), cyclohexylmethylene-methyl-amine (1.0 mmol, 125 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (70 mg, 26 % yield, AC: RC = 92:8, regioselectivity n.d.). R_f= 0.15 (1:3 hexanes: EtOAc).

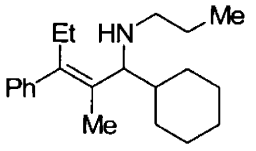


I-17

(1-Cyclohexyl-2-methyl-3-phenyl-pent-2-enyl)-propyl-amine (I-18)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), cyclohexylmethylene-propyl-amine (1.0 mmol, 170 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard

experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (138 mg, 46% yield, AC: RC = 94:6, regioselectivity 88:12). R_f= 0.39 (3:2 hexanes: EtOAc).

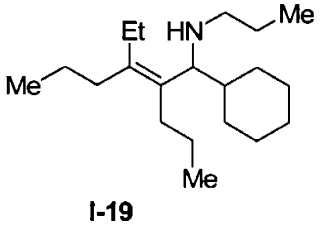


I-18

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.23 (m, 1H), 7.08 (m, 2H), 3.36 (d, J = 9.5 Hz, 1H), 2.55 (m, 1H), 2.43 (m, 2H), 2.15 (m, 1H), 1.72 (m, 4H), 1.51 (m, 2H), 1.30 (m, 8H), 0.95 (m, 5H), 0.85 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.4, 130.6, 129.0, 128.1, 126.0, 63.4, 49.5, 40.8, 31.4, 30.7, 26.94, 26.86, 26.7, 26.6, 23.8, 13.8, 13.3, 12.2. IR (film, CH_2Cl_2): 2858, 2925, 2852, 1599, 1449, 702 cm^{-1}. HR-MS (ESI) calcd for $C_{21}H_{33}N$ $(M+H)^+$ 300.2686 found 300.2682.

(1-Cyclohexyl-3-ethyl-2-propyl-hex-2-enyl)-propyl-amine (I-19)

In the alkylative coupling of 4-octyne (2.0 mmol, 293 μL), cyclohexylmethylene-propyl-amine (1.0 mmol, 153 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (153 mg, 52% yield, AC: RC = 95:5). R_f= 0.68 (1:2 hexanes: EtOAc).



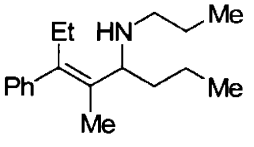
I-19

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (d, J = 9.5 Hz, 1H), 2.42 (m, 1H), 2.28 (m, 1H), 2.14-1.89 (m, 6H), 1.82-1.74 (m, 2H), 1.65(m, 2H), 1.55 (m, 1H), 1.48-1.31 (m, 7H), 1.26-1.19 (m, 2H),

1.13 (m, 2H), 0.94-0.87 (m, 12H), 0.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 132.7, 49.8, 41.1, 33.9, 31.4, 31.0, 26.9, 26.7, 26.6, 24.5, 23.7, 23.3, 22.1, 15.4, 14.8, 13.8, 12.1. IR (film, CH_2Cl_2): 3419, 2957, 2870, 1733, 1455, 1376, 1260, 1092, 1020, 803 cm^{-1}. HR-MS (ESI) calcd for $C_{20}H_{39}N$ $(M+H)^+$ 294.3155 found 294.3151.

(2-Methyl-3-phenyl-1-propyl-pent-2-enyl]-propyl-amine (I-20)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), butylidene-propyl-amine (1.0 mmol, 113 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (78 mg, 30% yield, AC: RC = 90:10, regioselectivity 91:9). R_f= 0.18 (1:3 hexanes: EtOAc).



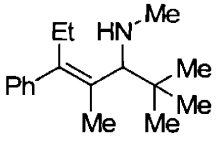
I-20

^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.22 (m, 1H), 7.08 (m, 2H), 3.74 (dd, J = 5.8, 8.2 Hz, 1H), 2.49 (m, 4H), 1.48 (m, 7H), 1.34 (s, 3H), 0.93 (m, 6H), 0.86 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 141.1, 131.3, 129.1, 128.2, 126.1, 57.8, 49.4, 36.9, 26.7, 23.8, 20.0, 14.7, 13.5, 13.1, 12.2. IR (film, CH_2Cl_2): cm^{-1}. HR-MS (ESI) calcd for $C_{18}H_{29}N$ $(M+H)^+$ 260.2373 found 260.2369.

(1-*tert*-Butyl-2-methyl-3-phenyl-pent-2-enyl]-methyl-amine (I-21)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), (2,2-dimethyl-propylidene)-methyl-amine (1.0 mmol, 147 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic

amines as colorless oil (44 mg, 18% yield, AC: RC = 95:5, regioselectivity= not determined). R_f = 0.12 (1:4 hexanes: EtOAc).

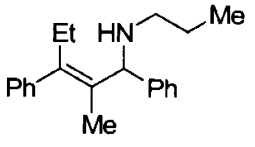


I-21

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 2H), 7.25-7.21 (m, 2H), 7.08-7.05 (m, 1H), 3.38 (s, 1H), 2.56 (m, 1H), 2.35 (s, 3H), 2.31 (m, 1H), 1.44 (bs, 1H), 1.36 (s, 3H), 1.02 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 143.3, 130.0, 129.2, 128.5, 126.3, 68.4, 35.31, 35.27, 28.7, 27.4, 15.7, 13.2. IR (film, CH_2Cl_2): 3356, 3019, 2959, 2869, 1599, 1575, 1476, 1104, 765 cm^{-1}. HR-MS (ESI) calcd for $C_{17}H_{27}N$ $(M+H)^+$ 246.2216 found 246.2210.

(2-Methyl-1,3-diphenyl-pent-2-enyl)-propyl-amine (I-22)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-propyl-amine (1.0 mmol, 147 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (282 mg, 96% yield, AC: RC = 95:5, regioselectivity 93:7). R_f= 0.80 (4:1 hexanes: EtOAc).



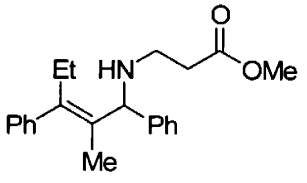
I-22

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (m, 2H), 7.37 (m, 4H), 7.25 (m, 2H), 7.11(m, 2H), 4.98 (s, 1H), 2.62 (m, 4H), 1.61 (m, 4H), 1.27 (s, 3H), 0.99 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 143.2, 140.8, 132.0, 129.1, 128.3, 128.2, 127.1, 126.7, 126.3, 61.7, 49.8, 27.2, 27.8, 14.3,

13.7, 12.2. IR (film, CH_2Cl_2): 3312, 3024, 2960, 2872, 1599, 1492, 1376, 1052, 1029, 765, 751 cm^{-1}. HR-MS (ESI) calcd for $C_{21}H_{27}N$ $(M+H)^+$ 294.2216 found 294.2218.

3-(2-Methyl-1,3-diphenyl-pent-2-enylamino)-propionic acid methyl ester (I-23)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), 3-(benzylidene-amino)-propionic acid methyl ester (1.0 mmol, 191 mg) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (230 mg, 75% yield, AC: RC = 94:6, regioselectivity 91:9). R_f= 0.58 (4:1 hexanes: EtOAc).



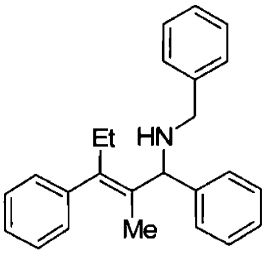
I-23

^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 2H), 7.37 (m, 4H), 7.28 (m, 2H), 7.14 (m, 2H), 5.02 (s, 1H), 3.75 (s, 3H), 3.05 (m, 1H), 2.90 (m, 1H), 2.65 (m, 4H), 1.31 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 143.6, 142.7, 141.0, 131.6, 129.0, 128.3, 128.2, 127.0, 126.7, 126.3, 61.6, 51.7, 43.0, 35.0, 27.1, 14.2, 13.7. IR (film, CH_2Cl_2): 3449, 3024, 2966, 1736, 1600, 1491, 1438, 1371, 1173, 766 cm^{-1}. HR-MS (ESI) calcd for $C_{22}H_{27}NO_2$ $(M+Na)^+$ 360.1934 found 360.1925.

Benzyl-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (I-24)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzyl-benzylidene-amine (2.0 mmol, 195 μL) and Et_3B (3 M in MeOAc, 3.0 mmol, 1 mL), the standard experimental

procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (181 mg, 53% yield, AC: RC = 92:8, regioselectivity 88:12). R_f= 0.39 (10:1 hexanes: EtOAc).

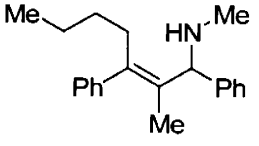


I-24

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (m, 2H), 7.54 (m, 2H), 7.48-7.19 (m, 12H), 5.14 (s, 1H), 3.96 (app q, J = 13.32 Hz, 2H), 2.60 (q, J = 7.41 Hz, 2H), 1.73 (s, 1H), 1.44 (s, 3H), 1.02 (t, J = 7.37 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.9, 141.4, 141.0, 131.5, 129.0, 128.6, 128.5, 128.4, 128.2, 127.3, 127.1, 126.8, 126.3, 61.0, 51.7, 27.1, 14.4, 13.6. IR (film, CH_2Cl_2): 3321, 3059, 3025, 2967, 1930, 1870, 2246, 1948, 1875, 1809, 1599, 1492, 1452, 1070, 1028, 911, 745 cm^{-1}. HR-MS (ESI) calcd for $C_{25}H_{27}N$ $(M-H)^+$ 340.2060 found 340.2068.

Methyl-(2-methyl-1,3-diphenyl-hept-2-enyl)-amine (I-25)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Bu_3B (3M MeOAc, 1mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (206 mg, 70% yield, AC: RC = 90:10, regioselectivity 91:9). R_f= 0.42 (1:2 hexanes: EtOAc).



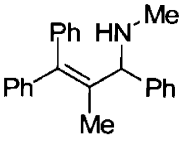
I-25

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.10 (m, 10H), 4.90 (s, 1H), 2.62 (m, 2H), 2.53 (s, 3H), 1.61 (bs, 1H), 1.43 (m, 4H), 1.28 (s, 3H), 0.89 (t, *J*= 7.5, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 142.8, 140.1, 131.8, 128.9, 128.4, 128.2, 127.0, 126.7, 126.2, 63.5, 34.6, 34.0, 31.1, 23.1, 14.3, 14.2. IR (film, CH_2Cl_2): 3334, 3024, 2954, 2858, 1599, 1574, 1491, 1148, 1102, 1029, 745 cm^{-1}. HR-MS (ESI) calcd for $C_{21}H_{27}N$ $(M+H)^+$ 294.2216 found 294.2224.

_N_,2-dimethyl-1,3,3-triphenylprop-2-en-1-amine (I-26)

Procedure using Ph_3B: In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and Ph_3B (1M MeOAc, 1mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (203 mg, 65% yield, AC: RC = >97%, regioselectivity 93:7). R_f= 0.62 (3:1 hexanes: EtOAc).

Procedure using phenyl boronic acid: In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and phenyl boronic acid (3M MeOAc, 1mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (225 mg, 72% yield, AC: RC = >97%, regioselectivity 92:8). R_f= 0.62 (3:1 hexanes: EtOAc).



I-26

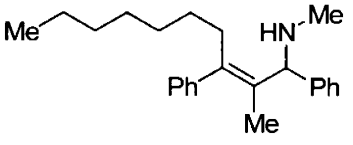
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.20 (m, 15H), 4.60 (s, 1H), 2.45 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.9, 142.5, 141.0, 135.4, 129.5, 129.4, 128.4, 128.3, 128.2, 127.2, 126.8, 126.7, 126.6, 65.1, 34.3, 14.1. IR (film, CH_2Cl_2): 3334, 3056, 3024, 2931, 2789,

1598, 1576, 1490, 1442, 754 cm^{-1}. HR-MS (ESI) calcd for $C_{23}H_{23}N$ $(M)^+$ 313.1825 found 313.1825.

Methyl-[-2-methyl-1,3-diphenyl-dec-2-enyl]amine (I-27)

Heptyl-(9-BBN) solution is MeOAc was prepared by adding heptene (1.5 mmol, 211 μL) and 9-BBN dimer (0.75 mmol, 183 mg) in 1ml THF at 0 °C. Reaction was slowly warm to room temperature and stir overnight. THF was removed under vacuo and MeOAc was added.

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and heptyl-(9-BBN) (3M MeOAc, 0.5 mL), the standard experimental procedure **B** was used, followed by $NaBO_3$ work-up. 5 ml CH_2Cl_2, 5 ml H_2O and $NaBO_3$ (3 mmol, 81.80 mg) were added to the reaction mixture and stir for 2 h. Organic layer was separated, dried with Na_2SO_4 and concentrated under vacuo. Silica gel chromatography afforded the allylic amines as colorless oil (100 mg, 30% yield, AC: RC = 94:6, regioselectivity 91:9). R_f = 0.36 (1:2 hexanes: EtOAc).



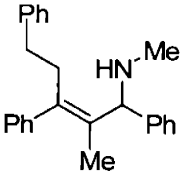
I-27

HR-MS (ESI) calcd for $C_{24}H_{33}N$ $(M+H)^+$ 336.2686 found 336.2593.

Methyl-(2-methyl-1,3,5-triphenyl-pent-2-enyl)-amine (I-28)

$PhCH_2CH_2$-(9-BBN) solution is MeOAc was prepared by adding styrene (1.5 mmol, 172 μL) and 9-BBN dimer (0.75 mmol, 183 mg) in 1ml THF at 0 °C. Reaction was slowly warm to room temperature and stir overnight. THF was removed under vacuo and MeOAc was added.

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and $PhCH_2CH_2$-(9-BBN) (3M MeOAc, 0.5 mL), the standard experimental procedure **B** was used, followed by $NaBO_3$ work-up. 5 ml CH_2Cl_2, 5 ml H_2O and $NaBO_3$ (3 mmol, 81.80 mg) were added to the reaction mixture and stir for 2 h. Organic layer was separated, dried with Na_2SO_4 and concentrated under vacuo. Silica gel chromatography afforded the allylic amines as colorless oil (230 mg, 28% yield, AC: RC = 92:8, regioselectivity 90:10). R_f = 0.43 (1:2 hexanes: EtOAc).



I-28

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.15 (m, 15H), 4.87 (s, 1H), 2.92 (m, 3H), 2.68 (m, 2H), 2.43 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.2, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 127.1, 126.8, 126.7, 126.6, 126.1, 63.9, 36.3, 34.9, 34.5, 14.5. IR (film, CH_2Cl_2): 3329, 3059, 3025, 2928, 2858, 2788, 1600, 1493, 1451, 1375, 1074, 1017, 750, 699 cm^{-1}. HR-MS (ESI) calcd for $C_{25}H_{27}N$ $(M+H)^+$ 342.2216 found 342.2227.

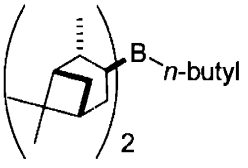
Experiments with chiral boranes:

Chiral borane **A** was synthesized by adding (-)-*β*-chlorodiisopinocampheylborane [(-)-IPC_2BCl] and *n*-BuLi in pentane at -78 °C, followed by slowly warming the reaction to room temperature and stirring overnight.[45]

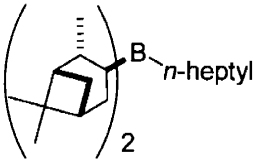
Chiral boranes **B** and **C** were synthesized from reaction between the corresponding alkene and freshly prepared (-)-diisopinocampheylborane [(-)-IPC_2BH] solution in THF.[46]

(45) Kramer, G. W.; Brown, H. C. *J. Organomet Chem.* **1974**, *73*, 1.

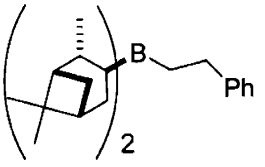
These chiral boranes (3M MeOAc, 0.5 ml) were tested in the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL) and benzylidene-methyl-amine (1.0 mmol, 125 μL) using the standard experimental procedure **B**. In all cases, <10% yield and 0% enantiomeric excess was obtained in the desired alkylative coupling products. Enantioselectivity was measure using HPLC (Chiralcel OD column) on the corresponding acetamide derivatives.



A



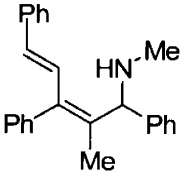
B



C

Methyl-(2-methyl-1,3,5-triphenyl-penta-2,4-dienyl)-amine (I-29)

In the alkylative coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-methyl-amine (1.0 mmol, 125 μL) and *trans*-styrylboronic acid (3M MeOAc, 1mL), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amines as colorless oil (230 mg, 68% yield, AC: RC = >97%, regioselectivity 91:9). R_f = 0.45 (1:1 hexanes: EtOAc).



I-29

(46) Singaram, B.; Brown, H. C. *J. Org. Chem.* **1984**, *49*, 945.

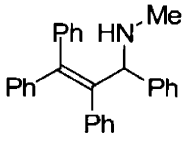
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J*= 15.7, 1H), 7.52 (m, 2H), 7.58-7.28 (m, 10H), 7.24 (m, 1H), 7.18 (m, 2H), 6.03 (d, *J*= 15.7, 1H), 5.32 (s, 1H), 2.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 140.9, 139.2, 137.9, 137.8, 132.3, 129.9, 128.7, 128.5, 127.5, 127.1, 126.92, 126.89, 128.81, 126.5, 63.1, 34.6, 15.4. IR (film, CH_2Cl_2): 3330, 3024, 2932, 1599, 1574, 1492, 1448, 1014, 957, 752 cm^{-1}. HR-MS (ESI) calcd for $C_{25}H_{25}N$ $(M+H)^+$ 340.2060 found 340.2069.

Standard Experimental Procedure C — Procedure for the intermolecular alkylative coupling of Ar-C≡C-Ar alkynes, imines and phenyl boronic acid (Table 1.10)

In a glovebox, $Ni(cod)_2$ (7 mg, 0.05 mmol), tricyclopentylphosphine (Cyp_3P, 7 μL, 0.05mmol) and $PhB(OH)_2$ (1mmol, 121 mg) were placed into an oven-dried 50mL flask, with teflon coated stir bar, which was then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere in 50 °C oil bath. Anhydrous MeOH (2.5 mL) was added followed by benzylidene-methyl-amine (0.5 mmol, 62.5 μL) and alkyne (0.75 mmol, 1 M solution in MeOAc). The reaction mixture was further stirred for 12 h at 50 °C, cooled to room temperature and opened to air. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines. Unless otherwise stated, yield refers to the combined isolated yield of all allylic amine products. Ratios of regioisomers and alkylative coupling (AC), reductive coupling (RC) were determined by ^{1}H NMR.

Methyl-(1,2,3,3-tetraphenyl-allyl)-amine (I-30)

Standard experimental procedure **C** — diphenylacetylene (0.75 mmol, 133 mg) was used as an alkyne with 20% $Ni(cod)_2$ and $(c\text{-}C_5H_9)_3P$. Silica gel chromatography afforded the allylic amines as slightly yellow solid (121 mg, 65 % yield). R_f= 0.41 (1:4 hexanes: EtOAc).

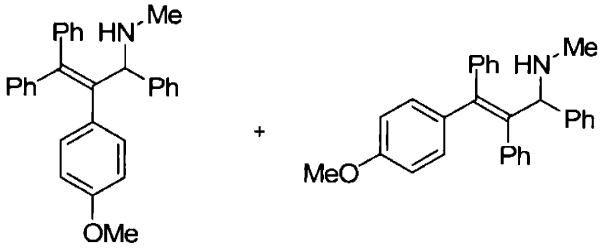


I-30

^1H NMR (400 MHz, CD_3OD): δ 7.50 (m, 3H), 7.37 (m, 1H), 7.25 (m, 3H), 7.13 (m, 2H), 7.01 (m, 3H), 6.93 (m, 5H), 6.71 (m, 2H), 4.87 (s, 1H), 3.36 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 144.7, 143.9, 143.8, 142.5, 142.1, 139.2, 132.3, 131.1, 130.9, 129.8, 129.2, 128.6, 128.5, 128.42, 128.38, 128.1, 127.8, 127.2, 65.9, 34.4. IR (film, CH_2Cl_2): 3364, 3054, 2859, 2669, 1596, 1492, 1454, 1444, 1385, 1144, 1077, 1031, 930 cm^{-1}. HR-MS (ESI) calcd for $C_{28}H_{25}N$ $(M+H)^+$ 376.2060 found 376.2065.

[2-(4-Methoxy-phenyl)-1,3,3-triphenyl-allyl]-methyl-amine and [3-(4-methoxy-phenyl)-1,2,3-triphenyl-alllyl]methyl-amine (I-31)

Standard experimental procedure **C** — 1-methoxy-4-phenylethynyl-benzene (0.75 mmol, 156 mg) was used as an alkyne. Silica gel chromatography afforded the allylic amines as slightly yellow oil (63 mg, 31 % yield, regioselectivity = 55:45). Two regioisomers could not be separated and were isolated together. R_f= 0.38 (1:4 hexanes: EtOAc).

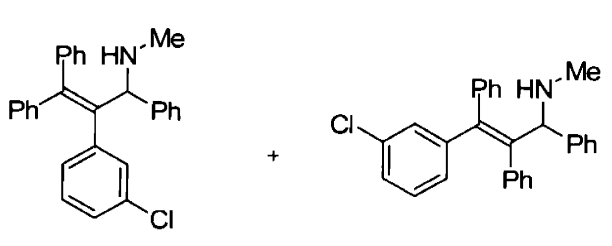


I-31

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.20 (m, 20H), 7.07 (m, 6H), 6.97 (d, J = 7.66 Hz, 2H), 6.86 (d, J = 7.58 Hz, 2H), 6.79 (d, J = 7.50 Hz, 2H), 6.70 (d, J = 7.86 Hz, 2H), 6.60 (d, J = 7.89 Hz, 2H), 6.56 (d, J = 7.79 Hz, 2H), 4.93 (s, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ158.4, 157.8, 142.8, 142.6, 132.0, 131.6, 130.9, 130.3, 129.83, 129.79, 128.72, 128.70, 128.3, 128.2, 127.7, 127.6, 127.3, 127.18, 127.15, 126.9, 126.84, 126.78, 126.2, 113.1, 113.0, 64.7, 64.6, 55.2, 34.39, 34.36. IR (film, CH_2Cl_2): 3419, 3056, 2933, 1605, 1508, 1492, 1442, 1246, 1178, 1031, 909, 731 cm^{-1}. HR-MS (ESI) calcd for $C_{29}H_{27}NO$ $(M+H)^+$ 406.2165 found 406.2038.

[2-(3-Chloro-phenyl)-1,3,3-triphenyl-allyl]-methyl-amine and [3-(3-chloro-phenyl)-1,2,3-triphenyl-alllyl]methyl-amine (I-32)

Standard experimental procedure **C** — 1-chloro-3-phenylethylnyl-benzene (0.75 mmol, 142 μL) was used as an alkyne. Silica gel chromatography afforded the allylic amines as slightly yellow oil (25 mg, 12 % yield, regioselectivity = 57:43). Two regioisomers could not be separated and were isolated together. R_f= 0.49 (1:4 hexanes: EtOAc).

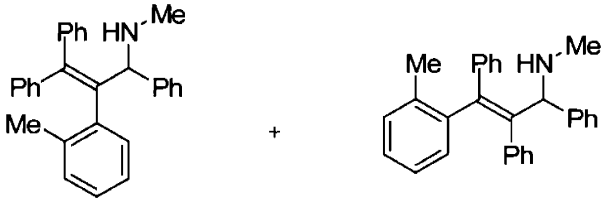


I-32

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-6.60 (m, 38H), 4.92 (s, 1H), 4.91 (s, 1H), 2.52 (s, 3H), 2.52 (s, 3H), 1.58 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.7, 142.2, 141.8, 141.6, 137.8, 133.4, 133.2, 130.9, 130.85, 130.2, 130.18, 129.8, 129.7, 129.4, 129.35, 129.1, 128.9, 128.8, 128.76, 128.70, 128.5, 128.32, 128.27, 127.8, 127.7, 127.5, 127.4, 127.3, 127.1, 126.92, 126.86, 126.5, 126.4, 64.8, 64.6, 34.5. IR (film, CH_2Cl_2): 3323, 3058, 3026, 2792, 1560, 1491, 1472, 1443, 1077, 909, 753, 734 cm^{-1}. HR-MS (ESI) calcd for $C_{28}H_{25}N$ 409.1597 found 409.1550.

Methyl-(1,3,3-triphenyl-2-*o*-tolyl-allyl)-amine and Methyl-(1,2,3-triphenyl-3-*o*-tolyl-allyl)-amine (I-33)

Standard experimental procedure **C** — 1-methyl-2-phenylethylnyl-benzene (0.75 mmol, 144 mg) was used as an alkyne. Silica gel chromatography afforded the allylic amines as slightly yellow oil (17 mg, 10% yield, regioselectivity = 67:33). Two regioisomers could not be separated and were isolated together. R_f= 0.42 (1:4 hexanes: EtOAc).

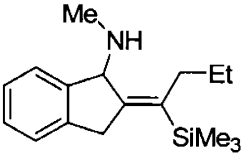


I-33

Methyl-[2-(1-trimethylsilanyl-butylidene)-indan-1-yl]-amine (I-37)

In a glovebox, $Ni(cod)_2$ (14 mg, 0.05 mmol) and tributylphosphine (Bu_3P, 12.5 μL, 0.05mmol) were placed into an oven-dried 50mL flask, with teflon coated stir bar, which was then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere in 50 °C oil bath. Anhydrous MeOH (3 mL) was added followed by 2 mL of 2M EtOAc solution of Et_3B. After 2 min, **I-36** (1.0 mmol, 229 mg) was added and reaction stirred for

12 h. The reaction mixture was cooled to room temperature and opened to air. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines. Silica gel chromatography afforded the allylic amines (138 mg, 49% yield and regioselectivity >98:2). R_f = 0.18 (1:5 hexanes: EtOAc).



I-37

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (m, 1H), 7.26 (m, 3H), 4.83 (s, 1H), 3.75 (d, J = 20.0 Hz, 1H), 3.56 (d, J = 20.0 Hz, 1H), 2.54 (m, 1H), 2.29 (s, 3H), 2.24 (m, 1H), 1.28 (bs, 1H), 1.02 (t, J = 7.50 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.4, 142.4, 138.5, 127.8, 126.4, 125.2, 124.5, 106.5, 64.1, 38.4, 31.7, 25.5, 15.9, -0.00. HRMS (ESI): *m/z* calcd for $C_{16}H_{25}NSi$ $(M+Na)^+$ 282.1658, found 282.1658. 2D NOESY was performed, and cross peak from the ethyl CH_2 protons to C-H next to the amine was observed.

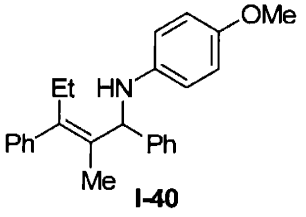
<u>Standard Experimental Procedure D</u> —Intermolecular alkylative coupling of alkynes and imines and organoboron reagents using (o-anisyl)$_3$P (Table 1.12 and 1.13)

In a glovebox, $Ni(cod)_2$ (14 mg, 0.05 mmol) and tri-o-anisylphosphine [(o-anisyl)$_3$P, 17.6 mg, 0.05mmol] were placed into an oven-dried 50mL flask, with teflon coated stir bar, which was then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere at room temperature. Anhydrous MeOH (5 mL) was added followed by 200 μL of 3M MeOAc solution of RBX_2 (where X = OH, or R). After 2 min, imine (1.0 mmol) was added followed by alkyne (0.4 mmol). Reaction was stirred for an hour. Additional alkyne (1.60 mmol) and RBX_2 (3 M in MeOAc, 2.40 mmol, 800 μL) were added in 4 equal portions over 4 h.

The reaction mixture was further stirred for 12 h at room temperature and opened to air. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines. Unless otherwise stated, yield refers to the combined isolated yield of all allylic amine products. Ratios of regioisomers and alkylative coupling (AC), reductive coupling (RC) were determined by ^{1}H NMR.

(4-Methoxy-phenyl)-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (I-40)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-(4-methoxy-phenyl)-amine (1.0 mmol, 212 mg) and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used at 50 °C. Silica gel chromatography afforded the allylic amines (278 mg, 78% yield and regioselectivity = 90:10). R_f = 0.62 (5:1 hexanes: EtOAc).

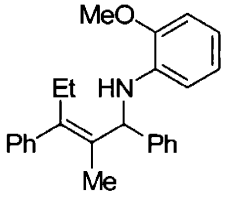


I-40

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (m, 2H), 7.32 (m, 6H), 7.15 (m, 2H), 6.80 (m, 2H), 6.62 (m, 2H), 5.55 (s, 1H), 3.78 (s, 3H), 2.58 (q, J = 7.50 Hz, 2H), 1.39 (s, 3H), 0.98 (t, J = 7.50 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.3, 143.2, 142.3, 142.2, 141.3, 131.2, 128.9, 128.7, 128.3, 127.2, 127.1, 126.5, 115.0, 114.9, 59.3, 56.0, 27.4, 15.7, 13.4. IR (film, CH_2Cl_2): 3392, 2965, 1599, 1511, 1492, 1243, 1179, 1038, 818, 766 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{27}NO$ $(M+Na)^+$ 380.1985, found 380.1982.

(2-Methoxy-phenyl)-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (I-41)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzylidene-(2-methoxy-phenyl)-amine (1.0 mmol, 212 mg), and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used at 50 °C. Silica gel chromatography afforded the allylic amines (217 mg, 60% yield and regioselectivity = 91:9). R_f = 0.58 (5:1 hexanes: EtOAc).

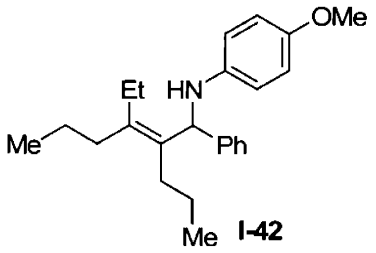


I-41

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (m, 1H), 7.35 (m, 8H), 7.18 (m, 1H), 6.85 (m, 2H), 6.71 (m, 1H), 6.63 (m, 1H), 5.63 (s, 1H), 4.74 (s, 1H), 3.91 (s, 3H), 2.62 (q, J = 7.40 Hz, 2H), 1.41 (s, 3H), 0.98 (t, J = 7.49 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 143.3, 142.2, 142.1, 137.8, 131.0, 129.0, 128.7, 128.2, 127.2, 127.1, 126.4, 121.4, 116.7, 111.0, 109.5, 58.2, 55.7, 27.4, 15.7, 13.3. IR (film, CH_2Cl_2): 3434, 3058, 2963, 1601, 1509, 1492, 1453, 1241, 1222, 1126, 1026, 736 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{27}NO$ $(M+Na)^+$ 380.1985, found 380.1987.

(3-Ethyl-1-phenyl-2-propyl-hex-2-enyl)-(4-methoxy-phenyl)-amine (I-42)

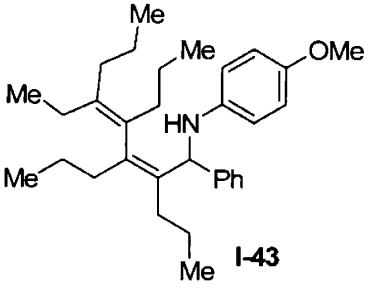
In the three-component coupling of 4-octyne (2.0 mmol, 300 μL), benzylidene-(4-methoxy-phenyl)-amine (1.0 mmol, 212 mg), and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (140 mg, 40% yield). R_f = 0.46 (9:1 hexanes: EtOAc). Also, isolated 10% product resulting from coupling reaction of 2 alkynes + 1 imine.



I-42

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 2H), 7.31 (m, 2H), 7.23 (m, 1H), 6.73 (m, 2H), 6.47 (m, 2H), 5.26 (s, 1H), 3.73 (s, 3H), 2.21 (m, 1H), 2.07 (m, 2H), 1.97 (m, 1H), 1.85 (m, 1H), 1.47 (m, 2H), 1.22 (m, 2H), 0.96 (m, 6H), 0.83 (m, 1H), 0.72 (t, J = 7.05 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.9, 143.0, 142.6, 140.1, 134.6, 128.4, 127.3, 126.7, 114.8, 114.5, 60.1, 55.9, 34.2, 31.9, 24.8, 23.9, 22.3, 15.0, 14.7, 14.2. IR (film, CH_2Cl_2): 3408, 3059, 3025, 2959, 2870, 2831, 1601, 1511, 1465, 1243, 1179, 1040, 817, 759, 738, 700 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{33}NO$ $(M)^+$ 351.2557, found 351.2561.

(5-Ethyl-1-phenyl-2,3,4-tripropyl-octa-2,4-dienyl)-(4-methoxy-phenyl)-amine (I-43)

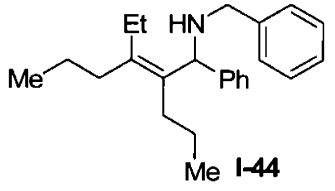


I-43

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (m, 2H), 7.27 (m, 2H), 7.19 (m, 1H), 6.64 (m, 2H), 6.31 (m, 2H), 5.12 (s, 1H), 3.69 (s, 3H), 2.38 (m, 1H), 2.19 (m, 2H), 2.10-1.90 (m, 7H), 1.71(m, 1H), 1.52 (m, 5H), 1.27 (m, 3H), 1.09 (m, 2H), 0.95 (m, 7H), 0.78 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.7, 143.2, 142.8, 142.4, 138.5, 133.6, 133.0, 128.3, 127.2, 126.5, 114.7, 114.5, 61.7, 56.0, 36.7, 34.7, 31.3, 30.8, 25.0, 24.0, 23.9, 21.6, 21.3, 15.3, 15.1, 14.9, 12.8. IR (film, CH_2Cl_2): 3411, 2958, 2931, 2870, 1511, 1464, 1244, 1040, 817, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{32}H_{47}NO$ $(M+H)^+$ 462.3730, found 462.3686.

Benzyl-(3-ethyl-1-phenyl-2-propyl-hex-2-enyl)-amine (I-44)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzyl-benzylidene-amine (0.5 mmol, 98 mg), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (34 mg, 20% yield). $R_f = 0.52$ (95:5 hexanes: EtOAc).

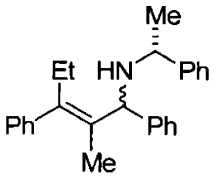


I-44

^1H NMR ($CDCl_3$, 400 MHz): δ 7.48 (m, 2H), 7.40-7.19 (m, 8H), 4.86 (s, 1H), 3.76 (AB q, J = 13.26 Hz, 2H), 2.17 (m, 2H), 2.04 (m, 2H), 1.95 (m, 1H), 1.78 (m, 1H), 1.52 (bs, 1H), 1.44 (m, 2H), 1.20 (m, 1H), 1.02 (t, J = 7.53 Hz, 3H), 0.94 (t, J = 7.33 Hz, 3H), 0.71 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 141.2, 139.5, 134.7, 128.5, 128.3, 128.2, 127.5, 127.0, 126.5, 61.7, 51.9, 34.2, 30.6, 24.2, 24.1, 22.2, 15.1, 14.7, 14.5. IR (film, CH_2Cl_2): 3330, 3084, 3061, 3026, 2959, 2930, 2870, 1701, 1601, 1493, 1453, 1375, 1070, 1028, 739, 699 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{33}N$ $(M+H)^+$ 336.2686, found 336.2684.

(2-Methoxy-phenyl)-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (I-45)

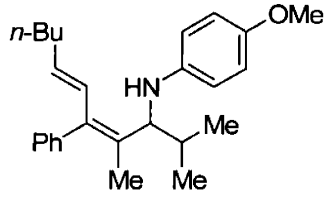
In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), (*R*)-benzylidene-(1-phenyl-ethyl)-amine (1.0 mmol, 209 mg), and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (217 mg, 60% yield and regioselectivity = 85:15, diastereoselectivity = 74:26. $R_f = 0.58$ (5:1 hexanes: EtOAc).



I-45

(1-Isopropyl-2-methyl-3-phenyl-nona-2,4-dienyl)-(4-methoxy-phenyl)-amine (I-46)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), isobutylidene-(4-methoxy-phenyl)-amine (1.0 mmol, 170 μL), and hexylboronic acid (2.0 mmol, 256mg), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (130mg, 36% yield and regioselectivity = 80:20). R_f = 0.64 (9:1 hexanes: EtOAc).

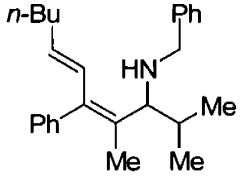


I-46

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (m, 2H), 7.23 (m, 1H), 6.96 (m, 2H), 6.86 (d, J = 15.25 Hz, 1H), 6.78 (m, 2H), 6.58 (m, 2H), 5.06 (m, 1H), 4.21 (d, J = 9.11 Hz, 1H), 3.77 (s, 3H), 3.46 (bs, 1H), 2.12 (q, J = 6.69 Hz, 2H), 1.81 (m, 1H), 1.33 (m, 3H), 1.30 (s, 3H), 1.20 (d, J = 6.54 Hz, 3H), 1.03 (d, J = 6.78 Hz, 3H), 0.91(m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 142.6, 142.0, 139.1, 134.8, 133.5, 129.7, 128.5, 128.2, 126.3, 114.9, 114.7, 60.6, 56.1, 33.2, 32.5, 31.8, 22.3, 20.7, 20.2, 15.0, 14.1. IR (film, CH_2Cl_2): 3403, 3027, 2956, 2028, 2871, 2831, 1618, 1511, 1465, 1441, 1240, 1070, 1041, 963, 817, 703 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{35}NO$ $(M+H)^+$ 378.2791, found 378.2792.

Benzyl-(1-isopropyl-2-methyl-3-phenyl-nona-2,4-dienyl)-amine (I-47)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzyl-isobutylidene-amine (1.0 mmol, 155 μL), and hexylboronic acid (2.0 mmol, 256mg), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (98 mg, 27% yield and regioselectivity = 75:25). R_f = 0.48 (9:1 hexanes: EtOAc).

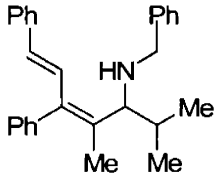


I-47

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.23 (m, 8H), 7.08 (m, 2H), 6.55 (d, J = 15.30 Hz, 1H), 4.97 (m, 1H), 3.83 (d, J = 13.38 Hz, 1H), 3.63 (d, J = 13.39 Hz, 1H), 3.54 (d, J = 9.48 Hz, 1H), 1.98 (q, J = 6.56 Hz, 2H), 1.73 (m, 1H), 1.33 (m, 3H), 1.44 (s, 3H), 1.25 (m, 4H), 1.13 (d, J = 6.49 Hz, 3H), 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5, 141.5, 140.2, 133.8, 133.5, 129.9, 128.9, 128.5, 128.4, 128.3, 126.9, 126.3, 63.4, 51.6, 33.1, 31.8, 31.5, 22.5, 20.8, 20.3, 14.7, 14.1. IR (film, CH_2Cl_2): 3346, 3060, 3027, 2955, 2926, 2870, 1603, 1493, 1454, 1441, 1378, 1364, 1103, 1071, 961, 774, 737 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{35}N$ $(M+H)^+$ 362.2842, found 362.2843.

Benzyl-(1-isopropyl-2-methyl-3,5-diphenyl-penta-2,4-dienyl)-amine (I-48)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), benzyl-isobutylidene-amine (1.0 mmol, 155 μL), and styryl boronic acid (1.5 mmol, 222 mg), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (153 mg, 40% yield and regioselectivity = 85:15). R_f = 0.52 (9:1 hexanes: EtOAc).

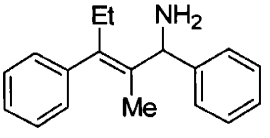


I-48

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.26 (m, 14H), 6.00 (d, J = 15.50 Hz, 1H), 4.05 (d, J = 14.0 Hz, 1H), 3.82 (m, 2H), 3.63 (d, J = 13.39 Hz, 1H), 1.92 (m, 1H), 1.71 (m, 2H), 1.69 (m, 3H), 1.33 (d, J = 6.50 Hz, 3H), 1.06 (d, J = 6.50 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6, 141.2, 140.4, 138.1, 137.5, 131.0, 129.8, 128.5, 128.4, 128.3, 127.5, 127.1, 126.9, 126.7, 126.5, 63.1, 51.2, 31.5, 20.8, 20.4, 15.1. IR (film, CH_2Cl_2): 3348, 3077, 3058, 3024, 2955, 2869, 1600, 1493, 1453, 1383, 1310, 1104, 1072, 1010, 957, 776, 753, 695 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{31}N$ $(M+H)^+$ 382.2529, found 382.2521.

2-Methyl-1,3-diphenyl-pent-2-enylamine (I-49)

Ceric ammonium nitrate (CAN) deprotection of allylic amine product (**I-40**) using procedure described by Overman and co-workers (Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J. *Org. Lett.* **2003**, *5*, 1809) afforded primary allylic amine **I-49** in 40% yield.

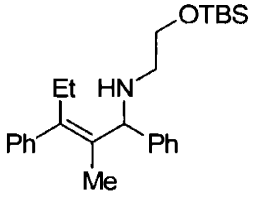


I-49

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (m, 2H), 7.36 (m, 4H), 7.26 (m, 2H), 7.15 (m, 2H), 5.30 (s, 1H), 2.60 (q, J = 7.52 Hz, 2H), 1.60 (bs, 1H), 1.31 (s, 1H), 1.01 (t, J = 7.51 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 143.6, 139.6, 133.5, 129.0, 128.4, 128.2, 126.6, 126.4, 126.3, 54.8, 27.3, 14.3, 14.0. IR (film, CH_2Cl_2): 3375 (d), 3024, 2965, 2930, 2870, 1599, 1492, 1449, 1462, 1376, 1028, 766, 750 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{18}H_{21}N$+Na 274.1566, found 274.1566.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (I-50)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (162 mg, 80% yield and regioselectivity = 93:7). R_f = 0.34 (10:1 hexanes: EtOAc).

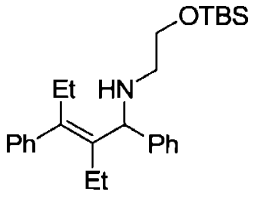


I-50

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (m, 2H), 7.39 (m, 4H), 7.29 (m, 2H), 7.16 (m, 2H), 5.05 (s, 1H), 3.91 (dd, *J* = 4.51, 6.28 Hz, 2H), 2.89 (m, 1H), 2.81 (m, 1H), 2.68 (q, *J* = 7.45 Hz, 2H), 1.33 (s, 3H), 1.05 (t, *J* = 7.43 Hz, 3H), 0.98 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 143.1, 140.8, 132.0, 129.1, 128.3, 128.2, 127.1, 126.6, 126.3, 62.8, 61.5, 49.7, 27.3, 26.1, 18.5, 14.2, 13.7, -5.02, -5.06. IR (film, CH_2Cl_2): 3329, 3058, 3024, 2929, 2956, 2857, 1945, 1600, 1492, 1471, 1462, 1377, 1360, 1256, 1085, 960, 836, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{39}NOSi$ $(M+H)^+$ 410.2874, found 410.2872.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-ethyl-1,3-diphenyl-pent-2-enyl)-amine (I-51)

In the three-component coupling of 1-phenyl-1-butyne (1.0 mmol, 142 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine as a single regioisomer (171 mg, 81% yield). R_f= 0.41 (95:5 hexanes: EtOAc).

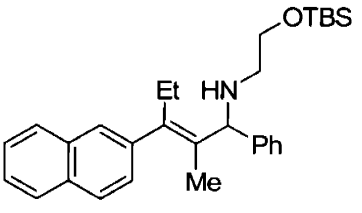


I-51

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (m, 2H), 7.35 (m, 4H), 7.25 (m, 2H), 7.14 (m, 2H), 4.99 (s, 1H), 3.85 (dd, J = 4.42, 6.32 Hz, 2H), 2.88 (m, 1H), 2.79 (m, 1H), 2.60 (m, 2H), 1.85 (m, 2H), 1.69 (m, 1H), 1.00 (t, J = 7.49 Hz, 3H), 0.95 (s, 9H), 0.47 (t, J = 7.53 Hz, 3H), 0.13 (s, 3H), 0.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 143.4, 141.5, 138.4, 129.0, 128.3, 128.1, 127.3, 126.6, 126.2, 62.9, 62.2, 50.2, 27.8, 26.2, 22.1, 18.5, 14.9, 13.5, -5.02, -5.06. IR (film, CH_2Cl_2): 3337, 3058, 3024, 2959, 2930, 2857, 1599, 1491, 1462, 1256, 1081, 835, 777, 702 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{41}NOSi$ $(M+H)^+$ 424.3030, found 424.3018.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-3-naphthalen-2-yl-1-phenyl--pent-2-enyl)-amine (I-52)

In the three-component coupling of 2-prop-1-ynyl-naphthalene (0.5 mmol, 83 mg), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.25 mmol, 68 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (184 mg, 80% yield, regioselectivity = 91:9). R_f = 0.34 (90:10 hexanes: EtOAc).

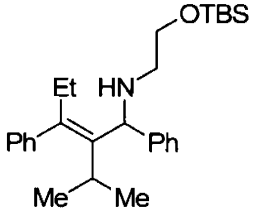


I-52

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (m, 3H), 7.52 (m, 5H), 7.41 (m, 2H), 7.29 (m, 2H), 5.08 (s, 1H), 3.90 (app t, J = 5.20 Hz, 2H), 2.92 (m, 1H), 2.81 (m, 1H), 2.75 (q, J = 7.46 Hz, 2H), 1.93 (bs, 1H), 1.34 (s, 3H), 1.05 (t, J = 7.49 Hz, 3H), 0.97 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 141.3, 140.7, 133.5, 132.6, 132.2, 128.4, 127.9, 127.8, 127.7, 127.4, 127.1, 126.7, 126.1, 125.6, 62.9, 61.6, 49.8, 27.3, 26.2, 18.6, 14.3, 13.8, -5.00, -5.03. IR (film, CH_2Cl_2): 3329, 3055, 2955, 2928, 2856, 1598, 1462, 1450, 1255, 1085, 835, 820, 778, 747, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{41}NOSi$ $(M+H)^+$ 460.3030, found 460.3033.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-isopropyl-1,3-diphenyl-pent-2-enyl)-amine (I-53)

In the three-component coupling of (3-methyl-but-1-ynyl)-benzene (1 mmol, 144 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine as a single regioisomer (22 mg, 10% yield). R_f= 0.48 (90:10 hexanes: EtOAc).



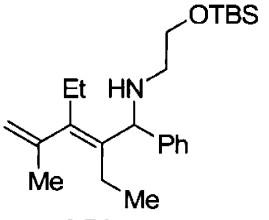
I-53

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 8.03 Hz, 2H), 7.32 (m, 4H), 7.23 (m, 2H), 7.08 (m, 2H), 4.44 (s, 1H), 3.87 (m, 2H), 2.91 (m, 2H), 2.50 (m, 2H), 2.18 (sep, J = 7.40 Hz, 1H), 1.70 (bs, 1H), 0.95 (m, 15H), 0.37 (t, J = 7.40 Hz, 3H), 0.13 (s, 3H), 0.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 143.9, 143.0, 141.9, 128.8, 128.1, 128.0, 127.4, 126.1, 125.9, 62.9, 60.1,

51.4, 31.7, 28.8, 26.2, 22.7, 22.1, 18.6, 11.5, -5.00, -5.07. IR (film, CH_2Cl_2): 3608, 3583, 3058, 3023, 2957, 2929, 2858, 1491, 1462, 1256, 1084, 833, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{43}NOSi$ $(M+H)^+$ 438.3187, found 438.3167.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2,3-diethyl-4-methyl-1-phenyl-penta-2,4-dienyl)-amine (I-54)

In the three-component coupling of 2-methyl-hex-1-en-3-yne (1 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **B** was used. Silica gel chromatography afforded the allylic amine as a single regioisomer (101 mg, 52% yield). R_f= 0.45 (95:5 hexanes: EtOAc).

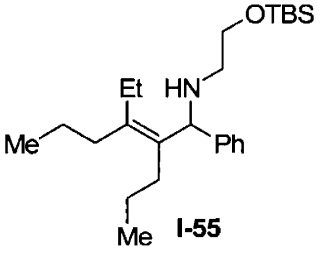


I-54

^1H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 4.93 (m, 1H), 4.79 (s, 1H), 4.65 (m, 1H), 3.80 (dd, *J* = 4.45, 6.27 Hz, 2H), 2.71 (m, 2H), 2.32 (m, 2H), 1.95 (m, 1H), 1.83 (m, 4H), 1.05 (t, *J* = 7.51 Hz, 3H), 0.92 (s, 9H), 0.65 (t, *J* = 7.51 Hz, 3H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.9, 143.5, 142.8, 136.1, 128.2, 127.3, 126.4, 113.1, 62.9, 62.0, 50.2, 26.1, 23.9, 23.2, 22.3, 18.5, 15.9, 13.9, -5.05, -5.09. IR (film, CH_2Cl_2): 3339, 3074, 3025, 2959, 2930, 2858, 2340, 2361, 1626, 1601, 1492, 1471, 1451, 1462, 1256, 1082, 895, 835, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{41}NOSi$ $(M+H)^+$ 388.3030, found 388.3046.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-ethyl-1-phenyl-2-propyl-hex-2-enyl)-amine (I-55)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (121 mg, 60% yield). R_f= 0.69 (10:1 hexanes: EtOAc).

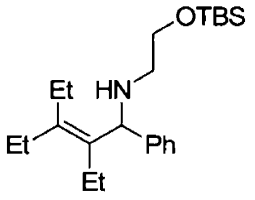


I-55

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (m, 2H), 7.29 (m, 2H), 7.20 (m, 1H), 4.78 (s, 1H), 3.77 (app t, J = 4.60 Hz, 2H), 2.67 (m, 2H), 2.27 (q, J = 7.39 Hz, 2H), 2.13 (m, 2H), 1.87 (m, 1H), 1.75 (m, 2H), 1.44 (m, 2H), 1.08 (t, J = 7.52 Hz, 3H), 0.94 (m, 12H), 0.65 (m, 4H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 138.9, 135.2, 128.1, 127.4, 126.3, 62.9, 62.3, 50.1, 34.2, 30.6, 26.1, 24.2, 24.1, 22.2, 18.5, 15.1, 14.7, 14.6, -5.07, -5.10. IR (film, CH_2Cl_2): 3337, 3025, 2958, 2930, 1463, 1256, 1082, 835, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{45}NOSi$ 403.3343, found $(M+H)^+$ 404.3335.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2,3-diethyl-1-phenyl-pent-2-enyl]-amine (I-56)

In the three-component coupling of 3-hexyne (1.0 mmol, 114 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (142 mg, 76% yield). R_f= 0.67 (90:10 hexanes: EtOAc).

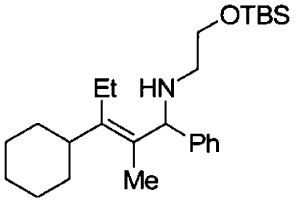


I-56

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (m, 2H), 7.30 (m, 2H), 7.20 (m, 1H), 4.80 (s, 1H), 3.77 (dd, J = 5.00, 5.50 Hz, 2H), 2.69 (m, 2H), 2.28 (q, J = 7.54 Hz, 2H), 2.10 (m, 2H), 1.95 (m, 1H), 1.83 (m, 1H), 1.70 (bs, 1H), 1.10 (t, J = 7.53 Hz, 3H), 1.02 (t, J = 7.48 Hz, 3H), 0.91 (s, 9H), 0.61 (t, J = 7.53 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 140.2, 135.6, 128.1, 127.4, 126.3, 62.9, 62.3, 50.0, 26.1, 24.7, 23.8, 20.6, 18.5, 15.4, 14.6, 13.6, -5.05, -5.09. IR (film, CH_2Cl_2): 3337, 3026, 2960, 2931, 2872, 1463, 1451, 1255, 1082, 835, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{23}H_{41}NOSi$ 376.3030, found $(M+H)^+$ 376.3043.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-cyclohexyl-2-methyl-1-phenyl-pent-2-enyl)-amine (I-57)

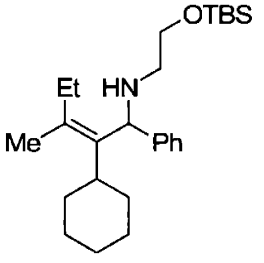
In the three-component coupling of prop-1-ynyl-cyclohexane (1.0 mmol, 137 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (125 mg, 60% yield, regioselectivity = 75:25). R_f = 0.64 (90:10 hexanes: EtOAc).



I-57

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (m, 2H), 7.30 (m, 2H), 7.21 (m, 1H), 4.77 (s, 1H), 3.79 (m, 2H), 2.68 (m, 2H), 2.47 (m, 1H), 2.22 (m, 2H), 1.81-1.52 (m, 9H), 1.40(s, 3H), 1.39-1.19 (m, 6H), 1.08 (t, J = 7.57 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 142.9, 128.9, 128.2, 127.2, 126.4, 62.9, 61.7, 49.7, 42.3, 31.5, 31.3, 27.1, 27.0, 26.5, 26.1, 21.1, 18.5, 16.2, 12.2, -5.04, -5.08. IR (film, CH_2Cl_2): 3332, 3083, 3060, 3025, 2928, 2854, 1702, 1601, 1491, 1471, 1462, 1448, 1255, 1090, 1062, 835, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NOSi$ 416.3343, found $(M+H)^+$ 416.3329.

Minor regioisomer: [2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-cyclohexyl-3-methyl-1-phenyl-pent-2-enyl)-amine

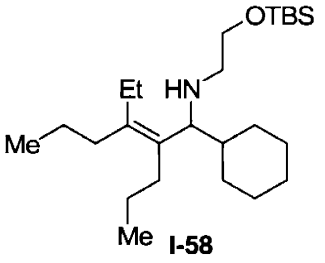


I-57 regioisomer

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (m, 2H), 7.27 (m, 2H), 7.16 (m, 1H), 4.65 (s, 1H), 3.79 (m, 2H), 2.79 (m, 1H), 2.71 (m, 1H), 2.18 (m, 3H), 1.77(s, 3H), 1.70 (m, 2H), 1.55 (m, 4H), 0.92 (s, 14H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 138.7, 134.5, 127.9, 127.3, 125.9, 63.1, 62.0, 50.5, 40.3, 31.9, 31.8, 28.7, 27.9, 27.6, 27.4, 26.5, 26.2, 22.9, 19.4, 18.6, 14.4, -5.05, -5.08. IR (film, CH_2Cl_2): 3360, 3083, 3060, 3025, 2928, 2854, 1701, 1471, 1462, 1448, 1256, 1092, 835, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NOSi$ 416.3343, found $(M+H)^+$ 416.3350.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-3-ethyl-2-propyl-hex-2-enyl)-amine (I-58)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclohexylmethylene-amine (0.5 mmol, 135 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (108 mg, 53% yield). R_f= 0.24 (90:10 hexanes: EtOAc).



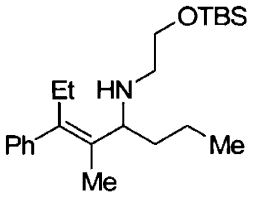
I-58

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.68 (m, 2H), 3.18 (d, J = 9.24 Hz, 1H), 2.59 (m, 1H), 2.42 (m, 1H), 2.07 (m, 6H), 1.91 (m, 1H), 1.80 (m, 2H), 1.62 (m, 4H), 1.43-1.10 (m, 10H), 0.92 (m, 9H), 0.89 (s, 9H), 0.78 (m, 1H), 0.053 (s, 3H), 0.050 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.7, 132.9, 63.0, 49.9, 41.2, 34.0, 31.4, 31.0, 27.0, 26.7, 26.6, 26.1, 24.5, 23.4, 22.1, 18.5, 15.5, 14.8, 13.9, -5.07, -5.10. IR (film, CH_2Cl_2): 3361, 2956, 2928, 2869, 2855, 1733, 1463, 1255, 1083, 834, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{51}NOSi$ $(M+H)^+$ 410.3813, found 410.3811.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-3-phenyl-1-propyl-pent-2-enyl)-amine (I-59)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-butylidene-amine (0.5 mmol, 115 mg) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded

the allylic amines (75 mg, 40% yield and regioselectivity = 93:7). R_f = 0.21 (10:1 hexanes: EtOAc).

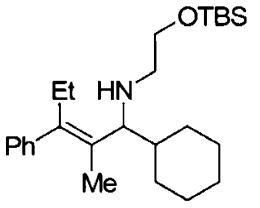


I-59

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (m, 2H), 7.23 (m, 1H), 7.08 (m, 2H), 3.74 (m, 3H), 2.72 (m, 1H), 2.60 (m, 1H), 2.42 (q, *J* = 7.50 Hz, 2H), 1.58-1.37 (m, 4H), 1.34 (s, 3H), 1.28 (m, 1H), 0.96 (t, *J* = 7.21 Hz, 3H), 0.90 (s, 9H), 0.88 (m, 3H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 141.1, 131.5, 129.1, 128.2, 126.1, 62.9, 57.7, 49.5, 36.9, 26.8, 26.1, 20.1, 18.5, 14.7, 13.5, 13.1, -5.04, -5.10. IR (film, CH_2Cl_2): 3331, 3077, 3056, 3020, 2956, 2930, 2858, 1599, 1574, 1491, 1463, 1441, 1361, 1255, 1080, 834, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{23}H_{41}NOSi$ $(M+H)^+$ 376.3030, found 376.3019.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-2-methyl-3-phenyl-pent-2-enyl)-amine (I-60)

In the three-component coupling of 1-phenyl-1-propyne (2.0 mmol, 250 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclohexylmethylene-amine (1 mmol, 280 μL) and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (374 mg, 90% yield and regioselectivity = 90:10). R_f = 0.47 (4:1 hexanes: EtOAc).

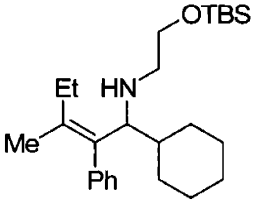


I-60

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (m, 2H), 7.23 (m, 1H), 7.08 (m, 2H), 3.75 (m, 2H), 3.38 (d, J = 9.48 Hz, 1H), 2.72 (m, 1H), 2.57 (m, 1H), 2.43 (m, 2H), 2.16 (bd, J = 12.57 Hz, 1H), 1.75 (m, 4H), 1.62 (bs, 1H), 1.34 (s, 3H), 1.25 (m, 3H), 1.10 (m, 2H), 0.92 (m, 10H), 0.86 (t, J = 7.48 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 141.5, 130.7, 129.1, 128.1, 126.0, 63.4, 62.9, 49.6, 40.8, 31.3, 30.7, 26.9, 26.8, 26.7, 26.6, 26.1, 18.4, 13.8, 13.3, -5.05, -5.10. IR (film, CH_2Cl_2): 3329, 3076, 3055, 3019, 2928, 2854, 1491, 1463, 1378, 1361, 1255, 1089, 1005, 948, 835, 811, 776, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NOSi$ $(M+H)^+$ 416.3343, found 416.3337.

Minor regioisomer:

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-3-methyl-2-phenyl-pent-2-enyl)-amine



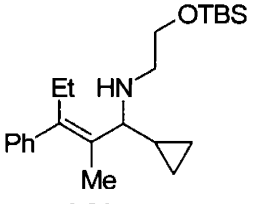
I-60 regioisomer

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (m, 2H), 7.23 (m, 1H), 7.05 (m, 2H), 3.74 (dd, J = 6.65, 4.69 Hz, 2H), 3.36 (d, J = 9.43 Hz, 1H), 2.96 (m, 1H), 2.57 (m, 1H), 2.53 (m, 1H), 2.24 (m, 2H), 2.05 (m, 1H), 1.95 (m, 1H), 1.66 (m, 3H), 1.43 (s, 3H), 1.13 (m, 3H), 1.07 (t, J = 7.55 Hz, 3H), 0.95 (m, 2H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ

141.0, 137.2, 134.4, 130.0, 128.0, 126.2, 63.7, 63.5, 50.1, 40.3, 31.8, 30.8, 27.1, 26.5, 26.4, 26.2, 20.1, 18.6, 13.3, -5.06. IR (film, CH_2Cl_2): 3326, 3078, 3055, 3016, 2926, 1854, 1471, 1462, 1450, 1255, 1073, 834, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NOSi$ $(M+H)^+$ 416.3343, found 416.3334.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclopropyl-2-methyl-3-phenyl-pent-2-enyl)-amine (I-61)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclopropylmethylene-amine (0.5 mmol, 140 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (84 mg, 45% yield and regioselectivity = 85:15). R_f = 0.64 (1:1 hexanes: EtOAc).

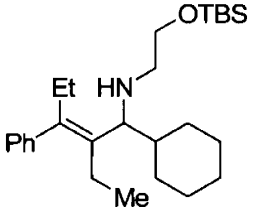


I-61

^1H NMR ($CDCl_3$, 400 MHz): δ 7.34 (m, 2H), 7.22 (m, 1H), 7.09 (m, 2H), 3.76 (m, 2H), 2.92 (d, *J* = 8.69 Hz, 1H), 2.69 (app t, *J* = 5.34 Hz, 2H), 2.35 (m, 2H), 1.73 (bs, 1H), 1.53 (s, 3H), 1.00 (m, 1H), 0.95 (s, 9H), 0.84 (t, *J* = 7.48 Hz, 3H), 0.63 (m, 1H), 0.46 (m, 1H), 0.35 (m, 1H), 0.22 (m, 1H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 140.0, 132.2, 129.2, 128.1, 126.1, 63.5, 62.3, 49.9, 26.7, 26.1, 18.5, 15.5, 14.6, 14.0, 5.2, 2.4, -5.03, -5.06. IR (film, CH_2Cl_2): 3332, 3077, 3057, 3002, 2929, 2956, 2857, 2929, 1492, 1463, 1441, 1373, 1255, 1083, 1016, 939, 834, 776, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{23}H_{39}NOSi$ $(M+H)^+$ 374.2874, found 374.2879.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-2-ethyl-3-phenyl-pent-2-enyl)-amine (I-62)

In the three-component coupling of But-1-ynyl-benzene (1.0 mmol, 142 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclohexylmethylene-amine (0.5 mmol, 135 μL) and Et_3B (3.0 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (182 mg, 85% yield and regioselectivity = 95:5). R_f = 0.53 (4:1 hexanes: EtOAc).

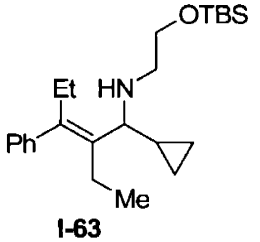


I-62

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (m, 2H), 7.24 (m, 1H), 7.12 (m, 2H), 3.75 (m, 2H), 3.35 (d, *J* = 9.60 Hz, 1H), 2.78 (m, 1H), 2.58 (m, 1H), 2.40 (m, 2H), 2.15 (bd, *J* = 12.55 Hz, 1H), 1.79 (m, 7H), 1.31 (s, 4H), 1.12 (m, 2H), 0.92 (m, 9H), 0.86 (t, *J* = 7.50 Hz, 3H), 0.74 (t, *J* = 7.54 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 142.4, 136.2, 129.2, 128.0, 126.0, 64.5, 63.0, 50.1, 41.3, 31.4, 31.1, 27.2, 27.0, 26.7, 26.6, 26.2, 26.1, 18.5, 14.9, 13.1, -5.05, -5.09. IR (film, CH_2Cl_2): 3358, 3076, 3055, 3018, 2928, 2854, 1490, 1463, 1449, 1255, 1089, 946, 835, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{47}NOSi$ $(M+H)^+$ 430.3500, found 430.3498.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclopropyl-2-ethyl-3-phenyl-pent-2-enyl)-amine (I-63)

In the three-component coupling of But-1-ynyl-benzene (1.0 mmol, 142 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclopropylmethylene-amine (0.5 mmol, 140 μL) and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (97 mg, 50% yield and regioselectivity = 90:10). R_f = 0.68 (1:1 hexanes: EtOAc).



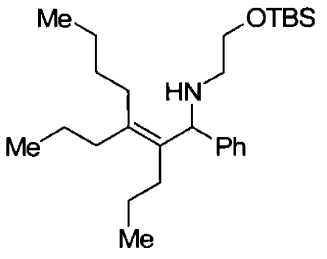
I-63

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 2H), 7.23 (m, 1H), 7.12 (m, 2H), 3.77 (m, 2H), 2.84 (d, *J* = 8.94 Hz, 1H), 2.75 (app t, *J* = 5.28 Hz, 2H), 2.34 (m, 2H), 2.00 (m, 2H), 1.77 (m, 1H), 1.04 (m, 1H), 0.93 (s, 9H), 0.84 (app dt, *J* = 7.50, 3.61 Hz, 6H), 0.66 (m, 1H), 0.46 (m, 1H), 0.34 (m, 1H), 0.23 (m, 1H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 140.9, 138.0, 129.2, 128.0, 126.0, 64.6, 62.7, 50.2, 27.1, 26.1, 21.9, 18.5, 16.0, 15.3, 13.7, 5.8, 2.8, -5.06, -5.09. IR (film, CH_2Cl_2): 3332, 3076, 3057, 2957, 1490, 1463, 1388, 1361, 1372, 1255, 1086, 1017, 960, 938, 835, 776, 703 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{41}NOSi$ $(M+H)^+$ 388.3036, found 380.3008.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-phenyl-2,3-dipropyl-hept-2-enyl)-amine (I-64)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Bu_3B (1.5 mmol, 3M in MeOAc),

the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (162 mg, 75% yield). R_f= 0.76 (10:1 hexanes: EtOAc).

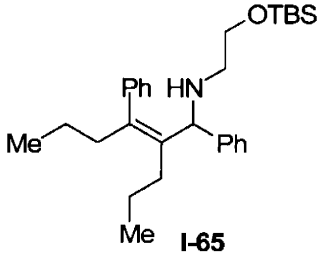


I-64

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (m, 2H), 7.29 (m, 2H), 7.20 (m, 1H), 4.79 (s, 1H), 3.78 (m, 2H), 2.69 (m, 2H), 2.24 (m, 2H), 2.02 (m, 2H), 1.81 (m, 3H), 1.43 (m, 7H), 0.97 (m, 4H), 0.92 (m, 10H), 0.68 (m, 4H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 137.7, 135.5, 128.1, 127.4, 126.3, 62.9, 62.3, 50.1, 34.6, 32.4, 31.2, 30.6, 26.1, 24.1, 23.5, 22.2, 18.5, 15.1, 14.7, 14.3, -5.07, -5.11. IR (film, CH_2Cl_2): 3337, 3061, 3025, 2957, 1602, 1492, 1463, 1255, 1084, 835, 777, 738 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{49}NOSi$ $(M+H)^+$ 432.3656, found 432.3640.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1,3-diphenyl-2-propyl-hex-2-enyl)-amine (I-65)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and $PhB(OH)_2$ (1 mmol, 121mg), the the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine (32 mg, 15% yield). R_f= 0.56 (10:1 hexanes: EtOAc).

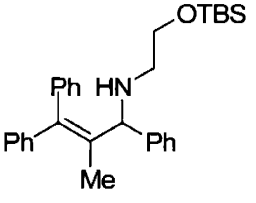


I-65

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (m, 4H), 7.27 (m, 3H), 7.19 (m, 3H), 4.36 (s, 1H), 3.66 (m, 2H), 2.58 (m, 1H), 2.45 (m, 1H), 2.33 (m, 2H), 2.07 (m, 1H), 1.92 (m, 1H), 1.65 (bs, 1H), 1.32 (m, 3H), 0.92 (s, 9H), 7.33 (t, J = 7.33 Hz, 3H), 0.78 (m, 4H), 0.075 (s, 3H), 0.072 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 139.9, 137.7, 129.1, 128.7, 128.2, 128.1, 127.3, 126.4, 126.3, 63.5, 62.8, 49.5, 36.8, 30.1, 26.1, 24.1, 21.3, 18.5, 15.1, 14.3, -5.07, -5.10. IR (film, CH_2Cl_2): 3334, 3059, 3024, 2957, 2929, 2869, 1689, 1600, 1491, 1463, 1256, 1090, 1062, 835, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{29}H_{45}NOSi$ $(M+H)^+$ 452.3343, found 452.3337.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-1,3,3-triphenyl-allyl)-amine (I-66)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and $PhB(OH)_2$ (0.5 mmol, 60.5 mg), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (87 mg, 38% yield and regioselectivity = 90:10). R_f = 0.41 (10:1 hexanes: EtOAc).



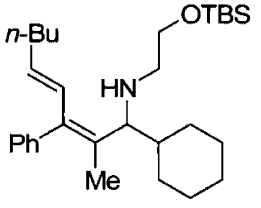
I-66

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (m, 2H), 7.24-7.05 (m, 13H), 4.57 (s, 1H), 3.66 (dd, J = 4.60, 5.75 Hz, 2H), 2.66 (m, 1H), 2.51 (dt, J = 4.44, 11.71 Hz, 1H), 1.75 (bs, 1H), 1.50 (s, 3H), 0.83 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.0, 142.94, 142.87, 140.5, 136.0, 129.6, 129.5, 128.5, 128.3, 128.2, 127.3, 126.7, 126.6, 63.1, 62.8, 49.5, 26.2, 18.6, 14.3, -5.02, -5.05. IR (film, CH_2Cl_2): 3329, 3078, 3057, 3025, 2953, 2928, 2856, 1491, 1471,

1462, 1443, 1255, 1082, 961, 836, 776, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{39}NOSi$ $(M+Na)^+$ 480.2693, found 480.2701.

[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-2-methyl-3-phenyl-nona-2,4-dienyl)-amine (I-67)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL) and hexenylboronic acid (1 mmol, 128 mg), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines (63 mg, 27% yield and regioselectivity = 80:20). R_f = 0.51 (9:1 hexanes: EtOAc).



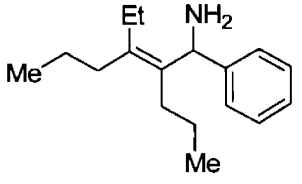
I-67

^1H NMR ($CDCl_3$, 500 MHz): δ 7.35 (m, 2H), 7.25 (m, 1H), 7.04 (m, 2H), 6.75 (d, *J* = 4.60 Hz, 1H), 4.96 (m, 1H), 3.76 (m, 1H), 3.69 (m, 1H), 3.63 (d, *J* = 9.50 Hz, 1H), 2.68 (m, 1H), 2.55 (m, 1H), 2.12 (ad, *J* = 13.0 Hz, 1H), 2.03 (d, *J* = 6.50 Hz, 2H), 1.85-1.60 (m, 7H), 1.30 (s, 3H), 1.26 (m, 6H), 0.90 (s, 10H), 0.89 (m, 3H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.5, 139.8, 133.9, 133.7, 129.8, 128.7, 128.2, 126.2, 62.7, 62.5, 49.5, 41.0, 33.2, 31.8, 31.2, 30.4, 26.9, 26.7, 26.5, 26.1, 22.4, 18.5, 14.7, 14.1, -5.03, -5.06. IR (film, CH_2Cl_2): 3358, 3077, 3030, 2954, 2927, 2854, 1463, 1449, 1255, 1092, 835, 776, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{51}NOSi$ $(M+H)^+$ 470.3813, found 470.3799.

Standard Experimental Procedure for Deprotection of N–(*tert*-butyldimethyl)silyloxy ethyl ($TBSOCH_2CH_2$–) allylic amines (Table 1.14)

Tetrabutylammoniumfluoride (TBAF 1M solution in THF, 150 mol%) was added to a solution of allylic amine product (1M in THF) at 0 °C and mixture stirred for 30 min. 5 mL H_2O was added, and extracted with ether. Concentration under vacuo afforded the *ß*-amino alcohol product. Without further purification, this product was dissolved in MeOH (0.2 M) and 40 % aq $MeNH_2$ (300 %), and solution of H_5IO_6 in water (360 mol%, 0.2M) were sequentially added. Reaction mixture was stirred 5 hr and then concentrated under vacuo. Add saturated $NaHCO_3$ solution to pH 9.0 and extract with CH_2Cl_2. Organic layer was concentrated in vacuo and silica gel chromatography (hexanes: EtOAc) yielded primary allylic amines products. Unless otherwise stated, yields refer to combined isolated yield with greater than >95% purity by ^1H NMR.

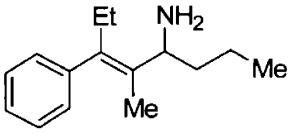
3-Ethyl-1-phenyl-2-propyl-hex-2-enylamine (I-68)



I-68

^1H NMR ($CDCl_3$, 400 MHz): δ 7.39 (m, 2H), 7.31 (m, 2H), 7.21 (m, 1H), 5.14 (s, 1H), 2.42 (m, 2H), 2.23 (m, 2H), 2.03 (m, 2H), 1.91 (ddd, J = 4.73, 12.03, 16.81 Hz, 1H), 1.75 (ddd, J = 4.97, 11.65 16.72 Hz, 1H), 1.45 (m, 3H), 1.23 (m, 1H), 1.07 (t, J = 7.53 Hz, 3H), 0.93 (t, J = 7.35 Hz, 3H), 0.88 (m, 1H), 0.75 (t, J = 7.22 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 138.3, 136.4, 128.2, 126.6, 126.4, 55.2, 34.4, 30.6, 24.8, 24.3, 22.2, 15.1, 14.8, 14.7. IR (film, CH_2Cl_2): 3376 (d), 3026, 2959, 2930, 2870, 1602, 1466, 1450, 1027 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{17}H_{27}N$+Na 268.2036, found 268.2043.

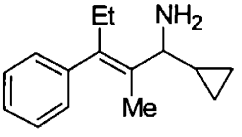
2-Methyl-3-phenyl-1-propyl-pent-2-enylamine (I-69)



I-69

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 2H), 7.23 (m, 1H), 7.07 (m, 2H), 3.96 (t, J = 6.97 Hz, 1H), 2.40 (m, 2H), 1.50 (m, 2H), 1.42 (s, 3H), 1.34 (m, 2H), 1.17 (bs, 2H), 0.98 (t, J = 7.18 Hz, 3H), 0.89 (t, J = 7.51 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 138.9, 133.8, 129.0, 128.2, 126.1, 51.5, 38.4, 26.9, 20.2, 14.6, 13.9, 13.1. IR (film, CH_2Cl_2): 3368, 3285, 3019, 2959, 2871, 1575, 1456, 1376, 1117, 1072, 765, 702 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{23}N$+H 218.1903, found 218.1907.

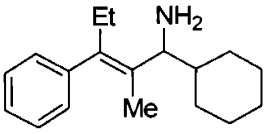
1-Cyclopropyl-2-methyl-3-phenyl-pent-2-enylamine (I-70)



I-70

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 2H), 7.30 (m, 1H), 7.11 (m, 2H), 3.18 (d, J = 8.54 Hz, 1H), 2.32 (m, 2H), 1.58 (s, 3H), 1.38 (bs, 1H), 1.0 (m, 1H), 0.86 (t, J = 7.52 Hz, 3H), 0.61 (m, 1H), 0.48(m, 1H), 0.35 (m, 1H), 0.21 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 138.5, 133.5, 129.2, 128.1, 126.2, 57.0, 26.9, 16.8, 14.4, 14.2, 4.5, 2.8. IR (film, CH_2Cl_2): 3373, 3288, 3076, 2965, 1599, 1575, 1441, 1016, 766 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{15}H_{21}N$–NH_2 199.1565, found 199.1500.

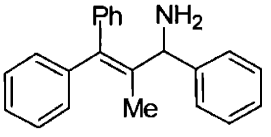
1-Cyclohexyl-2-methyl-3-phenyl-pent-2-enylamine (I-71)



I-71

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 2H), 7.23 (m, 1H), 7.07 (m, 2H), 3.55 (d, J = 9.62 Hz, 1H), 2.40 (q, J = 7.46 Hz, 2H), 2.12 (m, 1H), 1.72 (m, 4H), 1.41 (s, 3H), 1.29 (m, 6H), 0.99 (m, 2H), 0.88 (t, J = 7.46 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 139.7, 133.0, 129.0, 128.2, 126.1, 57.1, 41.9, 30.7, 27.0, 26.8, 26.7, 26.5, 17.8, 13.7. IR (film, CH_2Cl_2): 3377, 3055, 3018, 2926, 2851, 1491, 1448, 765 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{18}H_{27}N$+H 258.2216, found 258.2221.

2-Methyl-1,3,3-triphenyl-allylamine (I-72)



I-72

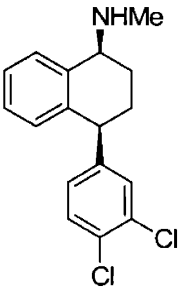
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (m, 15H), 5.00 (s, 1H), 1.60 (s, 3H), 1.58 (bs, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 142.9, 142.8, 139.6, 137.4, 129.6, 129.3, 128.6, 128.4, 128.2, 126.9, 126.7, 126.6, 126.5, 56.5, 14.2. IR (film, CH_2Cl_2): 3378, 3056, 3024, 2921, 1599, 1491, 1442, 1262, 1074, 1030, 763 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{22}H_{21}N$ 299.1669, found 299.1680.

Chapter 2

Catalytic Asymmetric Synthesis of Enantiomerically-Enriched Allylic Amines

A. Background

Enantiomerically pure amines are found in a large number of naturally occurring molecules (amino acids, opioid and non-opioid analgesics, vinblastine and strychnine alkaloids), and pharmaceuticals (antidepressant Sertraline or Zoloft®), and are useful synthetic building blocks in organic synthesis.[47] Optically pure allylic amines are a versatile sub-class and have found use as auxiliaries, resolving agents, and intermediates in the synthesis of both natural and unnatural compounds.[48]



Zoloft

Racemic chiral allylic amines can be resolved with classical methods and other methods of preparing optically enriched allylic amines involve the use of chiral auxiliary-based reactions and asymmetric catalytic methodology. Although several catalytic asymmetric methods for the synthesis of allylic alcohols from alkynes and aldehydes in high enantiomeric excess have been reported,[49] comparable success has not been achieved for the corresponding synthesis of allylic amines from imines.[50, 51]

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(47) (a) *World Review 2001*; Global sales of Zoloft® (Pfizer, Inc.) $2.2 billion in 2000. (b) Seyden-Penne, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; Wiley: New York, 1995.

(48) (a) Hagihara, M.; Anthony, N. J.; Clardy, S. J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 6568. (b) Takasago process: R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley: New York, 1994. (c) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

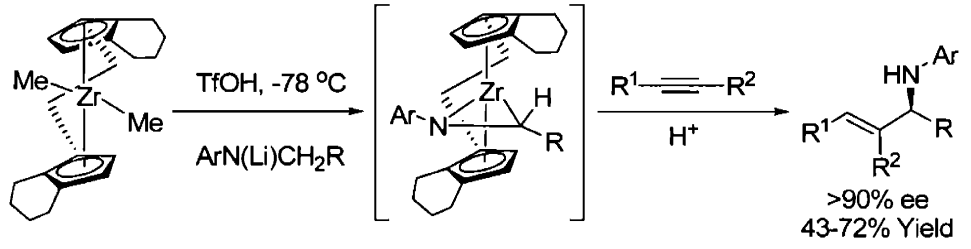
(49) (a) Miller, K. M.; Huang, W.–S.; Jamison, T. F. *J. Am. Chem. Soc.* **2003**, *125*, 3442. (b) Colby, E. A.; Jamison, T. F. *J. Org. Chem.* **2003**, *68*, 156. (c) For catalytic, asymmetric Nozaki-Hiyama-Kishi reactions, see: Choi, H. W.; Nakajima, K.; Demeke, D.; Kang, F. A.; Jun, H. S.; Wan, Z. K.; Kishi, Y.; *Org. Lett.* **2002**, *4*, 4435. For reactions that are catalytic in a chiral ligand, see: (d) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170. (e) Wipf, P.; Ribe, S. *J. Org. Chem.* **1998**, *63*, 6454.

(50) For catalytic, asymmetric rearrangement of prochiral allylic imidates to allylic amines, see: (a) Calter, M.; Hollis, T.; K. Overman, L. E.; Ziller, J.; Zipp, G. G. *J. Org. Chem.* **1997**, *62*, 1449. (b) Review: Hollis, T. K.; Overman, L. E. *J. Organomet. Chem.* **1999**, *576*, 290. For metal-catalyzed allylic amination, see: (a) Hayashi, T.; Yamamoto, Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. (b) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

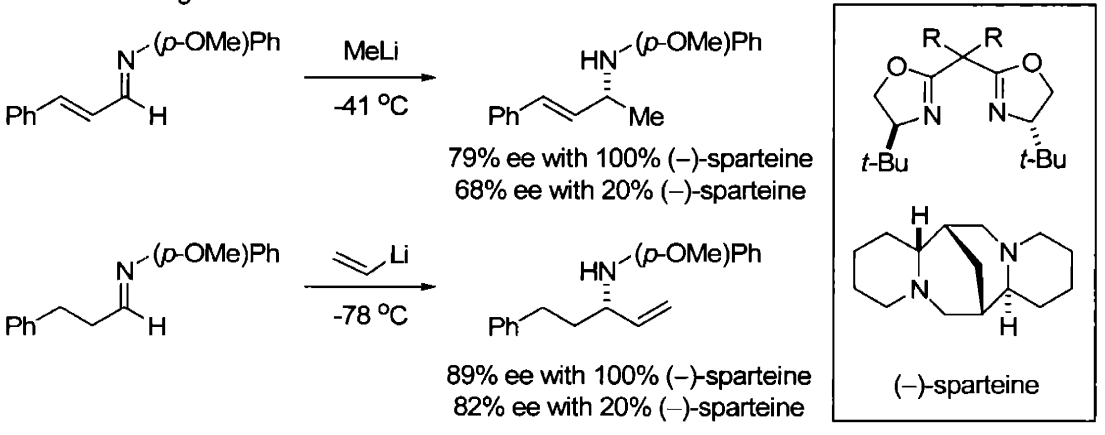
(51) Review on catalytic, enantioselective additions to imines, see: (a) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069. For diastereoselective additions to chiral imines, see: (b) Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.* **2002**, *35*, 984. (c) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407. (d) Enders, D.; Reinhold, U. *Tetrahedron Asymmetry* **1997**, *8*, 1895.

Buchwald and co-workers have reported stoichiometric reactions of chiral *ansa*-zirconocene imine complexes and alkynes provide trisubstituted allylic amines in high enantiomeric excess (Scheme 2.1).[52] High enantioselectivity (>90%) and moderate to good yields were reported with a wide variety of substrates the alkyne and the amine. However, the stoichiometric use of the transition metal and chiral ligand are drawbacks of this process.

Scheme 2.1 Enantioselective, Zirconium-Mediated Synthesis of Allylic Amines



Scheme 2.2. Bisoxazoline and (-)-sparteine promoted enantioselective additions of organolithium reagents to imines



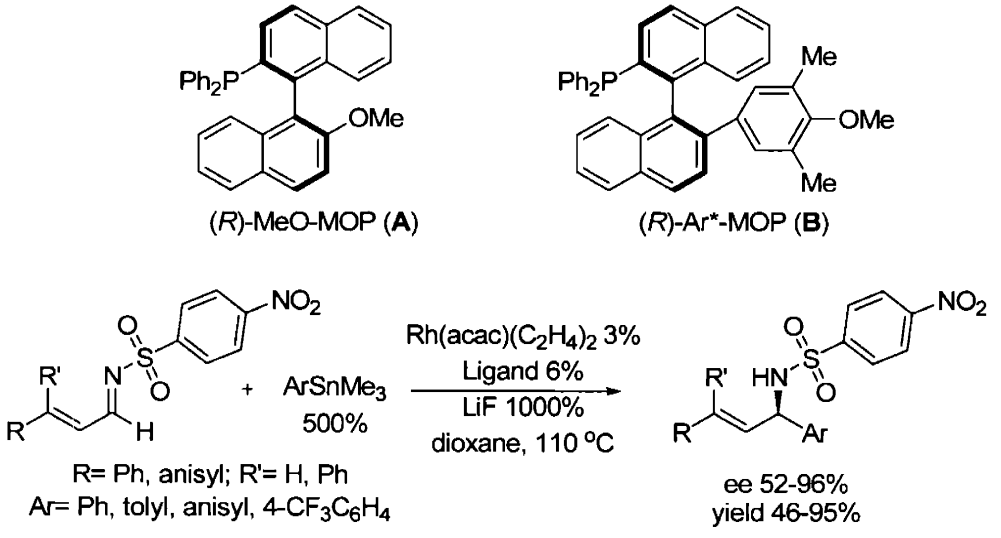
Denmark and co-workers have reported bisoxazoline and (–)-sparteine promoted methyl lithium addition to α, β-unsaturated imines and vinyl lithium addition to imines, however, the

(52) Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321.

use of catalytic amounts of (–)-sparteine in these reactions resulted in lower enantioselectivity (Scheme 2.2).[53]

Hayashi and co-workers have recently reported rhodium-catalyzed asymmetric arylation of α, β-unsaturated imines with arylstannanes to synthesize enantiomerically enriched allylic amines (Scheme 2.3). Highest enantioselectivities (>90%) were obtained when imines with two substituents at the β-position were employed. For substrates containing one substituent at the β-position, use of the (*R*)-Ar*-MOP ligand (Scheme 2.3, **B**) was necessary to obtain good enantioselectivities. Furthermore, five equivalents of aryltrimethyltin and ten equivalents of LiF were necessary for this reaction.[54]

Scheme 2.3. Rhodium-catalyzed asymmetric arylation of α,β- unsaturated imines with arylstannanes.

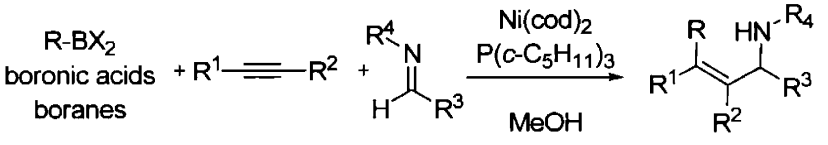


(53) (a) Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C. *J. Am. Chem. Soc.* **1994**, *116*, 8797. (b) Denmark, S. E.; Stiff, C. M. *J. Org. Chem.* **2000**, *65*, 5875. For amino-alcohol ligand promoted addition, see: (c) Tomioka, K.; Inoue, I.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1990**, *31*, 6681. (d) Tomioka, K.; Inoue, I.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1991**, *32*, 3095.

(54) (a) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976. (b) Hayashi, T.; Ishigedani, M. *Tetrahedron*, **2001**, *57*, 2589.

Other methods of preparing enantiomerically-enriched allylic amines include the Wittig olefination of α-amino aldehydes[55] and reduction of iodomethyl aziridines.[56] However, there are currently no examples of the *asymmetric* catalytic reductive or alkylative coupling of alkynes and imines. If this were feasible, the widely used starting materials of alkynes and imines could be joined in a single catalytic asymmetric operation to provide enantiomerically enriched, chiral allylic amines.

Scheme 2.4. Nickel-catalyzed three-component synthesis of allylic amines.



exclusive *cis*-addition across alkyne
up to 98% yield and up to >95:5 selectivity
aliphatic, aromatic and terminal alkynes; aliphatic and aromatic imines
functional group tolerance — aryl ketones, esters, and chlorides

We recently reported the first nickel-catalyzed three-component coupling reactions of alkynes, imines, and organoboron reagents (boronic acids and organoboranes), which afford tetrasubstituted allylic amines.[57] Excellent functional group tolerance, good to excellent yields, high regioselectivity, and complete (*E/Z*)-selectivity (*cis* addition to the alkyne) are obtained when electron-rich, tri-(*sec*-alkyl)-phosphine ligands were employed (Scheme 2.4). These studies provided the basis for future investigations directed toward asymmetric catalytic alkylative coupling of alkynes, imines and organoboron reagents. The aim of this chapter is the

(55) Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. *J. Org. Chem.* **1987**, *52*, 1487.
(56) Yadav, J. S.; Bandyopahdhyay, A; Reddy, B. V. S. *Synlett* **2001**, 1608.
(57) Patel, S. J.; Jamison, T. F. *Angew. Chem. Int. Ed.* **2003**, *42*, 1364.

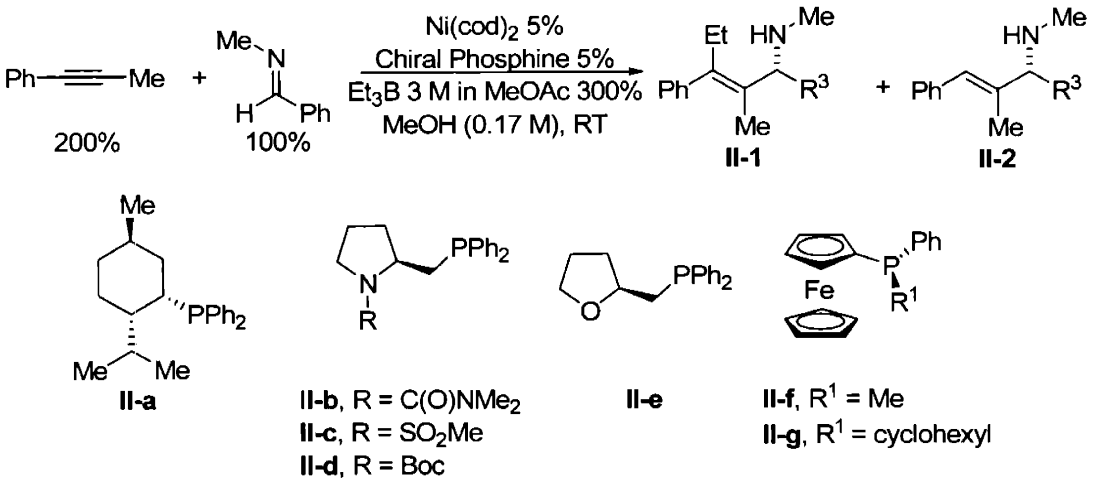
development of novel monodentate chiral phosphines that yield enantiomerically enriched allylic amines.

B. Initial Results with (–)-NMDPP and Mechanistic Discussions

Preliminary studies toward the development of a catalytic, highly enantioselective method of preparing allylic amines from alkynes and imines are summarized in this chapter. In our initial screening of chiral phosphines, we observed that chiral bisphosphine ligands (e.g. DuPhos, Me-BPE, BINAP) did not effect the catalytic alkylative coupling of imine derived from benzaldehyde and methylamine, 1-phenyl-1-propyne, and triethylborane, but several families of chiral monodentate phosphines were moderately effective (Table 2.1). The commercially available (*S*)-(neomenthyl)diphenylphosphine (*S*)-NMDPP (**II-a**) was the most effective in our initial studies and afforded modest enantioselectivity and good yield (Table 2.1, entry 1). *L*-Proline or (*R*)-tetrahydro-2-furoic acid-derived chelating monodentate phosphines (**II-b**, **II-c**, **II-d** and **II-e**) were moderately reactive and afforded <15% enantiomeric excess (entries 2-5). Furthermore, *P*-chiral ferrocenyl phosphines (**II-f** and **II-g**) were not selective in nickel-catalyzed coupling of imines (entries 6-7).[58]

(58) Ferrocenyl phosphine **II-f** was evaluated as a ligand in the asymmetric catalytic reductive coupling of alkynes and aldehydes and was found to provide the desired chiral allylic alcohols with good regioselectivity and moderate enantioselectivity. See ref 48b.

Table 2.1. Chiral monodentate phosphines screened for nickel-catalyzed synthesis of allylic amines.

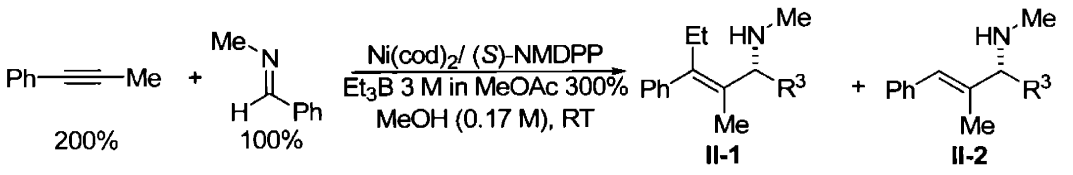


Entry	Ligand	ee %[a]	Yield %[b]	II-1:II-2[c]	Regioselectivity[c]
1	**II-a**	26	50	93:7	92:8
2	**II-b**	-2	28	96:4	95:5
3	**II-c**	-9	25	85:15	90:10
4	**II-d**	-14	10	80:20	92:8
5	**II-e**	-5	30	90:10	91:9
6	**II-f**	-9	22	>95:5	>95:5
7	**II-g**	14	44	>95:5	60:40

[a] ee in **II-1**, determined using HPLC (Chiralcel OD column) on the corresponding acetamide derivative. Negative ee refers to the opposite enantiomer as the major product. [b] Combined yields of allylic amines. [c] Determined using ^{1}H NMR.

Since (*S*)-NMDPP provided the best results in our initial screening, we further explored changes in reactivity and selectivity by varying reaction conditions. Yield and enantioselectivity were improved by increasing the catalyst loading from 5% to 10% $Ni(cod)_2$ and to 20% (*S*)-NMDPP (Table 2.2). Lowering the temperature to 0 °C provided a slight increase in enantioselectivity, but yields dropped dramatically (entry 5).

Table 2.2. Effects of catalyst loading and reaction temperature on reactivity and selectivity in nickel-catalyzed asymmetric reaction of alkynes, imines, and organoboron reagents.



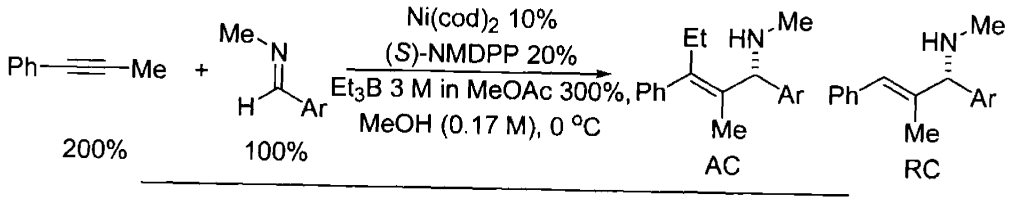
Entry	$Ni(cod)_2$ %	(*S*)-NMDPP %	ee %[a]	Yield %[b]	**II-1**:**II-2**[c]	Regioselectivity[c]
1	5	5	26	50	93:7	92:8
2	5	10	26	60	95:5	95:5
3	10	10	37	65	93:7	95:5
4	10	20	38	68	92:8	95:5
5[d]	10	20	41	33	95:5	95:5

[a] ee of alkylative product **II-1**, determined using HPLC (Chiralcel OD column) on the corresponding acetamide derivative. [b] Combined yields of allylic amine products. [c] Determined using ^{1}HNMR. [d] Reaction at 0 °C.

Additional imine substrates were evaluated using the above modified conditions and consistently moderate yields and enantioselectivities were observed (Table 2.3). However, we observed that the enantiomeric excess of the alkylative coupling product **II-1** was *identical* to that of the corresponding reductive coupling product **II-2** in every case. Moreover, in cases where the amount of the minor regioisomer of the reductive coupling product was detectable in the unpurified product mixtures (^{1}H NMR), the regioselectivity was also *identical* for alkylative and reductive coupling products.

These findings are consistent with the mechanistic pathway **A** (Chapter 1, Scheme 1.8), in which enantioselectivity and regioselectivity are determined in the same step and *before* a common intermediate azametallocyclopentene partitions into two pathways, leading to either alkylative or reductive coupling products.

Table 2.3. Enantioselectivities observed for alkylative and reductive coupling products using (*S*)-(+)-(neomenthyl)diphenylphosphine [(*S*)-NMDPP].[a]

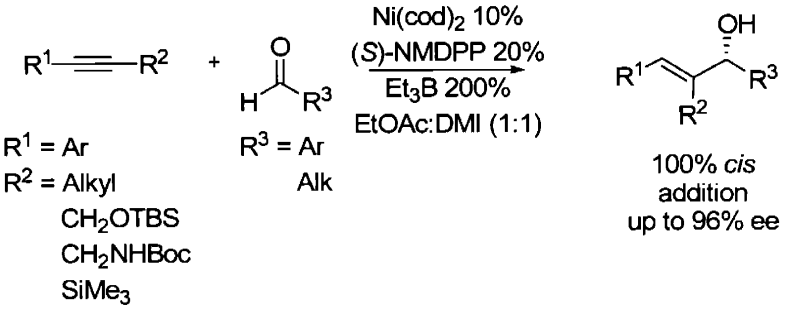


Entry	Ar	Yield %	AC:RC	ee %[b] AC	ee %[b] RC
1	Ph	33	95:5	41	42
2	(*p*-Cl)Ph	30	92:8	33	33
3	(*p*-CF_3)Ph	36	93:7	40	39

[a] AC = alkylative and RC = reductive coupling. [b] Enantiomeric excess determined on the corresponding acetamides (Ac_2O, Et_3N, cat. DMAP), Chiralcel OD column.

Our laboratory was recently successful in obtaining excellent enantioselectivities and yields in nickel-catalyzed reductive coupling reactions of alkynes and aldehydes using (*S*)-NMDPP, affording trisubstituted allylic alcohols (Scheme 2.5).[49a] The optimized reaction conditions involved using a solvent composed of equal volumes of ethyl acetate and 1,3-dimethylimidazolidinone (DMI) in conjunction with slow addition of the aldehydes at -25 °C over 8h. However, under analogous conditions to those reported in the aldehyde chemistry and other variations in solvents, additives, and mode of addition of the reaction components, we were unable to obtain good enantioselectivity and yield in nickel-catalyzed three-component coupling reactions of alkynes, imines and organoboron reagents.

Scheme 2.5. Catalytic asymmetric reductive coupling of alkynes and aldehydes using (neomenthyl)diphenylphosphine (*S*)-NMDPP

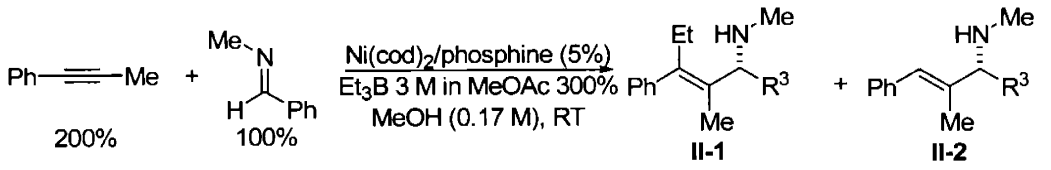


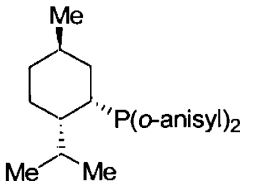
C. High enantioselectivities with novel *P*-chiral ferrocenyl phosphines and necessity of an alkyl group on imine nitrogen

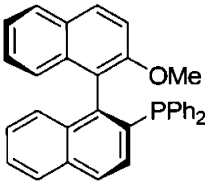
Since (*o*-anisyl)$_3$P showed improved reactivity and selectivity (Chapter 1, Table 1.9), we hypothesized that a similar improvement might be possible with an anisyl analog of the (*S*)-NMDPP ligand. The anisyl phosphine analog (**II-h**) was synthesized and tested in the nickel-catalyzed asymmetric assembly of allylic amine **II-1**. Unfortunately lower enantiomeric excess compared to (*S*)-NMDPP was observed (Table 2.4, entries 1 and 2). The commercially available (*R*)-MeO-MOP ligand (**II-i**) also displayed very low reactivity and 35% enantiomeric excess, and a planar chiral ferrocenyl phosphine (**II-j**) gave no enantioselectivity.[59]

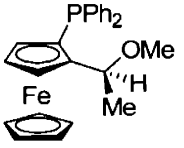
(59) (a) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.***1988**, *110*, 8153. (b) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354.

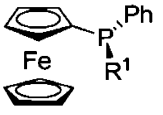
Table 2.4. Chiral monodentate phosphines screened for nickel-catalyzed synthesis of allylic amines.











II-k, R^1 = (*o*-anisyl)
II-l, R^1 = (*o*-tolyl)
II-m, R^1 = (*o*-biphenyl)

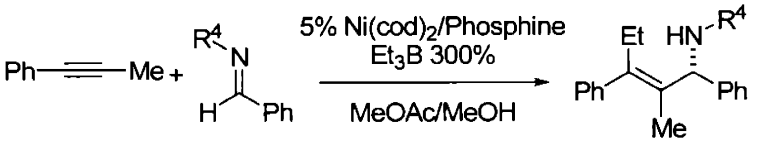
Entry	Ligand	ee %[a]	Yield %[b]	II-1:II-2[c]	Regioselectivity[c]
1	**II-a**	26	50	93:7	92:8
2	**II-h**	20	42	94:6	85:15
3	**II-i**	35	6	95:5	90:10
4	**II-j**	<2	35	86:14	80:20
5	**II-k**	-55	30	93:7	88:12
6	**II-l**	-73	40	91:9	88:12
7	**II-m**	-68	55	92:8	72:28

[a] ee in alkylative product **II-1**, determined using HPLC (Chiralcel OD column) on the corresponding acetamide derivative. Negative ee refers to the opposite enantiomer as the major product. [b] Combined yields of allylic amines. [c] Determined using ^{1}H NMR.

Nevertheless, the *P*-chiral ferrocenyl phosphines (**II-k**) increased the enantioselectivity of alkylative amine product to 55%. Remarkably, desymmetrization of $FcPPh_2$ by replacement of H with Me at the *ortho* position on one of the phenyl groups provided the allylic amine **II-l** in 73% ee and good yield (Table 2.4, entry 5). A ferrocenyl phosphine containing *o*-biphenyl substituent (**II-m**) provided higher yield but lower enantioselectivity (entry 6). These results indicated that differentiating the size of the small, medium, and large substituents on the *P*-chiral

phosphines was critical for obtaining high enantioselectivities. Several novel phosphines of this class were synthesized and tested.

Table 2.5. Effects of varying the group on nitrogen in asymmetric, catalytic assembly of allylic amines.



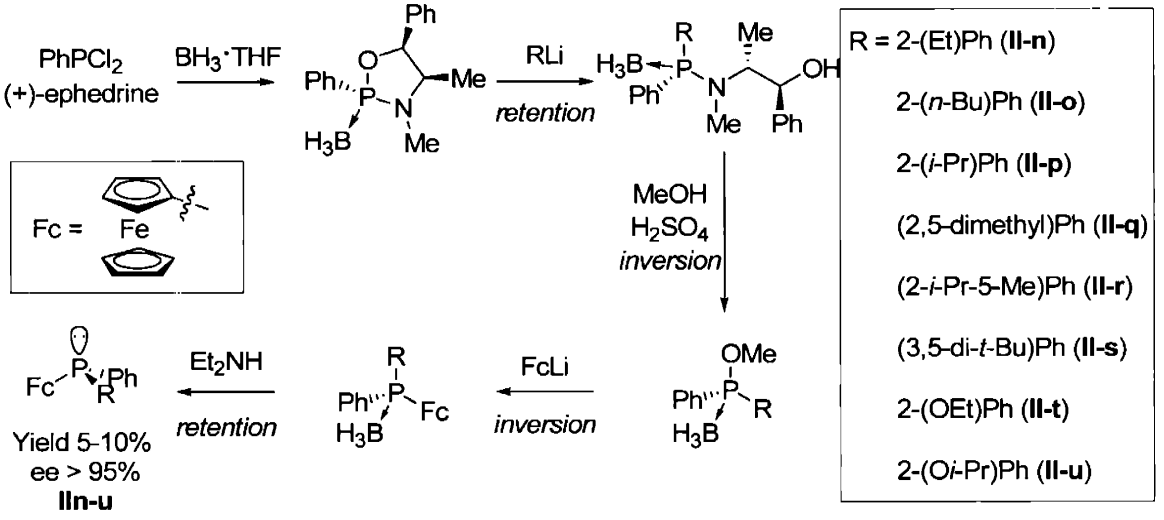
Entry	Phosphine	R^4	Product	Yield % (regio)[b]	ee %[c]
1	**II-h**	Me	**II-1**	50 (92:8)	-26
2	**II-h**	*p*-anisyl	**II-3**	10 (95:5)	0
3	**II-h**	*o*-anisyl	**II-4**	20 (97:3)	0
4	**II-k**	Me	**II-1**	30 (88:12)	55
5	**II-k**	*p*-anisyl	**II-3**	52 (85:15)	20
6	**II-l**	Me	**II-1**	40 (88:12)	73
7	**II-l**	$-CH_2CH_2OTBS$	**II-5**	74 (87:13)	73

[a] See Experimental Section for procedure. [b] Determined by ^1H NMR. [c] Enantioselectivity of major product determined by HPLC (Chiralcel OD column).

We also observed that the group on nitrogen had a dramatic effect on enantioselectivity (Table 2.5). With (*S*)-NMDPP (**II-h**) as a ligand, aryl substituents on the imine nitrogen afforded only racemic allylic amines (entries 2 and 3). With an *N*-aryl imine, a similar trend of lower enantioselectivities was observed when a *P*-chiral ferrocenyl phosphine (**II-k**) was utilized as ligand (entries 4 and 5). Interestingly, the enantioselectivity did not change with varying the *N*-alkyl substituent on the imine (entries 6 and 7). The imine derived from *N*–(*tert*-

butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2$–) group afforded identical enantioselectivity as the corresponding *N*-methyl imine. Since the $TBSOCH_2CH_2$– group would provide access to primary allylic amines (Chapter 1, Table 1.14), only imines derived from (*tert*-butyldimethyl)silyloxyethyl amine were examined in the subsequent optimizations.

Scheme 2.6. Synthesis of *P*-chiral phosphines using Jugé's ephedrine method.



Enantiomerically pure *P*-chiral ferrocenyl phosphines (**II-n-u**) were synthesized using a modification of Jugé's ephedrine-based method in which the ferrocenyl group was installed later in the synthesis (Scheme 2.6).[60] As the steric bulk on the aryl group increased, the overall yields of the phosphine synthesis decreased, but phosphines **IIn-u** were synthesized in >95 % enantioselectivity. The borane complex of phosphine **II-p** was analyzed by X-ray crystallography to determine the relative and absolute configurations (Figure 2.1).

(60) (a) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357. (b) Colby, E. A.; Jamison, T. F. *J. Org. Chem.* **2003**, *68*, 156.

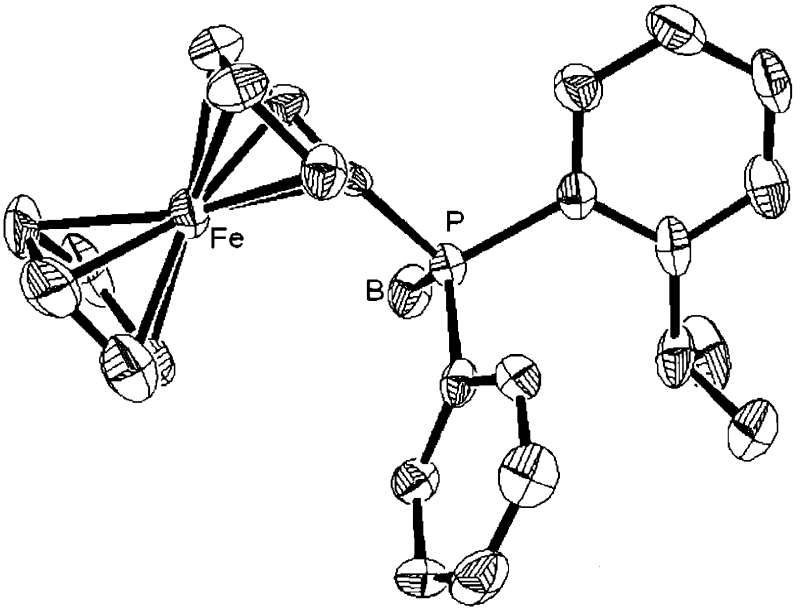


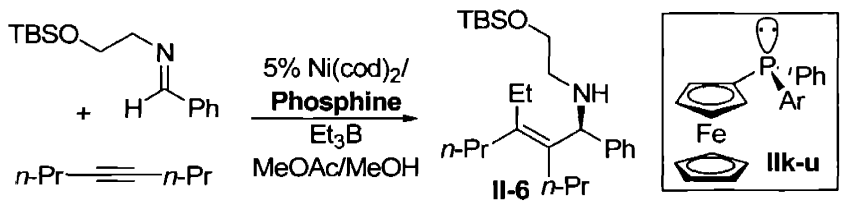
Figure 2.1. ORTEP illustration of phosphine **II-p**—borane complex (crystallization from EtOAc and hexanes; hydrogen atoms are omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

These sterically demanding phosphines (**IIn-u**) were examined in nickel-catalyzed three-component coupling reactions (Table 2.6). We observed that the enantioselectivity tended to increase as the steric bulk in the *ortho* position of the aryl group on the ligand increased (Table 2.6, entries 1-4). A phenyl substituent in the *ortho* position (i.e. Ar = *o*-biphenyl, entry 5) led to severely diminished yield (19%) and enantioselectivity (45%). Unfortunately, all efforts to synthesize more sterically demanding phosphines such as **II-v** (Ar = (2-*t*-butyl)Ph) or **II-w** (Ar = (2,6-dimethyl)Ph) were unsuccessful.[61] In addition, lower yields and enantioselectivities were

(61) (*o-tert*-Butyl)phenyllithium and (2,6-dimethyl)phenyllithium did not undergo addition to the oxazaphospholidine borane complex. Other groups have also reported similar difficulties with

obtained with other substitution patterns (entries 6-8) and with ligands possessing alkoxy groups in the *ortho* position (entries 9-11). Interestingly, under identical conditions no enantioselection was observed with (*S*)-NMDPP (**II-h**). Novel *P*-chiral triarylphosphines **II-x** and **II-y** afforded moderate enantioselectivity (Scheme 2.7).[62]

Table 2.6. Evaluation of *P*-chiral ferrocenyl phosphines in catalytic three-component assembly of allylic amines.[a]



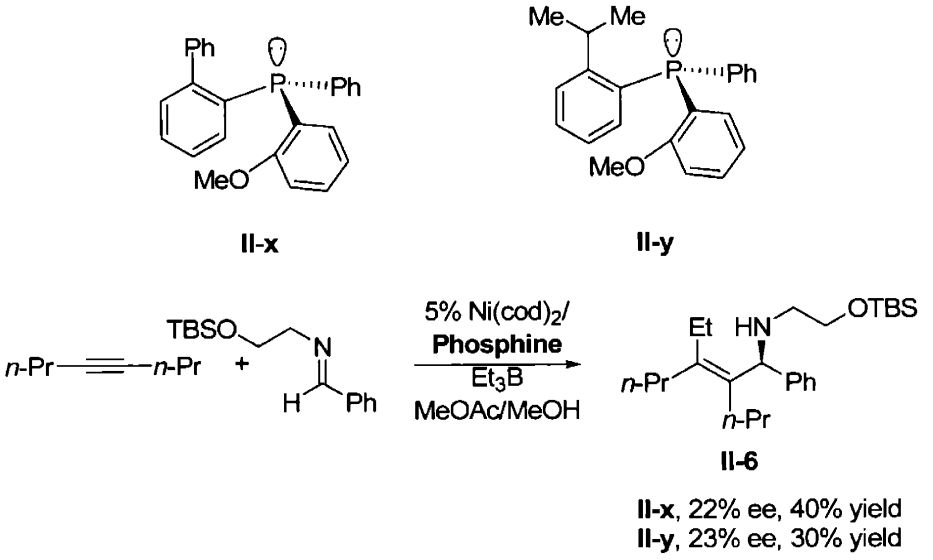
Entry	Phosphine (Ar)	Yield %	ee %[b]
1	*o*-tolyl (**II-l**)	88	75
2	2-(Et)Ph (**II-n**)	90	80
3	2-(*n*-Bu)Ph (**II-o**)	60	75
4	2-(*i*-Pr)Ph (**II-p**)	85	89
5	*o*-biphenyl(**II-m**)	19	45
6	(2,5-dimethyl)Ph (**II-q**)	85	75
7	(2-*i*-Pr-5-Me)Ph (**II-r**)	25	77
8	(3,5-di-*t*-Bu)Ph (**II-s**)	20	45
9	*o*-anisyl (**II-k**)	64	54
10	2-(OEt)Ph (**II-t**)	41	41
11	2-(O*i*-Pr)Ph (**II-u**)	73	51
12	(*S*)-NMDPP (**II-h**)	50	0

[a] See experimental section for details.
[b] Determined using HPLC (Chiralcel OD).

mesityllithium, 9-anthryllithium, and 2,4,6-trimethoxyphenyllithium: (a) Maienza, F.; Spindler, F.; Thommen, M.; Pugin, B.; Malan, C.; Mezzetti, A. *J. Org. Chem.* **2002**, *67*, 5239.

(62) These *P*-chiral triarylphosphines were synthesized using Jugé's ephedrine-based method (Scheme 2.6). Review on *P*-chiral phosphines of type Ar^1Ar^2PAlk, see: (a) Lagasse, F.; Kagan, H. B. *Chem. Pharm. Bull.* **2000**, *3*, 315.

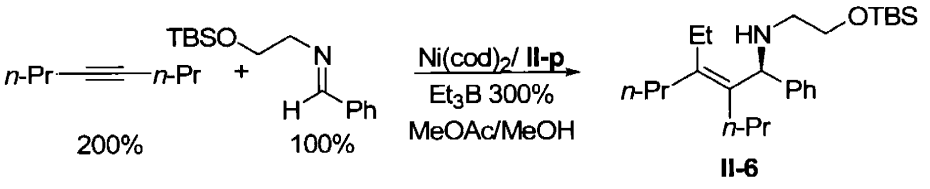
Scheme 2.7. Evaluation of *P*-chiral triaryl phosphines in asymmetric, nickel-catalyzed three-component coupling reaction.



II-x, 22% ee, 40% yield
II-y, 23% ee, 30% yield

Reactions run at room temperature afforded the highest yields and enantioselectivity as shown in Table 2.7 (entries 1-3). Reactions performed at 0 °C afforded no allylic amine products. At higher temperature the enantioselectivity dropped, while running the reaction at 15 °C over 48 h gave only 20% yield of the product, with no enhancement in enantioselectivity. The highest enantioselectivity and reactivity were obtained with 5% catalyst loading and 1:1 $Ni(cod)_2$ to **II-p** ratio (entries 1, 4 and 5).

Table 2.7. Effects of catalyst loading and temperature on enantioselectivity.[a]



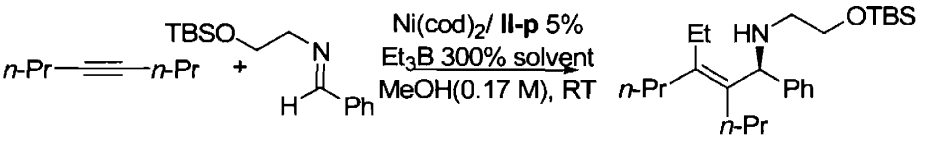
II-6

Entry	$Ni(cod)_2$ %	**II-p** %	Temperature	Yield %	ee %[b]
1	5	5	RT	89	89
2	5	5	15 °C	20	87
3	5	5	50 °C	90	83
4	5	10	RT	63	86
5	10	10	RT	70	83

[a] 0.5 mmol scale, see Experimental Section for procedure.
[b] Determined using HPLC (Chiralcel OD column).

Since $Ni(cod)_2$ and *P*-chiral ferrocenyl phosphine **II-p** were not soluble in MeOH until the Et_3B solution was added, the effect of different Et_3B solutions on enantioselectivity and reaction yield was examined (Table 2.8). Interestingly, toluene provided the lowest and enantiomeric excess, but the enantioselectivity was restored using electronically withdrawing trifluromethyltoluene solution (entries 6 and 8). Comparable enantioselectivities were also obtained using Et_3B 3 M solution in MeOAc (entry 2). Moreover, modifications of alkyne/imine stoichiometry, concentration, and modes of reagent addition reduced efficacy and/or selectivity. In summary, the highest yields and enantioselectivities were obtained with portion-wise addition of the alkyne and Et_3B as a solution in MeOAc (see Experimental Section for detailed reaction procedures).

Table 2.8. Effects of varying the Et_3B solution on enantioselectivity.[a]



II-6

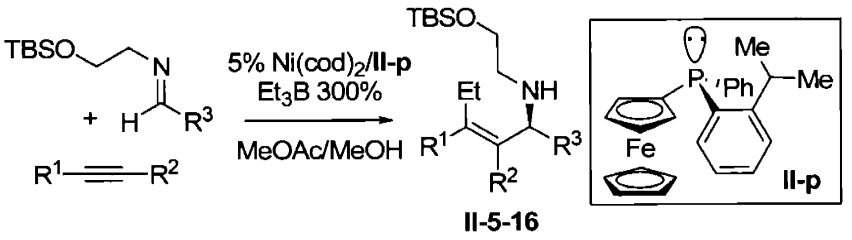
Entry	Solvent	Yield %[b]	ee %[b]
1	none	36	84
2	MeOAc	84	89
3	EtOAc	54	84
4	*t*-BuOAc	40	82
5	acetone	52	83
6	toluene	28	75
7	C_6F_6	15	82
8	trifluorotoluene	26	89
9	1,3-ditrifluoromethylbenzene	NR	NR

[a] See Experimental Section for procedure. [b] Determined using HPLC (Chiralcel OD column).

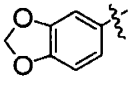
D. Substrate Scope

An extensive evaluation of a large number and variety of chiral monophosphines demonstrated that *P*-chiral ferrocenyl phosphines afforded the desired allylic amines in good yields and enantioselectivities, as long as the group on nitrogen was aliphatic in nature (Table 2.5 and Table 2.6). Ligand **II-p** proved to be the most selective phosphine in these studies, and it also afforded allylic amines from a variety of substrate combinations in moderate to very good enantioselectivity (Table 2.9).

Table 2.9. Enantiomerically enriched allylic amines prepared *via* catalytic intermolecular couplings of alkynes, imines, and triethylborane.[a]



II-5-16

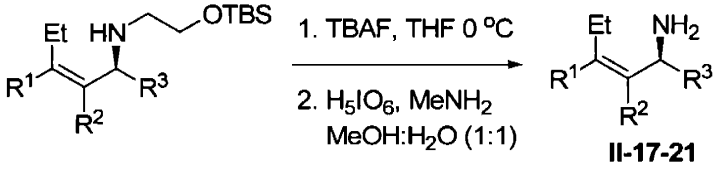
Entry	R^1	R^2	R^3	Product	Yield % (regio)[b]	ee %[c]
1	*n*-Pr	*n*-Pr	Ph	**II-6**	85	89
2	*n*-Bu	*n*-Bu	Ph	**II-7**	83	89
3	Et	Et	Ph	**II-8**	89	83
4	*n*-Pr	*n*-Pr	*o*-tolyl	**II-9**	74	85
5	*n*-Pr	*n*-Pr	*p*-anisyl	**II-10**	75	82
6	*n*-Pr	*n*-Pr	*p*-CF_3(Ph)	**II-11**	91	85
7	*n*-Pr	*n*-Pr	2-naphthyl	**II-12**	90	73
8	*n*-Pr	*n*-Pr		**II-13**	95	73
9	Et	Et	*c*-C_6H_{11}	**II-14**	53	51
10	Ph	Me	Ph	**II-5**	45 (80:20)	84
11	Ph	Et	Ph	**II-15**	62 (>98:2)	71
12	2-naphthyl	Me	Ph	**II-16**	42 (85:15)	70

[a] See experimental section for procedure. [b] Determined by ^{1}H NMR.
[c] Enantioselectivity of major product determined by HPLC or GC.

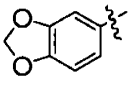
Both symmetrical dialkyl acetylenes (Table 2.9, entries 1-9) and unsymmetrical alkynes of the general form Aryl-C≡C-Alkyl (entries 10-12) were effective in these reactions, the latter allowing preparation of enantiomerically enriched tetrasubstituted allylic amines possessing four different substituents on the alkene with good to complete control of olefin geometry and regioselectivity. Several aromatic imines underwent three-component coupling reactions in both high enantiomeric excess and yield (entries 4-8). No significant difference in enantioselectivity

was observed with electron-donating (entries 4 and 5) or withdrawing (entry 6) substituents on the phenyl group. However, imines derived from 2-naphthaldehyde and piperonal afforded lower enantiomeric excess (entries 7 and 8). Notably, even an enolizable aliphatic imine was a compatible substrate, undergoing coupling in moderate enantioselectivity and yield (entry 9). Even though the electron-rich, bulky phosphine **II-p** was highly enantioselective, rapid polymerization of alkyne and lower regioselectivity were observed with Aryl-C≡C-methyl alkynes (entries 10 and 11).

Table 2.10. Deprotection of enantiomerically enriched *N*-(*tert*-butyldimethyl) silyloxyethyl allylic amines.



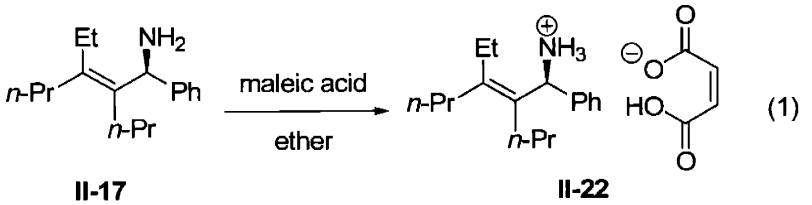
II-17-21

Entry	R^1	R^2	R^3	Product	Yield %	ee %[a]
1	*n*-Pr	*n*-Pr	Ph	**II-17**	73	89
2	*n*-Pr	*n*-Pr	*o*-tolyl	**II-18**	66	85
3	*n*-Pr	*n*-Pr	2-naphthyl	**II-19**	59	76
4	*n*-Pr	*n*-Pr		**II-20**	68	73
5	Ph	Me	Ph	**II-21**	63	84

[a] ee of major product, determined on the corresponding acetamide derivative using HPLC (Chiralcel OD and AD column).

The *N*–(*tert*-butyldimethyl)silyloxyethyl ($TBSOCH_2CH_2$–) allylic amine products were readily deprotected using a two-step protocol, a TBAF deprotection of the TBS ether and oxidative cleavage of the resulting 1,2-amino alcohol (Table 2.10).[42] Since the optical purity was conserved in this reaction sequence, enantiomerically enriched tetrasubstituted primary

allylic amines were obtained in both good overall yields and enantiomeric excess. These primary allylic amines could be recrystallized to optical purity as the maleic acid salt (eq 1).



II-17
89% ee

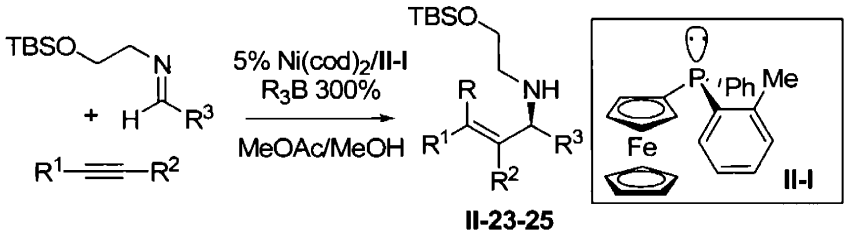
II-22
>99% ee, 71% yield

(1)

E. Limitations

P-chiral ferrocenyl phosphine **II-p** afforded high yields and enantioselectivity for several different substrate combinations (Table 2.9). Nevertheless, the high selectivity of this electron-rich, bulky phosphine had some drawbacks with respect to reactivity. Aryl-C≡C-alkyl alkynes rapidly polymerized and did not react with aliphatic imines. Additionally, other organoboranes and boronic acids did not undergo coupling using the protocol described in Table 2.9. However, with sterically less bulky phosphine **II-l**, moderate yield and enantioselectivity were obtained when Aryl-C≡C-alkyl alkynes were coupled with aliphatic imines and when $PhB(OH)_2$ was employed (Table 2.11).

Table 2.11. Enantiomerically enriched allylic amines prepared *via* catalytic intermolecular couplings of alkynes, imines, and organoboran reagents.[a]



II-23-25

Entry	R^1	R^2	R^3	R	Product	Yield %[b]	ee %[c]
1	Ph	Me	*c*-C_3H_5	Et	**II-23**	10	50
2	Ph	Me	*c*-C_6H_{11}	Et	**II-24**	24	20
3[d]	Ph	Me	Ph	Ph	**II-25**	36	63

[a] See experimental section for procedure. [b] Combined yield of both regioisomers, regioselectivity was not determined except in entry 3 (80:20). Major regioisomer as shown. Determined by ^{1}H NMR. [c] Enantioselectivity of major product determined by HPLC. [d] 100% $PhB(OH)_2$, and alkylne used.

F. Conclusions

In conclusion, the asymmetric nickel-catalyzed coupling of alkynes and imines afforded enantiomerically enriched tetrasubstituted allylic amines in a single step. An extensive evaluation of a variety of chiral monophosphines demonstrated that *P*-chiral ferrocenyl phosphines provided the desired allylic amines in good yields and enantioselectivities, as long as the group on nitrogen was aliphatic in nature. It exhibited a broad substrate scope with respect to both alkynes and imines, and high reaction yields (up to 95%) and enantioselectivities (up to 89%) were observed. Furthermore, removal of the *N*–(*tert*-butyldimethyl)silyloxy ethyl group provided direct access to versatile, primary allylic amines that can be further recrystallized to >99% ee.

G. Experimental Section

Unless stated otherwise, all compounds were purchased from commercial suppliers (Aldrich, Alfa Aesar, or Strem) and used without further purification. THF, Et_2O and toluene were distilled from sodium/benzophenone ketyl. MeOH was distilled from magnesium methoxide. All other anhydrous grade solvents were purchased from Aldrich Chemical Co. Triethylborane was obtained neat and solutions were prepared using freshly distilled, thoroughly degassed solvents. Imines were prepared by condensation of aldehydes and amines in the presence of molecular sieves, and then purified by distillation or crystallization.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates precoated with a fluorescent indicator. TLC plates were analyzed with UV light, stained with 12-molybdophosphoric (PMA) stain and developed by heating for 10 sec with a heat gun. Flash chromatography was performed using silica gel 60 (40-63 μm) from Silicycle. All ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz or Varian 500 MHz spectrometers at ambient temperature. IR spectra were recorded as a thin film between NaCl plates on a Perkin-Elmer Model 2000 FTIR instrument. HPLC was performed on a Hewlett-Packard 1100 chromatograph equipped with a variable wavelength detector and Chiralcel OD, AD, or OJ column. GC analysis was performed on a Varian CP-3800 gas chromatograph fitted with Chiraldex B-PH, B-DA, and G-TA capillary columns. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Tesla Fourier Transform Mass Spectrometer of the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility.

Standard Experimental Procedure A — Used in Table 2.1, 2.2 and Table 2.4.

For an exact proportion of reagents please refer to appropriate table and all reactions were performed on 0.5 mmol scale.

In a glovebox, $Ni(cod)_2$ and chiral phosphine were placed into an oven-dried 50 mL flask, with teflon coated stir bar, which was sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere at room temperature. Anhydrous MeOH (2.5 mL) was added followed by 100 μL of 3M MeOAc solution of Et_3B. After 2 min, benzylidene-methyl-amine (0.5 mmol, 62.5 μL) was added followed by 1-phenyl-1-propyne (0.2 mmol, 25 μL). Reaction was stirred for an hour. Additional alkyne (0.80 mmol, 100 μL) and Et_3B (3M MeOAc, 2.40 mmol, 400 μL) were added in 4 equal portions over 4 h. The reaction was further stirred for 12 h and the flask was opened to the air and concentrated *in vacuo*. Silica gel chromatography (hexanes:EtOAc) yielded allylic amines **II-1** and **II-2**. The corresponding acetamides were prepared [acetic anhydride (110%), triethylamine (120%) and 4-dimethylaminopyridine (DMAP, 5%) in CH_2Cl_2 (5 mL)]. 10 mL CH_2Cl_2 and 5 mL $NaHCO_3$ solution was added to the reaction flask and the organic layer was separated, dried with $MgSO_4$ and the solvent was removed under reduced pressure. Enantiomeric excess was measured using Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol = 99:1 t_R (minor) = 23 min, t_R (major) = 33 min, t_R (minor) = 50 min, t_R (major) = 54 min.

Standard Experimental Procedure B — Asymmetric Intermolecular Alkylative Coupling of 1-phenyl-1-propyne, *aromatic imines* and triethylborane using (*S*)-NMDPP (Table 2.3)

In a glovebox, $Ni(cod)_2$ (28 mg, 0.10 mmol) and (*S*)-(+)-(neomenthyl)diphenylphosphine [(*S*)-NMDPP, 64 mg, 0.20mmol] were placed into an oven-dried 50 mL flask, with teflon coated stir

bar, which was sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Anhydrous MeOH (5 mL) was added followed by 200 μL of 3M MeOAc solution of R_3B and the flask was placed in 0 °C ice bath. After 10 min, imine (1.0 mmol) was added followed by 1-phenyl-1-propyne (0.4 mmol, 50 μL). Reaction was stirred for an hour. Additional alkyne (1.60 mmol, 200 μL) and R_3B (3M MeOAc, 2.40 mmol, 800 μL) were added in 4 equal portions over 4 h. The reaction was further stirred for 20 h at 0 °C, and the flask was opened to the air and quenched with 5 mL water. The product was extracted with ethyl acetate, dried over $MgSO_4$ and concentrated *in vacuo*. Silica gel chromatography (hexanes:EtOAc) yielded allylic amines. The corresponding acetamides were prepared [acetic anhydride (110%), triethylamine (120%) and 4-dimethylaminopyridine (DMAP, 5%) in CH_2Cl_2 (5 mL)]. 10 mL CH_2Cl_2 and 5 mL $NaHCO_3$ solution was added to the reaction flask and the organic layer was separated, dried with $MgSO_4$ and the solvent was removed under reduced pressure. The amides were analyzed by Chiralcel OD column to measure the enantiomeric excess.

Table 2.3, entry 1

Enantiomeric excess was measured using Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol = 99:1 t_R [AC minor] = 23 min, t_R [AC major] = 33 min, t_R [RC minor] = 50 min, t_R [RC major] = 54 min.

Table 2.3, entry 2

Enantiomeric excess was measured using Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol = 99:1 t_R [AC minor] = 15 min, t_R [AC major] = 17 min, t_R [RC minor] = 28 min, t_R [RC major] = 32 min.

Table 2.3, entry 3

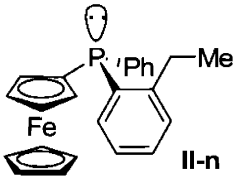
Enantiomeric excess was measured using Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol= 99:1 for first 45 min then hexane: *i*-propanol= 99:2, t_R [AC minor] = 31 min, t_R [AC major] = 34 min, t_R [RC minor] = 59 min, t_R [RC major] = 62 min.

Synthesis of *P*-chiral ferrocenyl phosphines

All *P*-chiral ferrocenyl phosphines were prepared using methods described by Jamison group. (Colby, E. A.; Jamison, T.F. *J. Org. Chem.* **2003**, *68*, 156-166).

(*R*)-Ferrocenyl(2-ethylphenyl)phenylphosphine (II-n)

The *P*-chiral ferrocenyl phosphine (**II-n**) was prepared starting from an ephedrine-based oxazaphospholidine complex in 8% overall yield over four steps in 92% ee. After one crystallization enantioselectivity of >97% was achieved.



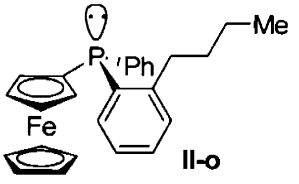
II-n

R_f(10:1 hexane/EtOAc) = 0.68. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48 (m, 2H), 7.36 (m, 3H), 7.25 (m, 2H), 7.10 (dt, *J* = 7.2, 1.5 Hz, 1H), 6.99 (ddd, *J* = 1.5, 4.2, 7.5 Hz, 1H), 4.45 (m, 1H), 4.35 (m, 2H), 4.13 (s, 5H), 3.82 (m, 1H), 2.82 (m, 2H), 1.11 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.3 (d, *J* = 23.3 Hz), 137.9 (d, *J* = 11.9 Hz), 137.7 (d, *J* = 8.1 Hz), 134.2 (d, *J* = 19.7 Hz), 132.6, 128.7, 128.6, 128.2 (d, *J* = 7.35 Hz), 128.0 (d, *J* = 4.2 Hz), 125.6, 76.3 (d, *J* = 4.95 Hz), 74.3 (d, *J* = 28.1 Hz), 72.1, 71.4 (d, *J* = 6.5 Hz), 70.5, 69.3 (d, *J* = 0.7 Hz 5C), 27.3 (d, *J* = 21.6 Hz), 15.4 (d, *J* = 2.4 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ -25.5 (s). IR (film, CH_2Cl_2):

3053, 2962, 2930, 2870, 1726, 1467, 1434, 1160, 1106, 1026, 820, 747, 698 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{23}FeP$ 398.0960, obsd 398.0883. Enantiomeric excess: 92% ee, chiral HPLC analysis of phosphine borane complex (Chiralcel AD, isocratic 1ml/min, hexane/i-propanol = 99.5:0.5, t_R [(*R*)-**II-n**] = 19.6 min, t_R [(*S*)-**II-n**] = 22.2 min). $[\alpha]_D = -182.1$ (*c* 0.71, $CHCl_3$).

(*R*)-Ferrocenyl(2-*n*-butylphenyl)phenylphosphine (II-o)

The *P*-chiral ferrocenyl phosphine (**II-o**) was prepared starting from an ephedrine-based oxazaphospholidine complex in 2% overall yield over four steps.

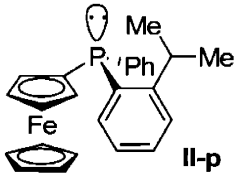


II-o

R_f(10:1 hexane/EtOAc) = 0.72. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (m, 2H), 7.35 (m, 3H), 7.24 (dt, *J* = 1.42, 7.38 Hz, 1H), 7.16 (m, 1H), 7.08 (dt, *J* = 1.17, 7.38 Hz, 1H), 6.98 (m, 1H), 4.43 (m, 1H), 4.37 (m, 1H), 4.34 (m, 1H), 4.10 (s, 5H), 3.82 (m, 1H), 2.8(m, 2H), 1.50 (m, 1H), 1.27(m, 3H), 0.82 (d, *J* = 7.20 Hz, 3H). ^{31}P NMR ($CDCl_3$, 121 MHz): δ -25.1 (s). HRMS (ESI): *m/z* calcd for $C_{26}H_{27}FeP$ 426.1200, obsd 426.1257.

(*R*)-Ferrocenyl(2-*i*-propylphenyl)phenylphosphine (II-p)

The *P*-chiral ferrocenyl phosphine (**II-p**) was prepared starting from an ephedrine-based oxazaphospholidine complex in 5% overall yield over four steps in >97% ee.

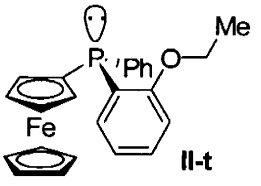


II-p

R_f(10:1 hexane/EtOAc) = 0.65. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (m, 2H), 7.35 (m, 3H), 7.28 (m, 2H), 7.08 (m, 1H), 6.99 (m, 1H), 4.43 (m, 1H), 4.38 (m, 2H), 4.11 (s, 5H), 3.81 (m, 1H), 3.63(sep, J = 6.9 Hz, 1H), 1.31(d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.2 (d, J = 22.0 Hz), 138.3 (d, J = 7.6 Hz), 137.5 (d, J = 11.2 Hz), 134.5 (d, J = 19.9 Hz), 132.6, 128.9, 128.8, 128.3 (d, J = 7.5 Hz), 125.7, 125.3 (d, J = 4.0 Hz), 76.5 (d, J = 6.0 Hz), 74.5 (d, J = 29.0 Hz), 72.1, 71.4 (d, J = 6.59 Hz), 70.6, 69.3 (s, 5C), 31.3 (d, J = 24.3 Hz), 23.9 (d, J = 28.0 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ -25.7 (s). IR (film, CH_2Cl_2): 3053, 2959, 2246, 1586, 1470, 1435, 1160, 1106, 1026, 909, 819, 761, 741 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}FeP$ 414.1194, obsd 414.1149. Enantiomeric excess: >97% ee, chiral HPLC analysis of phosphine borane complex (Chiralcel AD, isocratic 1ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)-**II-p**] = 10.7 min, t_R [(*S*)-**II-p**] = 12.5 min). $[\alpha]_D = -36.4$ (*c* 0.71, $CHCl_3$).

(*R*)-Ferrocenyl(2-ethoxy-phenyl)phenylphosphine (II-t)

The *P*-chiral ferrocenyl phosphine (**II-t**) was prepared starting from an ephedrine-based oxazaphospholidine complex in 9% overall yield over four steps.



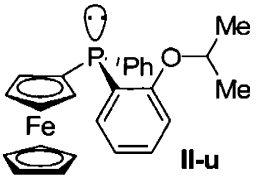
II-t

R_f(10:1 hexane/EtOAc) = 0.59. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (m, 2H), 7.35 (m, 3H), 7.28 (m, 1H), 6.93 (m, 1H), 6.85 (m, 1H), 6.77 (m, 1H), 4.43 (m, 1H), 4.36 (m, 2H), 4.09 (s, 5H), 3.97 (m, 1H), 3.86 (m, 1H), 3.78(m, 1H), 1.13(d, J = 7.34 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.9, 159.8, 138.3, 134.0, 133.8, 133.3 (d, J = 11.2 Hz), 129.9, 128.6, 128.0, 127.9 (d, J = 32.4 Hz), 120.6, 111.1, 74.9, 74.6, 72.1, 71.1 (d, J = 26.0 Hz), 70.7, 69.2, 63.9, 14.5. ^{31}P

NMR ($CDCl_3$, 121 MHz): δ -25.7 (s). HRMS (ESI): *m/z* calcd for $C_{24}H_{23}FeOP$ 415.0909, obsd 415.0903.

(*R*)-Ferrocenyl(2-*i*-propoxy-phenyl)phenylphosphine (II-u)

The *P*-chiral ferrocenyl phosphine (**II-u**) was prepared starting from an ephedrine-based oxazaphospholidine complex in 6% overall yield over four steps.



II-u

R_f(10:1 hexane/EtOAc) = 0.61. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52 (m, 2H), 7.25 (m, 4H), 6.98 (m, 1H), 6.83 (m, 1H), 6.76 (m, 1H), 4.41 (m, 4H), 4.13 (s, 5H), 3.88 (m, 1H), 1.13 (d, *J* = 6.94 Hz, 3H), 0.76 (d, *J* = 6.94 Hz, 3H). ^{31}P NMR ($CDCl_3$, 121 MHz): δ -24.6 (s). HRMS (ESI): *m/z* calcd for $C_{25}H_{25}FeOP$ 429.1065, obsd 429.1072.

Standard Experimental Procedure C — Asymmetric, Catalytic Three-component Coupling of Alkynes, Imines and Triethylborane using *P*-Chiral Ferrocenyl Phosphine (Table 2.5-2.8) For an exact proportion of reagents please refer to appropriate table and all reactions were performed on 0.5 mmol scale.

In a glovebox, an oven-dried 50mL flask was charged with $Ni(cod)_2$ and *P*-chiral ferrocenylphosphine, teflon coated stir bar and then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Distilled MeOH (2.5 mL) was added followed by 100 μL of 3M solution of Et_3B. After 2 min, the imine (0.5 mmol) and alkyne (0.2 mmol) were added, and the mixture was stirred 10 min. Additional alkyne (0.80 mmol) and

3M solution of Et_3B (1.20 mmol, 400 μL) were added in four equal portions every 10 min. The mixture was stirred 12 h at room temperature and opened to air for 10 min. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines. Unless otherwise stated, yields refer to combined isolated yield with greater than >95% purity by ^1H NMR. Enantioselectivities were measured on HPLC (Chiralcel OD column).

(4-Methoxy-phenyl)-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (II-3)

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-40**.

Enantiomeric excess was measured using HPLC (Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol = 99:1 t_R (minor) = 10.4 min, t_R (major) = 12.4 min).

(2-Methoxy-phenyl)-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (II-4)

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-41**.

Enantiomeric excess was measured using HPLC (Chiralcel OD, isocratic 1 ml/min, hexane: *i*-propanol = 99:1 t_R = 6.9 min, t_R = 9.8 min).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (II-5)

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-50**.

Enantiomeric excess was measured using HPLC (Chiralcel OD, isocratic 0.6ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.9 min, t_R [(*S*)] = 10.1 min). Absolute configuration of **II-5** was determined by Mosher ester analysis of the corresponding free amine **II-21**.

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-ethyl-1-phenyl-2-propyl-hex-2-enyl)-amine (II-6)

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-55**.

Enantiomeric excess was measure using HPLC (Chiralcel OD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 10.0 min, t_R [(*S*)] = 10.7 min). Absolute configuration was assigned by analogy to **II-5**.

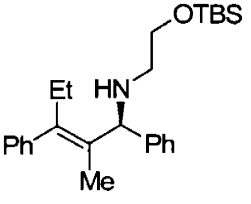
Standard Experimental Procedure D — Evaluation of Substrate Scope in Nickel-catalyzed Asymmetric Coupling of Alkynes, Imines and Triethylborane using *P*-Chiral Ferrocenyl Phosphine II-p (Table 2.9).

In a glovebox, an oven-dried 50mL flask was charged with $Ni(cod)_2$ (7 mg, 0.025 mmol) and (*R*)-Ferrocenyl(2-*i*-propylphenyl)phenylphosphine **II-p** (10.5 mg, 0.025 mmol), teflon coated stir bar and then sealed with a rubber septum. The flask was removed from the glovebox and placed under Ar atmosphere. Distilled MeOH (2.5 mL) was added followed by 100 μL of 3M solution of Et_3B in MeOAc. After 2 min, the imine (0.5 mmol) and alkyne (0.2 mmol) were added, and the mixture was stirred 10 min. Additional alkyne (0.80 mmol) and Et_3B in MeOAc (1.20 mmol, 400 μL) were added in four equal portions every 10 min. The mixture was stirred 12 h at room temperature and opened to air for 10 min. Concentration in vacuo and silica gel chromatography (hexanes: EtOAc) yielded allylic amines **II-5-16**. Unless otherwise stated, yields refer to combined isolated yield with greater than >95% purity by ^{1}H NMR. Enantiomeric excess measured using HPLC or GC (Chiralcel OD, AD, or OJ columns and Chiraldex B-PH, B-DA, and G-TA columns). Absolute configuration of **II-5** was determined by Mosher ester analysis of the corresponding free amine **II-21**. Absolute configuration of **II-6-16** and **II-23-25** was assigned

by analogy. Racemic starting materials were prepared using the identical procedure as above using achiral tricyclopentylphosphine (c-$C_5H_{11})_3P$.

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-1,3-diphenyl-pent-2-enyl)-amine (II-5)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines **II-5** (92 mg, 45% yield and 80:20 regioisomer, major shown). $R_f = 0.34$ (10:1 hexanes: EtOAc).



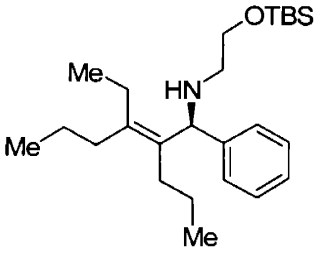
II-5

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-50**. Enantiomeric excess: 84% ee, HPLC analysis (Chiralcel OD, isocratic 0.6ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.9 min, t_R [(*S*)] = 10.1 min). $[\alpha]_D = -26.4$ (c 17.8, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-ethyl-1-phenyl-2-propyl-hex-2-enyl)-amine (II-6)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the

standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **2** (172 mg, 85 % yield). R_f= 0.69 (10:1 hexanes: EtOAc).

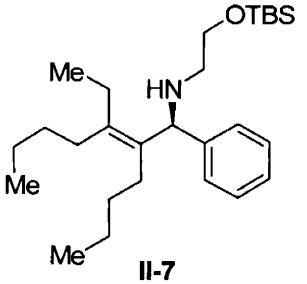


II-6

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-55**. Enantiomeric excess: 89% ee, HPLC analysis (Chiralcel OD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 10.0 min, t_R [(*S*)] = 10.7 min). $[\alpha]_D$ = –57.8 (*c* 6.4, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-butyl-3-ethyl-1-phenyl-hept-2-enyl]-amine (II-7)

In the three-component coupling of 5-decyne (1.0 mmol, 179 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-7** as colorless oil (180 mg, 83% yield). R_f= 0.72 (90:10 hexanes: EtOAc).



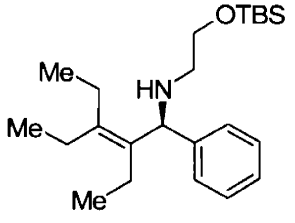
II-7

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (m, 2H), 7.30 (m, 2H), 7.22 (m, 1H), 4.80 (s, 1H), 3.77 (app t, *J* = 5.24 Hz, 2H), 2.69 (m, 2H), 2.29 (m, 2H), 2.05 (m, 2H), 1.89 (m, 1H), 1.76 (m, 2H), 1.38

(m, 4H), 1.12 (m, 6H), 0.93 (m, 12H), 0.73 (t, J = 7.23 Hz, 3H), 0.61 (m, 1H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 138.9, 135.0, 128.1, 127.4, 126.3, 62.9, 62.3, 50.1, 32.9, 31.7, 31.3, 27.8, 26.1, 24.3, 23.6, 23.4, 18.5, 14.6, 14.3, 13.9, -5.07, -5.11. IR (film, CH_2Cl_2): 3337, 3061, 3025, 2958, 2957, 1491, 1463, 1378, 1256, 1125, 1081, 1061, 963, 835, 777, 701 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{49}NOSi$ 432.3656, found $(M+H)^+$ 432.3635. Enantiomeric excess: 89% ee, HPLC analysis (Chiralcel OD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.4 min, t_R [(*S*)] = 9.1 min). $[\alpha]_D$ = – 45.8 (*c* 6.4, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2,3-diethyl-1-phenyl-pent-2-enyl]-amine (II-8)

In the three-component coupling of 3-hexyne (1.0 mmol, 114 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-8** (169 mg, 89% yield). R_f= 0.67 (90:10 hexanes: EtOAc).

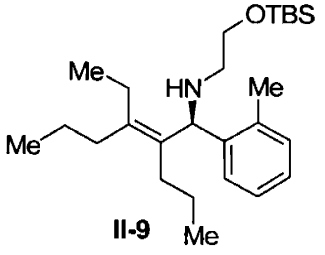


II-8

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-56**. Enantiomeric excess: 83% ee, HPLC analysis (Chiralcel OD, isocratic 0.3ml/min, hexane/*i*-propanol = 99.6:0.4, t_R [(*R*)] = 13.3 min, t_R [(*S*)] = 14.6 min). $[\alpha]_D$ = –60.7 (*c* 2.8, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-ethyl-2-propyl-1-*o*-tolyl-hex-2-enyl)-amine (II-9)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-benzylidene)-amine (0.5 mmol, 139 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-9** (154 mg, 74% yield). R_f= 0.57 (90:10 hexanes: EtOAc).

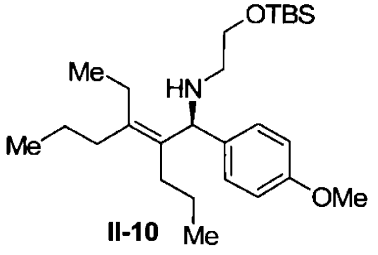


II-9

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.42 Hz, 1H), 7.21 (t, *J* = 7.46 Hz, 1H), 7.13 (dt, *J* = 1.34, 7.32 Hz, 1H), 7.07 (d, *J* = 7.17 Hz, 1H), 4.72 (s, 1H), 3.74 (t, *J* = 5.02 Hz, 2H), 2.62 (m, 2H), 2.41 (m, 1H), 2.23 (m, 1H), 2.18 (s, 3H), 2.04 (t, *J* = 7.95 Hz, 2H), 1.76 (m, 2H), 1.57 (bs, 1H), 1.41 (m, 3H), 1.09 (t, *J* = 7.54 Hz, 3H), 0.91 (m, 12H), 0.58(t, *J* = 7.24 Hz, 3H), 0.4 (m, 1H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.8, 139.4, 136.8, 133.9, 130.0, 127.2, 126.2, 125.7, 62.9, 60.4, 50.4, 33.8, 31.2, 26.1, 24.0, 23.5, 22.2, 19.7, 18.5, 14.8, 14.7, 13.9, -5.07, -5.09. IR (film, CH_2Cl_2): 3345, 2957, 2930, 2870, 1462, 1255, 1091, 1059, 833, 776, 745 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{47}NOSi$ 418.3500, found 418.3496. Enantiomeric excess: enantiomeric excess was measured on the trifluoro-acetamide of the deprotected primary allylic amine [*N*-(3-Ethyl-2-propyl-1-*o*-tolyl-hex-2-enyl)-2,2,2-trifluoro-acetamide] 85% ee, HPLC analysis (Chiralcel AD, isocratic 1 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 4.4 min, t_R [(*S*)] = 5.5 min). $[\alpha]_D$ = –44.7 (*c* 3.8, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-[3-ethyl-1-(4-methoxy-phenyl)-2-propyl-hex-2-enyl]-amine (II-10)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-(4-methoxy-benzylidene)-amine (0.5 mmol, 147 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-10** (162 mg, 75% yield). R_f= 0.37 (90:10 hexanes: EtOAc).

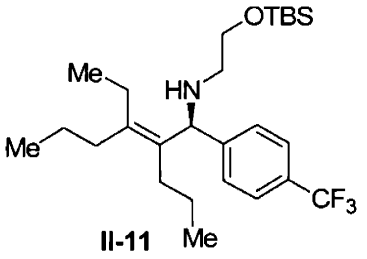


II-10

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (m, 2H), 6.84 (m, 2H), 4.73 (s, 1H), 3.80 (s, 3H), 3.76 (dd, *J* = 4.64, 5.73 Hz, 2H), 2.67 (m, 2H), 2.24 (m, 2H), 2.02 (m, 2H), 1.83 (m, 1H), 1.74 (m, 1H), 1.65(bs, 1H), 1.43 (m, 2H), 1.07 (t, *J* = 7.52 Hz, 3H), 0.91 (m, 12H), 0.69 (m, 4H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2 138.7, 135.7, 135.3, 128.3, 113.4, 62.9, 61.6, 55.4, 50.0, 34.2, 30.5, 26.1, 24.1, 24.0, 22.2, 18.5, 15.1, 14.7, 14.6, -5.07, -5.10. IR (film, CH_2Cl_2): 3334, 2957, 2931, 2870, 1610, 1584, 1509, 1464, 1246, 1103, 1074, 1040, 834, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{47}NO_2Si$ 434.3449, found 434.3444. Enantiomeric excess: 82% ee, HPLC analysis (Chiralcel AD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.7 min, t_R [(*S*)] = 11.2 min). $[\alpha]_D$ = –48.9 (*c* 9.2, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-[3-ethyl-2-propyl-1-(4-trifluoromethyl-phenyl)-hex-2-enyl]-amine (II-11)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-(4-trifluoromethyl-benzylidene)-amine (0.5 mmol, 143 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-11** (214 mg, 91% yield). R_f= 0.82 (90:10 hexanes: EtOAc).

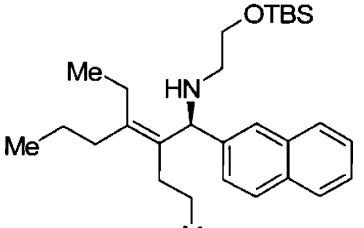


II-11

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (m, 4H), 4.76 (s, 1H), 3.72 (dd, *J* = 4.10, 6.44 Hz, 2H), 2.68 (m, 1H), 2.57 (m, 1H), 2.22 (m, 2H), 1.99 (m, 2H), 1.81 (m, 1H), 1.63 (m, 2H), 1.41(m, 2H), 1.04 (t, *J* = 7.52 Hz, 3H), 0.87 (m, 13H), 0.65 (m, 4H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1, 139.9, 134.4, 128.6, 127.7, 126.0, 125.00, 62.8, 62.4, 50.1, 34.2, 30.6, 26.1, 24.3, 24.1, 22.2, 18.5, 15.0, 14.7, 14.6, -5.08, -5.12. IR (film, CH_2Cl_2): 3338, 2959, 2931, 2871, 1618, 1464, 1325, 1256, 1163, 1126, 1068, 1017, 833, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{44}F_3NOSi$ 472.3217, found 472.3229. Enantiomeric excess: 85% ee, HPLC analysis (Chiralcel AD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.1:0.1, t_R [(*R*)] = 7.8 min, t_R [(*S*)] = 9.6 min). $[\alpha]_D$ = –65.8 (*c* 2.4, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(3-ethyl-1-naphthalen-2-yl-2-propyl-hex-2-enyl)-amine (II-12)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL) and [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-naphthalen-2-ylmethylene-amine (0.5 mmol, 157 mg), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-12** (204 mg, 90% yield). R_f= 0.38 (90:10 hexanes: EtOAc).

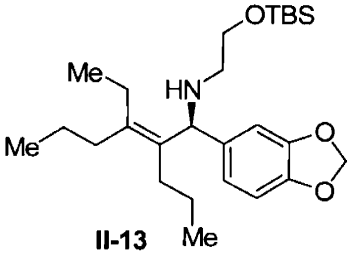


II-12

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H), 7.83 (app dd, J = 7.75, 10.45 Hz, 2H), 7.76 (d, J = 8.53 Hz, 1H), 7.45 (m, 3H), 4.96 (s, 1H), 3.84 (m, 2H), 2.75 (m, 2H), 2.35 (m, 2H), 2.07 (m, 2H), 1.92 (m, 1H), 1.78 (m, 1H), 1.48 (m, 2H), 1.22 (m, 1H), 1.14 (t, J = 7.50 Hz, 3H), 0.95 (m, 12H), 0.65 (m, 4H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2, 139.5, 134.8, 133.7, 132.6, 128.1, 127.7, 127.5, 126.6, 125.9, 125.4, 125.2, 62.8, 62.5, 50.1, 34.2, 30.6, 26.2, 24.3, 24.1, 22.2, 18.5, 15.1, 14.7, 14.6, -5.04, -5.07. IR (film, CH_2Cl_2): 3335, 2957, 2929, 2869, 1507, 1463, 1255, 1091, 954, 834, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{29}H_{47}NOSi$ 454.3500, found 454.3491. Enantiomeric excess: 73% ee, HPLC analysis (Chiralcel AD, isocratic 0.4 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 9.8 min, t_R [(*S*)] = 11.8 min). $[\alpha]_D$ = –78.7 (*c* 10.8, $CHCl_3$).

(*S*)-(1-Benzo[1,3]dioxol-5-yl-3-ethyl-2-propyl-hex-2-enyl)-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (II-13)

In the three-component coupling of 4-octyne (1.0 mmol, 150 μL), benzo[1,3]dioxol-5-ylmethylene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 154 mg), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-13** (212 mg, 95% yield). R_f= 0.46 (90:10 hexanes: EtOAc).

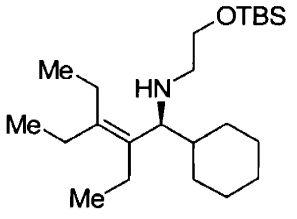


II-13

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.93 (d, *J* = 1.28 Hz, 1H), 6.87 (d, *J* = 8.10 Hz, 1H), 6.75 (d, *J* = 8.02 Hz, 1H), 5.93 (s, 2H), 4.68 (s, 1H), 3.75 (t, *J* = 5.11 Hz, 2H), 2.65 (m, 2H), 2.23 (q, *J* = 7.51 Hz, 2H), 2.01 (m, 2H), 1.86 (m, 1H), 1.72 (m, 1H), 1.59 (bs, 1H), 1.43 (m, 2H), 1.22 (m, 1H), 1.07 (t, *J* = 7.52 Hz, 3H), 0.91 (m, 12H), 0.72 (m, 4H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 145.9, 138.9, 137.8, 135.2, 120.2, 108.0, 107.9, 100.9, 62.9, 62.0, 50.0, 34.2, 30.5, 26.1, 24.2, 24.1, 22.2, 18.5, 15.1, 14.7, 14.6, -5.08, -5.11. IR (film, CH_2Cl_2): 3335, 2957, 2930, 2870, 1503, 1486, 1471, 1251, 1236, 1086, 1042, 940, 835, 810, 777 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{26}H_{45}NO_3Si$ 448.3241, found 448.3239. Enantiomeric excess: 73% ee, HPLC analysis (Chiralcel AD, isocratic 0.4 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.9 min, t_R [(*S*)] = 12.3 min). $[\alpha]_D$ = –48.7 (*c* 15.6, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-2,3-diethyl-pent-2-enyl)-amine (II-14)

In the three-component coupling of 3-hexyne (2.0 mmol, 228 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclohexylmethylene-amine (1 mmol, 270 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** used. Silica gel chromatography afforded the allylic amine **II-14** (202 mg, 53% yield). R_f= 0.81 (95:5 hexanes: EtOAc).

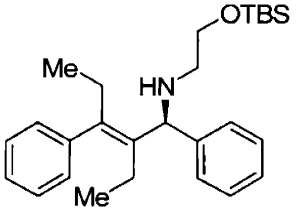


II-14

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.65 (m, 2H), 3.16 (d, J = 3.16 Hz, 1H), 2.57 (m, 1H), 2.42 (m, 1H), 2.08 (m, 7H), 1.9 (m, 1H), 1.62 (m, 5H), 1.2 (m, 5H), 0.98 (m, 6H), 0.91 (t, J = 7.54 Hz, 3H), 0.88 (s, 9H), 0.76(m, 1H), 0.03 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 133.2, 64.3, 62.9, 49.9, 41.2, 31.3, 31.0, 26.9, 26.8, 26.7, 26.6, 26.1, 24.4, 22.9, 18.4, 15.6, 13.8, 13.6, -5.11, -5.14. IR (film, CH_2Cl_2): 3361, 2959, 2928, 2854, 1463, 1449, 1255, 1094, 834, 776 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{23}H_{47}NOSi$ 382.3500, found 382.3492. Enantiomeric excess: 51% ee, chiral GC analysis. Column: cyclodextrin dialkyl B-DA, 20m* .25mm, isocratic 3.5 ml/min, 105 °C, t_R (major) = 148 min, t_R (minor) = 152 min. (Analysis performed on Trifluoroacetate derivative of amino-alcohol: Treat product with TBAF, followed by Tf_2O, Et_3N). $[\alpha]_D$ = –6.3 (*c* 26.8, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-ethyl-1,3-diphenyl-pent-2-enyl)-amine (II-15)

In the three-component coupling of 1-phenyl-1-butyne (1.0 mmol, 142 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.5 mmol, 135 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amine **II-15** as a single regioisomer (132 mg, 62% yield). R_f = 0.41 (95:5 hexanes: EtOAc).

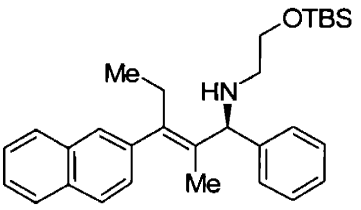


II-15

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-51**. Enantiomeric excess: 71% ee, HPLC analysis (Chiralcel OD, isocratic 0.5ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 8.1 min, t_R [(*S*)] = 9.9 min). $[\alpha]_D$ = –31.6 (*c* 3.8, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-3-naphthalen-2-yl-1-phenyl--pent-2-enyl)-amine (II-16)

In the three-component coupling of 2-prop-1-ynyl-naphthalene (0.5 mmol, 83 mg), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (0.25 mmol, 68 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** was used. Silica gel chromatography afforded the allylic amines **II-16** (regioselectivity: 85:15, 48 mg, 42% yield). R_f = 0.34 (90:10 hexanes: EtOAc).



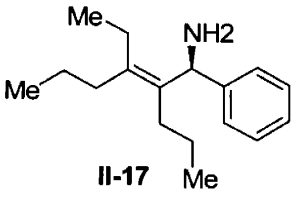
II-16

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-52**. Enantiomeric excess: 70% ee, HPLC analysis (Chiralcel OD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 12.9 min, t_R [(*S*)] = 15.3 min). $[\alpha]_D = -23.3$ (*c* 3.0, $CHCl_3$).

Standard Experimental Procedure for Deprotection of N–(*tert*-butyldimethyl)silyloxy ethyl ($TBSOCH_2CH_2$–) allylic amines (Table 2.10)

Tetrabutylammoniumfluoride (TBAF 1M solution in THF, 150 mol%) was added to a solution of allylic amine product (1M in THF) at 0 °C and mixture stirred for 30 min. 5 mL H_2O was added, and extracted with ether. Concentration under vacuo afforded the *β*-amino alcohol product. Without further purification, this product was dissolved in MeOH (0.2 M) and 40 % aq $MeNH_2$ (300 %), and solution of H_5IO_6 in water (360 mol%, 0.2M) were sequentially added. Reaction mixture was stirred 5 hr and then concentrated under vacuo. Add saturated $NaHCO_3$ solution to pH 9.0 and extract with CH_2Cl_2. Organic layer was concentrated in vacuo and silica gel chromatography (hexanes: EtOAc) yielded primary allylic amines **II-17-21**. Unless otherwise stated, yields refer to combined isolated yield with greater than >95% purity by ^{1}H NMR. Enantioselectivity was measured with HPLC (Chiralcel OD) on the corresponding trifluoroacetamide derivatives of primary allylic amines.

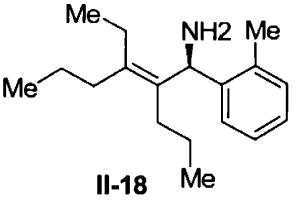
(*S*)-3-Ethyl-1-phenyl-2-propyl-hex-2-enylamine (II-17)



II-17

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-68**. Enantiomeric excess: 89% ee, HPLC analysis (Chiralcel OD, isocratic 1 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 5.0 min, t_R [(*S*)] = 9.7 min). $[\alpha]_D = -80.0$ (*c* 10.0, $CHCl_3$).

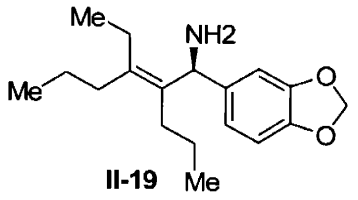
(*S*)-3-Ethyl-2-propyl-1-*o*-tolyl-hex-2-enylamine (II-18)



II-18

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 7.62, 1H), 7.24 (dt, *J* = 1.16, 7.58, Hz, 1H), 7.15 (dt, *J* = 1.36, 7.35, Hz, 1H), 7.07 (d, *J* = 7.27, 1H), 5.15 (s, 1H), 2.42 (m, 2H), 2.21 (m, 4H), 2.04 (m, 2H), 1.81 (m, 2H), 1.46 (m, 5H), 1.11 (t, *J* = 7.54 Hz, 3H), 1.10 (m, 1H), 0.93 (t, *J* = 7.35 Hz, 3H), 0.59 (t, *J* = 7.22 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.6, 138.8, 136.2, 134.5, 130.0, 126.4, 126.0, 125.9, 52.7, 33.9, 30.8, 23.8, 23.7, 22.2, 20.0, 14.9, 14.7, 14.1. IR (film, CH_2Cl_2): 3379 (d), 2959, 2930, 2870, 1604, 1464, 1036, 742 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{18}H_{29}N$+H 260.2373, found 260.2361. Enantiomeric excess: 85% ee, HPLC analysis (Chiralcel OD, isocratic 0.4ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 4.4 min, t_R [(*S*)] = 5.5 min). $[\alpha]_D = -73.8$ (*c* 8.4, $CHCl_3$).

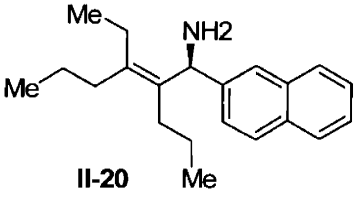
(*S*)-1-Benzo[1,3]dioxol-5-yl-3-ethyl-2-propyl-hex-2-enylamine (II-19)



II-19

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (m, 2H), 6.75 (dd, J = 0.75, 7.65 Hz, 1H), 5.94 (s, 2H), 5.03 (s, 1H), 2.20 (m, 2H), 2.03 (m, 2H), 1.91 (ddd, J = 4.79, 12.04, 16.82 Hz, 1H), 1.74 (ddd, J = 4.98, 11.84, 16.81 Hz, 1H), 1.45 (m, 4H), 1.25 (m, 1H), 1.06 (t, J = 7.54 Hz, 3H), 0.96 (m, 1H), 0.94 (t, J = 7.32 Hz, 3H), 0.77 (t, J = 7.27 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 146.0, 138.9, 138.2, 136.4, 119.4, 107.9, 107.5, 101.0, 54.9, 34.4, 30.5, 24.9, 24.3, 22.2, 15.1, 14.8, 14.7. IR (film, CH_2Cl_2): 3382 (d), 2958, 2930, 2870, 1502, 1486, 1234, 1040, 940, 810 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{18}H_{27}NO_2$+H 290.2115, found 290.2123. Enantiomeric excess: 73% ee, HPLC analysis (Chiralcel OD, isocratic 1ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 7.4 min, t_R [(*S*)] = 14.7 min).

(*S*)-3-Ethyl-1-naphthalen-2-yl-2-propyl-hex-2-enylamine (II-20)

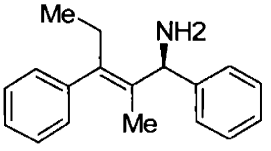


II-20

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1H), 7.84 (m, 2H), 7.76 (d, J = 8.55 Hz, 1H), 7.45 (m, 3H), 5.29 (s, 1H), 2.30 (m, 2H), 2.08 (m, 2H), 1.96 (ddd, J = 4.82, 12.1, 16.9 Hz, 1H), 1.76 (ddd, J = 4.96, 11.8, 16.8 Hz, 1H), 1.93 (bs, 2H), 1.50 (m, 2H), 1.27 (m, 1H), 1.12 (t, J = 7.53 Hz, 3H), 0.97 (t, J = 7.35 Hz, 3H), 0.89 (m, 1H), 0.69 (t, J = 7.29 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.3, 138.7, 136.2, 133.6, 132.5, 128.1, 127.7, 127.6, 126.1, 126.0, 125.5, 124.3,

55.4, 34.4, 30.7, 24.8, 24.4, 22.2, 15.1, 14.9, 14.7. IR (film, CH_2Cl_2): 3377(d), 2959, 2929, 2869, 1602, 1506, 1466, 1455, 1374, 1058, 855, 817, 754 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{21}H_{29}N+H$ 296.2373, found 296.2389. Enantiomeric excess: 76% ee, HPLC analysis (Chiralcel OD, isocratic 1 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 7.5 min, t_R [(*S*)] = 17.4 min). $[\alpha]_D = -123.3$ (*c* 9.0, $CHCl_3$).

(*S*)-2-Methyl-1,3-diphenyl-pent-2-enylamine (II-21)



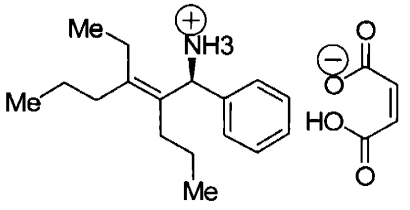
II-21

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-49**. Enantiomeric excess: 84% ee, HPLC analysis (Chiralcel OD, isocratic 0.7 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 17.2 min, t_R [(*S*)] = 23.5 min). $[\alpha]_D = -27.8$ (*c* 1.8, $CHCl_3$).

Determination of absolute configuration *via* mosher ester analysis.

Primary allylic amine **II-21** (6 mg, 0.03 mmol, 73% ee) was dissolved in CH_2Cl_2 (1 mL). (*R*)-Mosher's chloride (11.5 μL, 0.06 mmol), cat DMAP (~1 mg) and Et_3N (15 μL, 0.1 mmol) were added sequentially, and the reaction was stirred at room temperature for 5 hr. Reaction was diluted with 5 mL CH_2Cl_2 and washed with saturated $NaHCO_3$ solution. The organic layer was dried and concentrated, then subjected to silica gel chromatography (hexanes: EtOAc = 99: 1) to yield mixture of diastereomers (6 mg, ~85:15 diastereoselectivity). Shielding of the H and deshielding of the alkenyl group in the major diastereomer suggests an absolute configuration of (*S*).

Maleic Acid Salt (II-22)



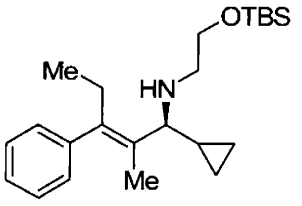
II-22

White crystals from ether at 0° C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (bs, 3H), 7.32 (m, 5H), 5.99 (s, 2H), 5.54 (s, 1H), 2.37 (m, 1H), 2.07 (m, 5H), 1.42 (m, 2H), 1.20 (m, 1H), 1.08 (t, J = 7.50 Hz, 3H), 0.93 (t, J = 7.29 Hz, 3H), 0.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 145.0, 136.7, 135.8, 129.0, 128.6, 128.3, 126.3, 55.2, 34.1, 30.2, 24.5, 23.9, 21.8, 14.8, 14.7, 14.2. Enantiomeric excess: Recrystallized maleic salt was treated with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. Corresponding triflamide was made to measure enantiomeric excess. >99% ee, HPLC analysis (Chiralcel OD, isocratic 1 ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 5.0 min, t_R [(*S*)] = 9.7 min). $[\alpha]_D = -59.4$ (*c* 3.2, $CHCl_3$).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclopropyl-2-methyl-3-phenyl-pent-2-enyl)-amine (II-23)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclopropylmethylene-amine (0.5 mmol, 140 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** with (*R*)-ferrocenyl(2-methyl)phenylphosphine **II-l**) was used. Silica gel chromatography afforded the allylic amine **II-23** (17 mg, 10% yield, regioselectivity not determined). R_f= 0.64 (1:1 hexanes: EtOAc).

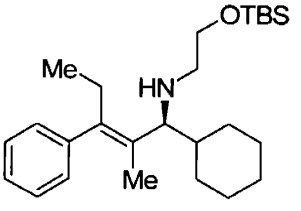


II-23

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-61**. The corresponding acetamide was prepared to measure enantiomeric excess (acetic anhydride, triethylamine and 4-dimethylaminopyridine in CH_2Cl_2). Enantiomeric excess: 50% ee, HPLC analysis (Chiralcel OD, isocratic 0.5ml/min, hexane/*i*-propanol = 99.6:0.4, t_R [(*R*)] = 25 min, t_R [(*S*)] = 27 min).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(1-cyclohexyl-2-methyl-3-phenyl-pent-2-enyl)-amine (II-24)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), [2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-cyclohexylmethylene-amine (0.5 mmol, 140 μL), and Et_3B (1.5 mmol, 3M in MeOAc), the standard experimental procedure **D** with (*R*)-ferrocenyl(2-methyl)phenylphosphine **II-l**) was used. Silica gel chromatography afforded the allylic amine **II-24** (50 mg, 24 % yield, regioselectivity not determined). R_f= 0.46 (4:1 hexanes: EtOAc).

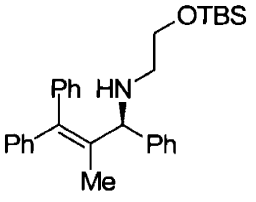


II-24

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-60**. Enantiomeric excess: 20 % ee, HPLC analysis (Chiralcel AD-H, isocratic 0.4 ml/min, hexane/*i*-propanol = 99.9:0.1, t_R [(*R*)] = 11.1 min, t_R [(*S*)] = 12.5 min).

(*S*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-(2-methyl-1,3,3-triphenyl-allyl)-amine (II-25)

In the three-component coupling of 1-phenyl-1-propyne (1.0 mmol, 125 μL), benzylidene-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-amine (1.0 mmol, 270 μL), and $PhB(OH)_2$ (1.0 mmol, 121 mg), the standard experimental procedure **D** with (*R*)-ferrocenyl(2-methyl)phenylphosphine **II-l**) was used. Silica gel chromatography afforded the allylic amine **II-25** (165 mg, 36 % yield, regioselectivity 80:20). R_f= 0.41 (9:1 hexanes: EtOAc).



II-25

For ^{1}HNMR, ^{13}CNMR, IR and HRMS data, see Chapter 1, **I-66**. Enantiomeric excess: 63 % ee, HPLC analysis (Chiralcel AD-H, isocratic 0.7ml/min, hexane/*i*-propanol = 99.5:0.5, t_R [(*R*)] = 6.3 min, t_R [(*S*)] = 11.6 min).

Curriculum Vitae

Sejal J. Patel

Education:

1998 B.S. (Chemistry and Biology), University of California, Irvine

2004 Ph.D. (Chemistry), Massachusetts Institute of Technology

Thesis title: "Asymmetric Nickel-Catalyzed Three-Component Assembly of Allylic Amines from Alkynes, Imines and Organoboron Reagents"

Supervisor: Professor Timothy F. Jamison

Research and Professional Experience:

1995-97	Undergraduate Research, UC Irvine (Prof. Allen Gibbs)
1997-98	Undergraduate Research, UC Irvine (Prof. Christopher Grayce)
1998-99	Research Associate, Kosan Biosciences
1999-04	Graduate Student, MIT (Prof. Timothy F. Jamison)

Teaching and Mentoring Experience:

1995-97	Group Tutor in Chemistry and Biology, UC Irvine
1997-98	Peer Academic Advisor, Department of Physical Sciences, UC Irvine
1999-02	Teaching Assistant, Chemistry Department, MIT

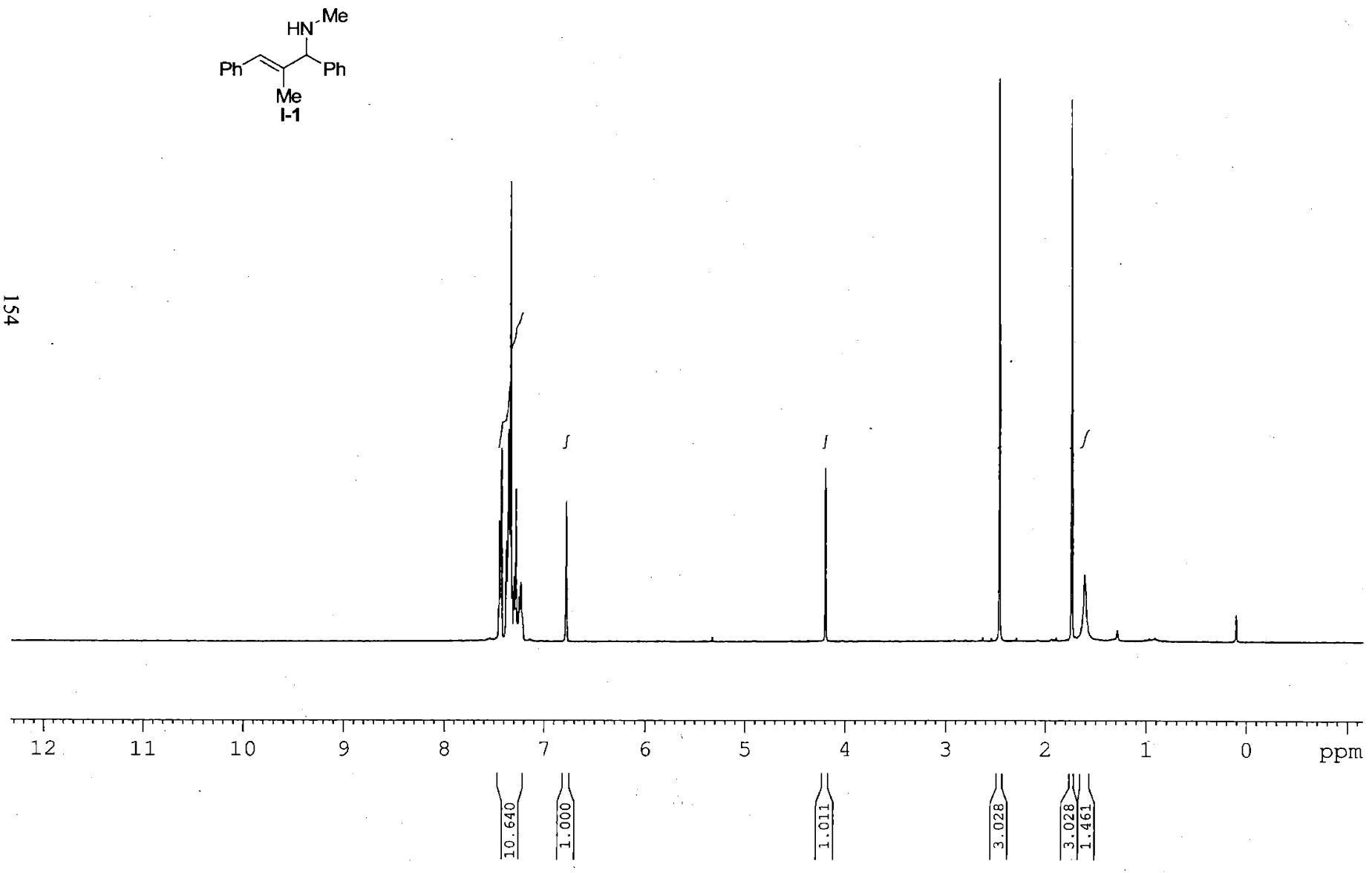
Honors, Awards and Leadership Opportunities:

1997	School of Biological Sciences Excellence in Research Award, UC Irvine
1997	Phi Beta Kappa (Top 2% of Junior Class), UC Irvine
1998	American Institute of Chemists Foundation Award, UC Irvine
1998	Honors in Chemistry (Outstanding Achievements in Research), UC Irvine
1998	Cum Laude Graduate in Chemistry and Biology, UC Irvine
2001	Greenlaw Predoctoral Fellowship
2000-02	President of Women In Chemistry Program at MIT
2000-02	Graduate Student Council Representative, Chemistry Department, MIT
2002	Excellence in Teaching by a Graduate Student (MIT)
2002	American Chemical Society Women Chemist Committee Travel Grant
2004	Morse Travel Grant

Publications and Presentations:

1) **Patel, S. J.**; Jamison, T. F. "Asymmetric Catalytic Coupling of Organoboranes, Alkynes, and Imines Possessing A Removable (Trialkylsilyloxy)ethyl Group — Direct Access to Enantiomerically Pure Primary Allylic Amines," *manuscript submitted.*
2) **Patel, S. J.**; Jamison, T. F. "Asymmetric, catalytic three-component assembly of allylic amines", 227th ACS National Meeting, Anaheim, CA, April 1, 2004.
3) **Patel, S. J.**; Jamison, T. F. "Catalytic, Three-Component Assembly of Allylic Amines: Selective Imine Addition in the Presence of Hydroxyl Groups, Ketones, and Esters," *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 1364.
4) **Patel, S. J.**; Jamison, T. F. "Catalytic, Three-Component Assembly of Allylic Amines," 225th ACS National Meeting, New Orleans, LA, March 23, 2003.

5) **Patel, S.**; Nelson, D. R.; Gibbs, A. G. "Chemical and physical analyses of wax ester properties," *J. Insect Science* (**2001**), *1*, Article 4 (online journal).
6) Chung, L.; Liu, L.; **Patel, S. J.**; Carney, J. R.; Reeves, C. D. "Deletion of rapQONML from the rapamycin gene cluster of Streptomyces hygroscopicus gives production of the 16-O-desmethyl-27-desmethoxy analog," *J. Antibiotics* (**2001**), *54*, 250.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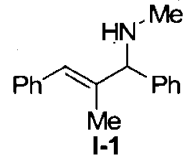
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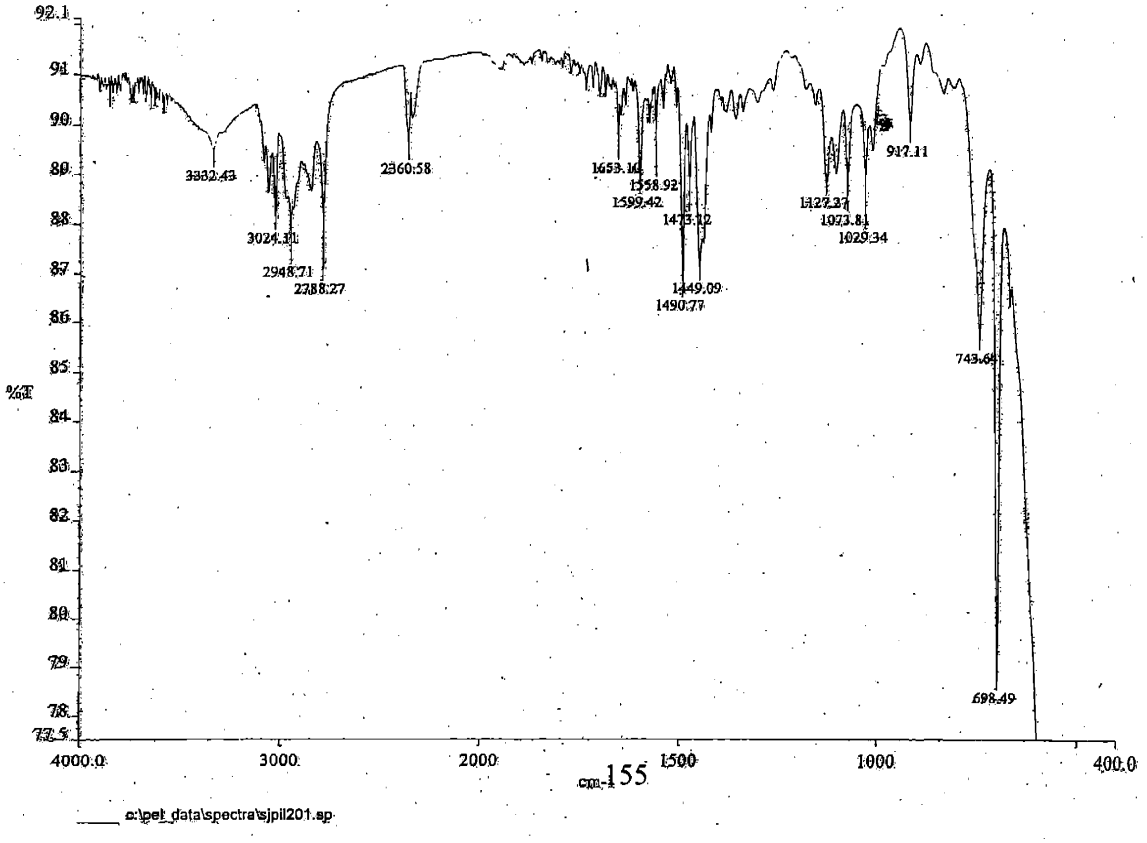
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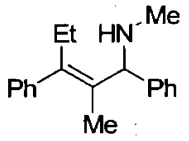
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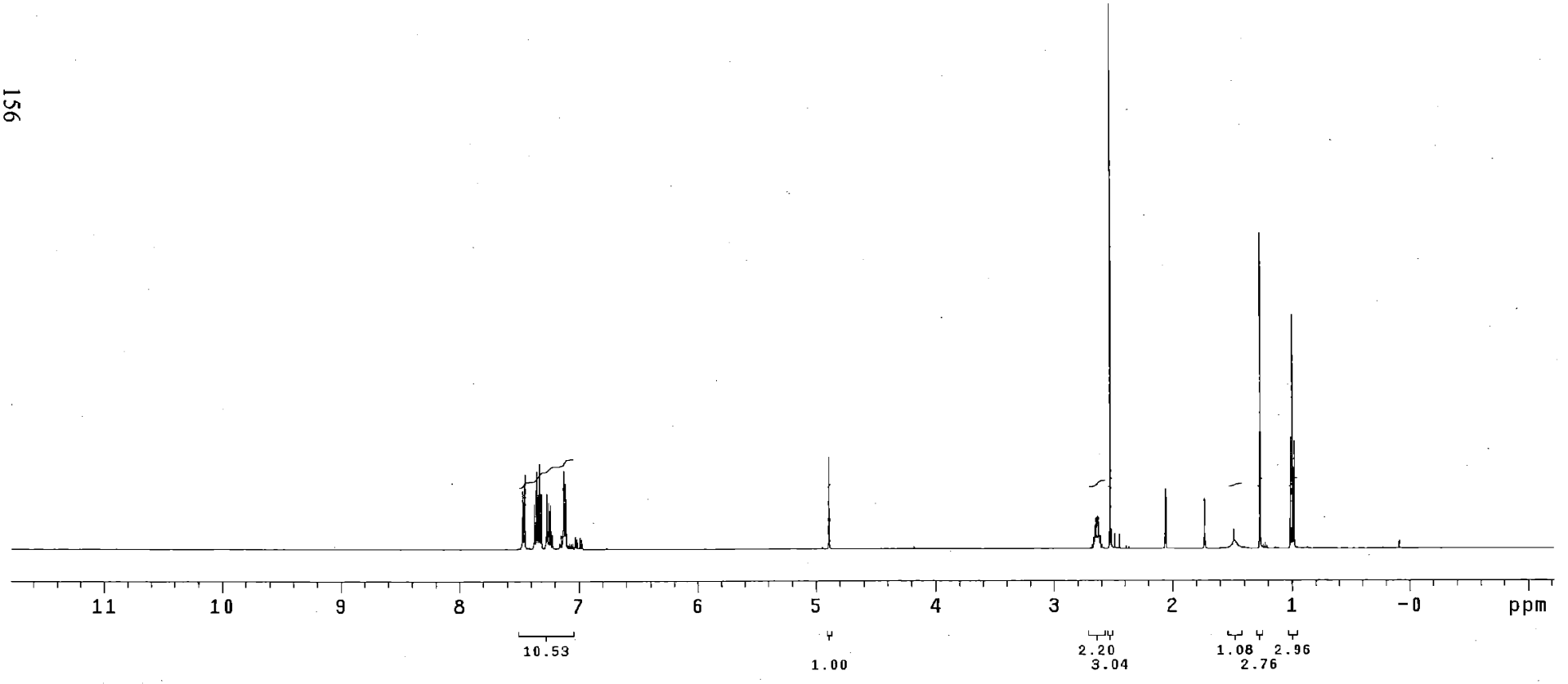
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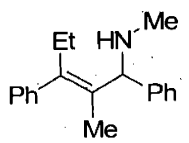
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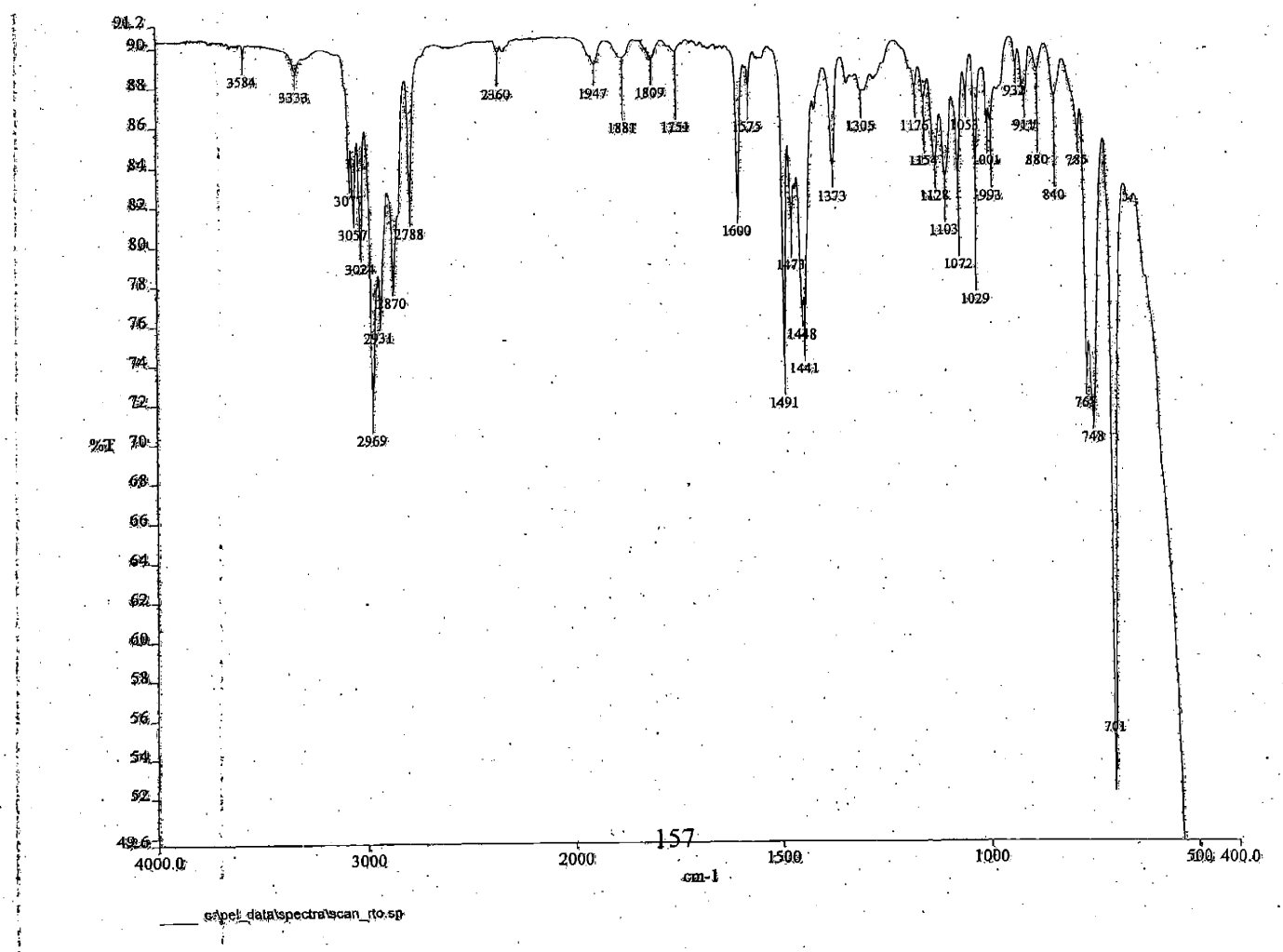
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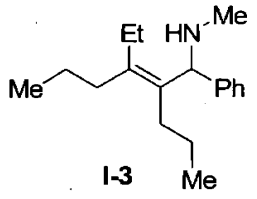
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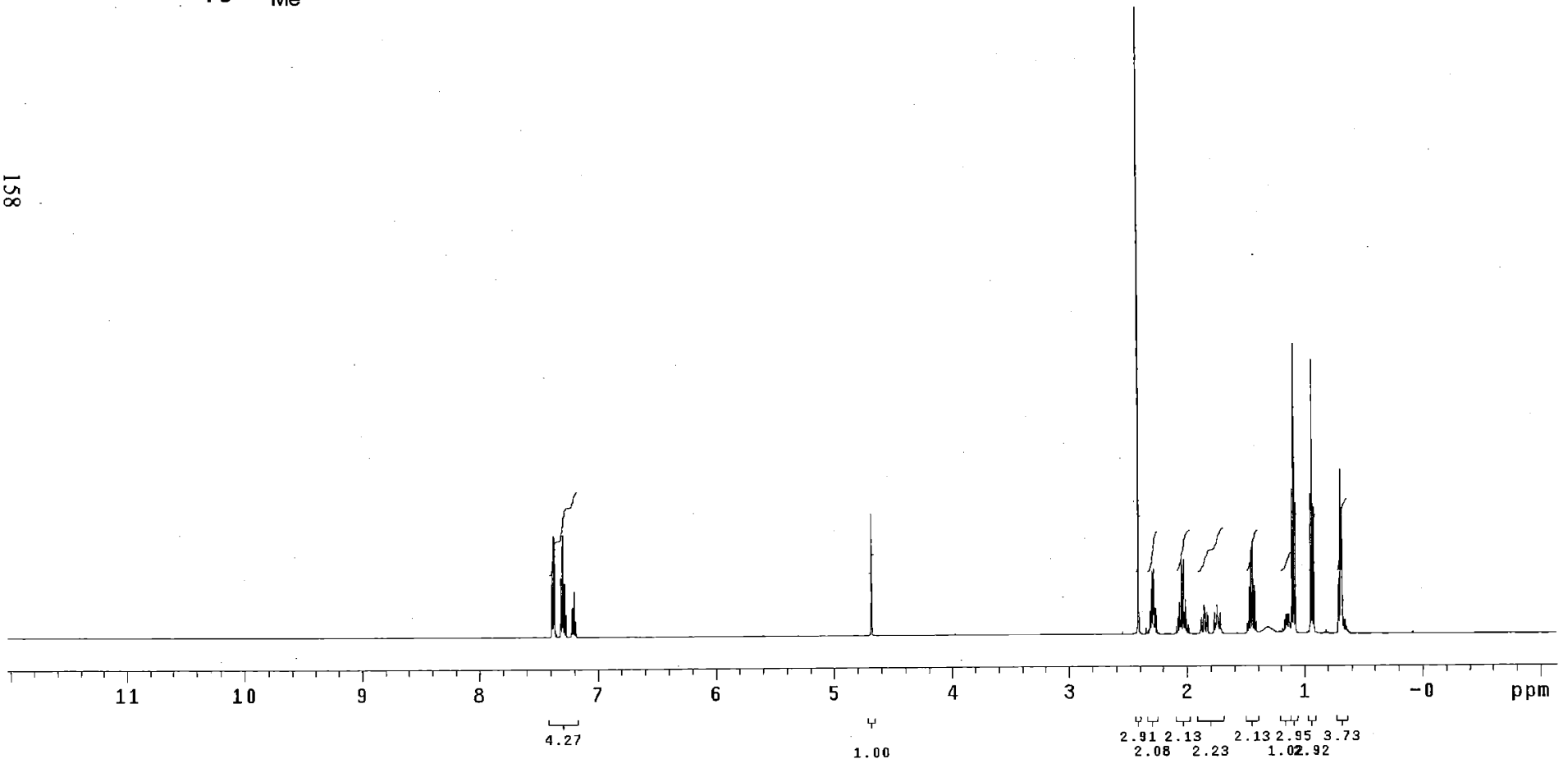
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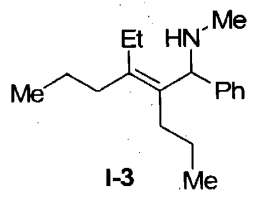
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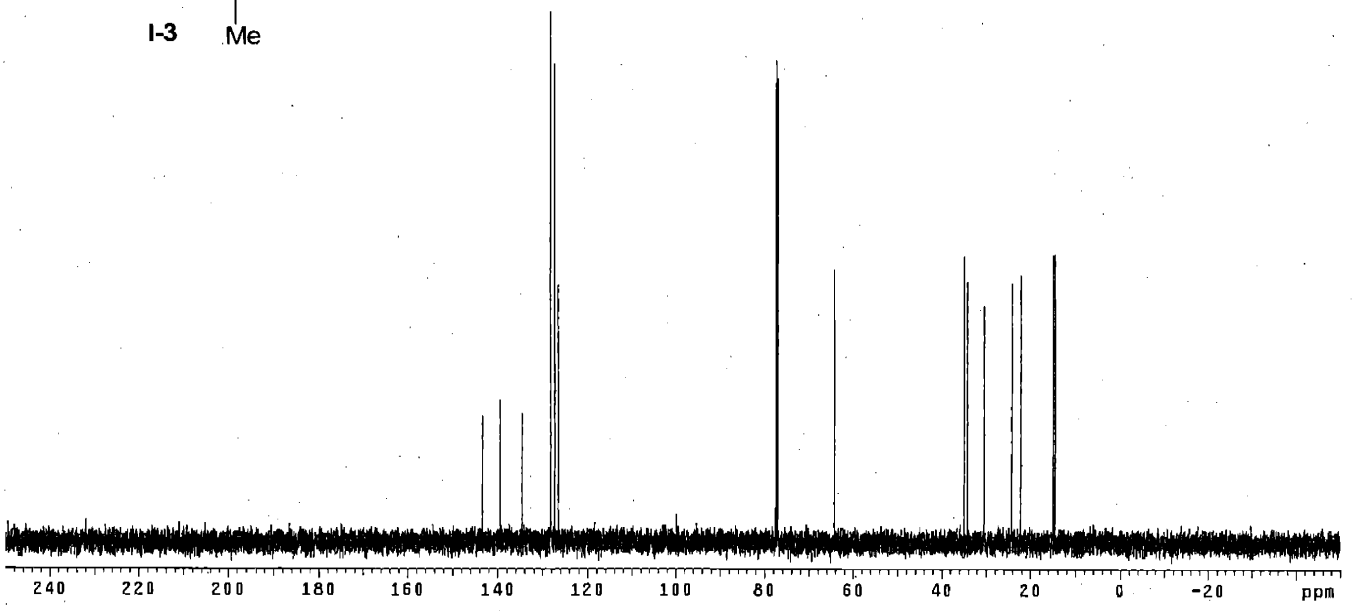
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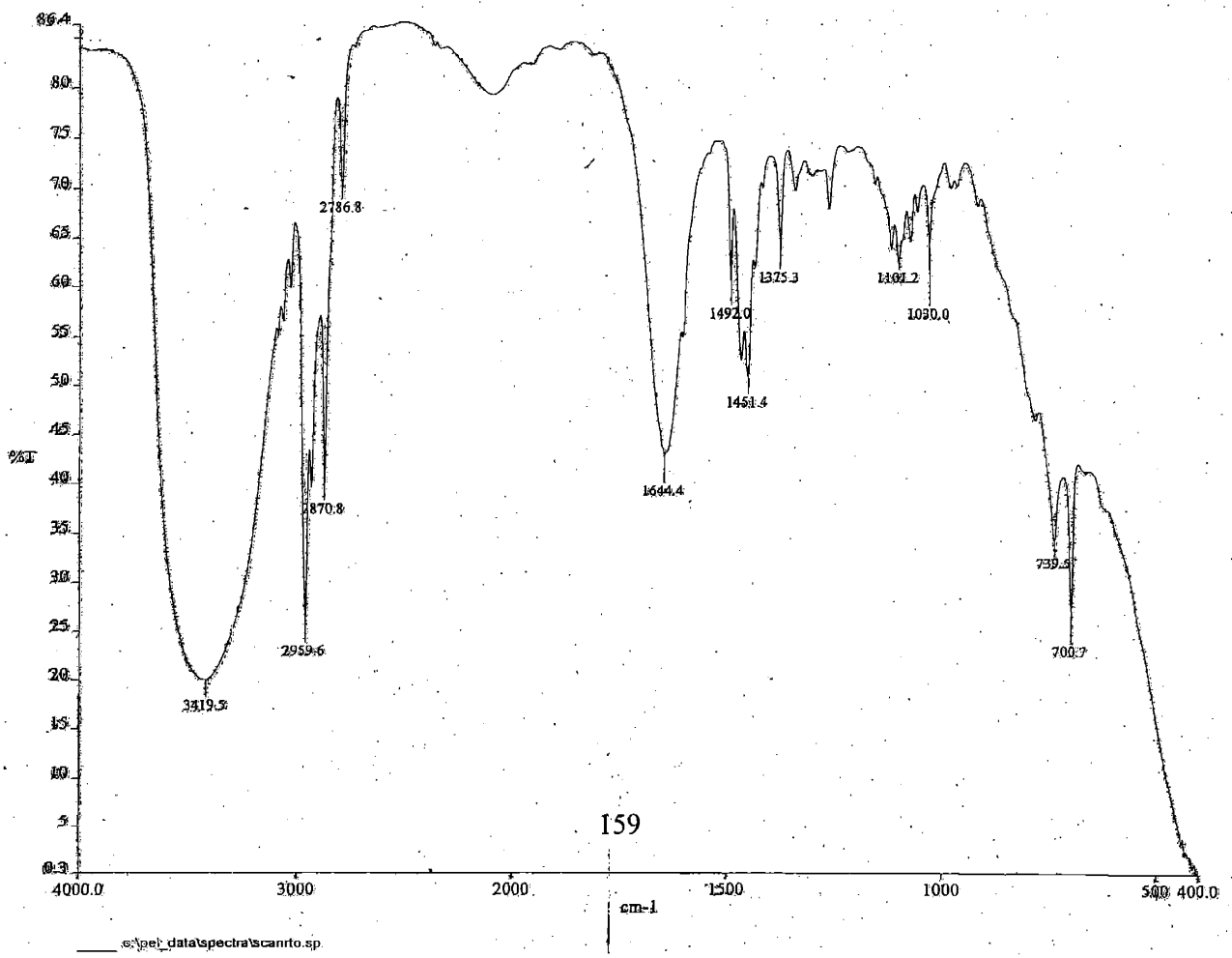
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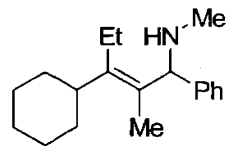
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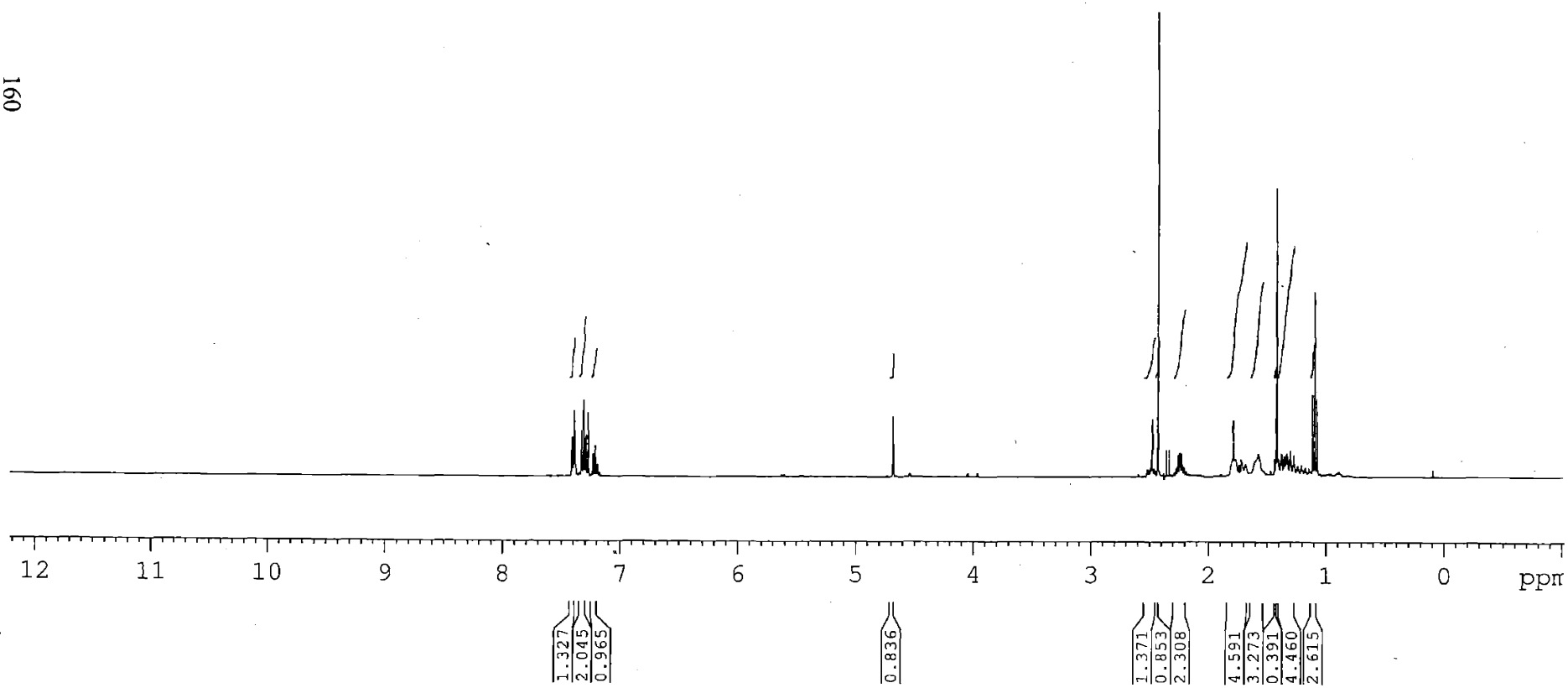
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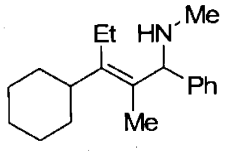
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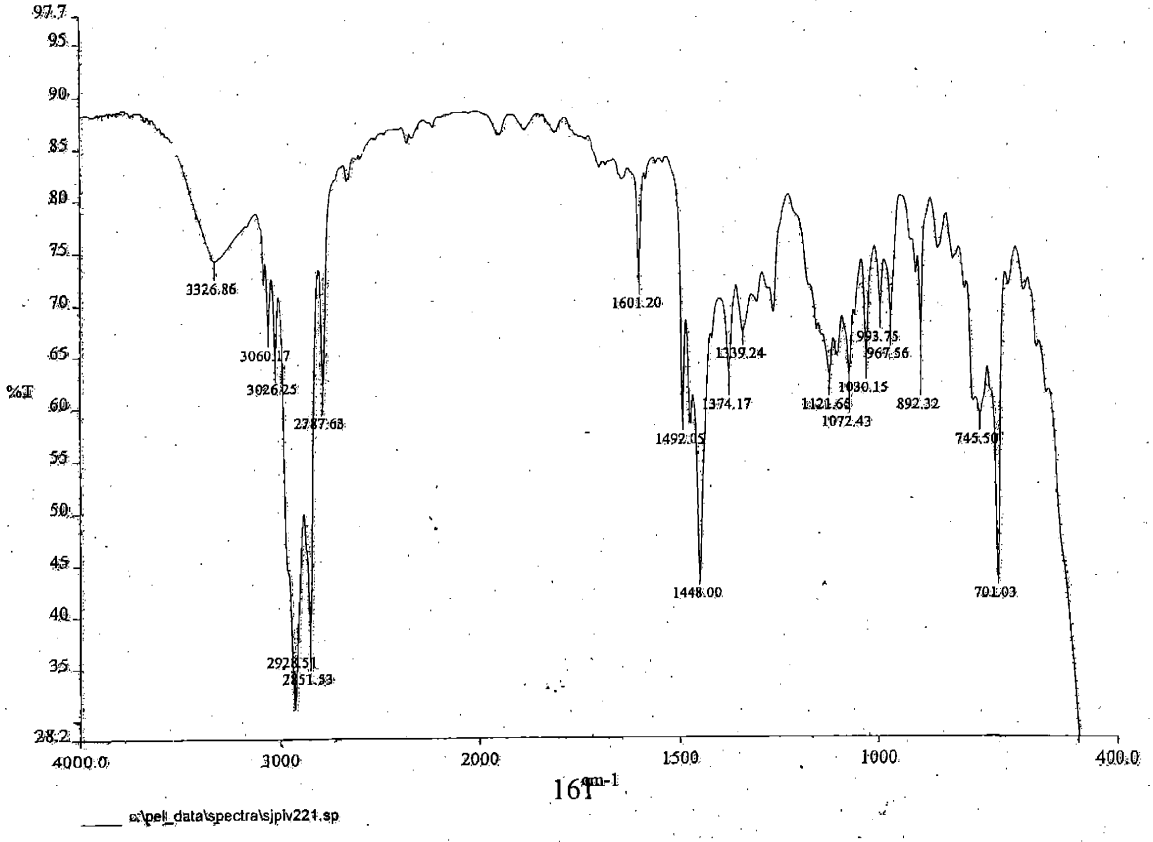
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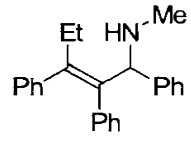
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I-6

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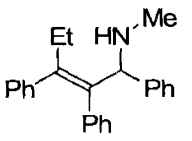
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I-6

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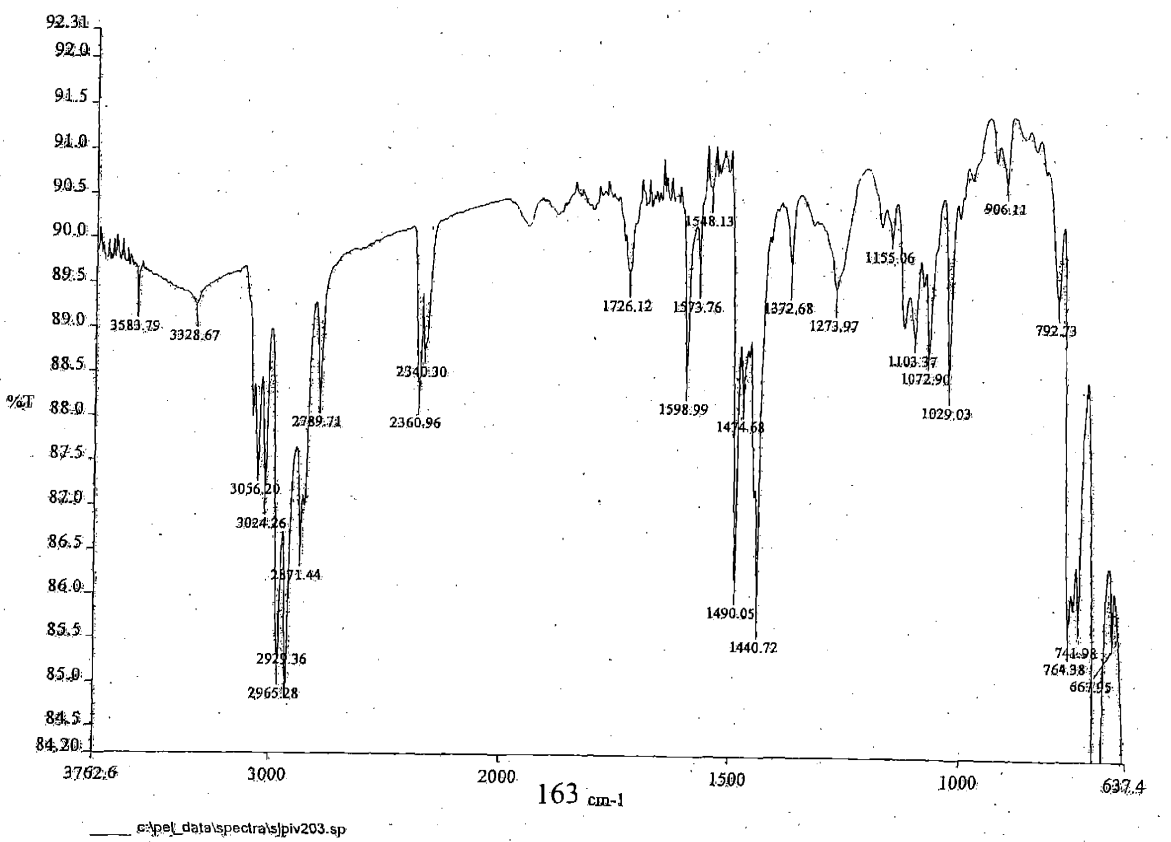
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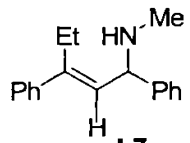
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Ph
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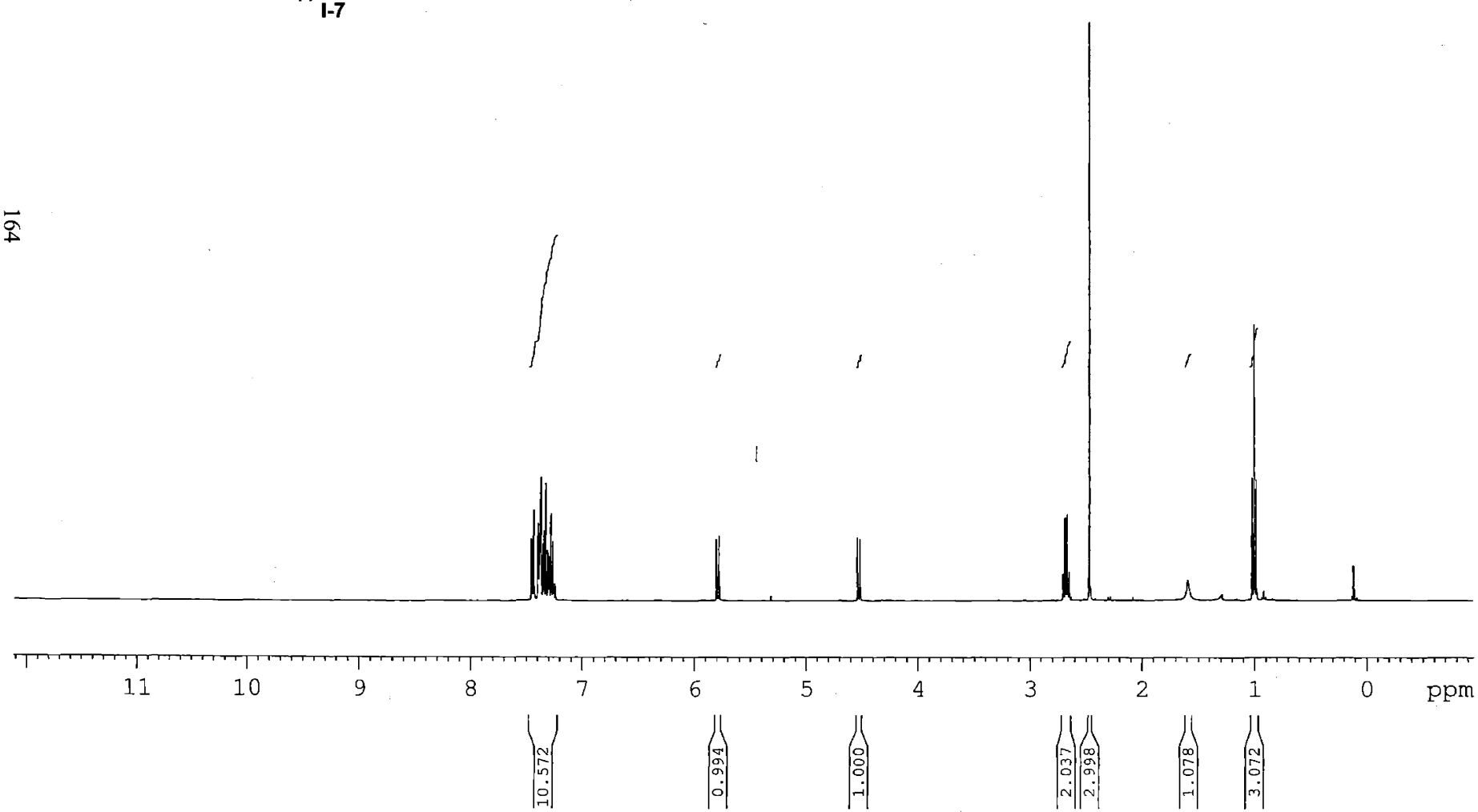
I-7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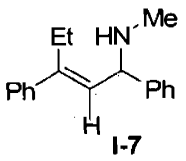
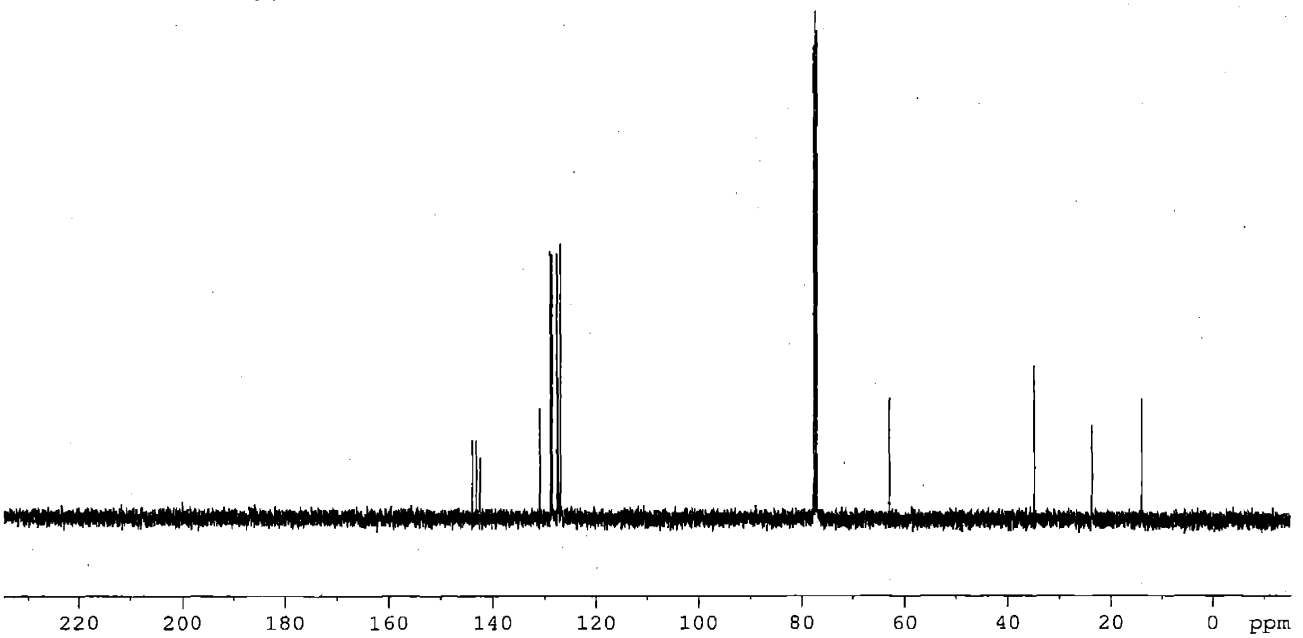
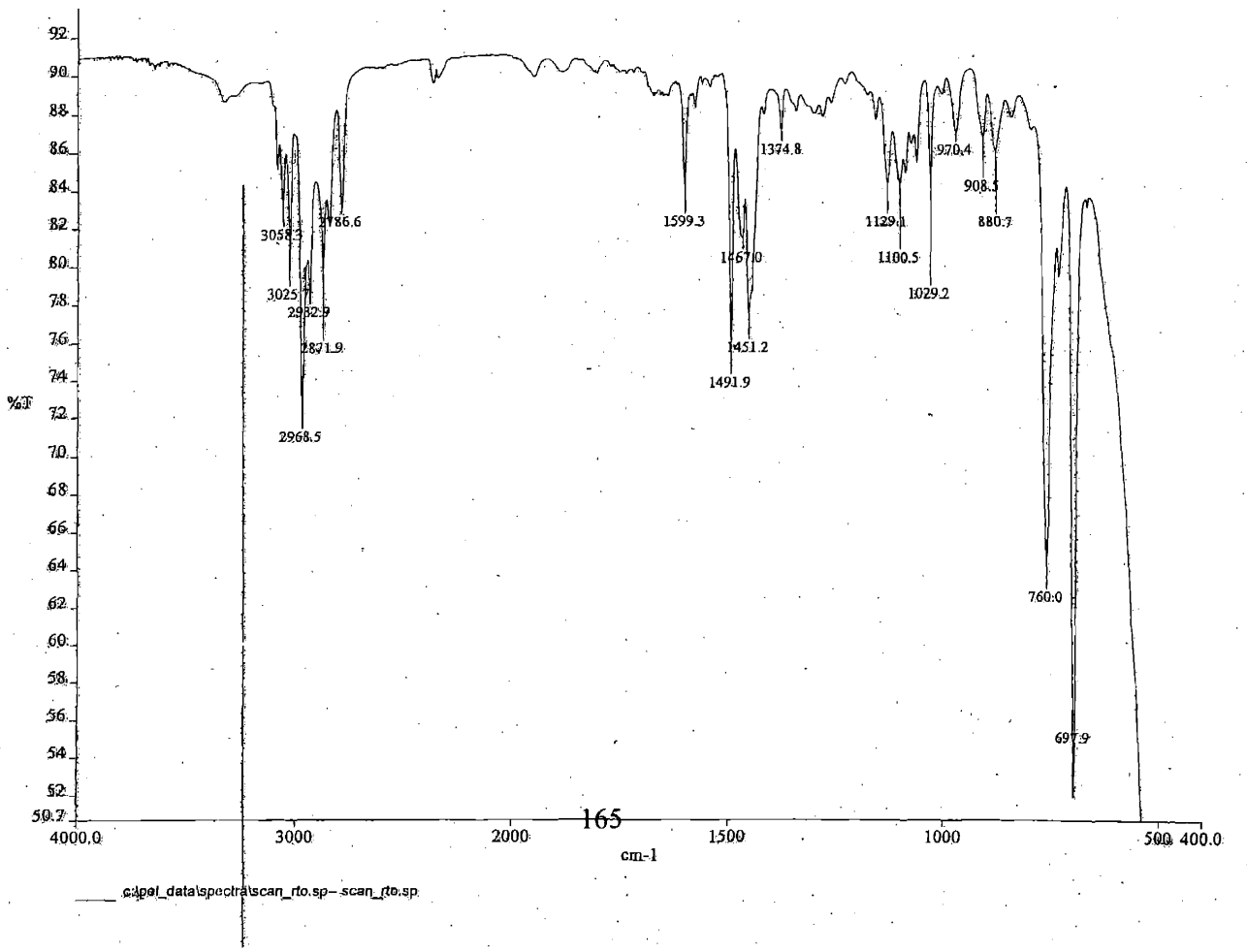
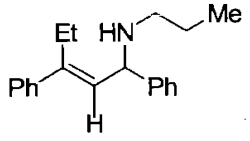
3.072


Et
HN
Me
Ph
Ph
H

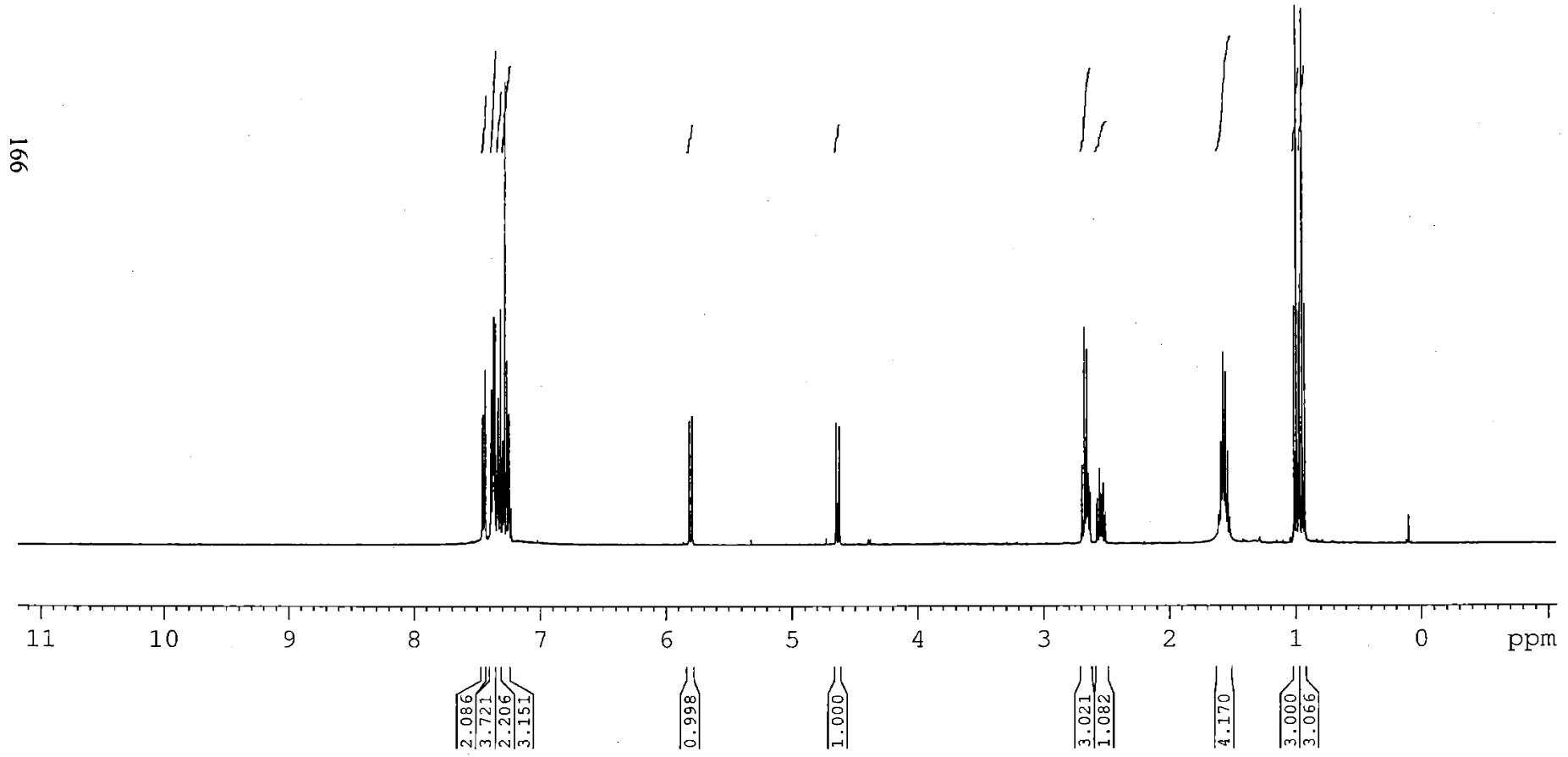
I-7

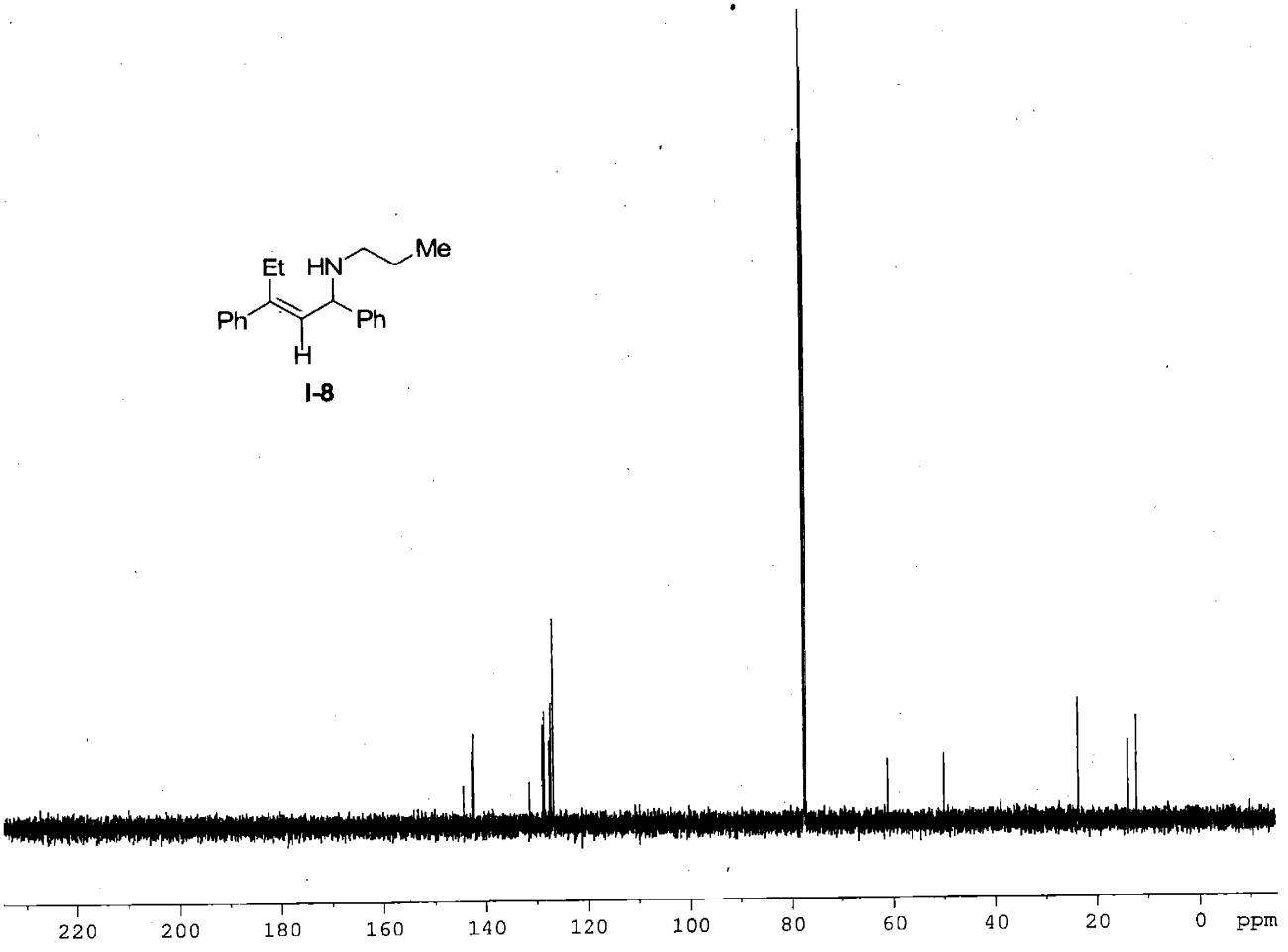

220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3058.3
3025.7
2932.9
2871.9
2968.5
3086.6
1599.3
1491.9
1451.2
1467.0
1374.8
1129.1
1100.5
1029.2
970.4
908.5
880.7
760.0
697.9
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pol_data\spectra\scan_rto.sp - scan_rto.sp

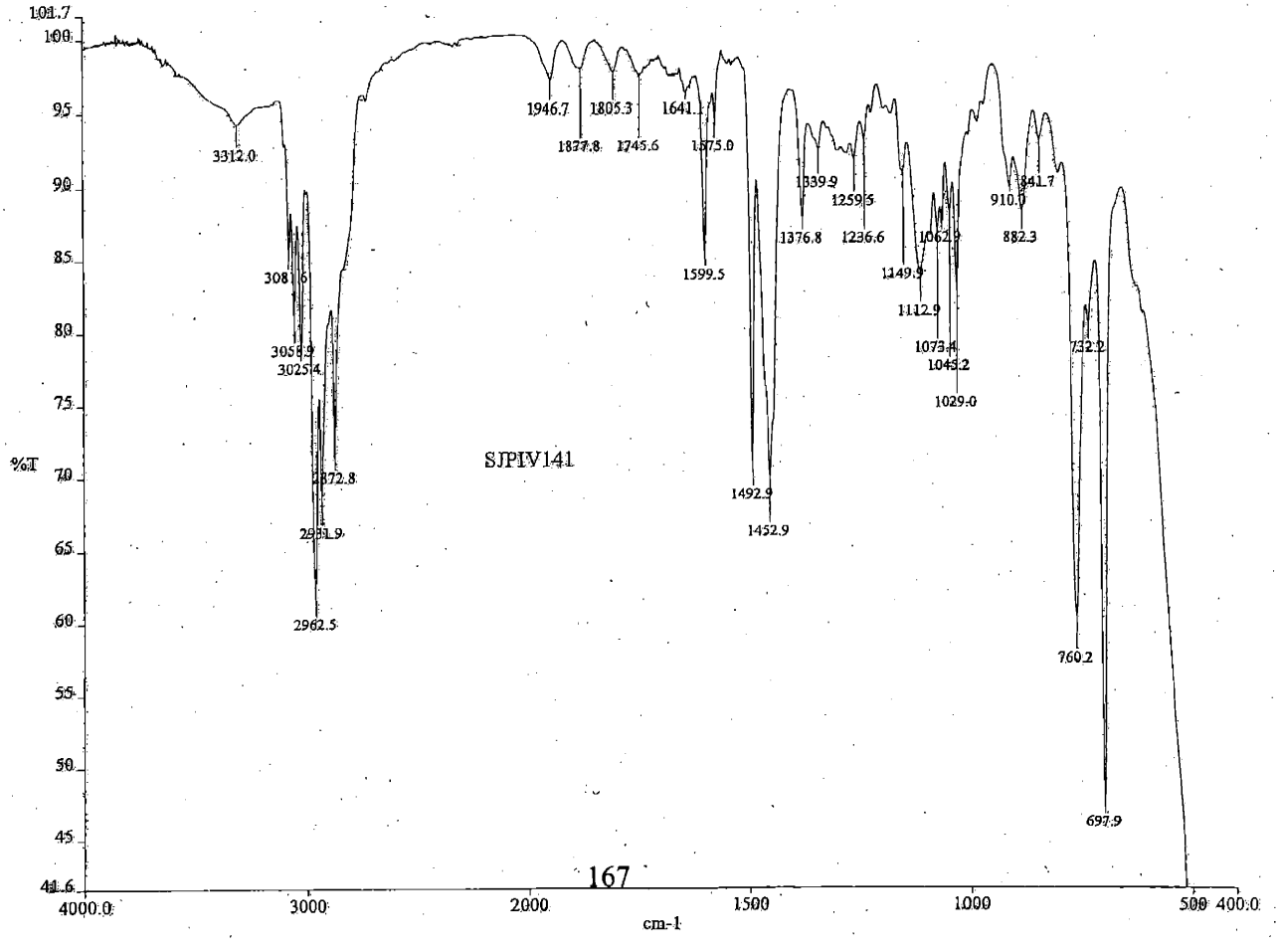

Et
HN
Me
Ph
Ph
H

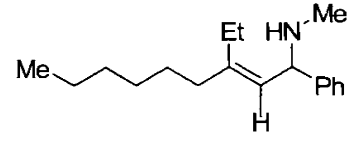
I-8


166
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.086
3.721
2.206
3.151
0.998
1.000
3.021
1.082
4.170
3.000
3.066

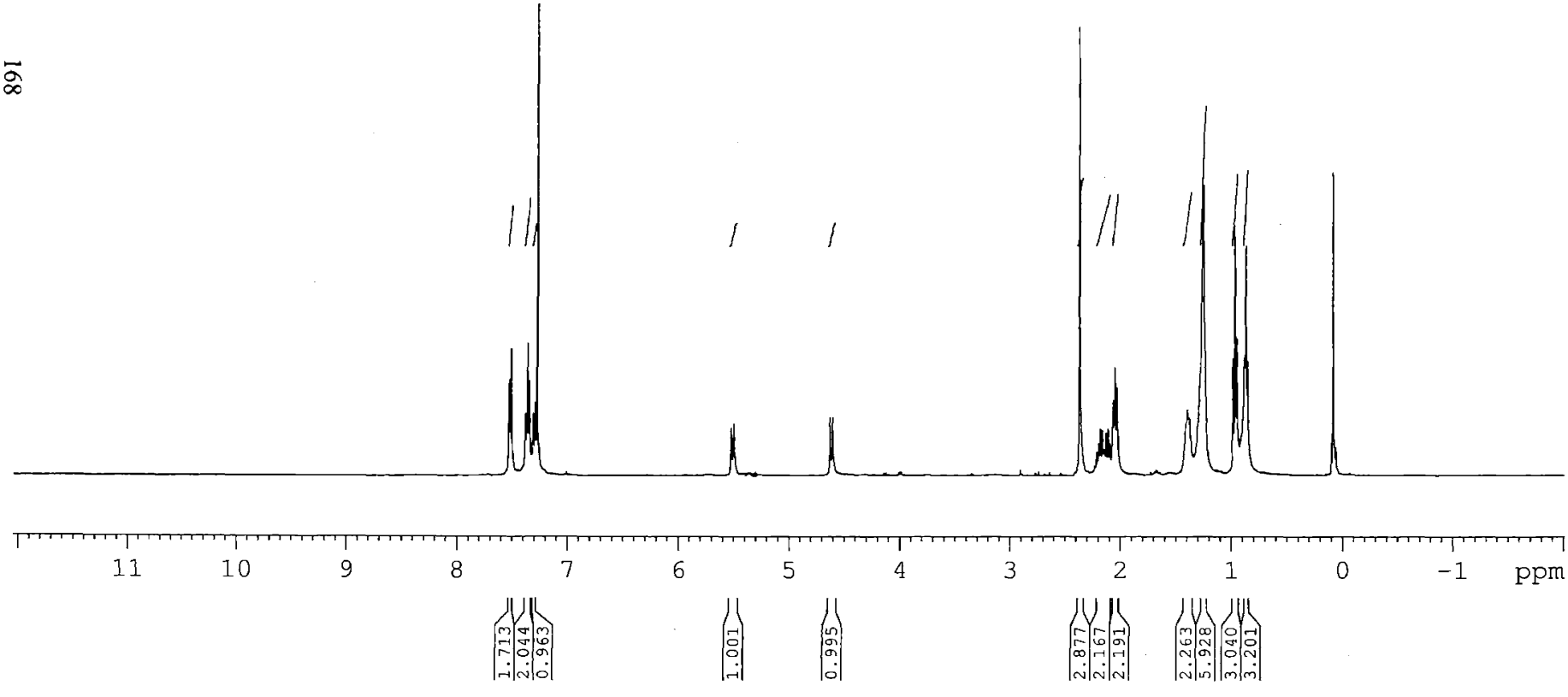

Et
HN
Me
Ph
Ph
H
220
200
180
160
140
120
100
80
60
40
20
0
ppm

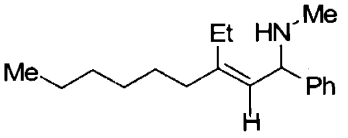
I-8


101.7
100
95
90
85
80
75
70
65
60
55
50
45
41.6
%T
3312.0
3081.6
3058.9
3025.4
2962.5
2931.9
2872.8
1946.7
1877.8
1805.3
1745.6
1641.1
1599.5
1575.0
1492.9
1452.9
1376.8
1339.9
1259.5
1236.6
1149.9
1112.9
1073.4
1045.2
1029.0
1062.9
910.0
882.3
841.7
760.2
732.2
697.9
SJPIV141
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pet_data\spectra\scan_rto.sp - scan_rto.sp


Et
HN
Me
Me
Ph
H

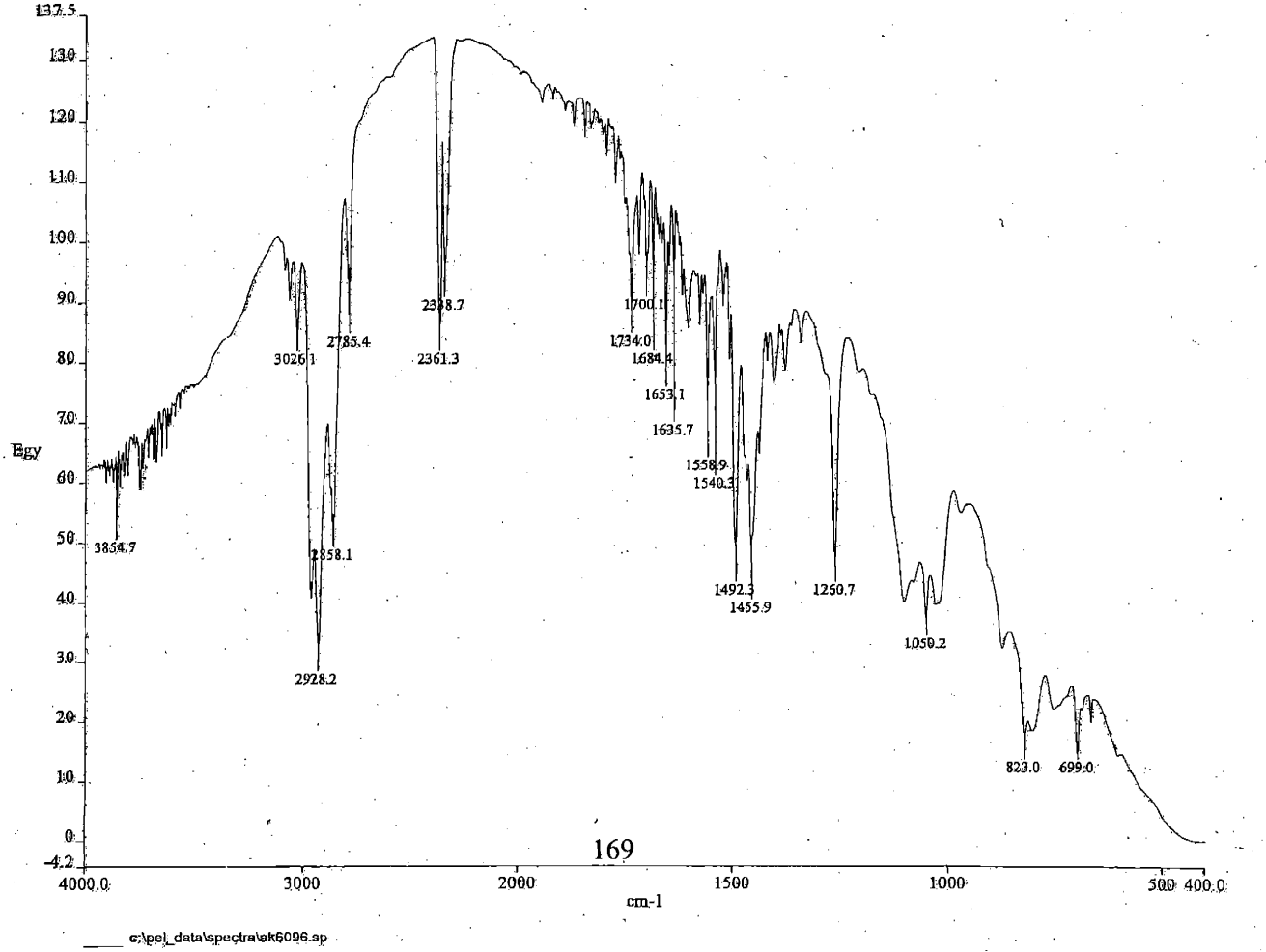
I-10

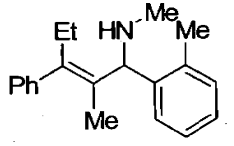

11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.713
2.044
0.963
1.001
0.995
2.877
2.167
2.191
2.263
5.928
3.040
3.201


Et
HN
Me
Me
Ph
H

I-10

150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


137.5
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-4.2
Egy
3854.7
3026.1
2928.2
2858.1
2785.4
2361.3
2338.7
1700.1
1734.0
1684.4
1653.1
1635.7
1558.9
1540.3
1492.3
1455.9
1260.7
1050.2
823.0
699.0
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\ak6096.sp

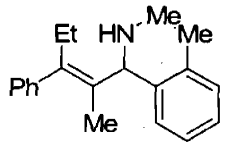


I-11

170

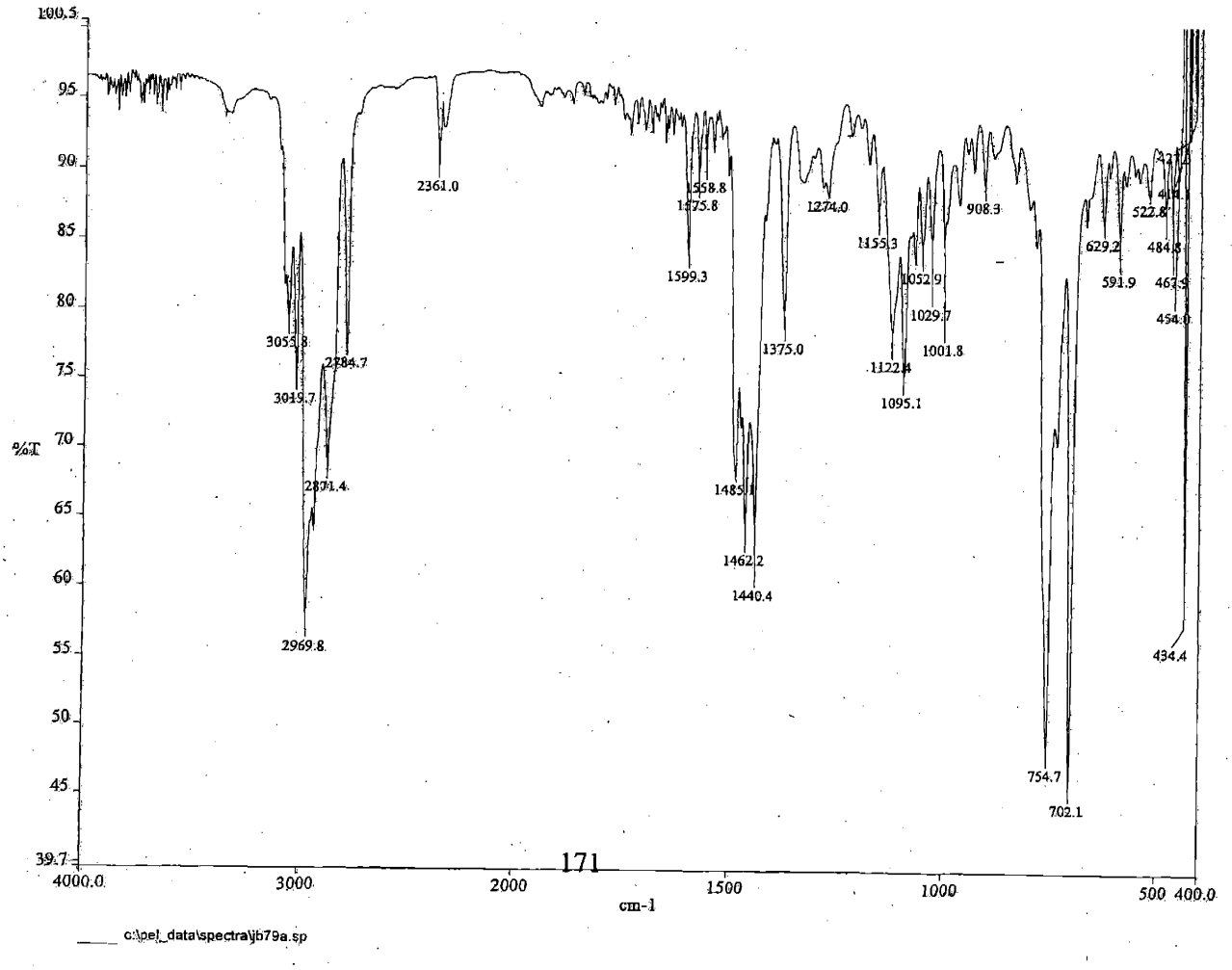
11 10 9 8 7 6 5 4 3 2 1 0 ppm

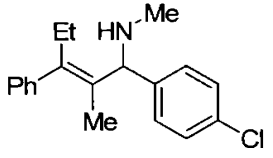
1.001 8.890 1.000 2.123 2.977 2.938 3.014 3.014


Et
HN
Me
Me
Ph
Me

I-11

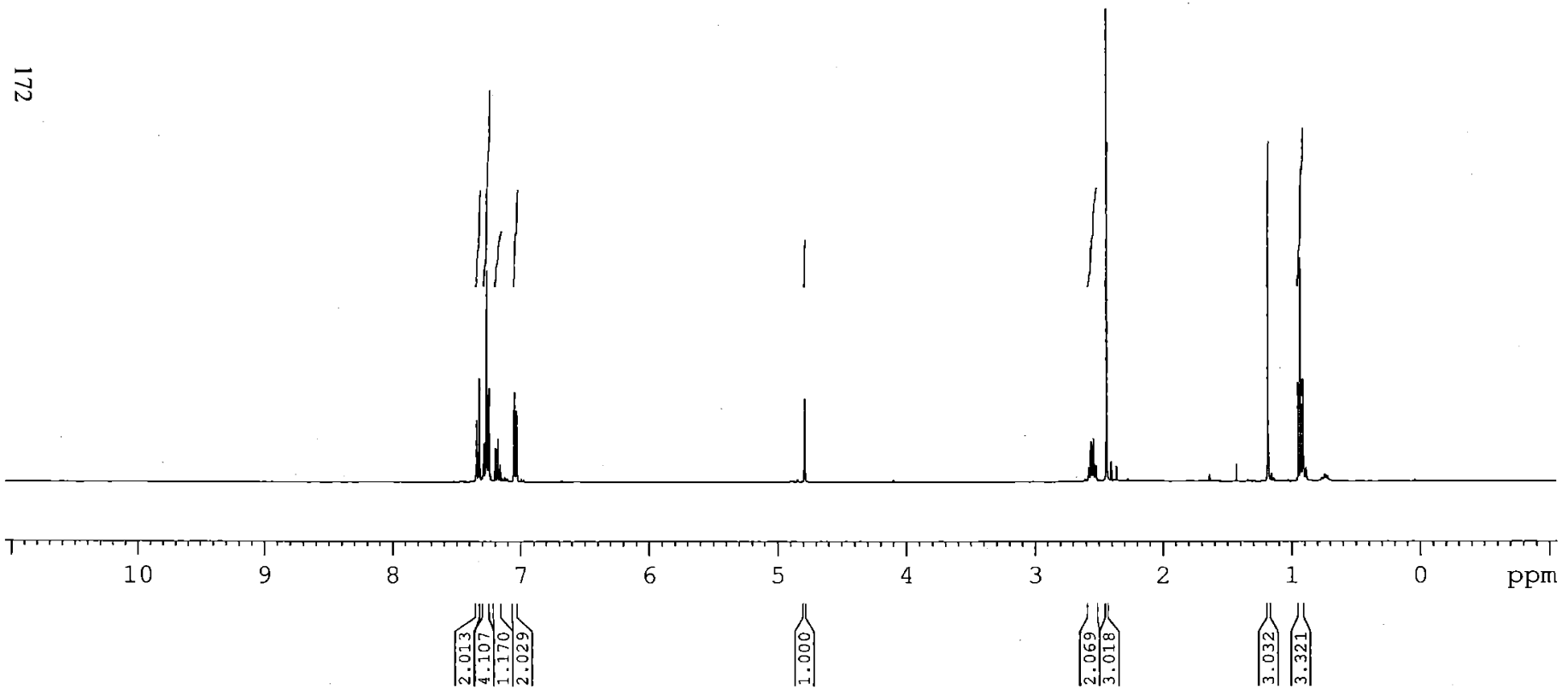
220
200
180
160
140
120
100
80
60
40
20
0
ppm

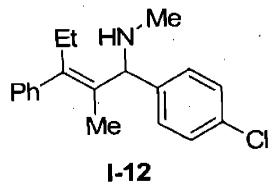

100.5
95
90
85
80
75
70
65
60
55
50
45
39.7
%T
4000.0
3000
2000
1500
1000
500
400.0
cm-1
2361.0
1599.3
1558.8
1375.8
1274.0
1155.3
1122.4
1095.1
1052.9
1029.7
1001.8
908.3
1375.0
1462.2
1440.4
3055.8
3019.7
2969.8
2884.7
2831.4
754.7
702.1
629.2
591.9
522.8
484.8
463.9
454.0
434.4
c:\pe_data\spectra\jb79a.sp


Et
HN
Me
Ph
Me
Cl

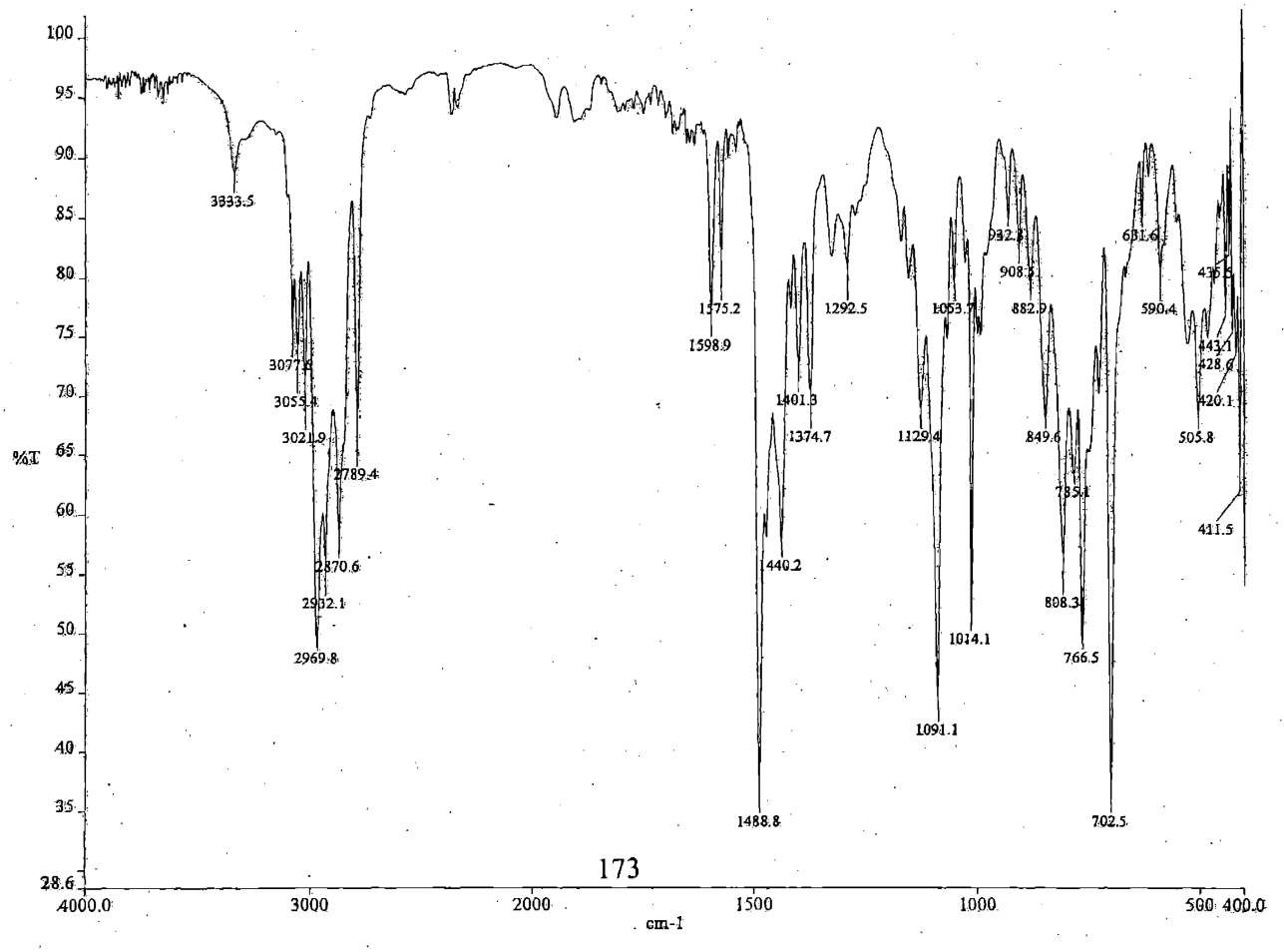
I-12

172

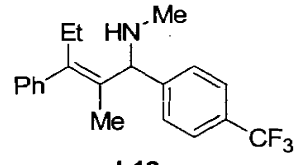

10
9
8
7
6
5
4
3
2
1
0
ppm
2.013
4.107
1.170
2.029
1.000
2.069
3.018
3.032
3.321



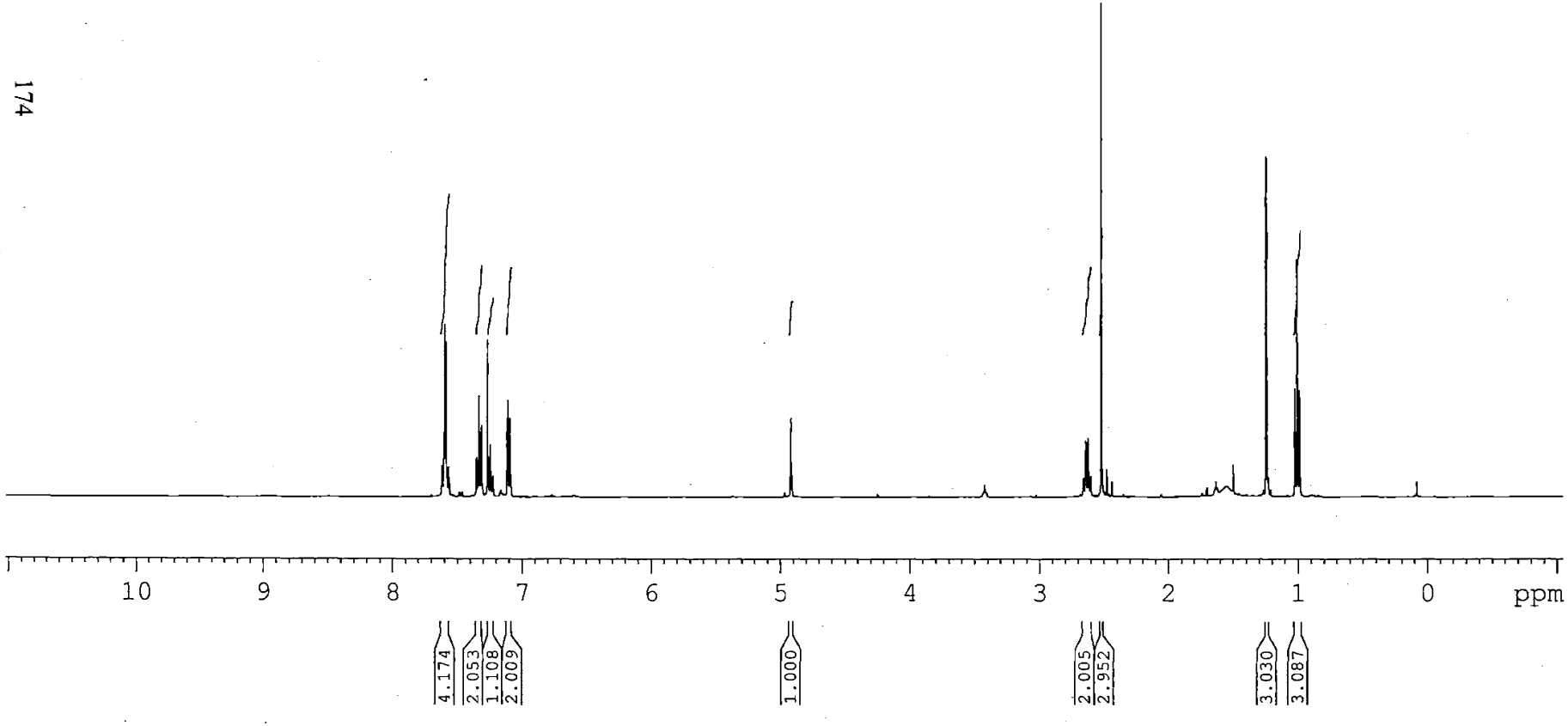
I-12

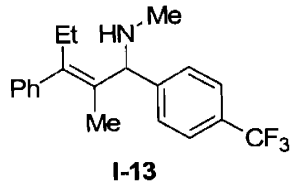


c:\pel_data\spectra\groups\jamison\sjpiv87.sp

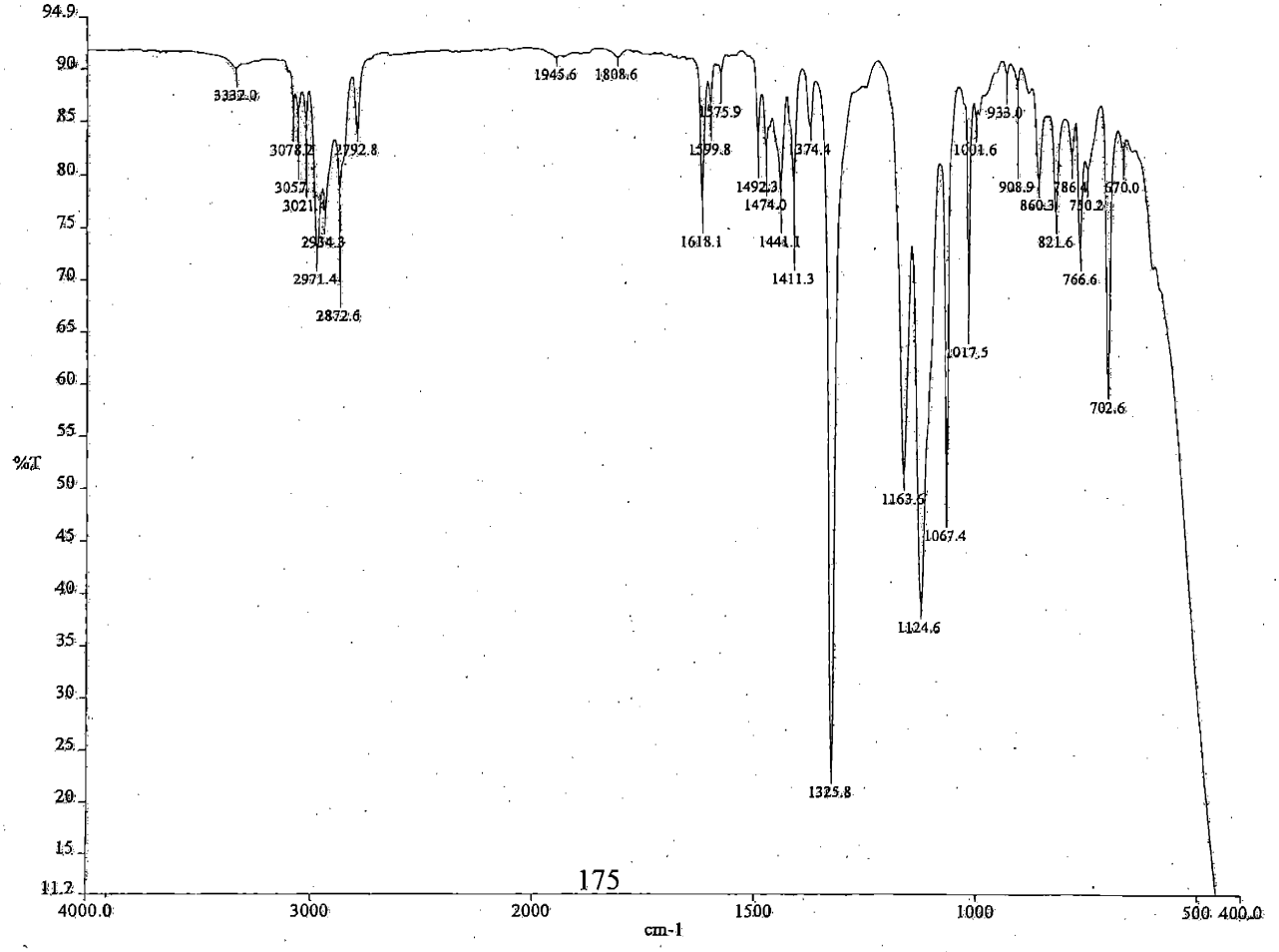

Et
HN
Me
Ph
Me
CF3

I-13

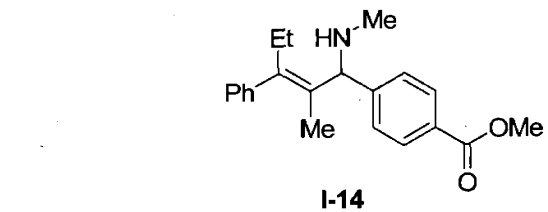

10
9
8
7
6
5
4
3
2
1
0
ppm
4.174
2.053
1.108
2.009
1.000
2.005
2.952
3.030
3.087



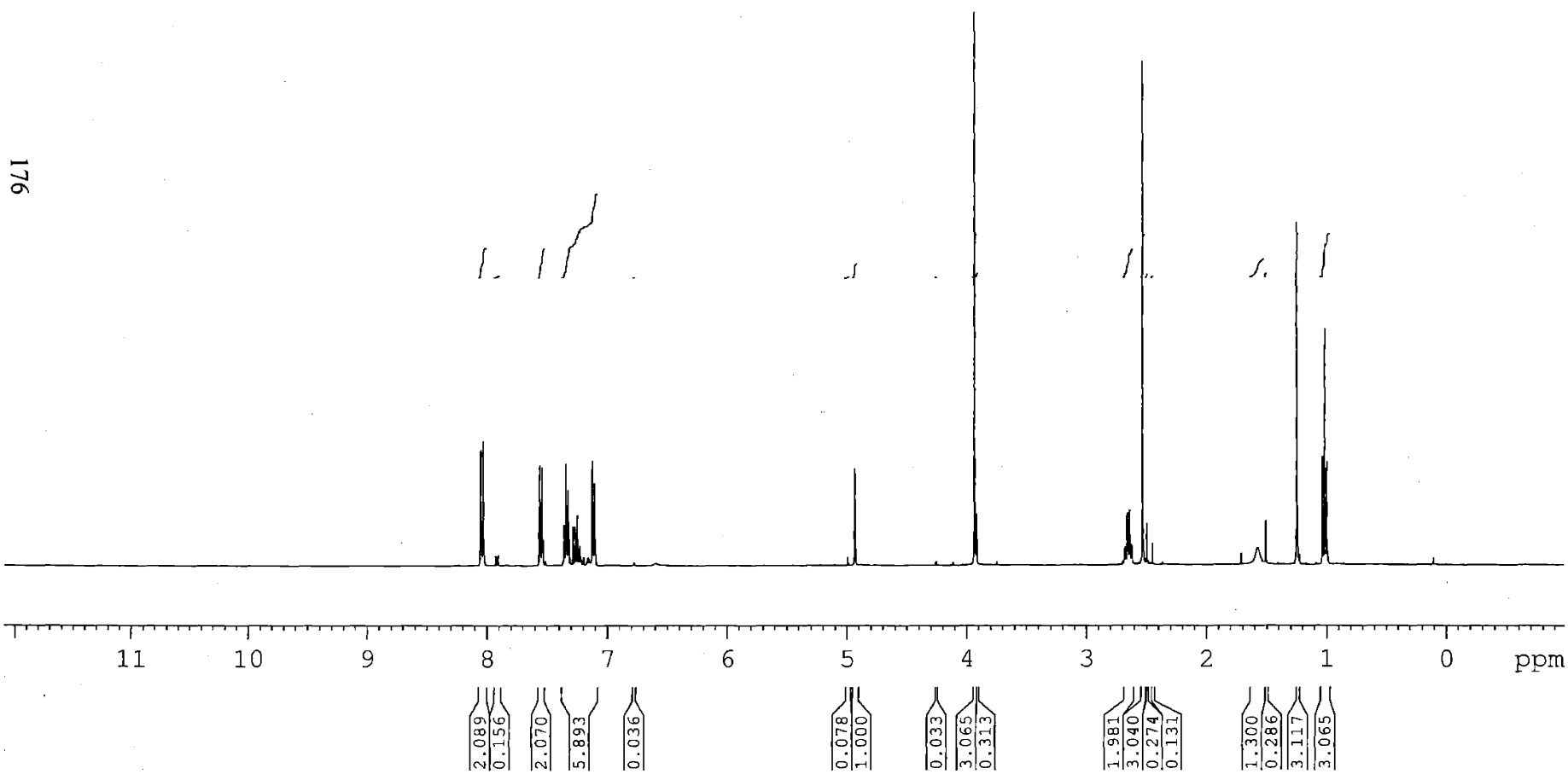
I-13

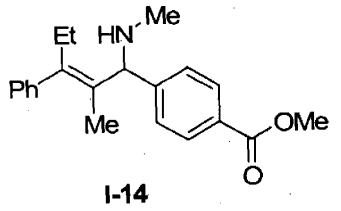


c:\pe_data\spectra\scan_rto.sp - scan_rto.sp

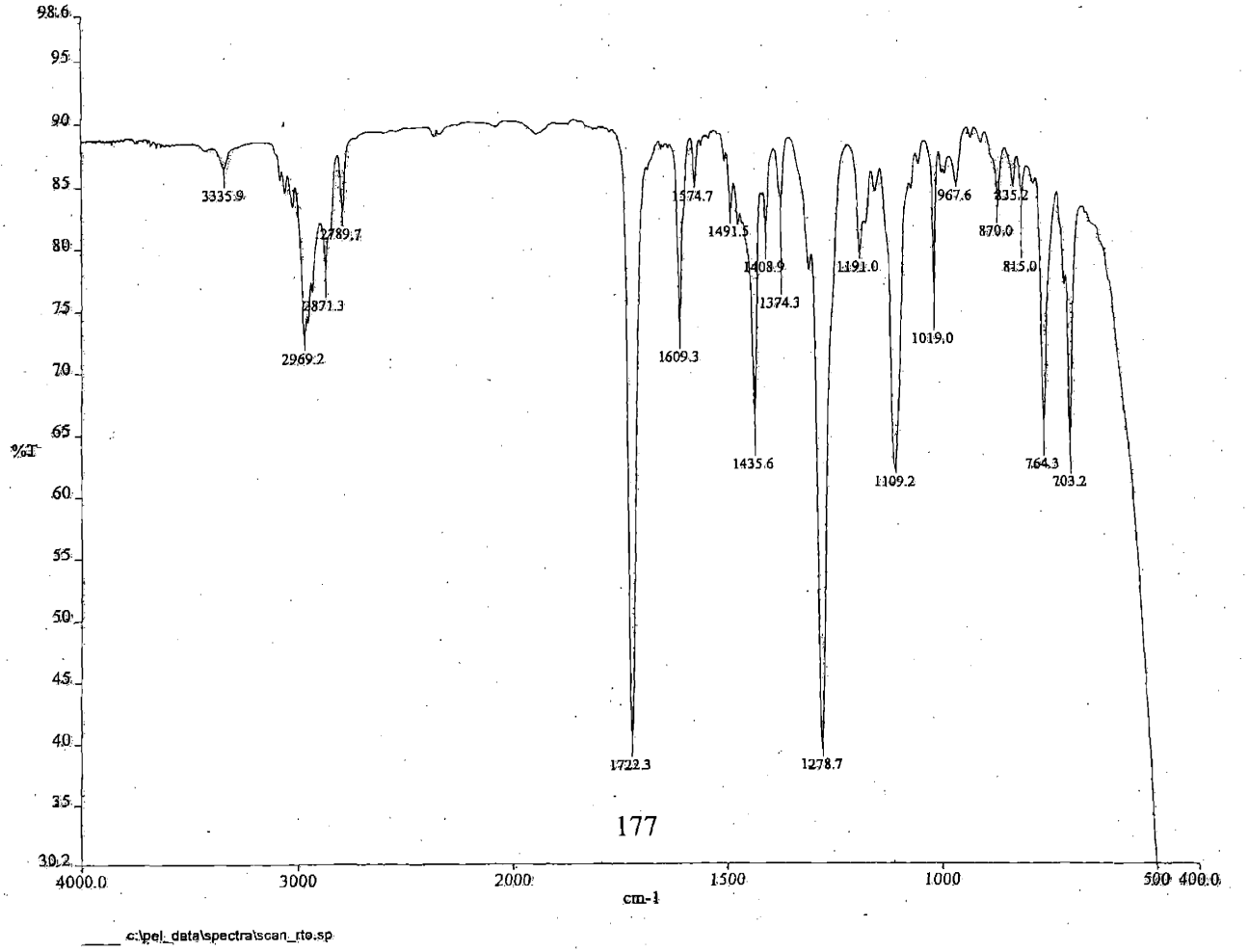

Et
HN
Me
Ph
Me
OMe
O

I-14

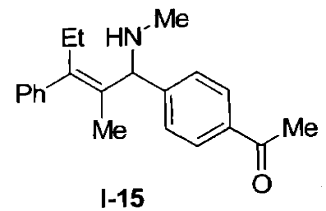

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.089
0.156
2.070
5.893
0.036
0.078
1.000
0.033
3.065
0.313
1.981
3.040
0.274
0.131
1.300
0.286
3.117
3.065



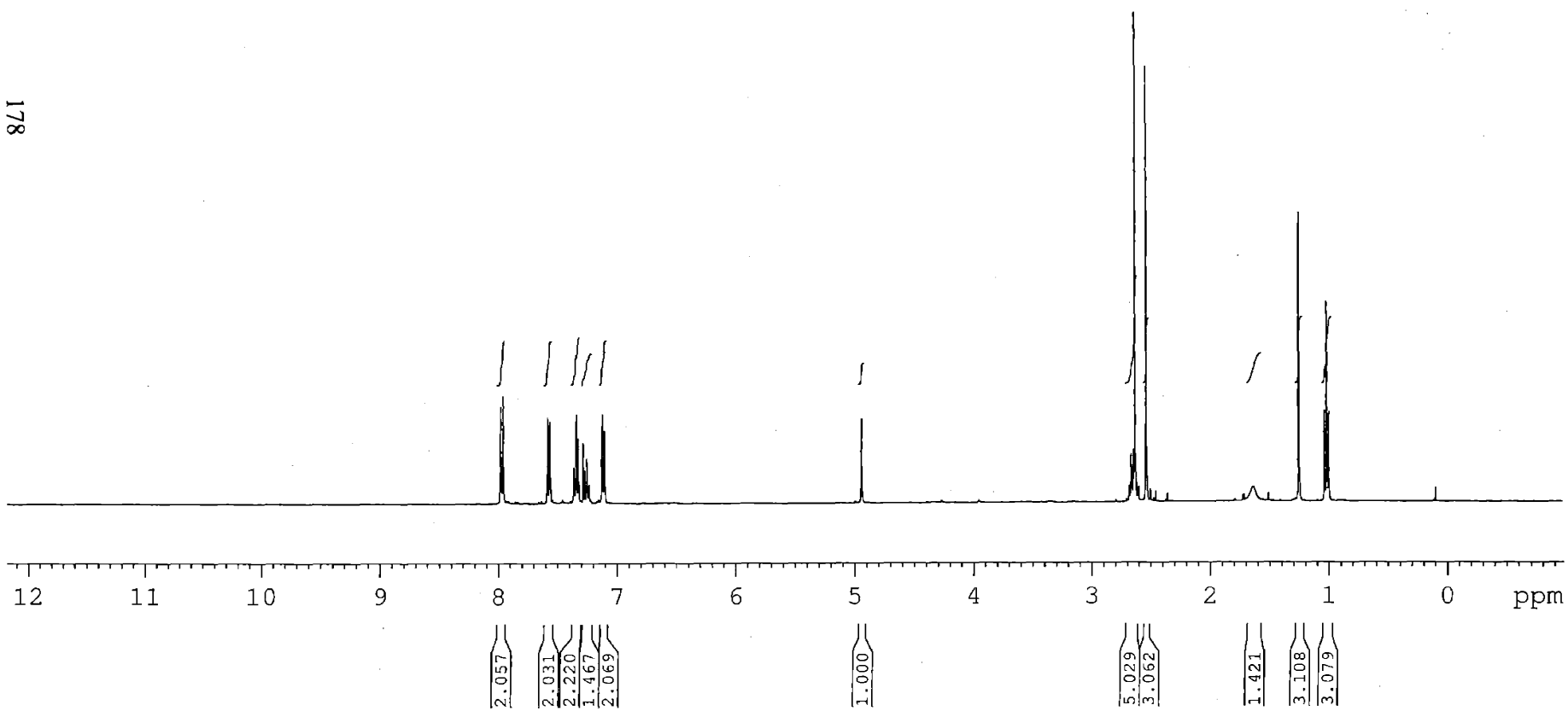
I-14

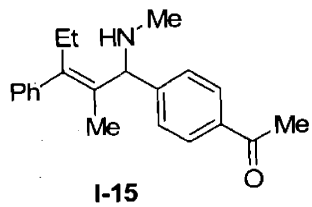


c:\pel_data\spectra\scan_rte.sp


Et
HN
Me
Ph
Me
Me
O

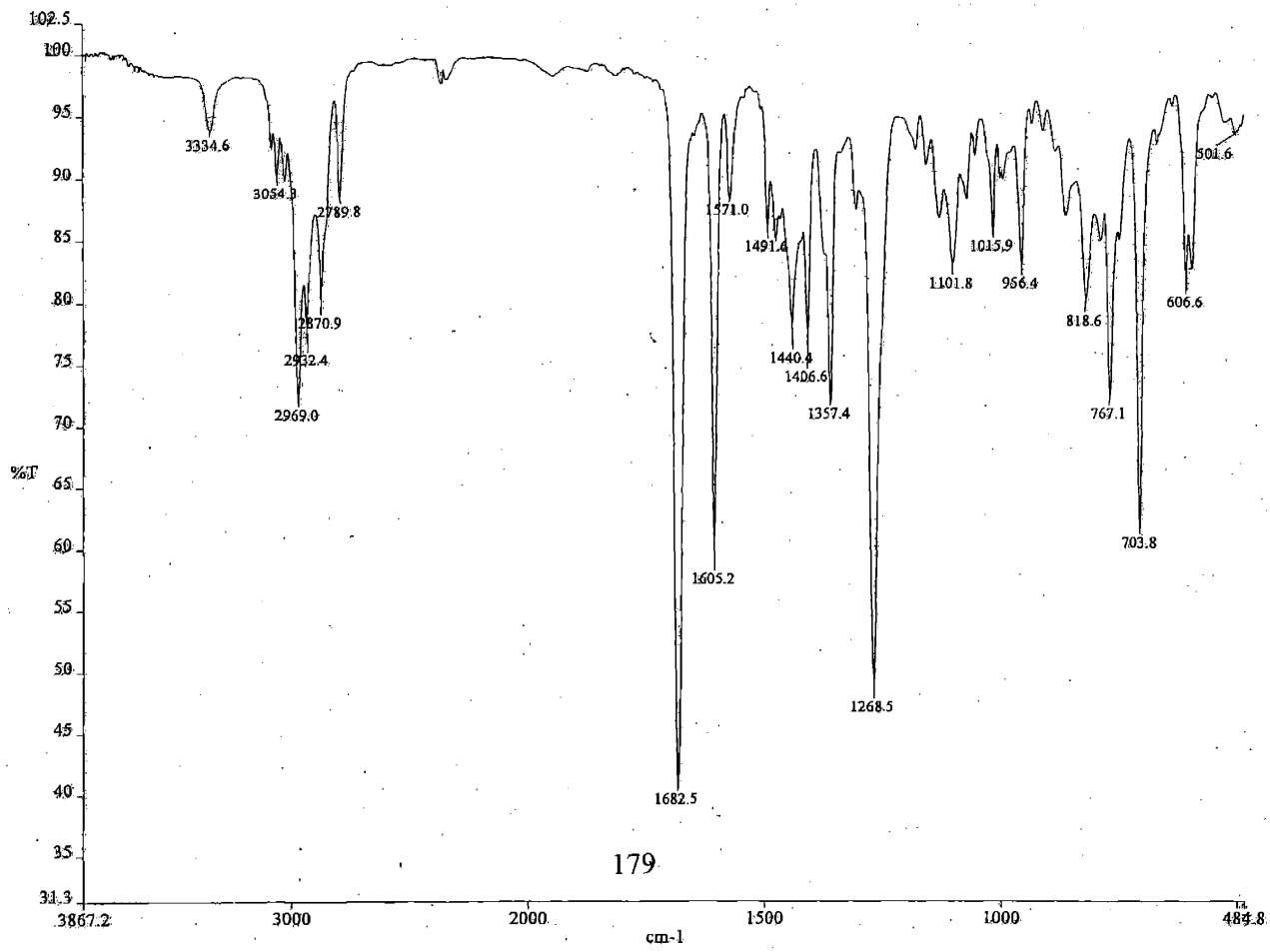
I-15

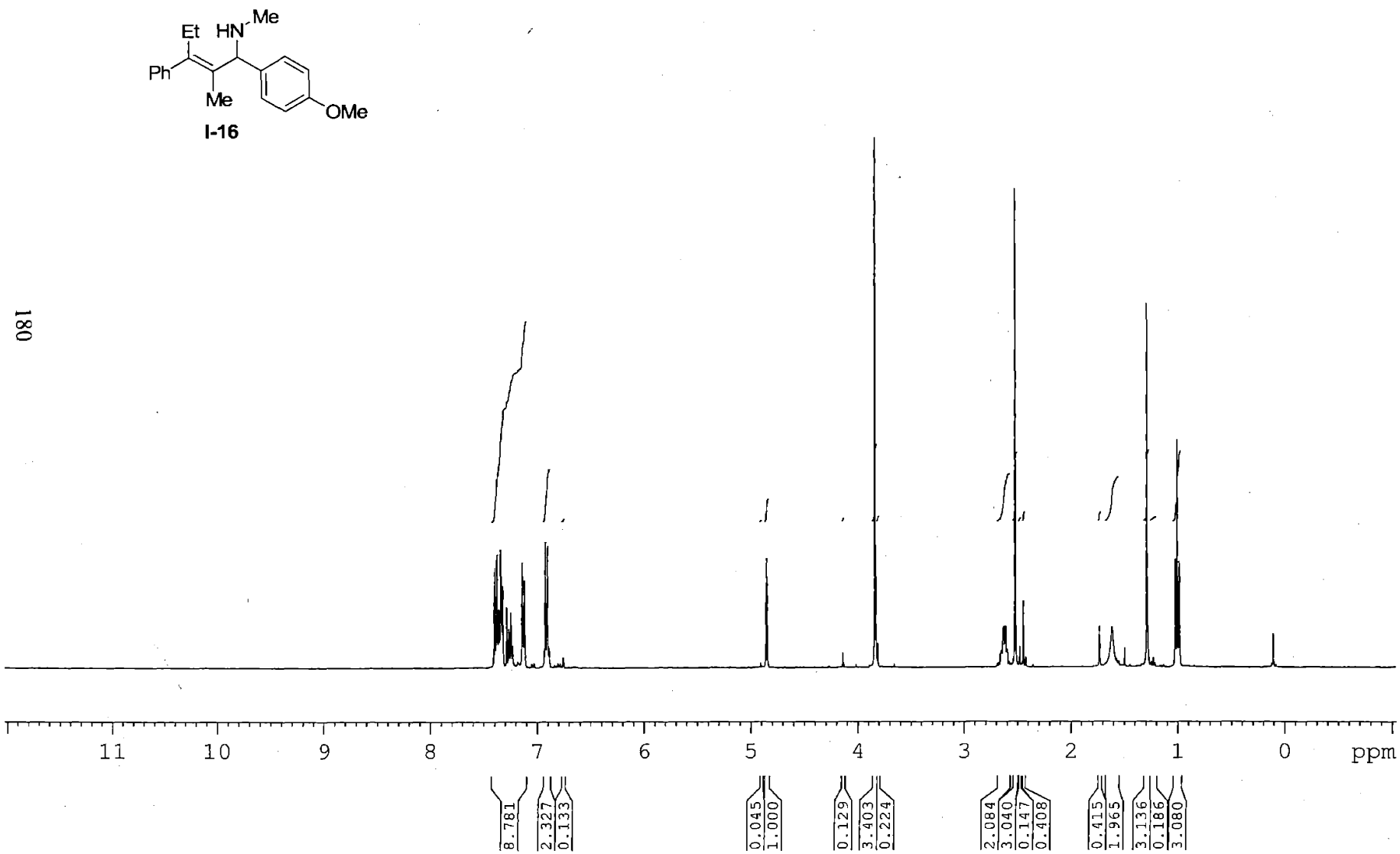

12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.057
2.031
2.220
1.467
2.069
1.000
5.029
3.062
1.421
3.108
3.079

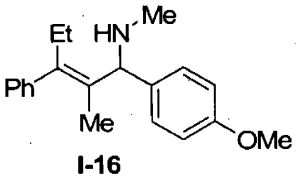

Et
HN
Me
Ph
Me
Me
O

I-15

220
200
180
160
140
120
100
80
60
40
20
0
ppm

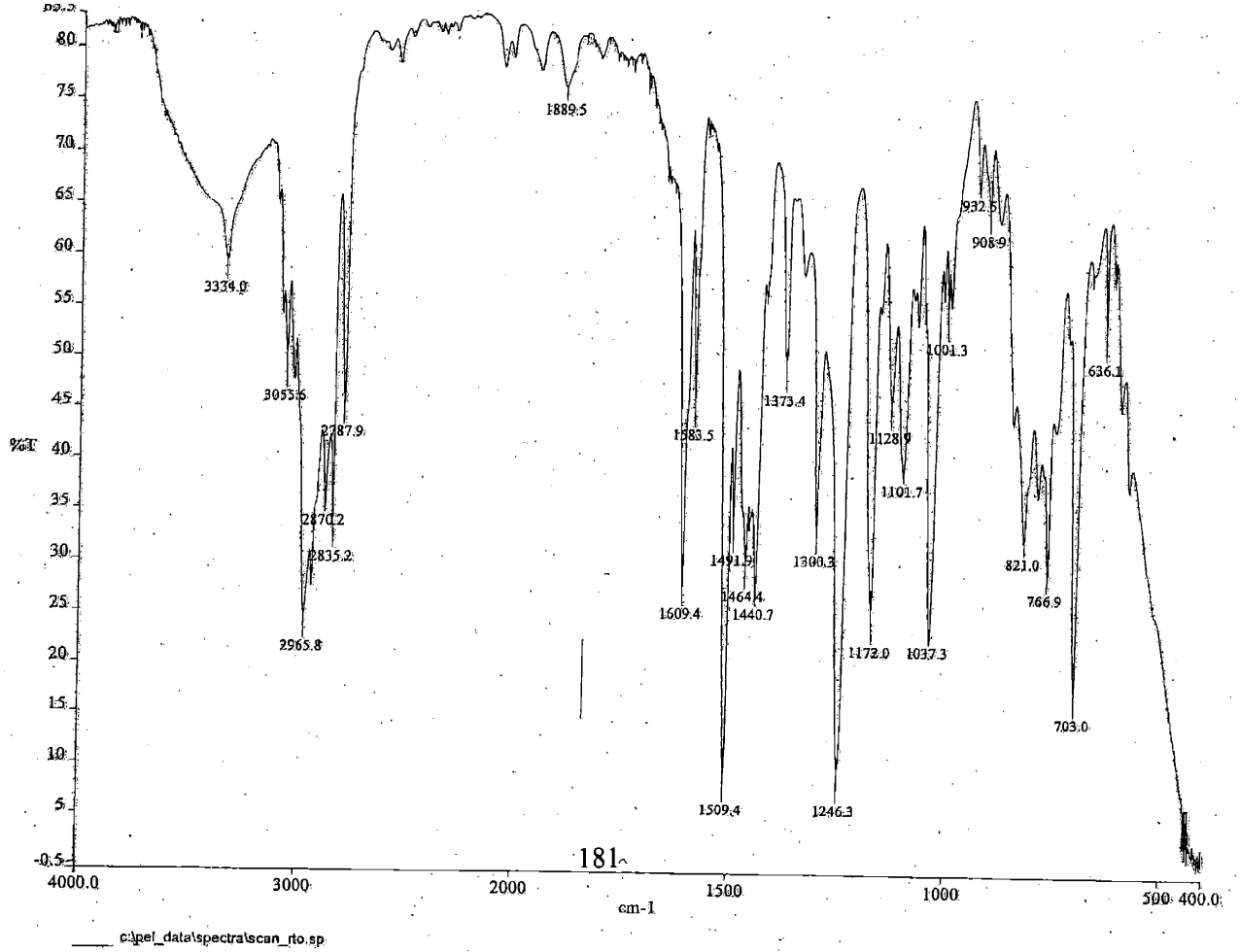

%T
102.5
100
95
90
85
80
75
70
65
60
55
50
45
40
35
31.3
3334.6
3054.3
2932.4
2969.0
2870.9
2789.8
1682.5
1605.2
1571.0
1491.4
1440.4
1406.6
1357.4
1268.5
1101.8
1015.9
956.4
818.6
767.1
703.8
606.6
501.6
3867.2
3000
2000
1500
1000
484.8
cm-1
c:\pel_data\spectra\scan_rto.sp

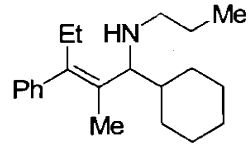

Et
HN
Me
Ph
Me
OMe
I-16
180
11
10
9
8
7
6
5
4
3
2
1
0
ppm
8.781
2.327
0.133
0.045
1.000
0.129
3.403
0.224
2.084
3.040
0.147
0.408
0.415
1.965
3.136
0.186
3.080


Et
HN
Me
Ph
Me
OMe

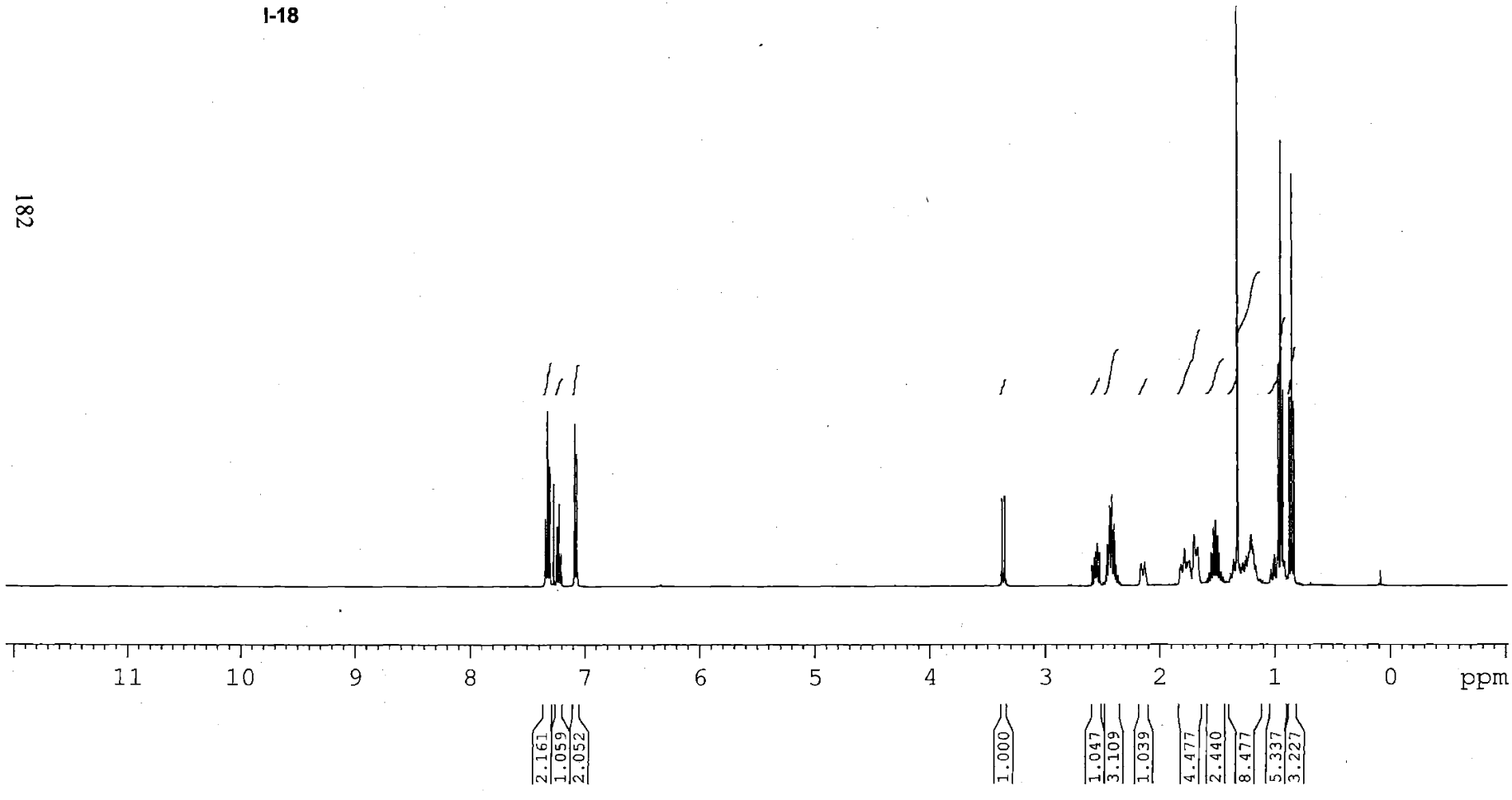
I-16

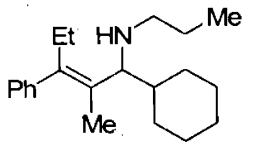
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3334.0
3055.6
2965.8
2870.2
2835.2
2787.9
1889.5
1609.4
1583.5
1509.4
1491.9
1464.4
1440.7
1373.4
1300.3
1246.3
1172.0
1128.9
1101.7
1037.3
1001.3
932.5
908.9
821.0
766.9
703.0
636.1
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\scan_rto.sp


Et
HN
Me
Ph
Me

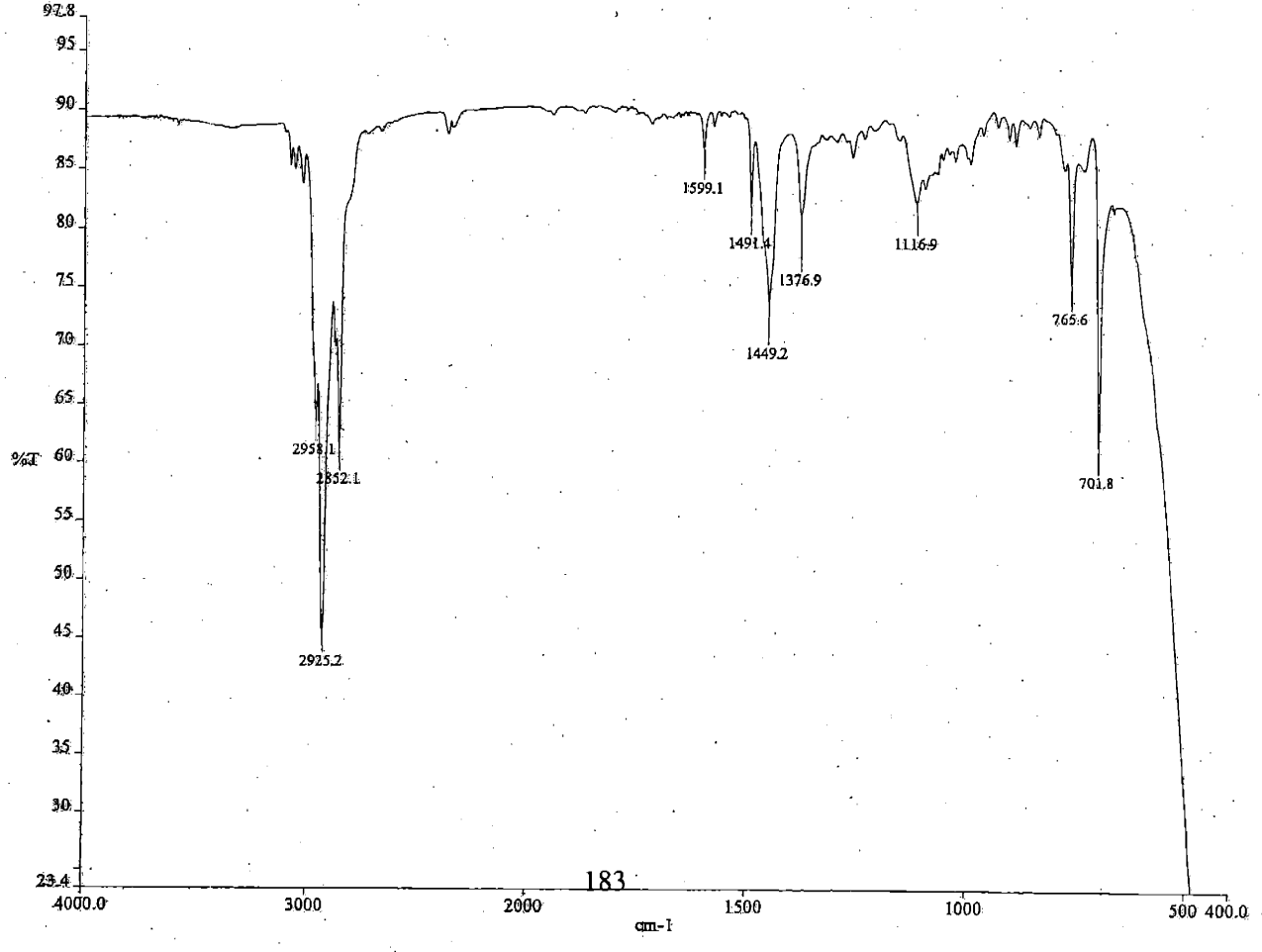
I-18

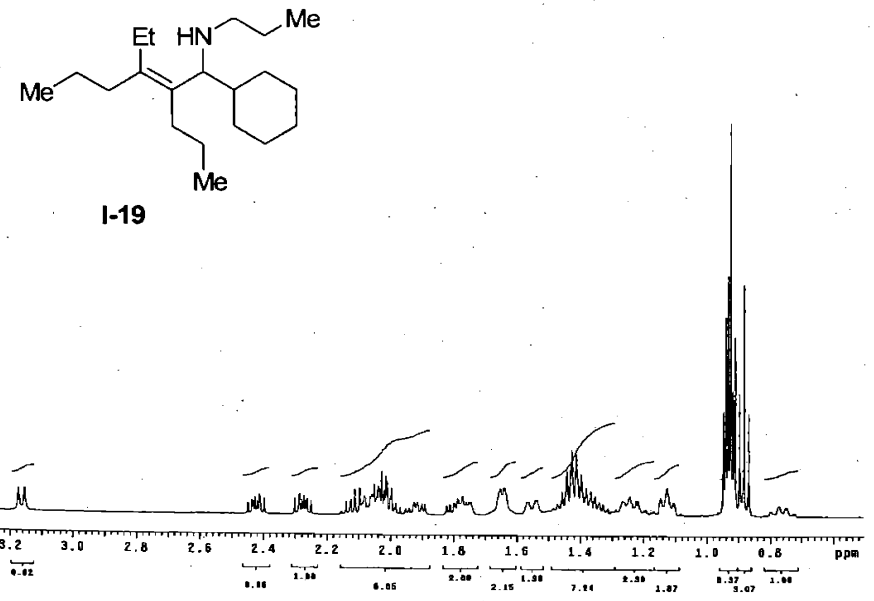

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.161
1.059
2.052
1.000
1.047
3.109
1.039
4.477
2.440
8.477
5.337
3.227


Et
HN
Me
Ph
Me

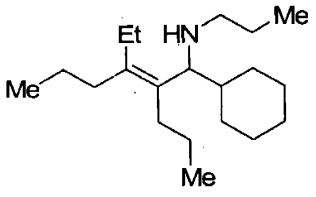
I-18

220
200
180
160
140
120
100
80
60
40
20
0
ppm

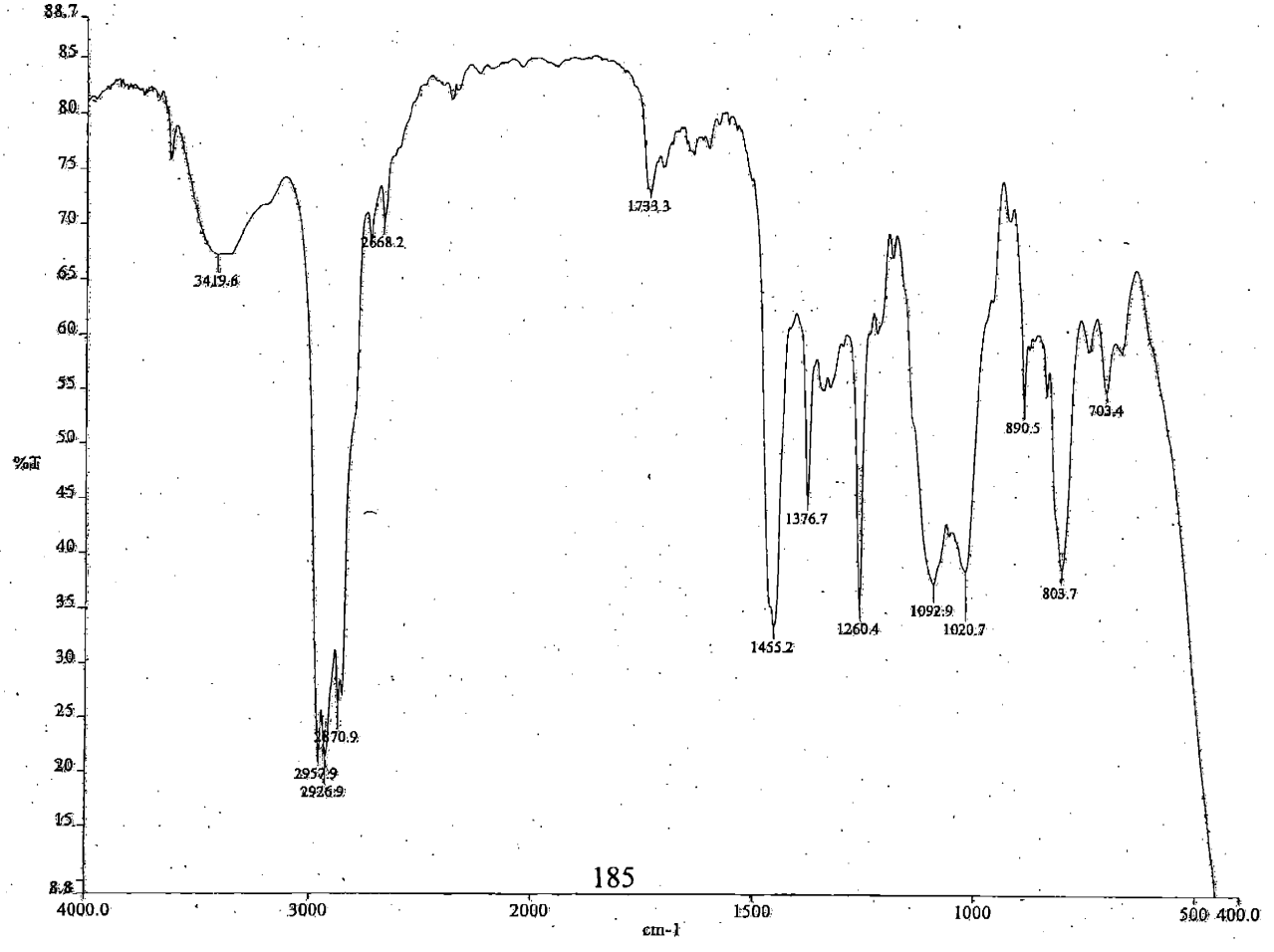

97.8
95
90
85
80
75
70
65
60
55
50
45
40
35
30
23.4
%T
2958.1
2852.1
2925.2
1599.1
1491.4
1449.2
1376.9
1116.9
765.6
701.8
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\scan_rto.sp



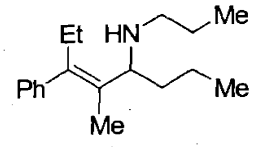
I-19



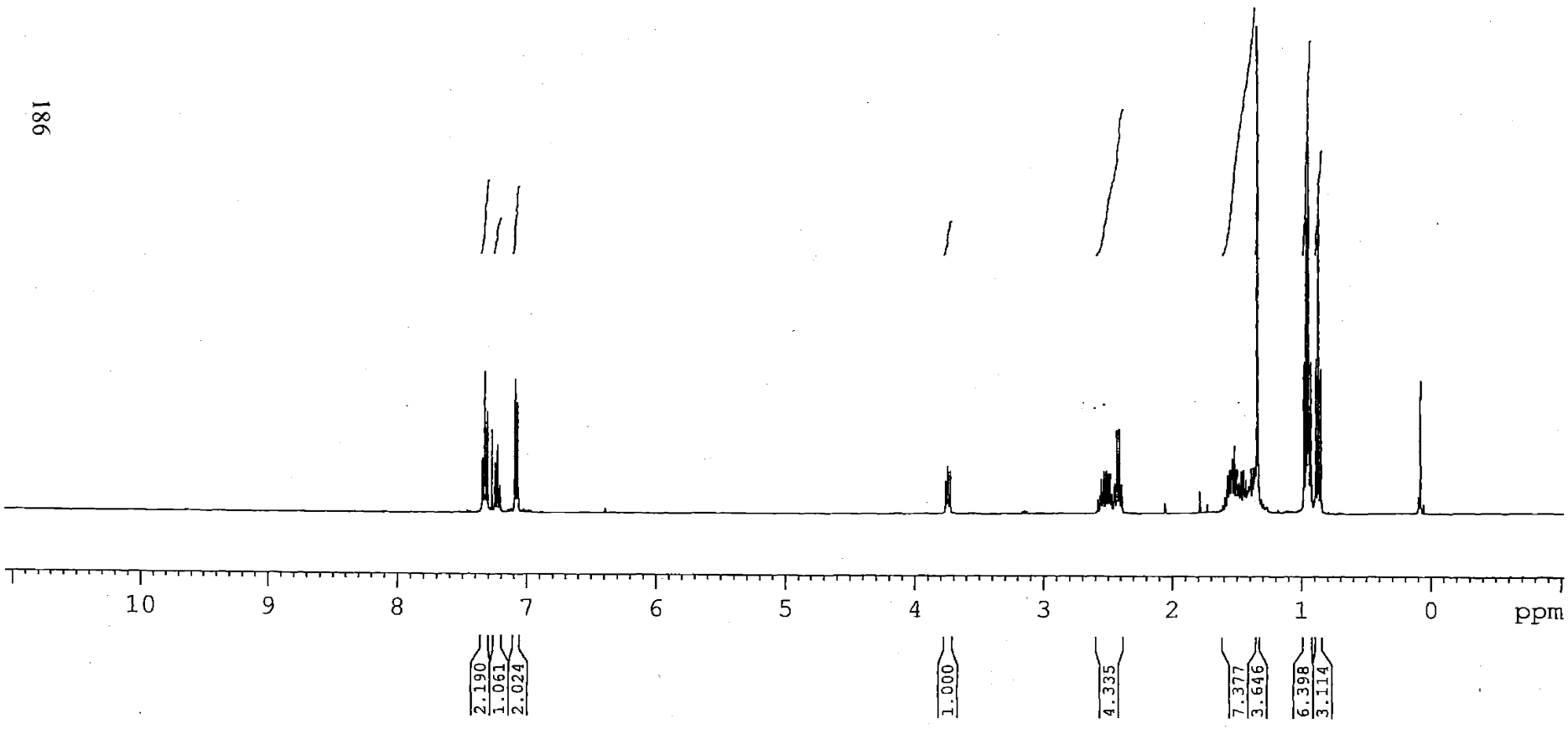
I-19

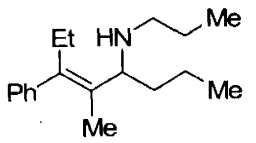


c:\pel_data\spectra\scan_rto.sp

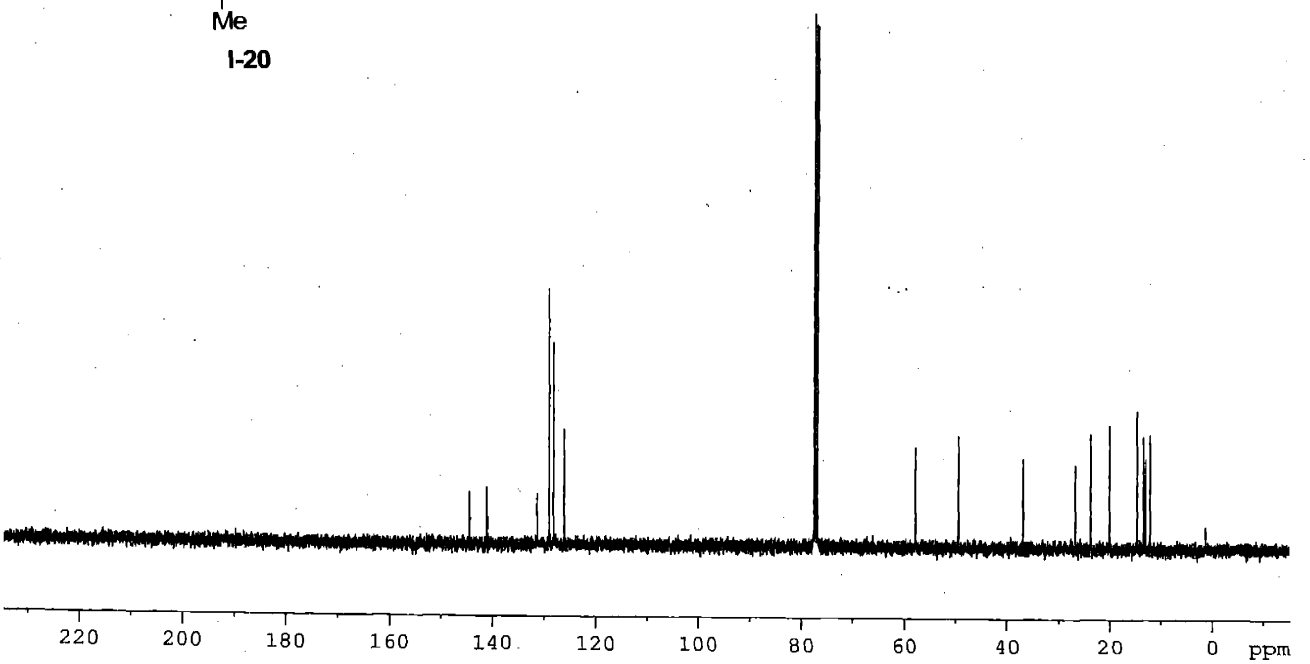

Et
HN
Me
Ph
Me
Me

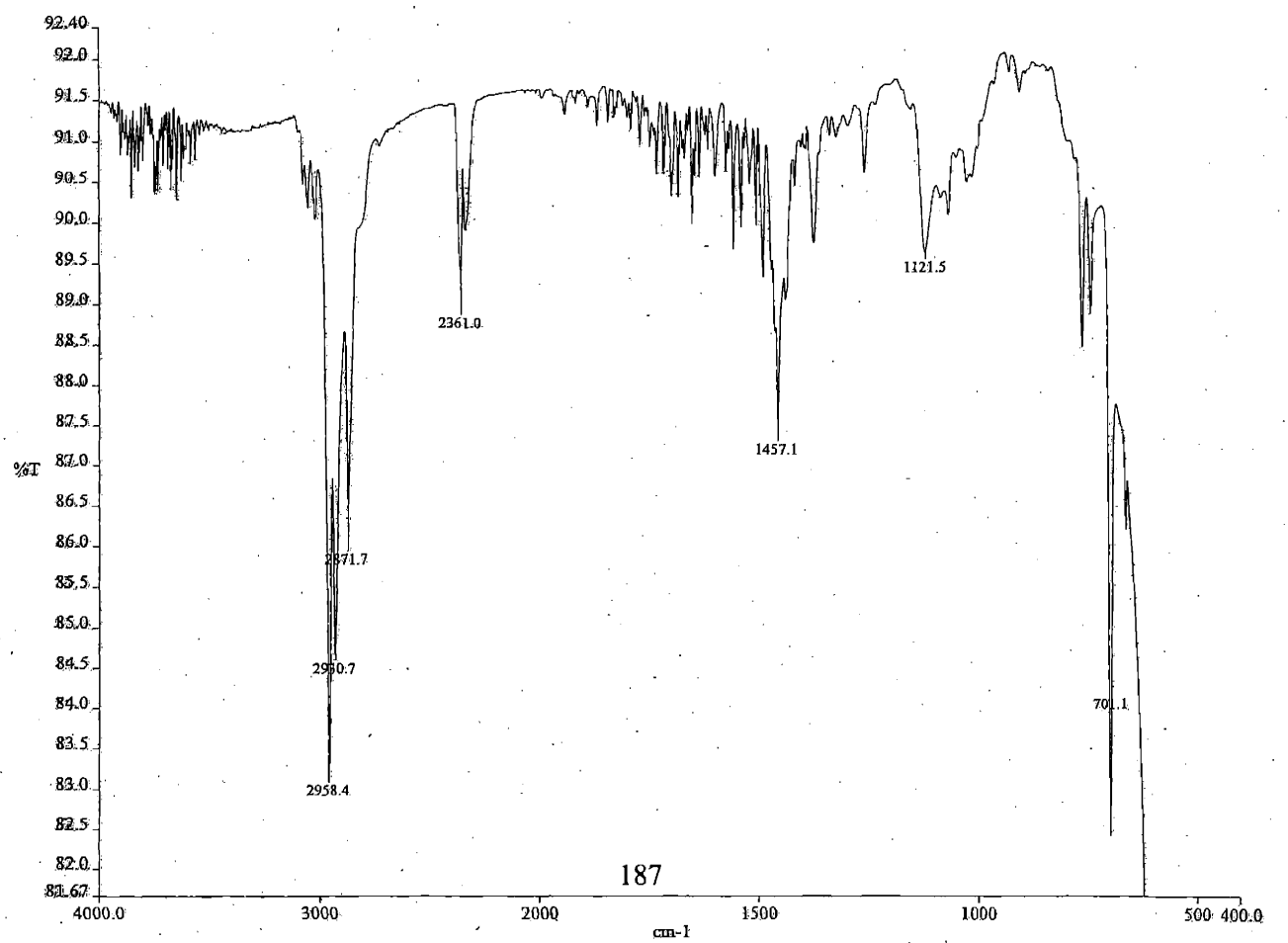
I-20

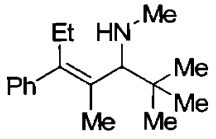

10
9
8
7
6
5
4
3
2
1
0
ppm
2.190
1.061
2.024
1.000
4.335
7.377
3.646
6.398
3.114


Et
HN
Me
Ph
Me
Me

I-20

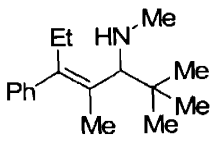

220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
2871.7
2960.7
2958.4
2361.0
1457.1
1121.5
701.1
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\scan_rto.sp - scan_rto.sp


Et
HN
Me
Ph
Me
Me
Me
Me

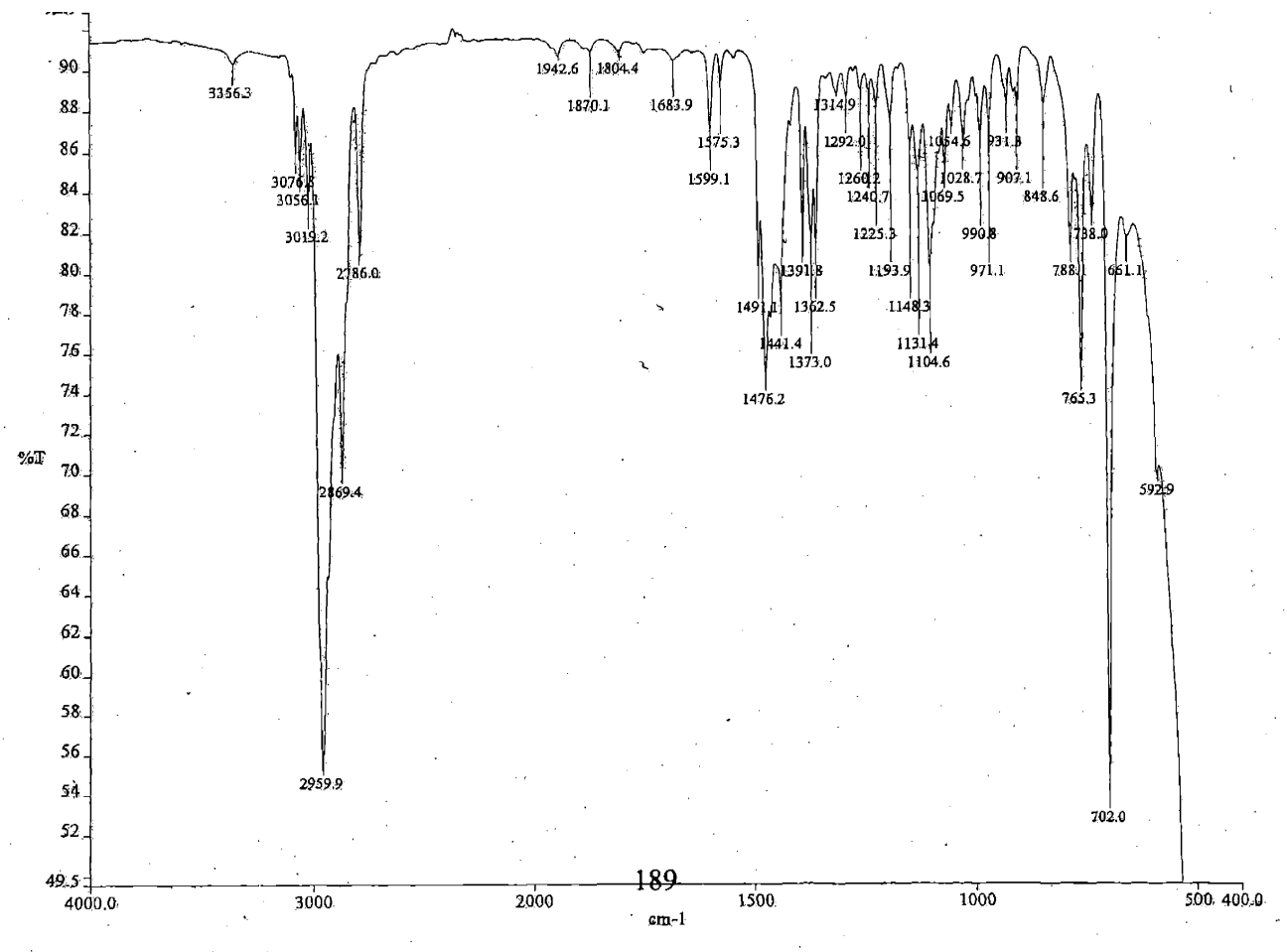
I-21

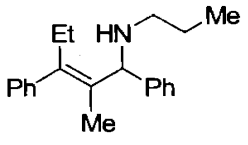
10
9
8
7
6
5
4
3
2
1
0
ppm
2.161
1.075
2.022
1.000
3.080
1.131
1.248
3.164
9.323
3.310


Et
HN
Me
Ph
Me
Me
Me
Me

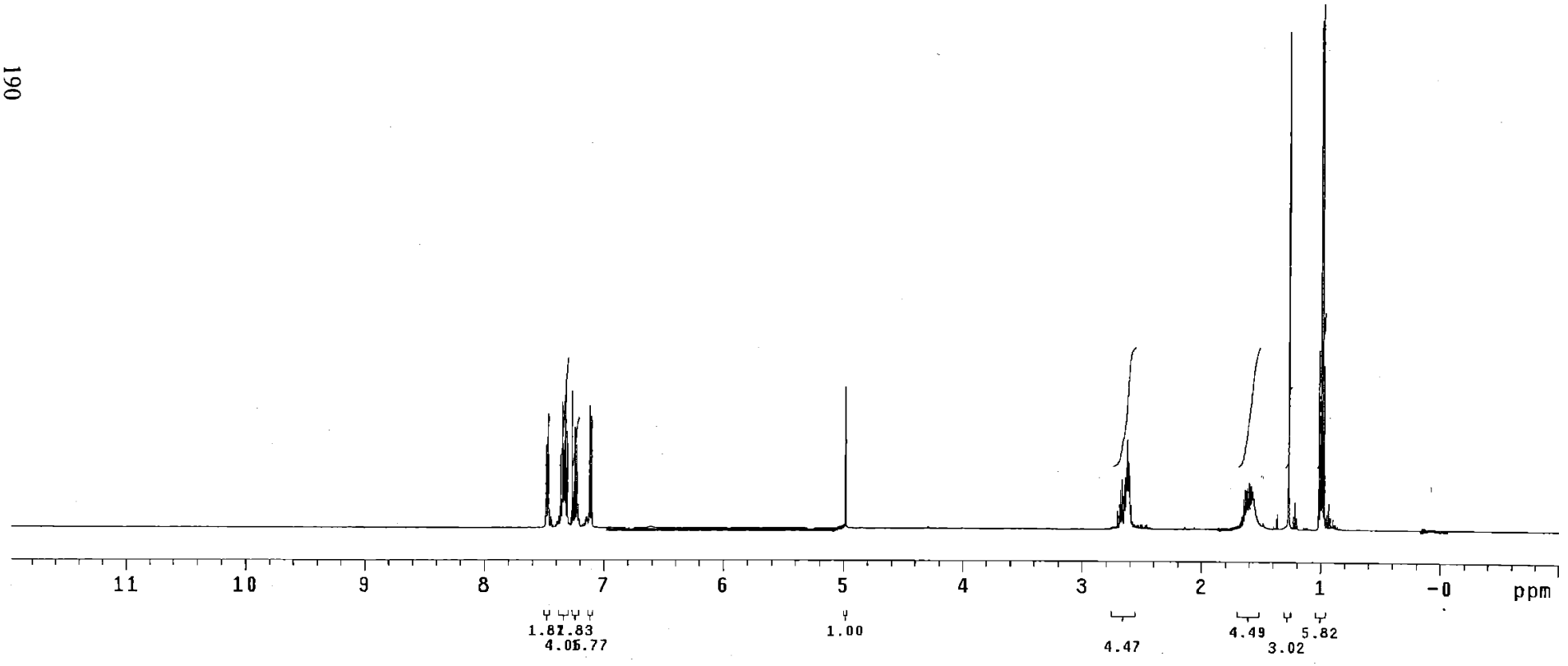
I-21

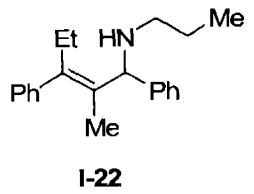
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3356.3
3076.8
3056.3
3019.2
2959.9
2869.4
2786.0
1942.6
1870.1
1804.4
1683.9
1599.1
1575.3
1491.1
1476.2
1441.4
1391.8
1373.0
1362.5
1314.9
1292.0
1260.2
1240.7
1225.3
1193.9
1148.3
1131.4
1104.6
1069.5
1064.6
1028.7
990.8
971.1
931.3
902.1
848.6
788.1
765.3
738.0
702.0
661.1
592.9
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\scan_rto.sp - scan_rto.sp

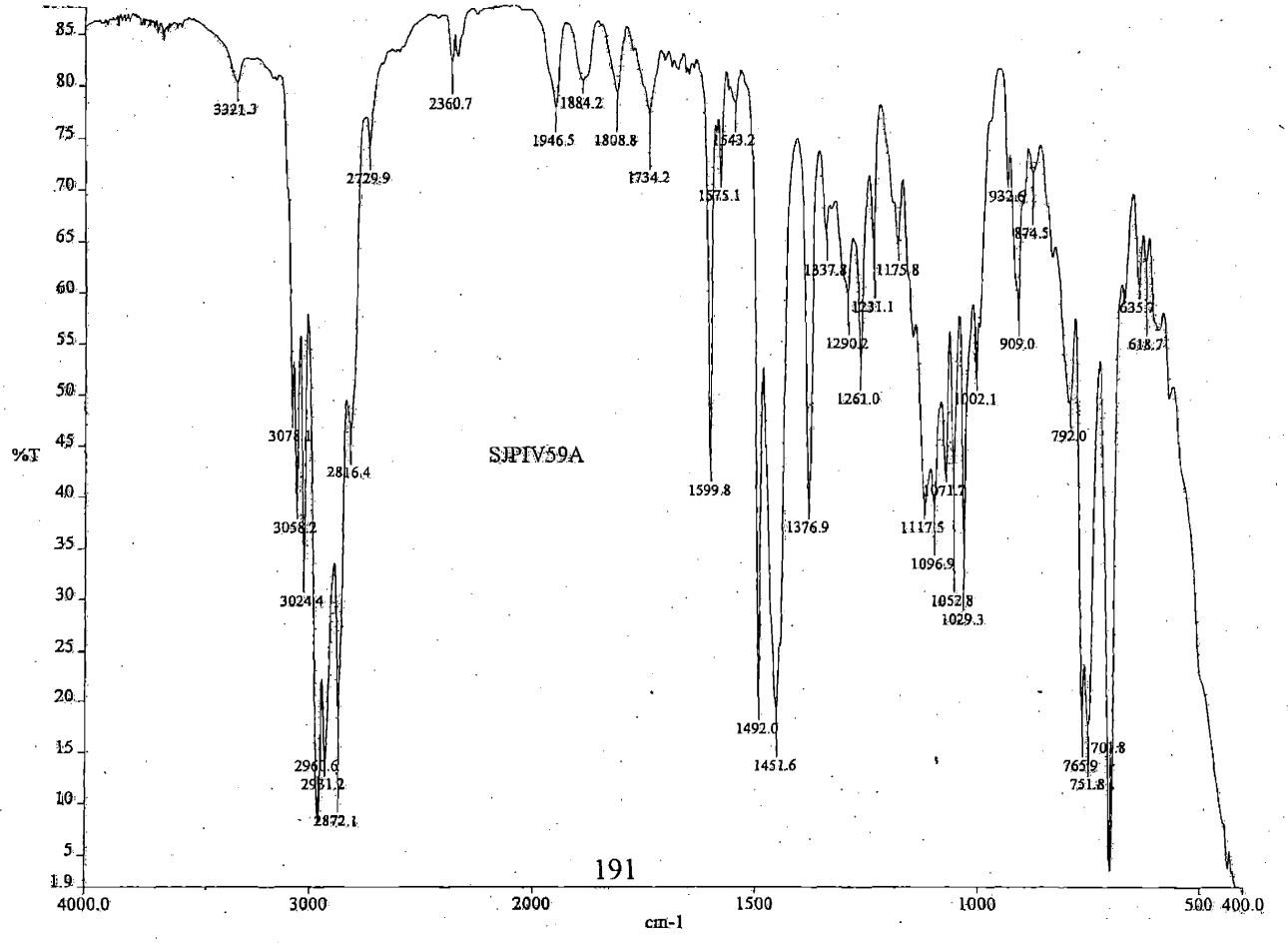

Et
HN
Me
Ph
Ph
Me

I-22

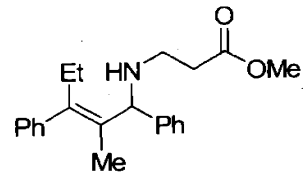

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.87
1.83
4.05
5.77
1.00
4.47
4.49
3.02
5.82



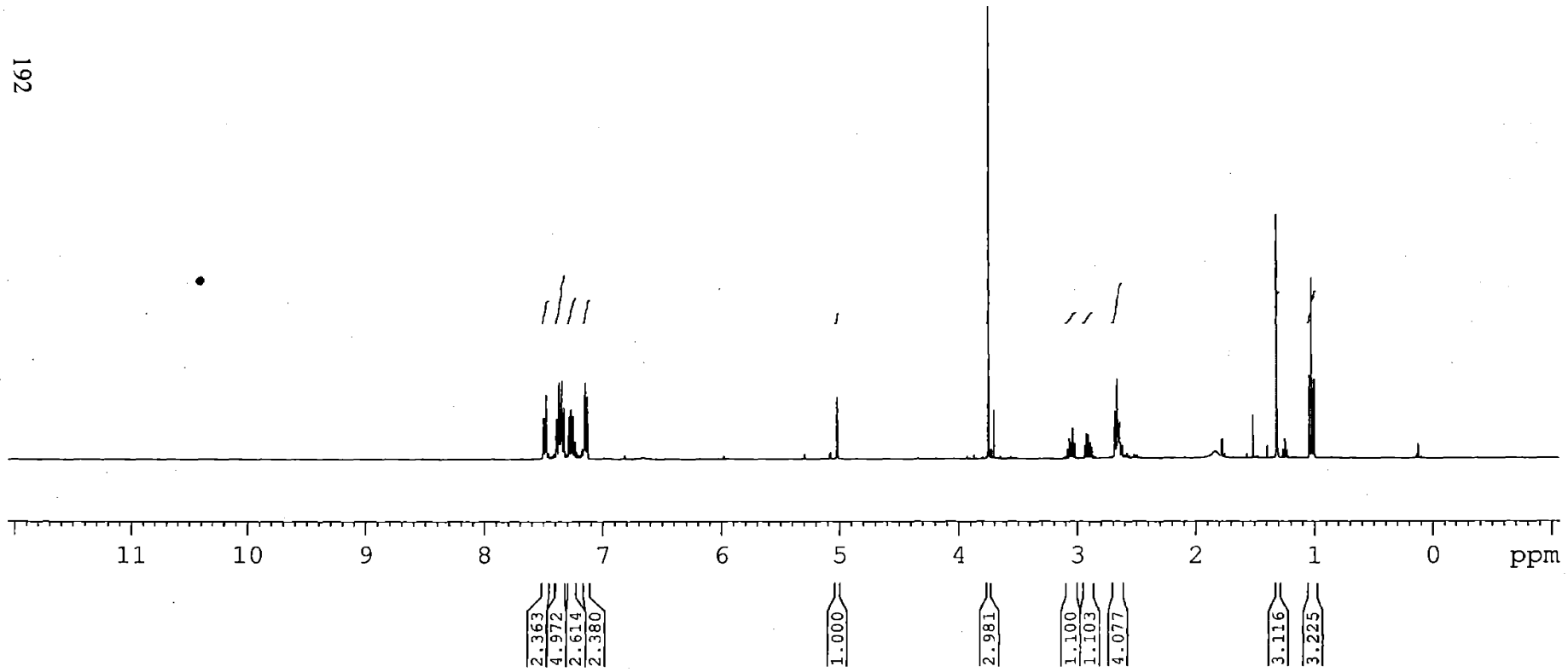
I-22

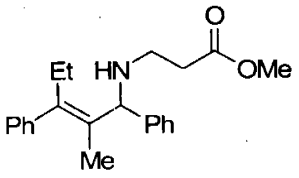


c:\pe_data\spectra\scan_rto.sp - scan_rto.sp

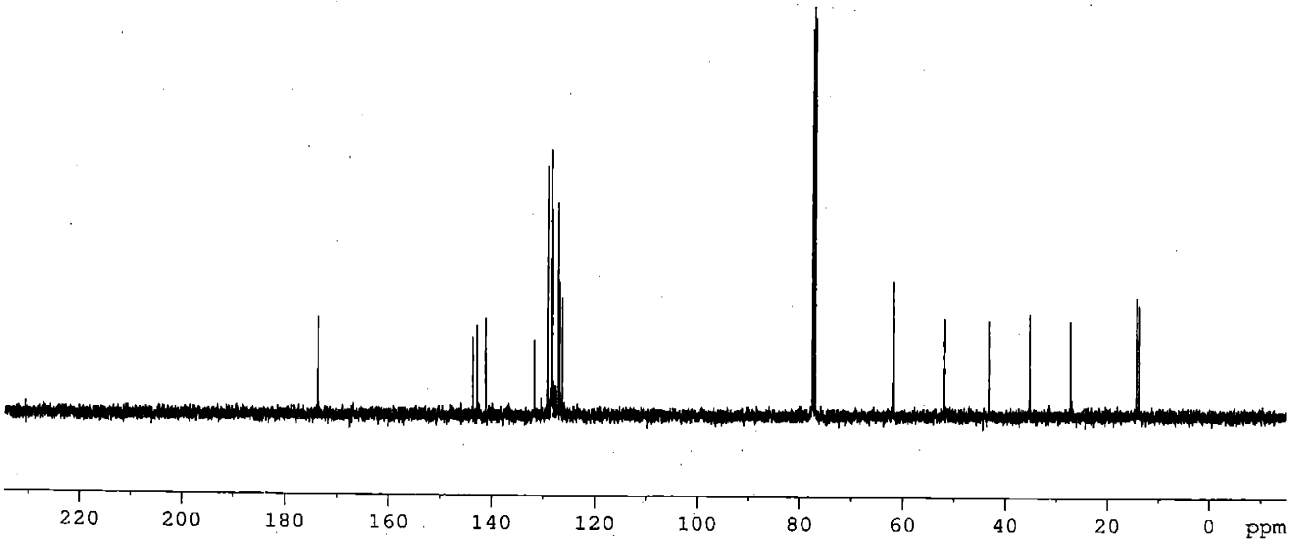

O
Et
HN
OMe
Ph
Ph
Me

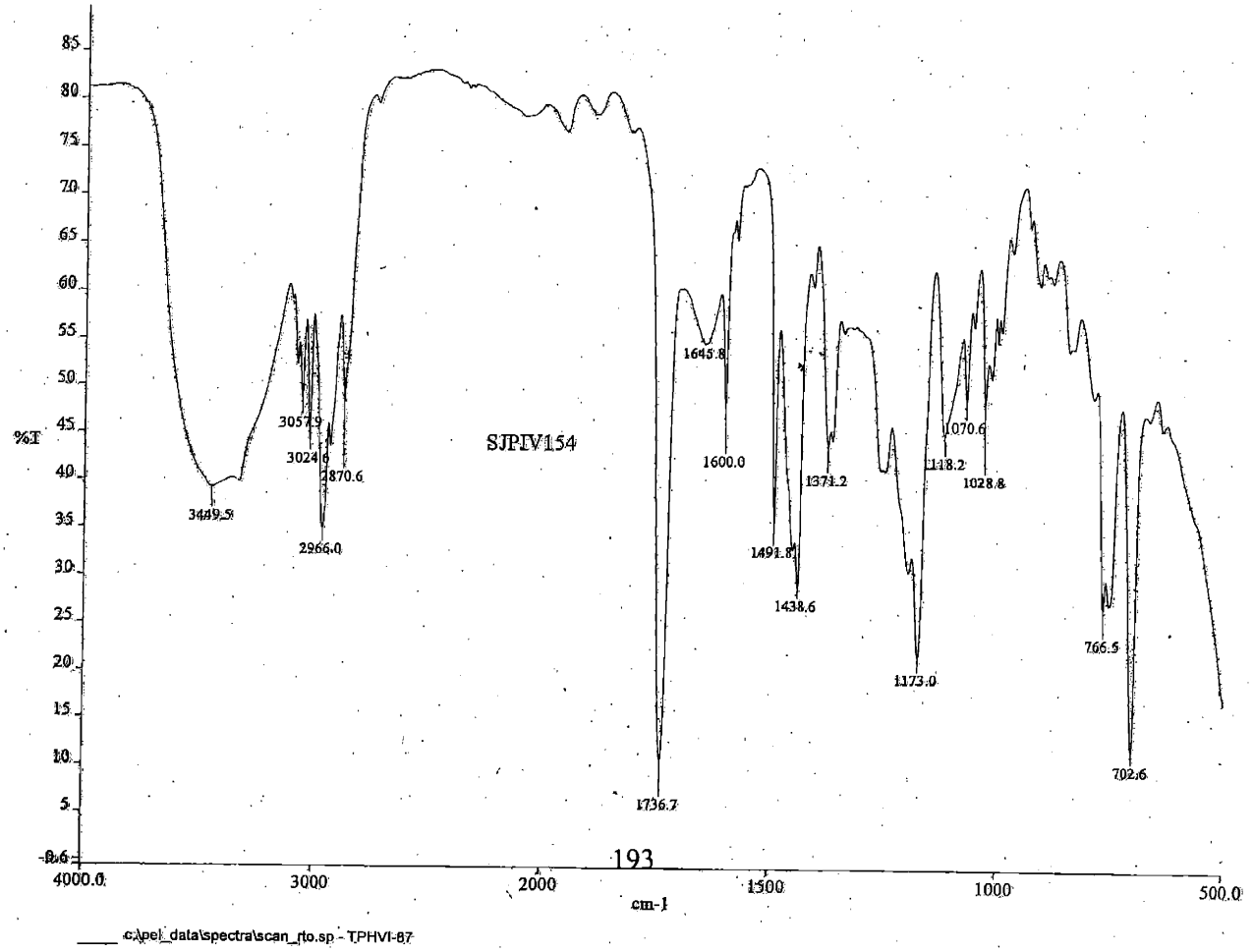
I-23

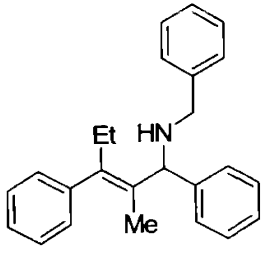

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.363
4.972
2.614
2.380
1.000
2.981
1.100
1.103
4.077
3.116
3.225


O
Et
HN
OMe
Ph
Ph
Me

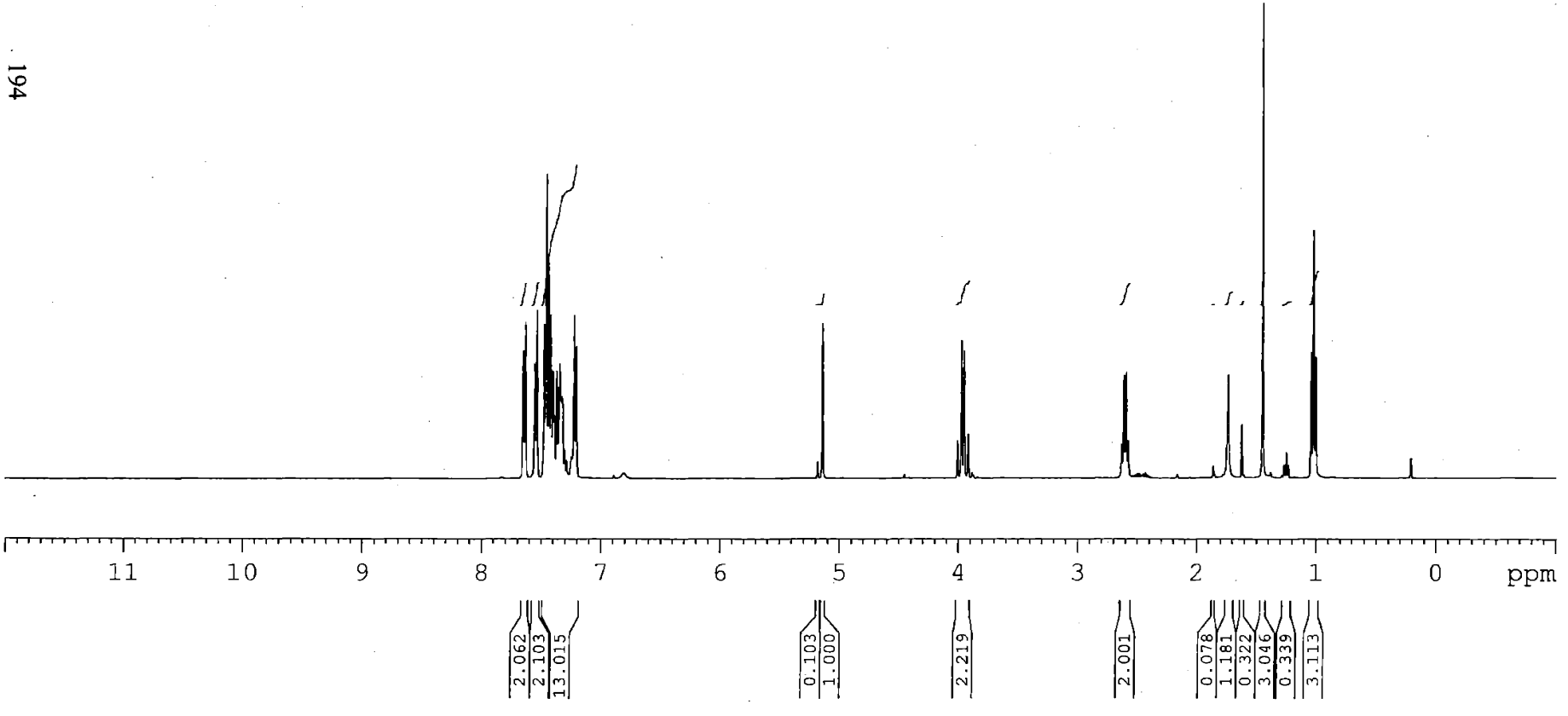
I-23

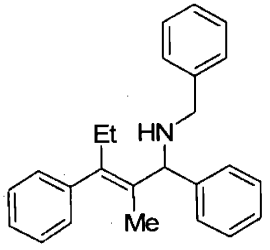

220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
SJPIV154
3449.9
3057.9
3024.6
2870.6
2966.0
1645.8
1600.0
1491.8
1438.6
1371.2
1173.0
1118.2
1070.6
1028.8
766.5
702.6
1736.7
4000.0
3000
2000
1500
1000
500.0
cm-1
c:\pei_data\spectra\scan_rto.sp - TPHVI-87


Et
HN
Me

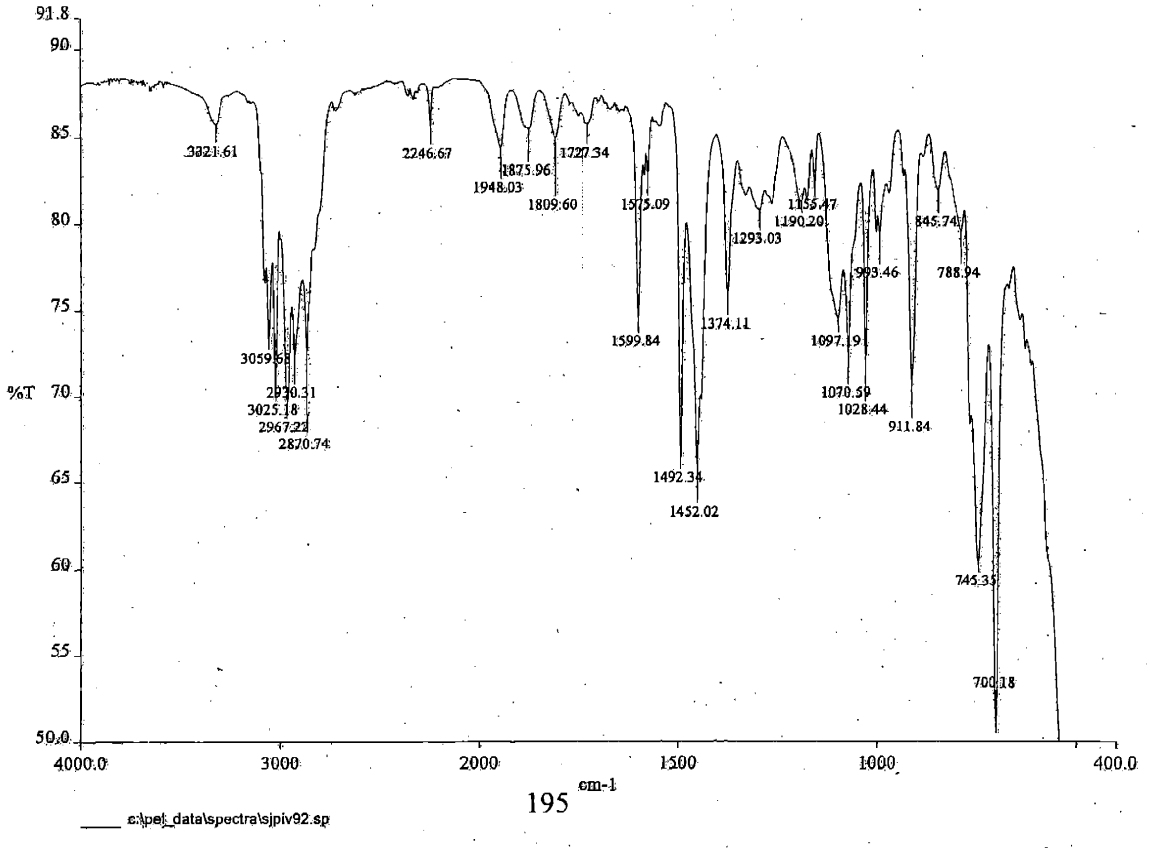
I-24

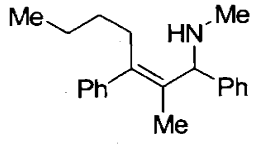

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.062
2.103
13.015
0.103
1.000
2.219
2.001
0.078
1.181
0.322
3.046
0.339
3.113


Et
HN
Me

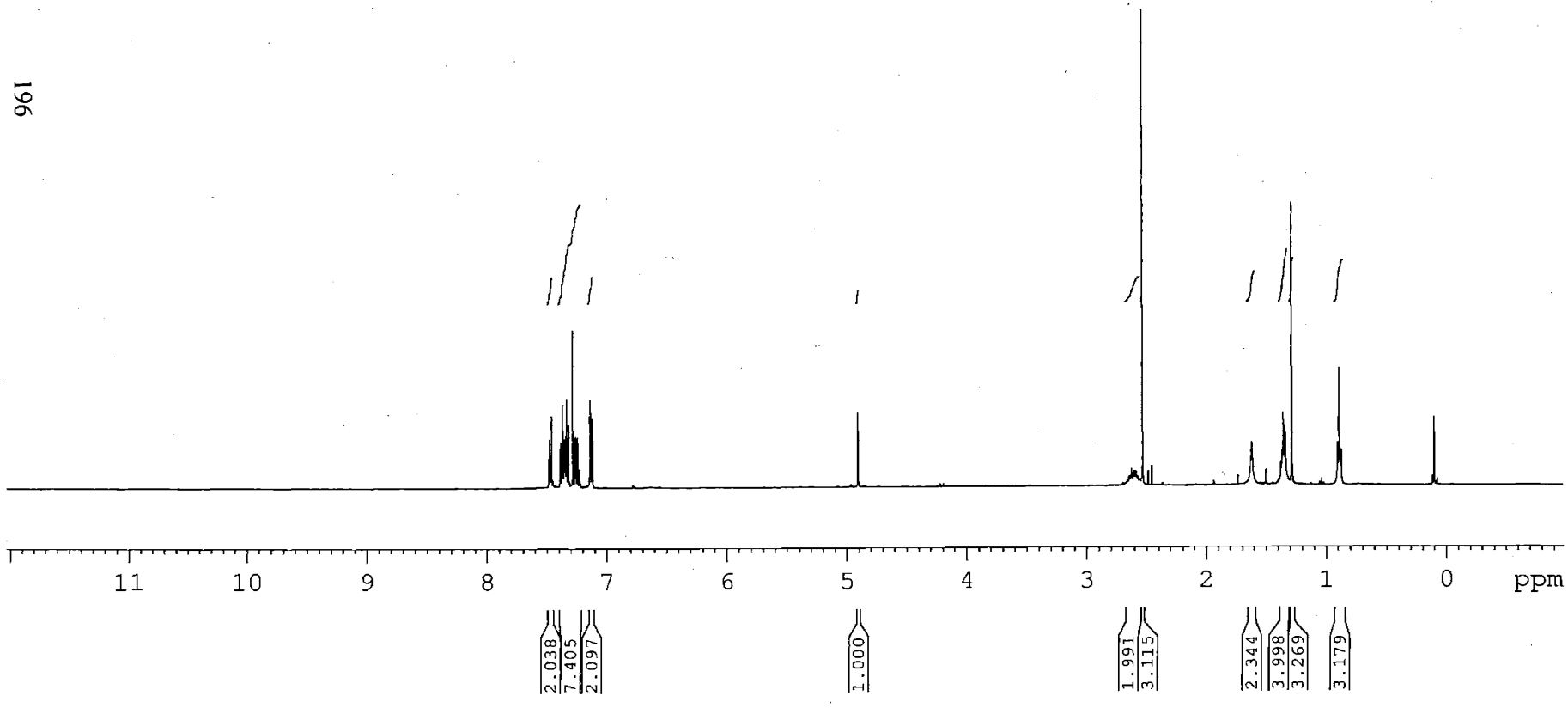
I-24

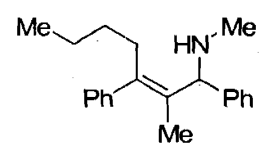
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
91.8
90
85
80
75
70
65
60
55
50.0
4000.0
3000
2000
1500
1000
400.0
cm-1
3821.61
3059.58
3025.18
2967.22
2930.31
2870.74
2246.67
1948.03
1875.96
1809.60
1727.34
1599.84
1575.09
1492.34
1452.02
1374.11
1293.03
1190.20
1155.47
1097.19
1070.59
1028.44
993.46
911.84
845.74
788.94
745.33
700.18
c:\pe_data\spectra\sjpiv92.sp


Me
HN
Me
Ph
Ph
Me

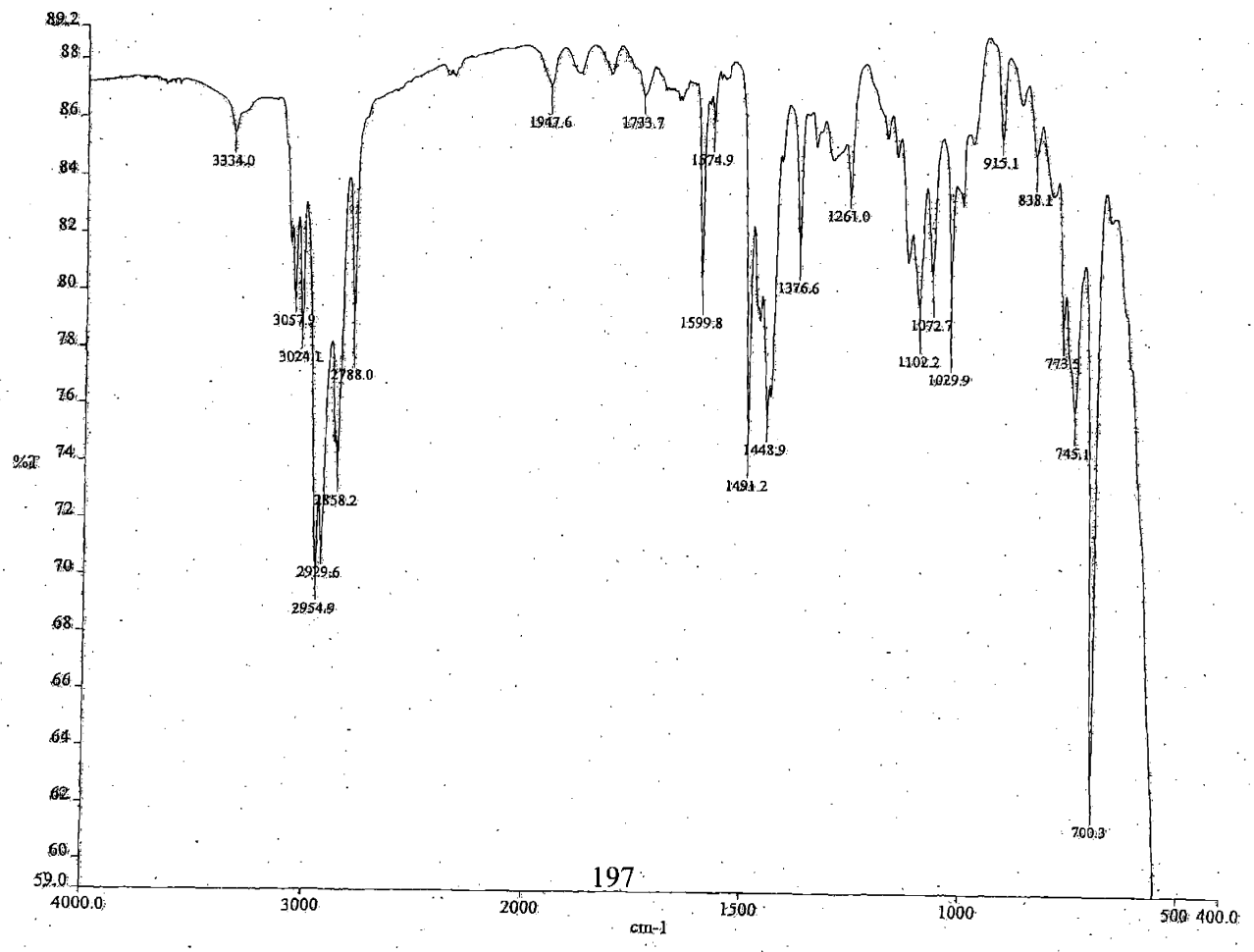
I-25

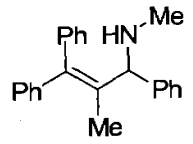

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.038
7.405
2.097
1.000
1.991
3.115
2.344
3.998
3.269
3.179


Me
HN
Me
Ph
Ph
Me

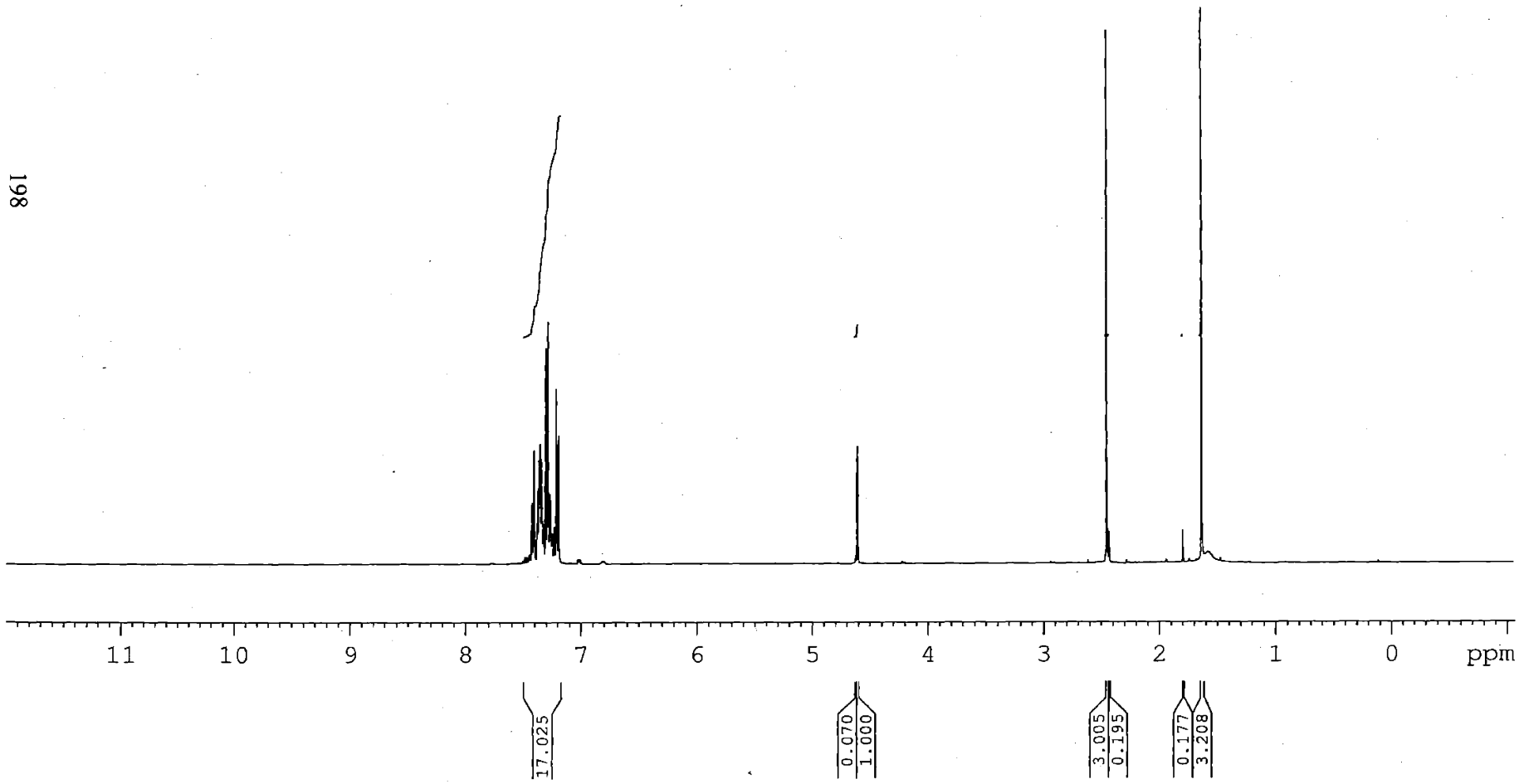
I-25

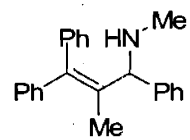
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3334.0
3057.9
3024.1
2929.6
2954.9
2858.2
2788.0
1947.6
1793.7
1599.8
1491.2
1448.9
1376.6
1261.0
1102.2
1072.7
1029.9
915.1
838.1
775.5
745.1
700.3
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\scan_rto.sp

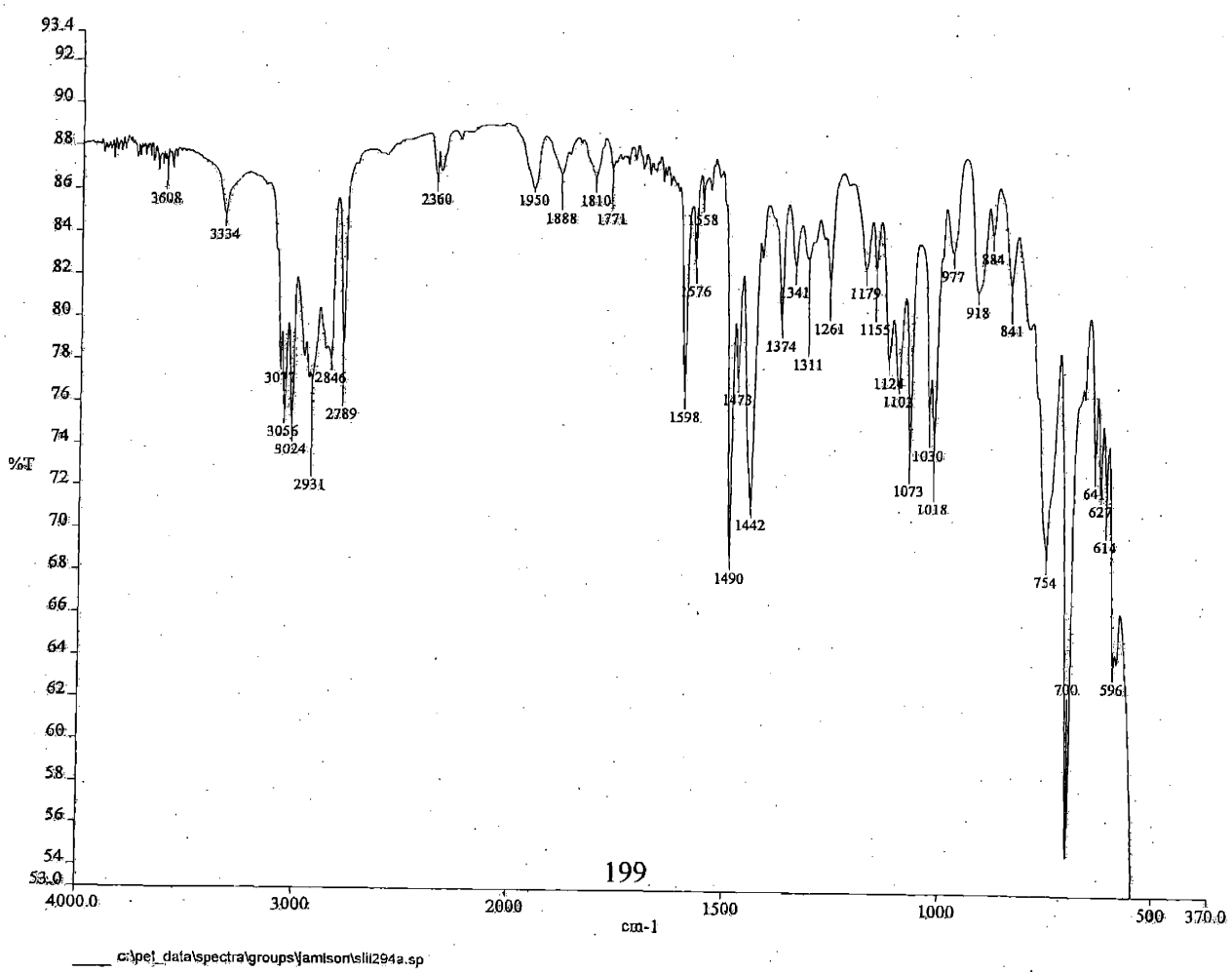

Ph
HN
Me
Ph
Ph
Me

I-26

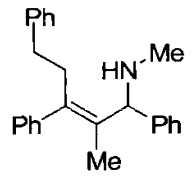

11
10
9
8
7
6
5
4
3
2
1
0
ppm
17.025
0.070
1.000
3.005
0.195
0.177
3.208



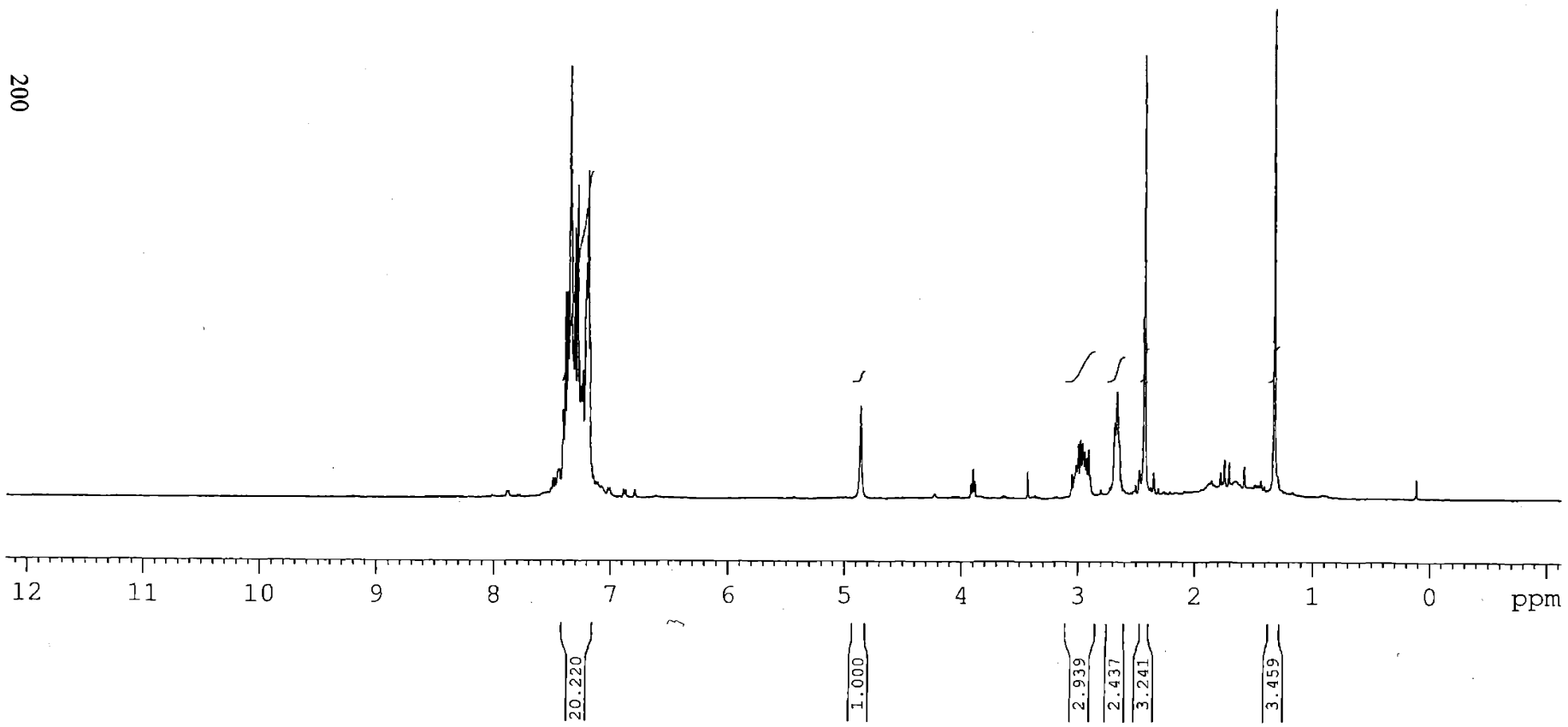
I-26

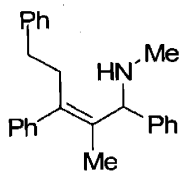


c:\pet_data\spectra\groups\jamison\slil294a.sp


Ph
HN
Me
Ph
Ph
Me

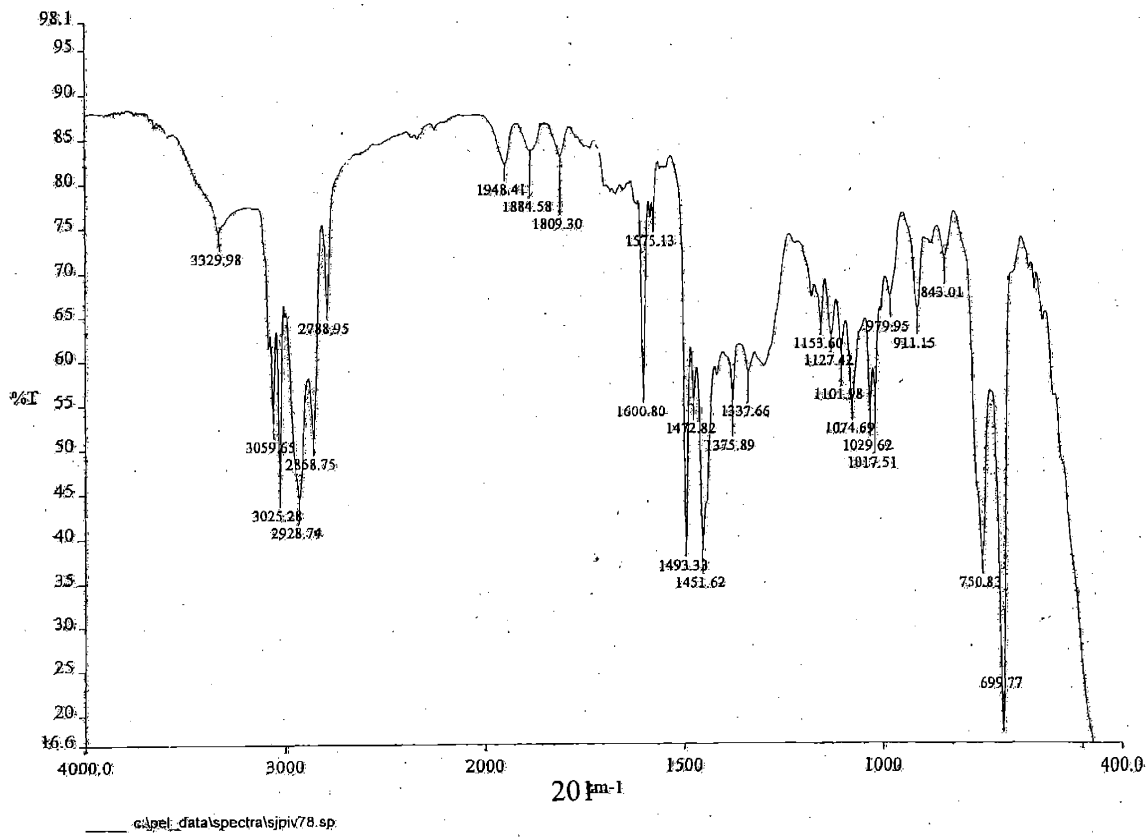
I-28

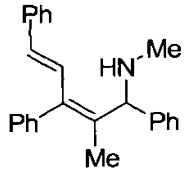

200
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
20.220
1.000
2.939
2.437
3.241
3.459


Ph
HN
Me
Ph
Ph
Me

I-28

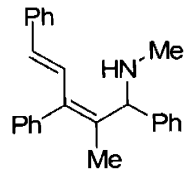
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
98.1
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
16.6
4000.0
3000
2000
1500
1000
400.0
cm-1
3329.98
3059.65
3025.28
2928.74
2858.75
2788.95
1948.41
1884.58
1809.30
1575.13
1600.80
1472.82
1493.33
1451.62
1337.66
1375.89
1153.60
1127.42
1101.98
1074.69
1029.62
1017.51
979.95
911.15
843.01
750.83
699.77
c:\pel_data\spectra\sjpiv78.sp


Ph
HN
Me
Ph
Ph
Me

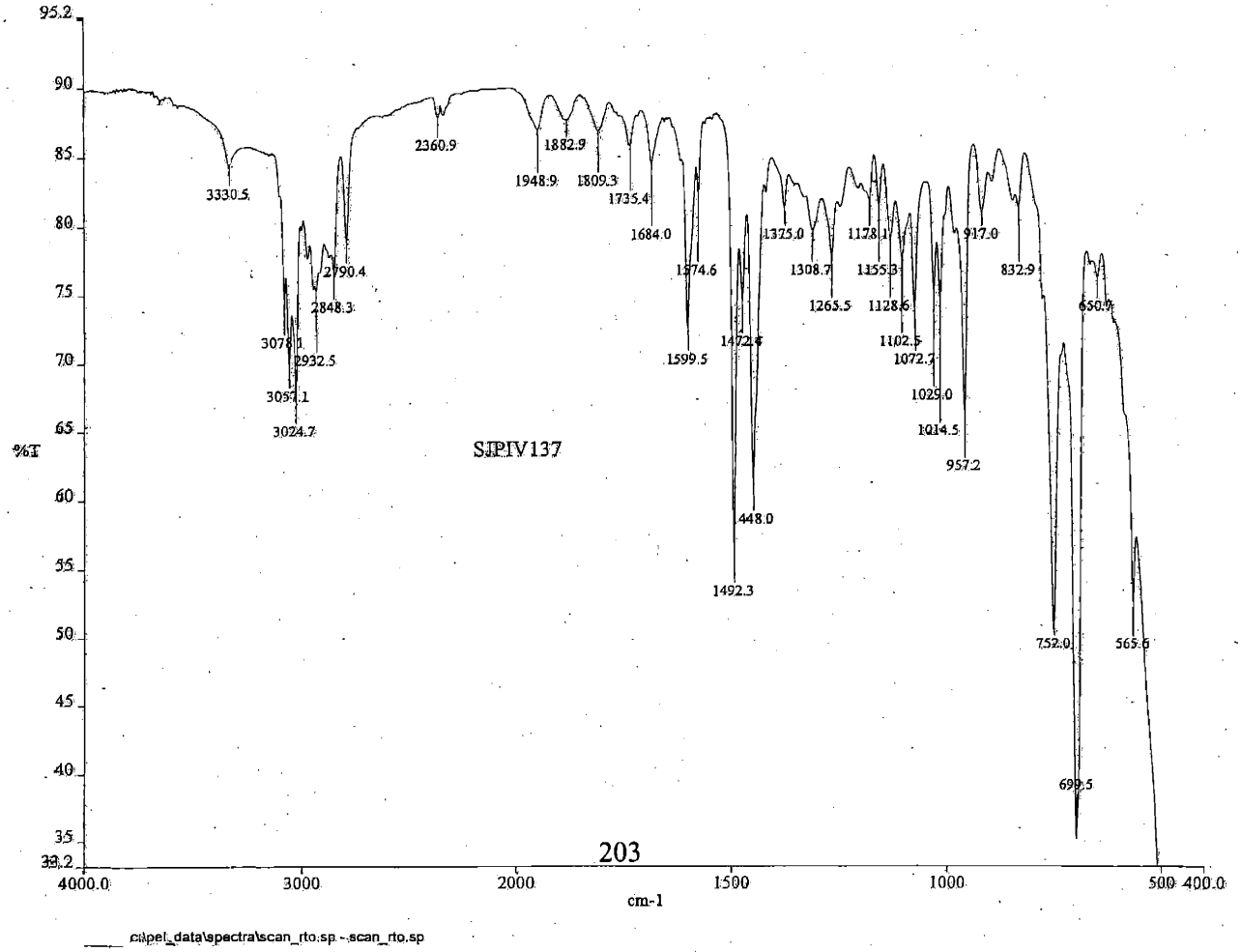
I-29

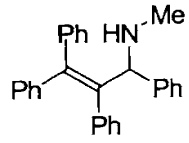
202
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.921
10.049
1.375
1.932
0.935
1.039
2.730
2.824


Ph
HN
Me
Ph
Ph
Me

I-29

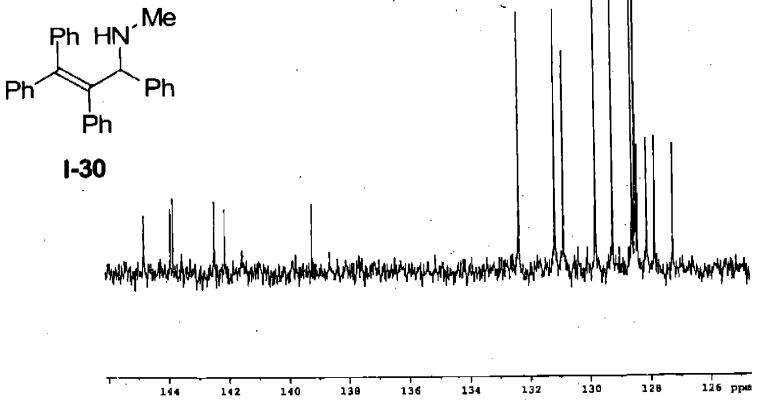
220
200
180
160
140
120
100
80
60
40
20
0
ppm


95.2
90
85
80
75
70
65
60
55
50
45
40
35
33.2
%T
3330.5
3078.1
3057.1
3024.7
2932.5
2848.3
2790.4
2360.9
1948.9
1882.9
1809.3
1735.4
1684.0
1599.5
1574.6
1492.3
1472.6
1448.0
1375.0
1308.7
1265.5
1178.1
1155.3
1128.6
1102.5
1072.7
1029.0
1014.5
957.2
917.0
832.9
752.0
699.5
650.9
565.6
SJPIV137
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pei_data\spectra\scan_rto.sp - scan_rto.sp


Ph
HN
Me
Ph
Ph
Ph

I-30

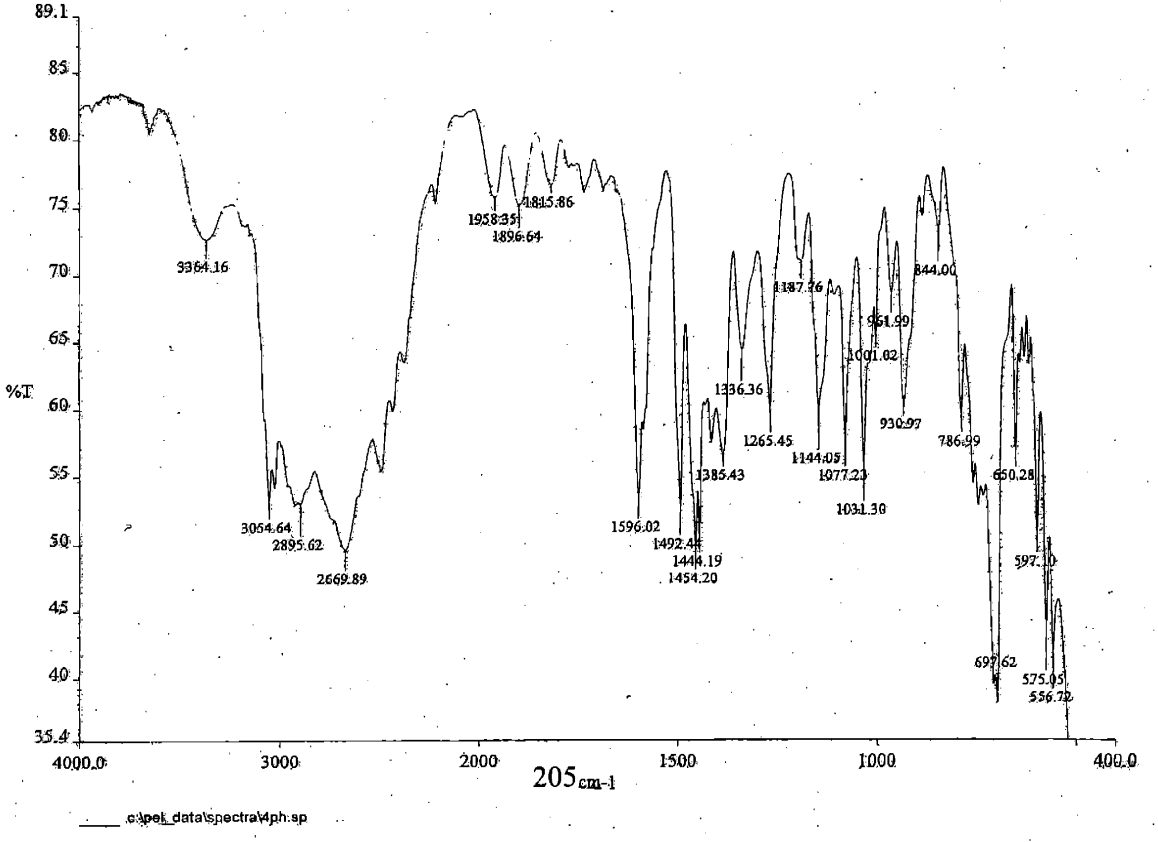
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.024
3.088
2.047
2.978
4.937
1.999
0.991
0.119
3.000

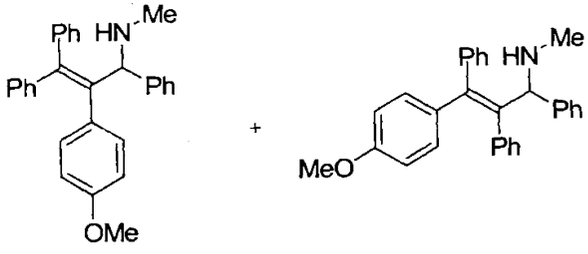

Ph
HN
Me
Ph
Ph
Ph

I-30

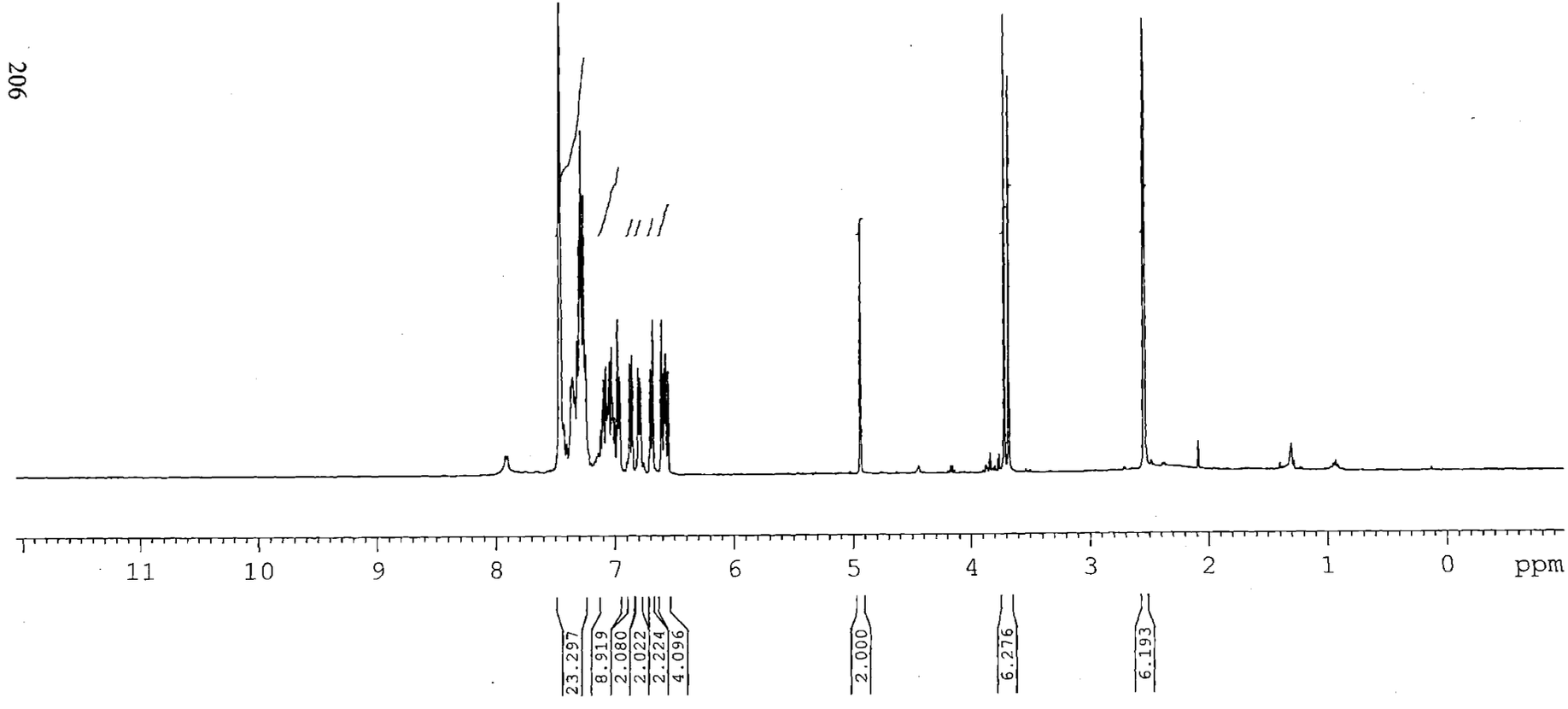
144
142
140
138
136
134
132
130
128
126 ppm

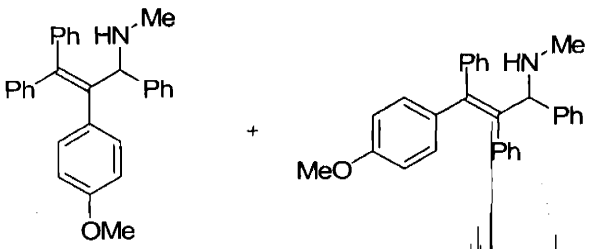
220
200
180
160
140
120
100
80
60
40
20
0 ppm


%T
89.1
85
80
75
70
65
60
55
50
45
40
35.4
4000.0
3000
2000
1500
1000
400.0
205 cm-1
3364.16
3054.64
2895.62
2669.89
1958.35
1896.64
1815.86
1596.02
1492.44
1446.19
1454.20
1385.43
1336.36
1265.45
1187.76
1144.05
1077.23
1031.30
1001.02
961.99
930.97
844.00
786.99
697.62
650.28
597.10
575.05
556.72
c:\pei_data\spectra\4ph.sp


Ph
HN
Me
Ph
Ph
OMe
+
Ph
HN
Me
Ph
Ph
MeO

I-31


206
11
10
9
8
7
6
5
4
3
2
1
0
ppm
23.297
8.919
2.080
2.022
2.224
4.096
2.000
6.276
6.193

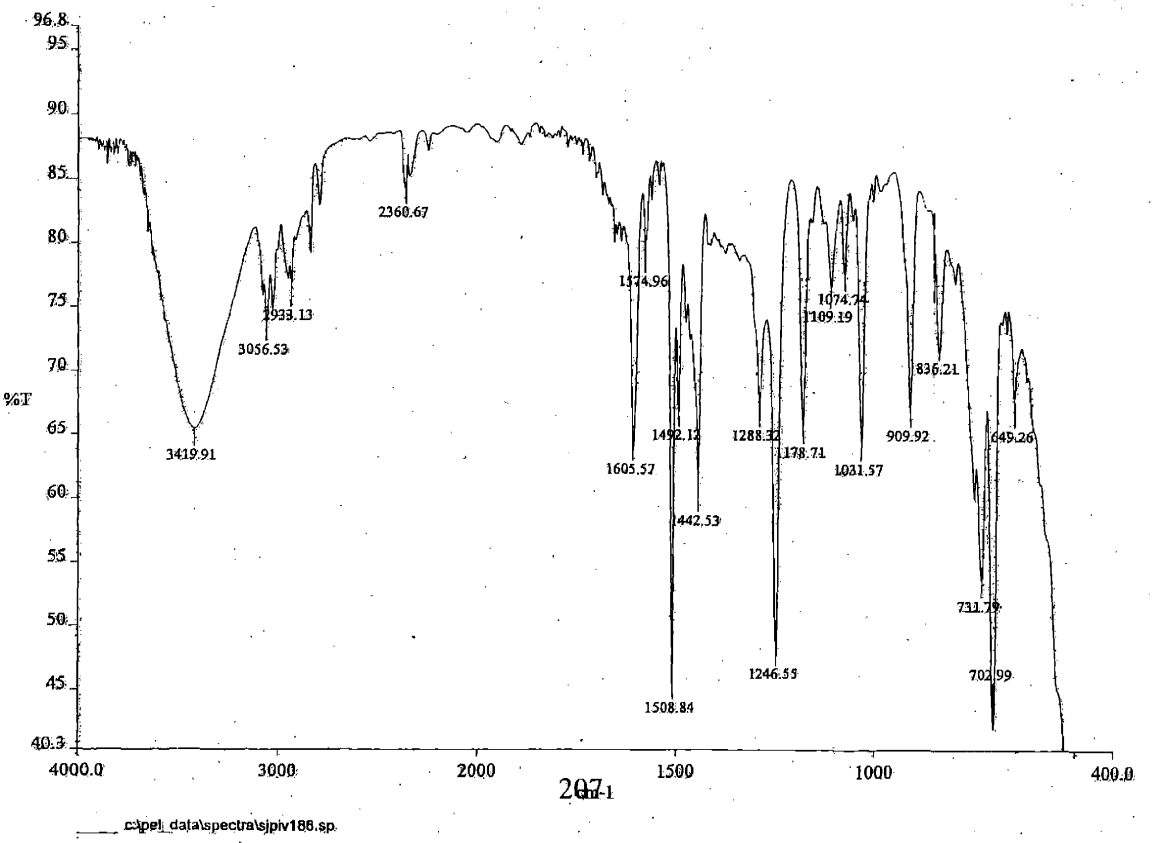

Ph
HN
Me
Ph
Ph
OMe

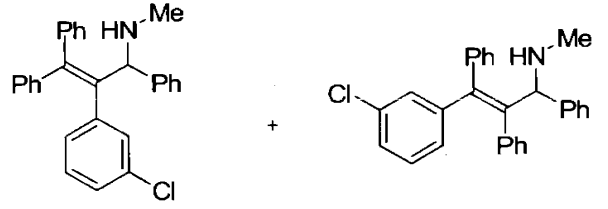
+

Ph
HN
Me
Ph
Ph
MeO

I-31

240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

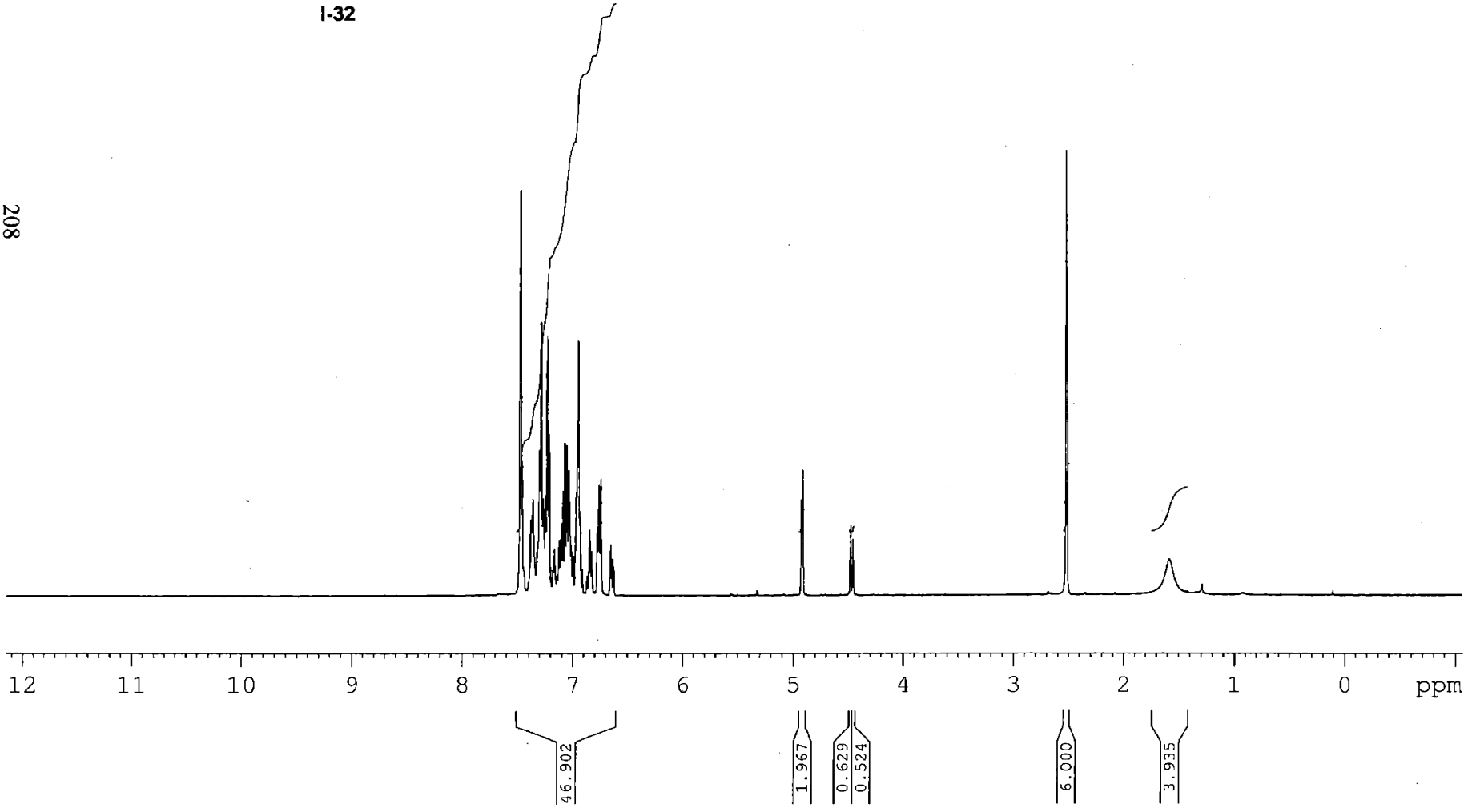

%T
96.8
95
90
85
80
75
70
65
60
55
50
45
40.3
4000.0
3000
2000
1500
1000
400.0
3419.91
3056.53
2933.13
2360.67
1574.96
1605.57
1492.12
1442.53
1508.84
1288.32
1246.55
1178.71
1109.19
1074.24
1031.57
909.92
836.21
731.79
702.99
649.26
c:\pel_data\spectra\sjpiv186.sp

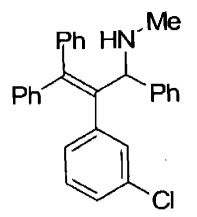

Ph
HN
Me
Ph
Ph
Cl

+

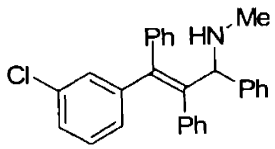
Ph
HN
Me
Cl
Ph
Ph

I-32


12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
46.902
1.967
0.629
0.524
6.000
3.935

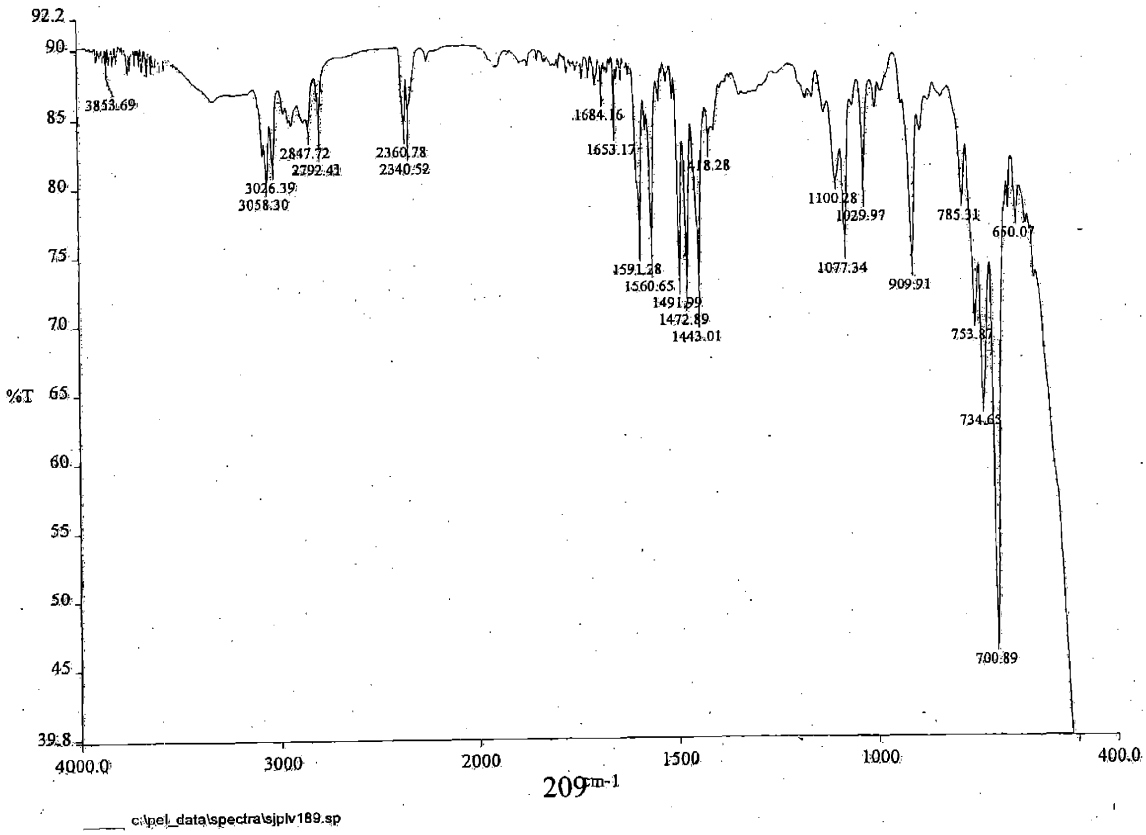

Ph
HN
Me
Ph
Ph
Cl

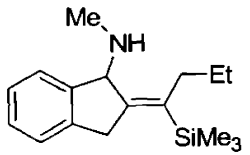
+


Cl
Ph
HN
Me
Ph
Ph

I-32

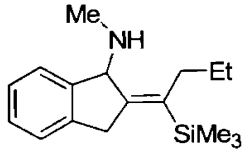
220
200
180
160
140
120
100
80
60
40
20
0
ppm


92.2
90
85
80
75
70
%T
65
60
55
50
45
39.8
3853.69
3026.39
3058.30
2847.72
2792.41
2360.78
2340.52
1684.16
1653.17
1591.28
1560.65
1491.99
1472.89
1443.01
1100.28
1029.97
1077.34
909.91
785.31
753.87
734.65
700.89
650.07
4000.0
3000
2000
1500
1000
400.0
cm-1
c:\pel_data\spectra\sjplv189.sp

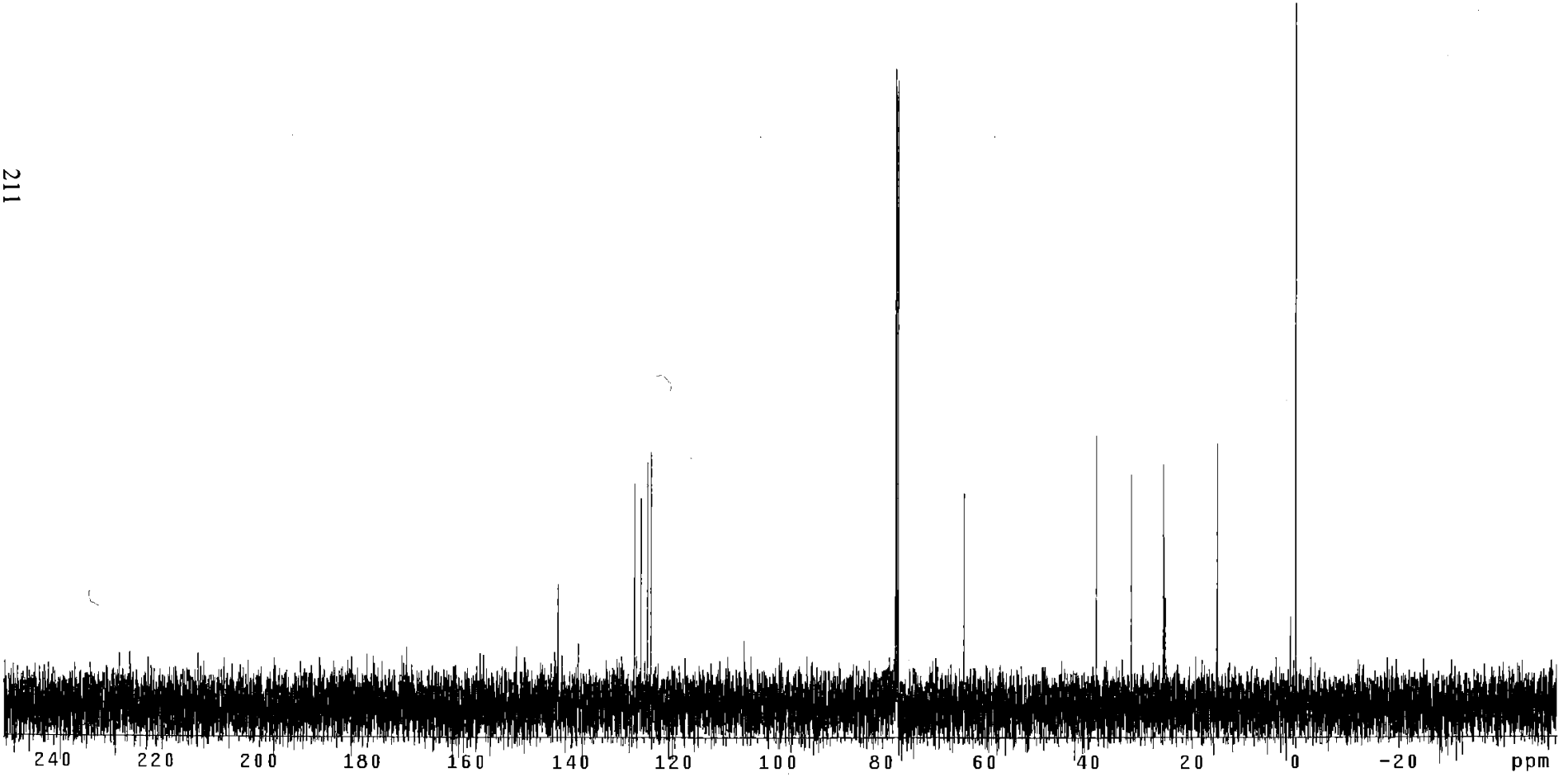

Me
NH
Et
SiMe3

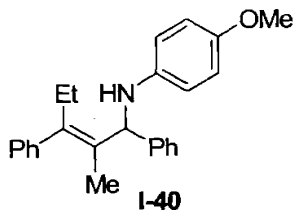
I-37

7
6
5
4
3
2
1
0
ppm
0.81
2.21
1.00
1.24
1.22
1.27
2.98
1.19
0.49
3.05
6.74

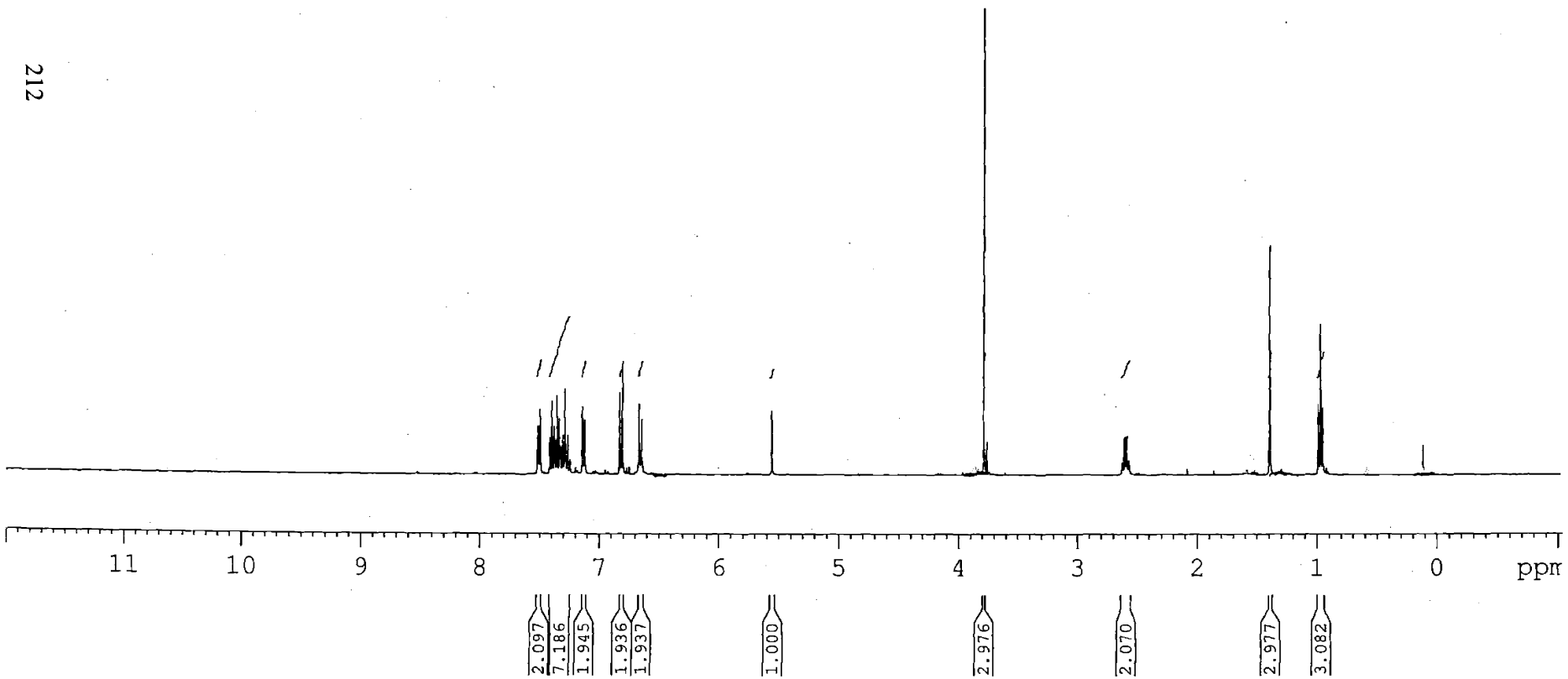


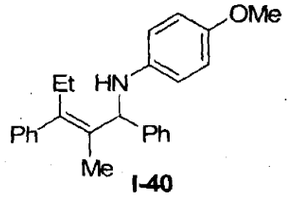
I-37



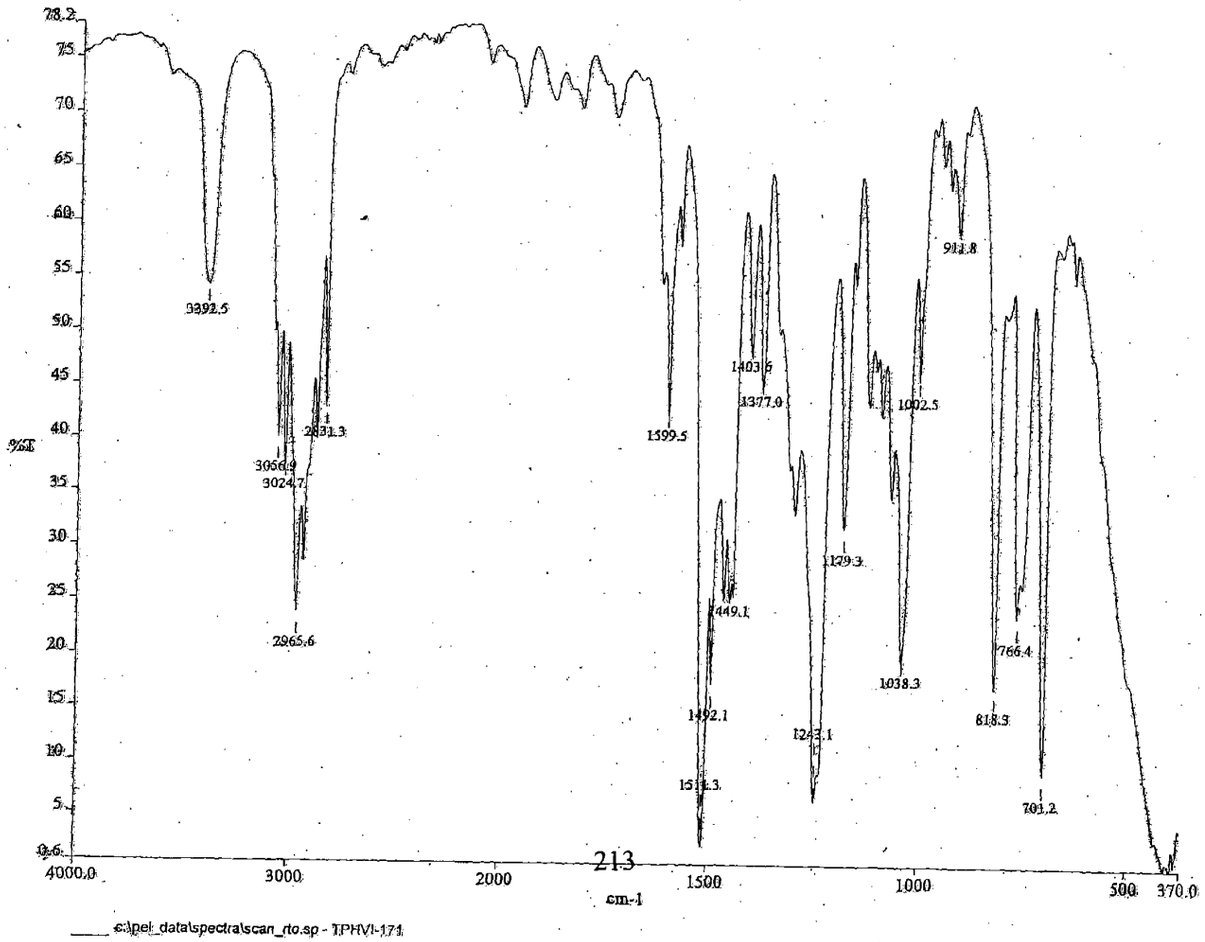

OMe
Et
HN
Ph
Ph
Me

I-40

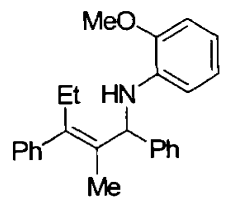

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.097
7.186
1.945
1.936
1.937
1.000
2.976
2.070
2.977
3.082



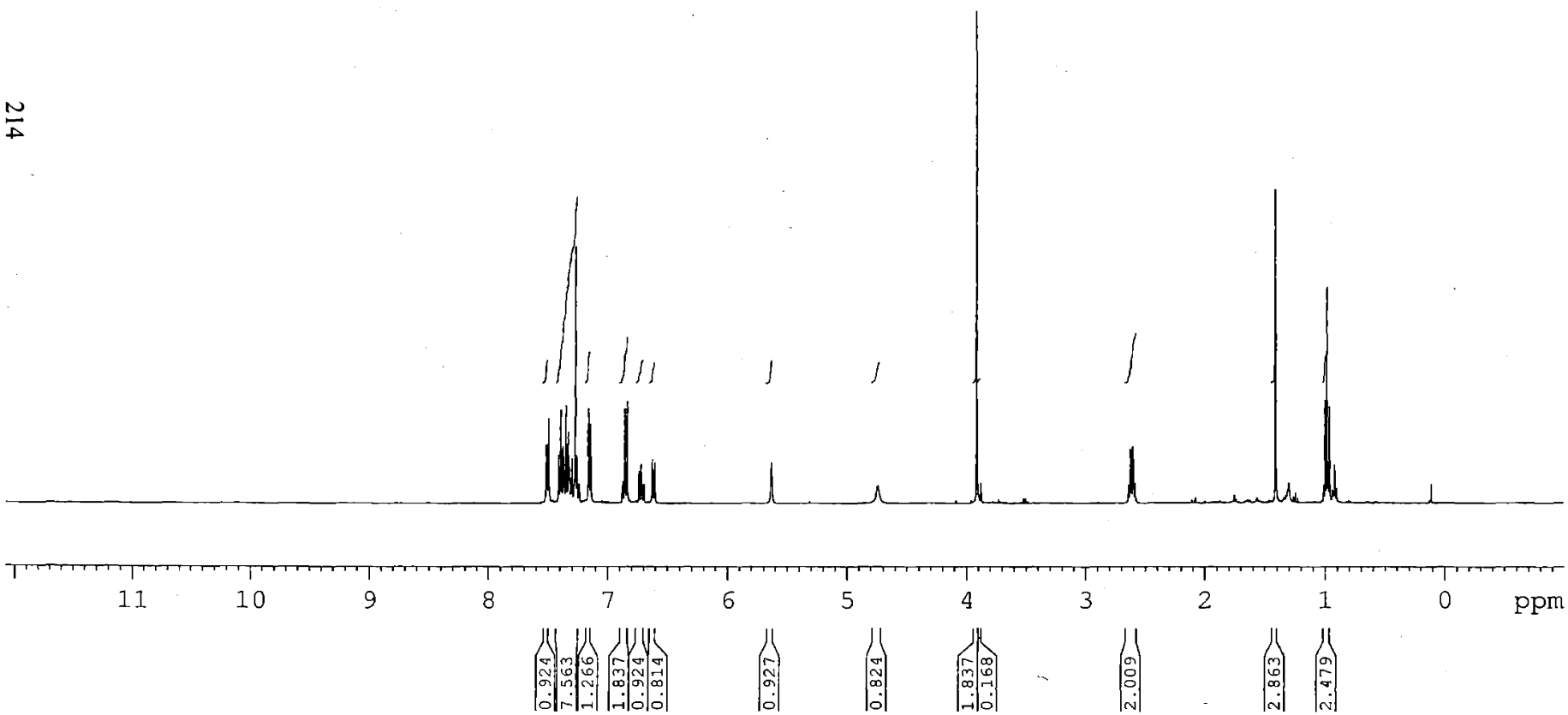
I-40

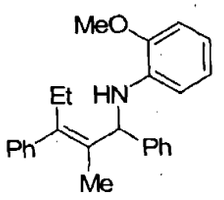


c:\pel_data\spectra\scan_rto.sp - TPHVI-171

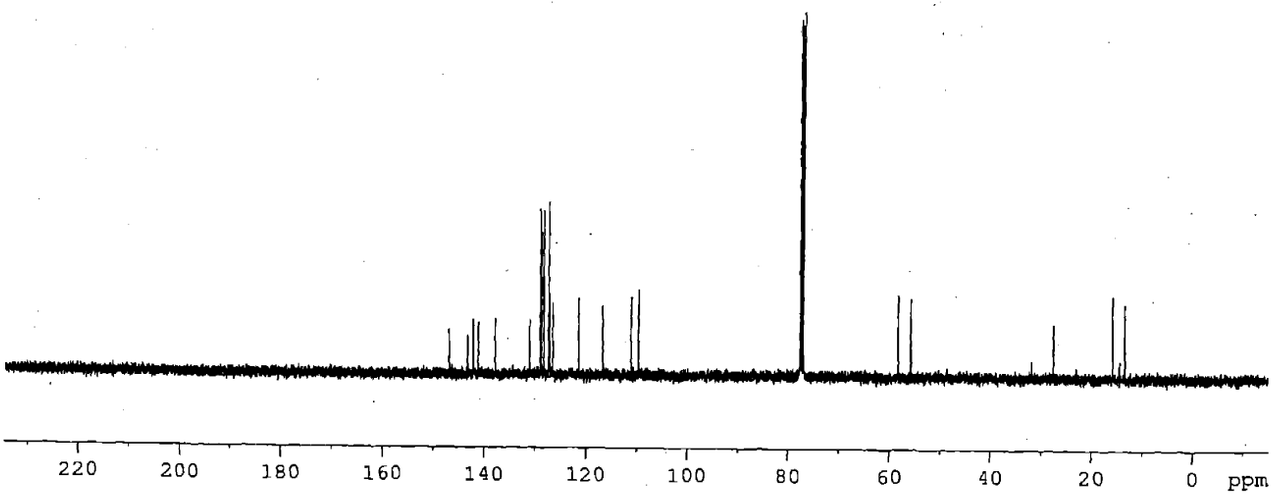

MeO
Et
HN
Ph
Ph
Me

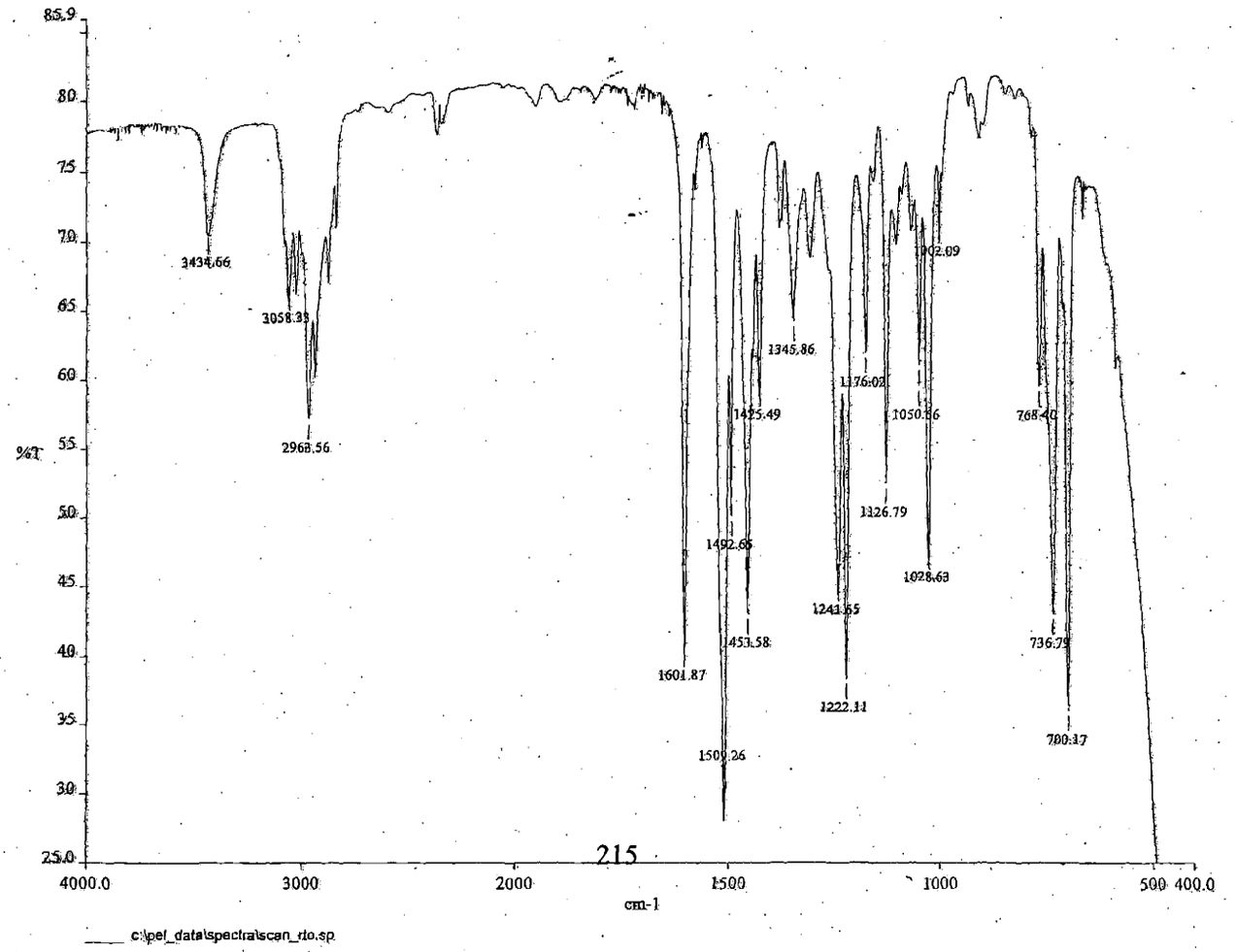
I-41

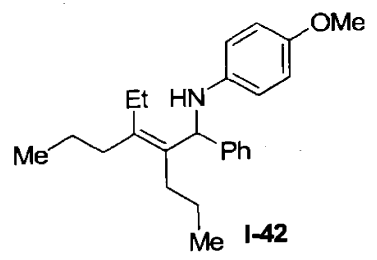

11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.924
7.563
1.266
1.837
0.924
0.814
0.927
0.824
1.837
0.168
2.009
2.863
2.479


MeO
Et
HN
Ph
Ph
Me

I-41

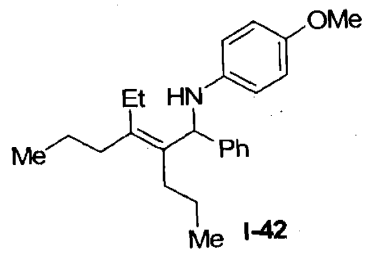

220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
85.9
80
75
70
65
60
55
50
45
40
35
30
25.0
3434.66
3058.33
2968.56
1601.87
1500.26
1492.65
1453.58
1425.49
1345.86
1241.55
1222.11
1176.02
1126.79
1050.56
1028.63
768.40
736.72
700.17
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\scan_rio.sp


OMe
Et
HN
Ph
Me
Me

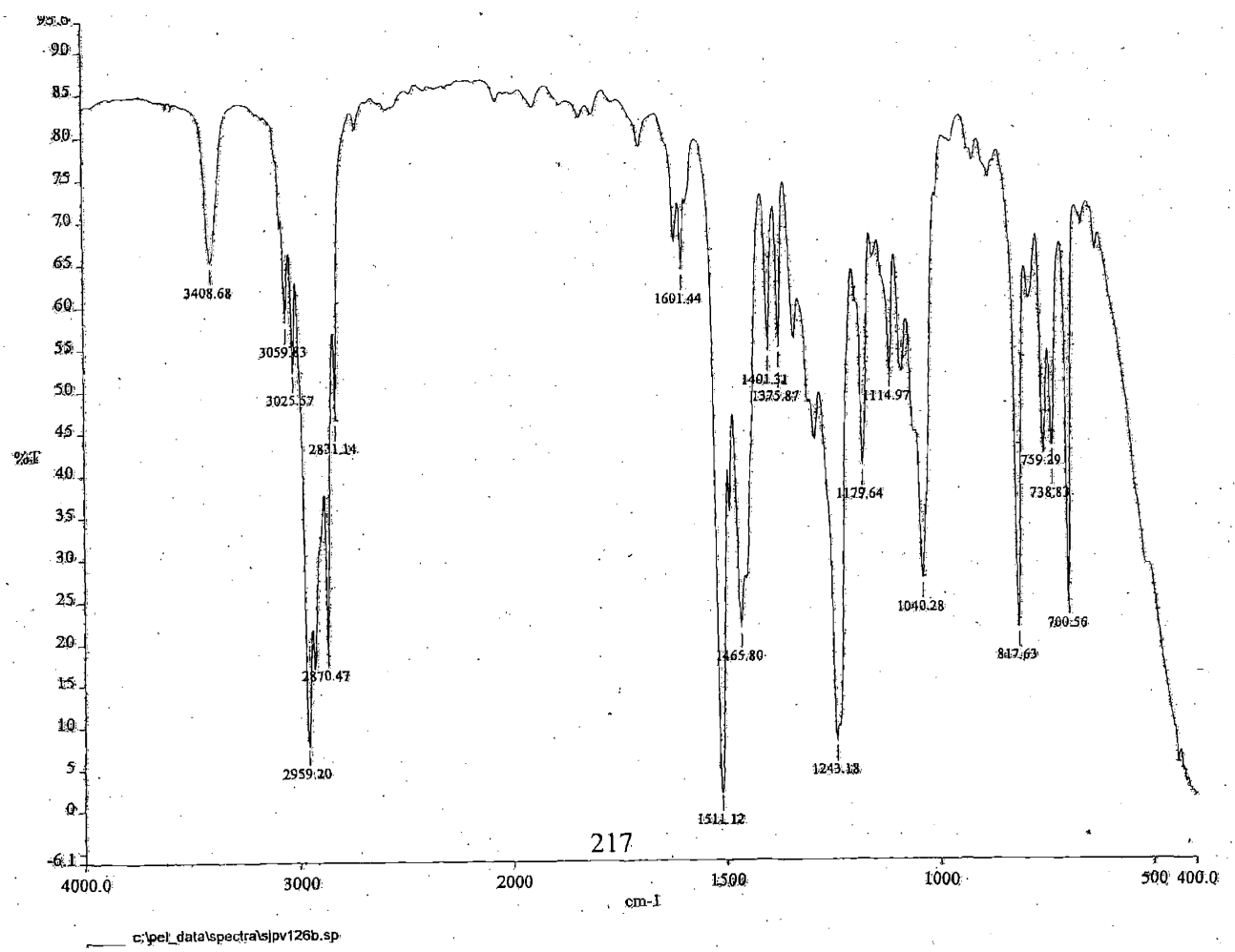
I-42

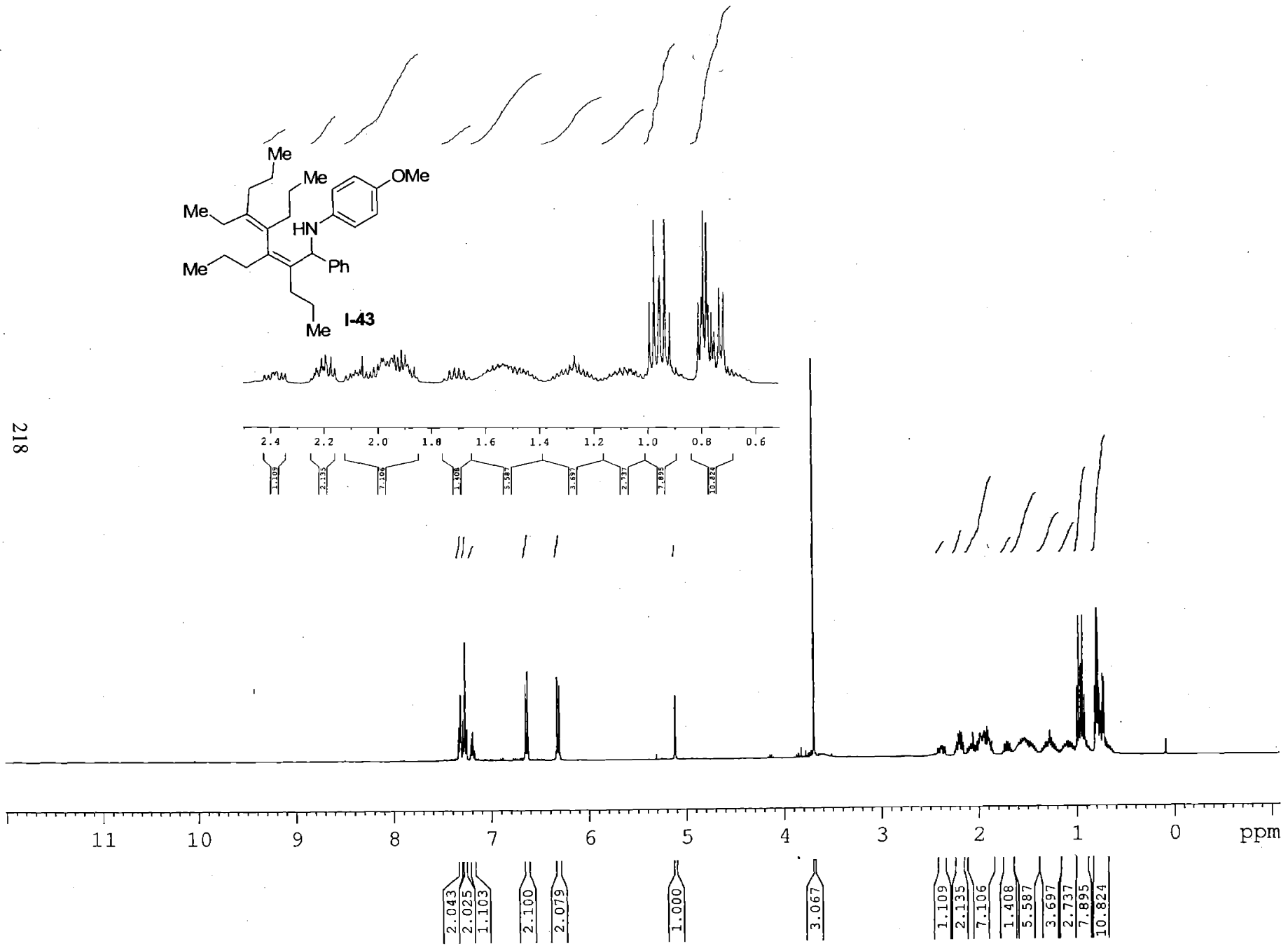
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.068
2.033
1.040
2.018
2.035
1.000
2.992
2.096
2.023
1.120
1.056
2.240
1.438
6.360
1.310
3.052

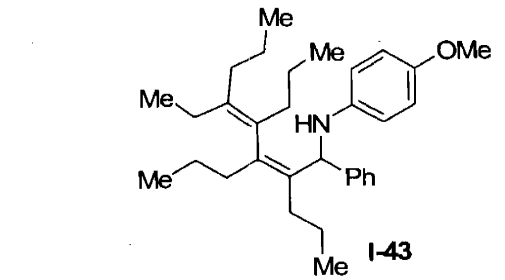

OMe
Et
HN
Ph
Me
Me

I-42

220
200
180
160
140
120
100
80
60
40
20
0
ppm

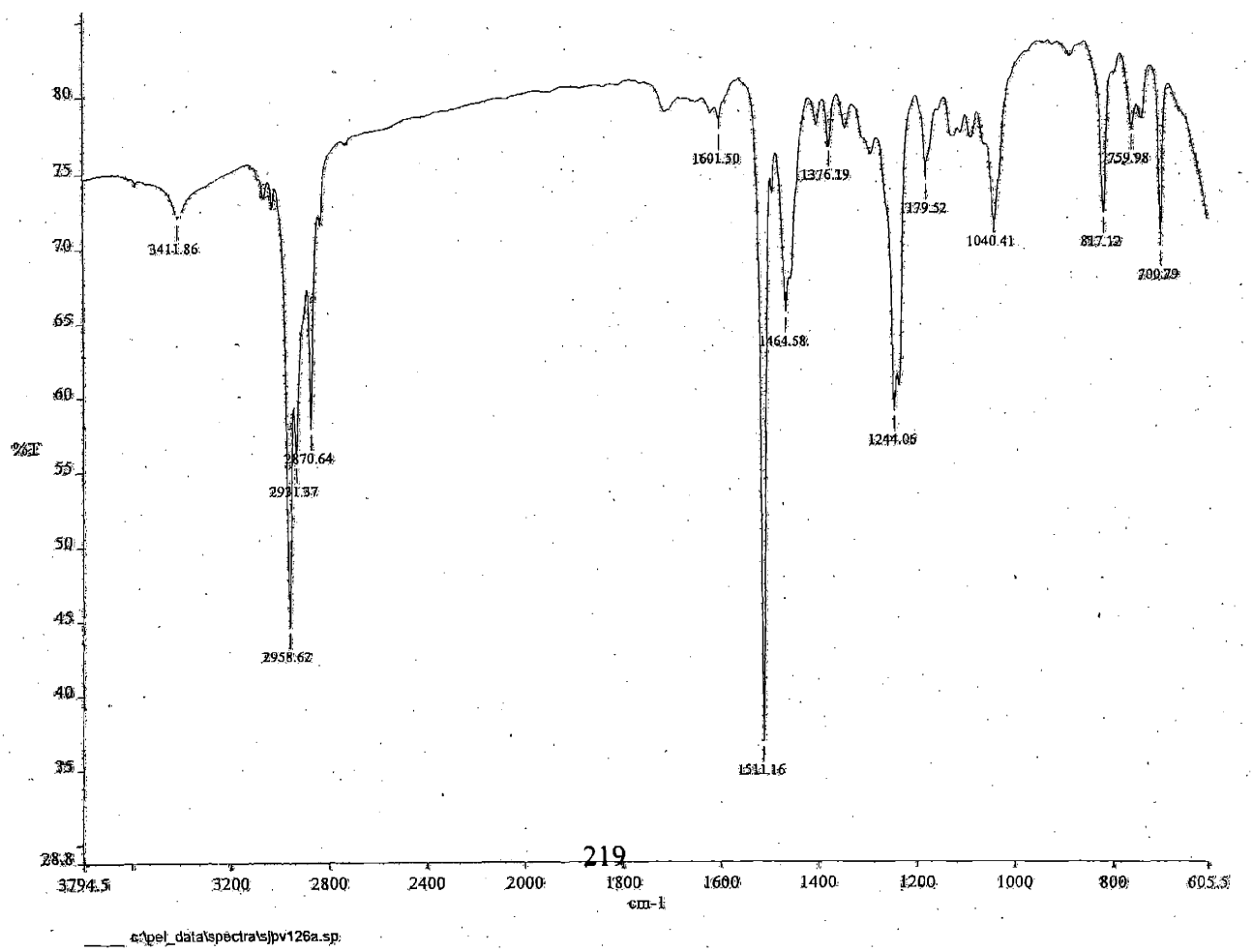

%T
3408.68
3059.43
3025.57
2931.14
2870.47
2959.20
1601.44
1511.12
1465.80
1401.31
1375.87
1314.97
1179.64
1243.13
1040.28
847.63
759.29
738.81
700.56
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\sjpv126b.sp

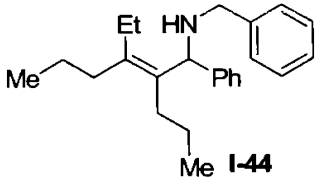

Me
Me
OMe
Me
HN
Ph
Me
Me
I-43
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.043
2.025
1.103
2.100
2.079
1.000
3.067
1.109
2.135
7.106
1.408
5.587
3.697
2.737
7.895
10.824


Me
Me
OMe
Me
HN
Me
Ph
Me

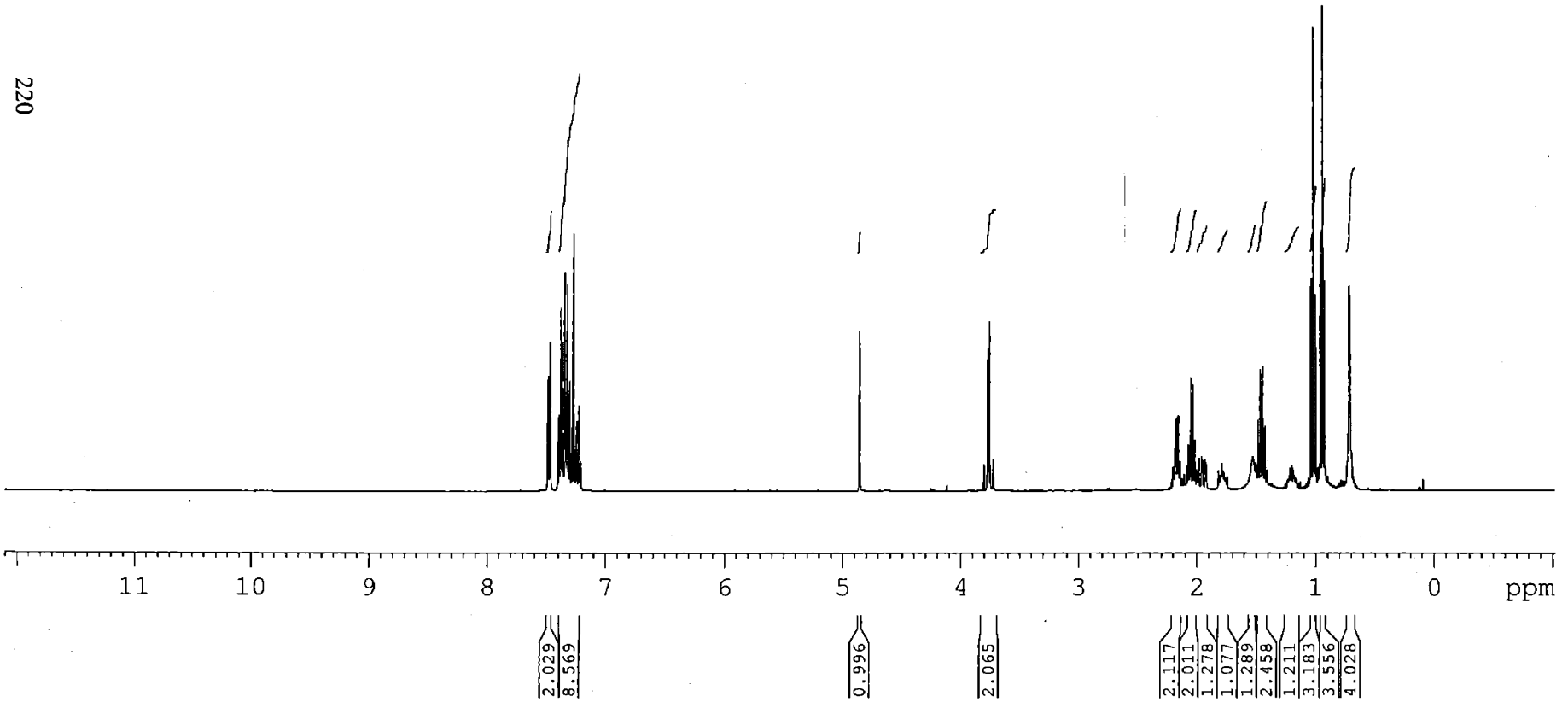
I-43

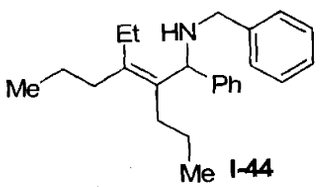
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
80
75
70
65
60
55
50
45
40
35
28.8
3411.86
2958.62
2931.37
2870.64
1601.50
1511.16
1464.58
1376.19
1244.06
1179.52
1040.41
817.12
759.98
700.29
3794.5
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
605.5
cm-1
c:\pel_data\spectra\sjpv126a.sp


Et
HN
Me
Ph
Me

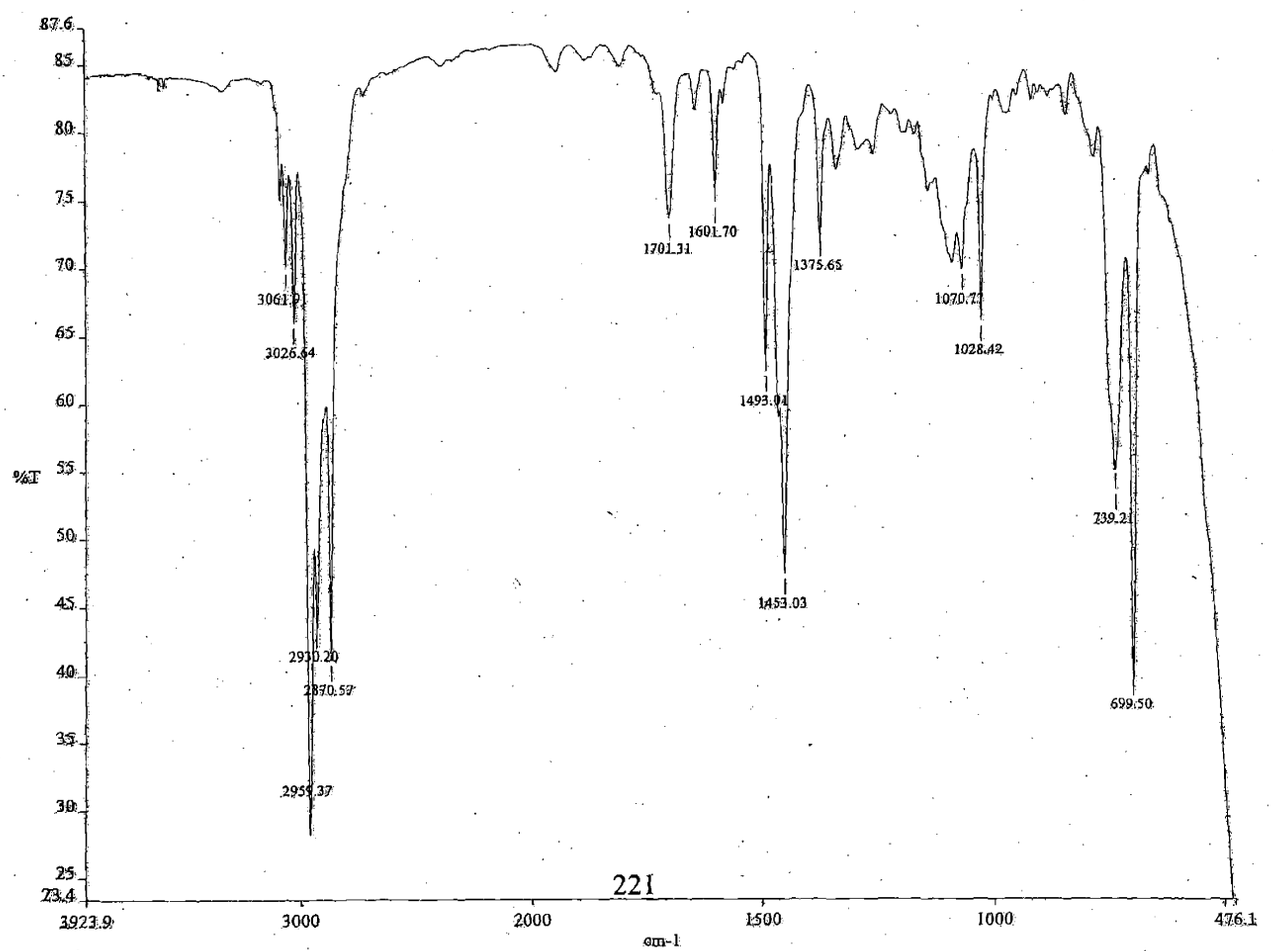
I-44

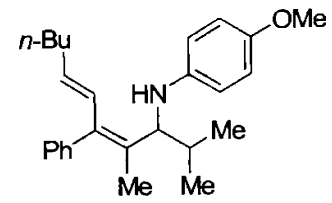

220
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.029
8.569
0.996
2.065
2.117
2.011
1.278
1.077
1.289
2.458
1.211
3.183
3.556
4.028


Et
HN
Me
Ph
Me

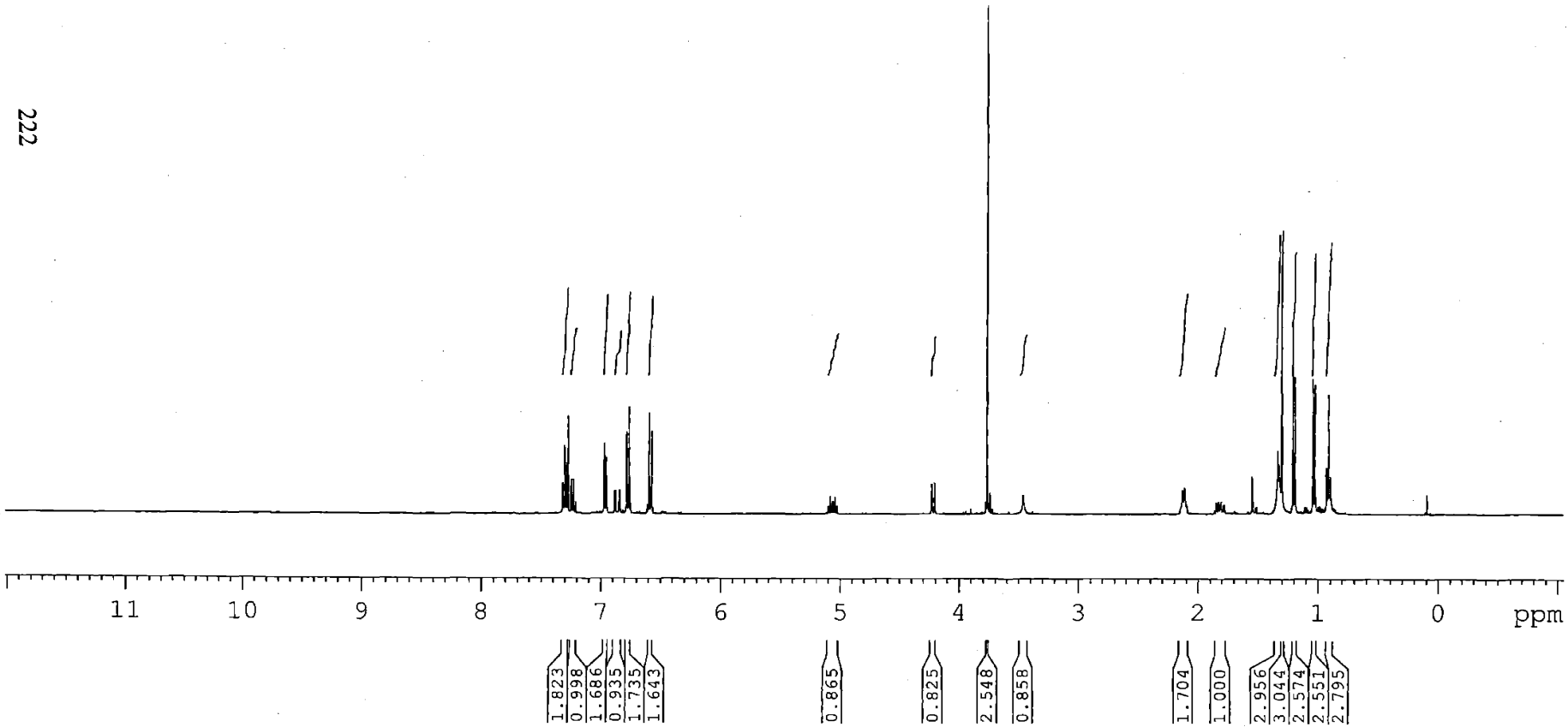
I-44

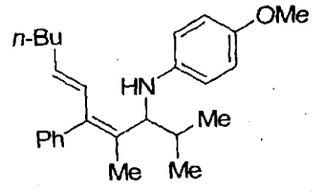
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
87.6
85
80
75
70
65
60
55
50
45
40
35
30
25
23.4
3061.9
3026.64
2930.20
2870.59
2959.37
1701.31
1601.70
1375.65
1493.01
1453.03
1070.77
1028.42
739.21
699.50
3923.9
3000
2000
1500
1000
476.1
cm-1
c:\pe_data\spectra\sjpv135a.sp


n-Bu
OMe
HN
Me
Ph
Me
Me

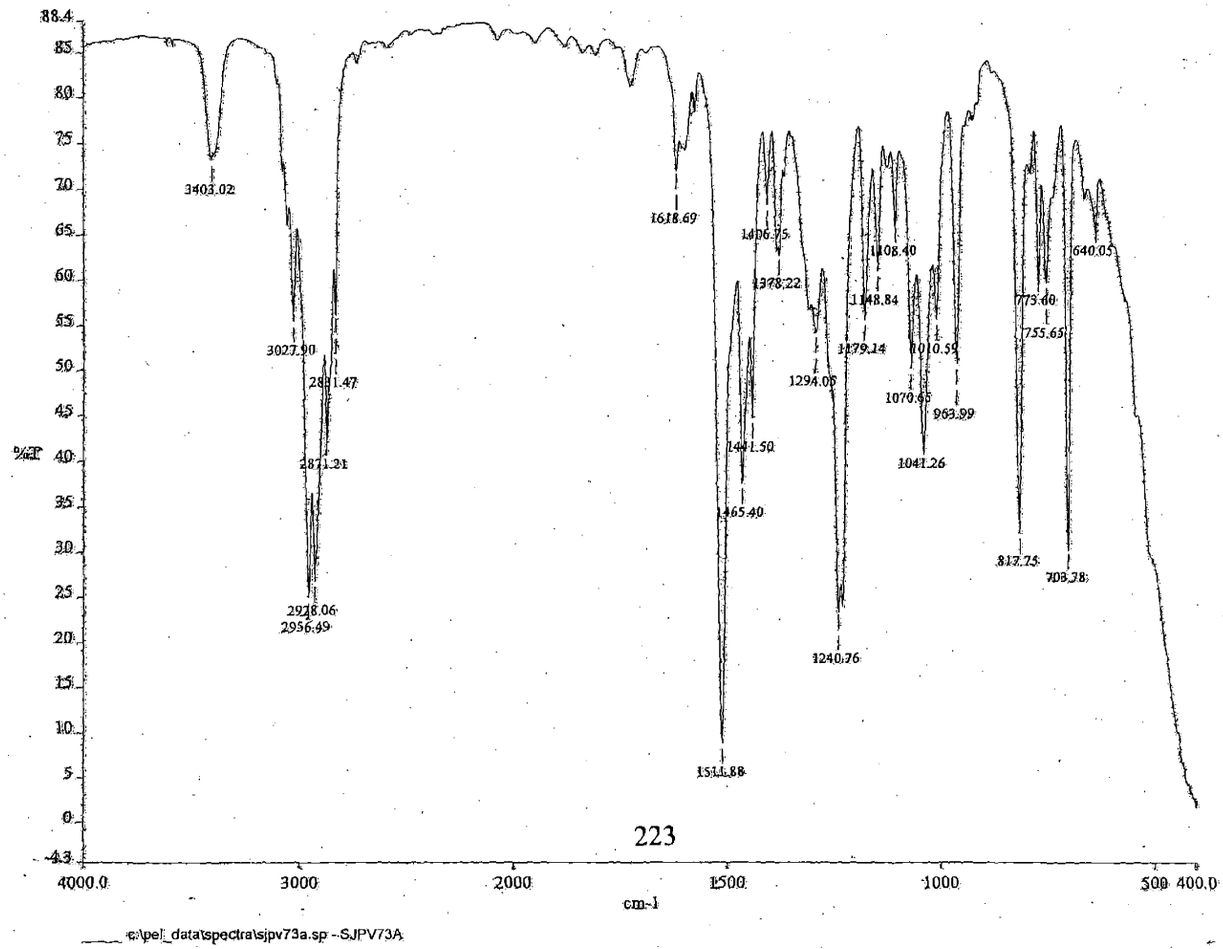
I-46

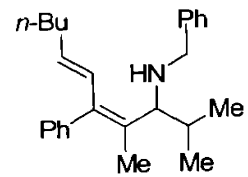

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.823
0.998
1.686
0.935
1.735
1.643
0.865
0.825
2.548
0.858
1.704
1.000
2.956
3.044
2.574
2.551
2.795


n-Bu
OMe
HN
Me
Ph
Me
Me

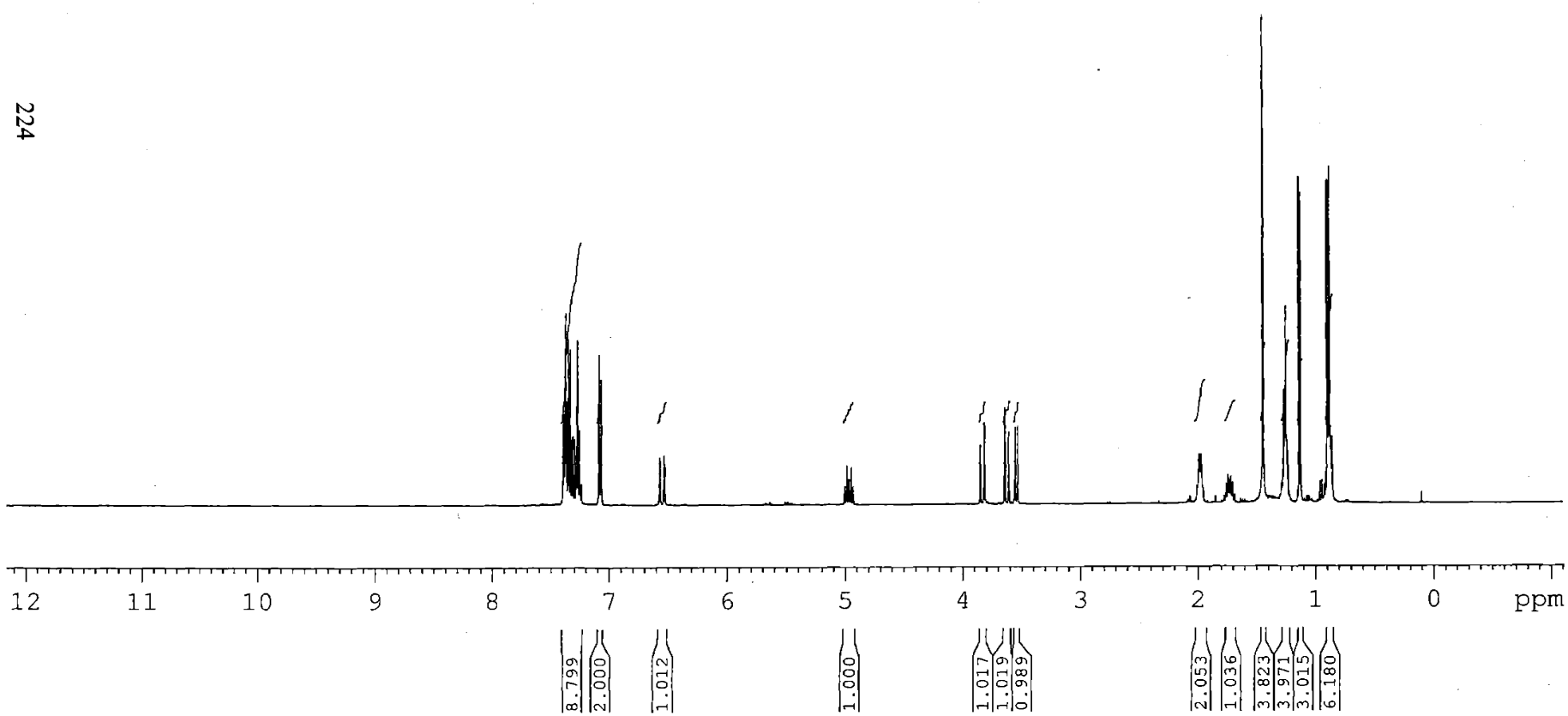
I-46

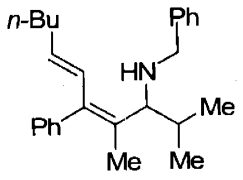
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3403.02
3027.90
2956.49
2918.06
2871.31
2831.47
1618.69
1606.75
1496.40
1465.40
1441.50
1378.22
1294.05
1240.76
1179.14
1148.84
1108.40
1070.65
1041.26
1010.59
963.99
817.75
773.00
755.65
708.38
640.05
1511.88
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\sjpv73a.sp - SJPV73A


n-Bu
Ph
HN
Me
Ph
Me
Me

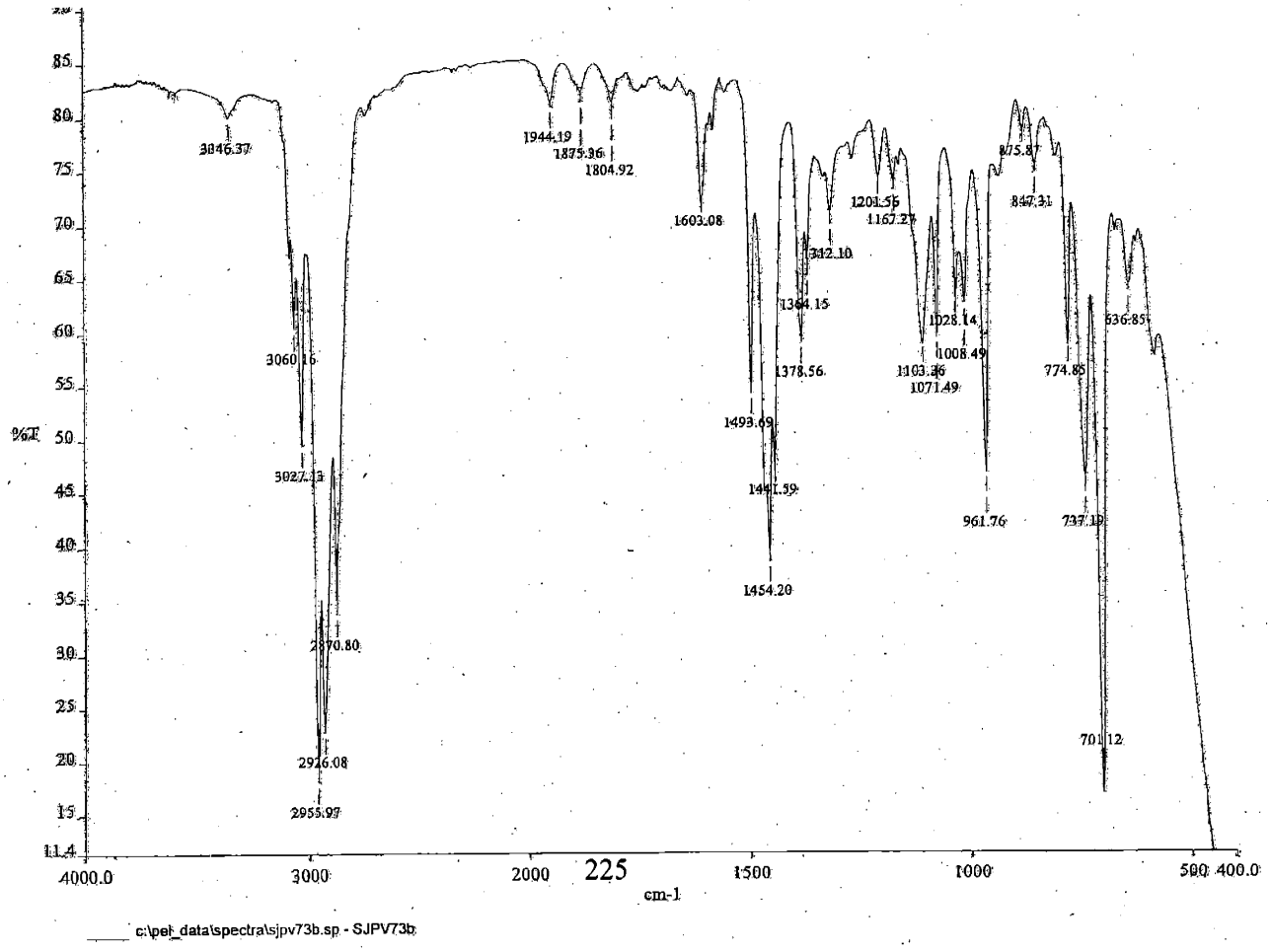
I-47

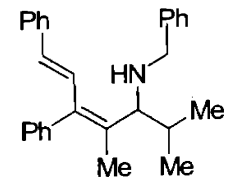

12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
8.799
2.000
1.012
1.000
1.017
1.019
0.989
2.053
1.036
3.823
3.971
3.015
6.180


n-Bu
Ph
HN
Me
Ph
Me
Me

I-47

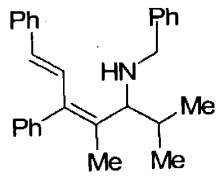
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3846.37
1944.19
1875.36
1804.92
1603.08
1201.55
1167.27
1312.10
1364.15
1378.56
1493.69
1447.59
1454.20
1103.36
1071.49
1028.14
1008.49
961.76
875.87
847.31
774.85
737.19
701.12
636.85
3060.16
3027.13
2870.80
2926.08
2955.97
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv73b.sp - SJPV73b


Ph
Ph
HN
Me
Ph
Me
Me

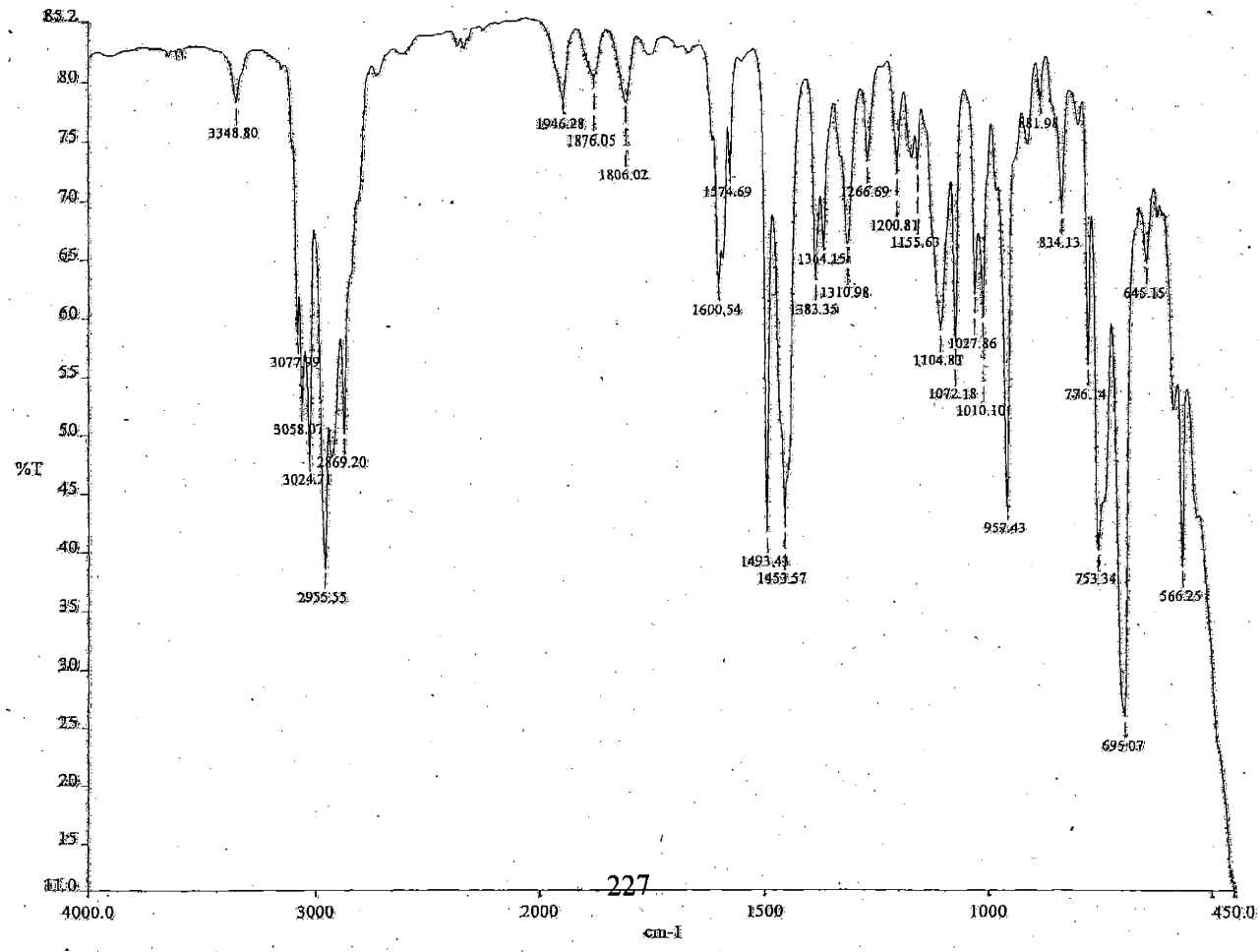
I-48

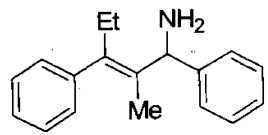
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
14.05
0.90
1.00
1.94
1.17
3.72
2.74
2.83


Ph
Ph
HN
Me
Ph
Me
Me

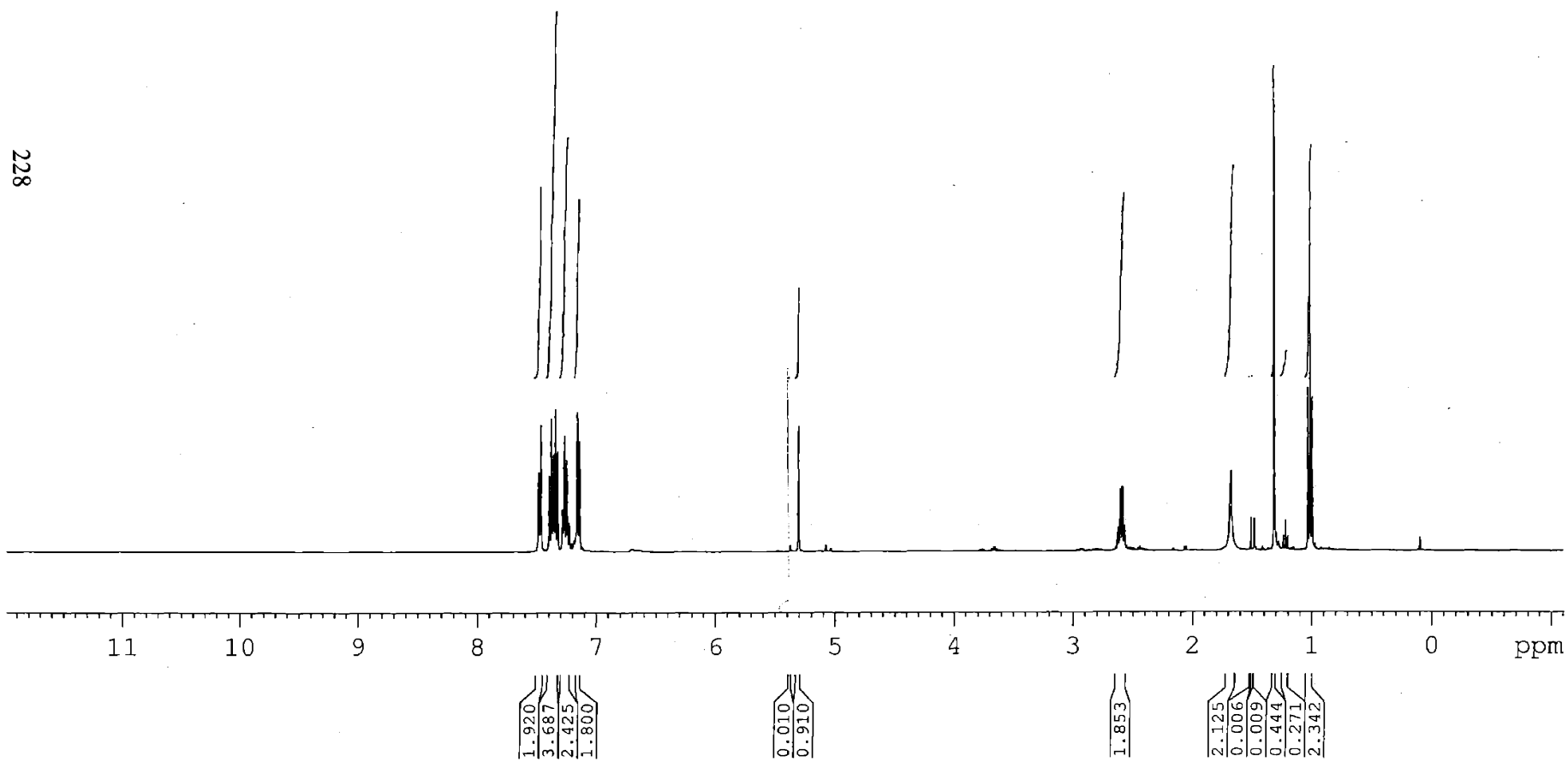
I-48

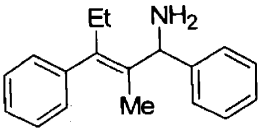
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm


%T
3348.80
3077.99
3058.07
3024.71
2956.55
2869.20
1946.28
1876.05
1806.02
1600.54
1574.69
1493.41
1453.57
1383.35
1364.15
1310.98
1266.69
1200.81
1155.63
1104.81
1072.18
1027.86
1010.10
957.43
881.98
834.13
776.14
753.34
695.07
645.15
566.25
4000.0
3000
2000
1500
1000
450.0
cm-1
c:\pef_data\spectra\sjp80.sp - SJPV80


Et
NH2
Me

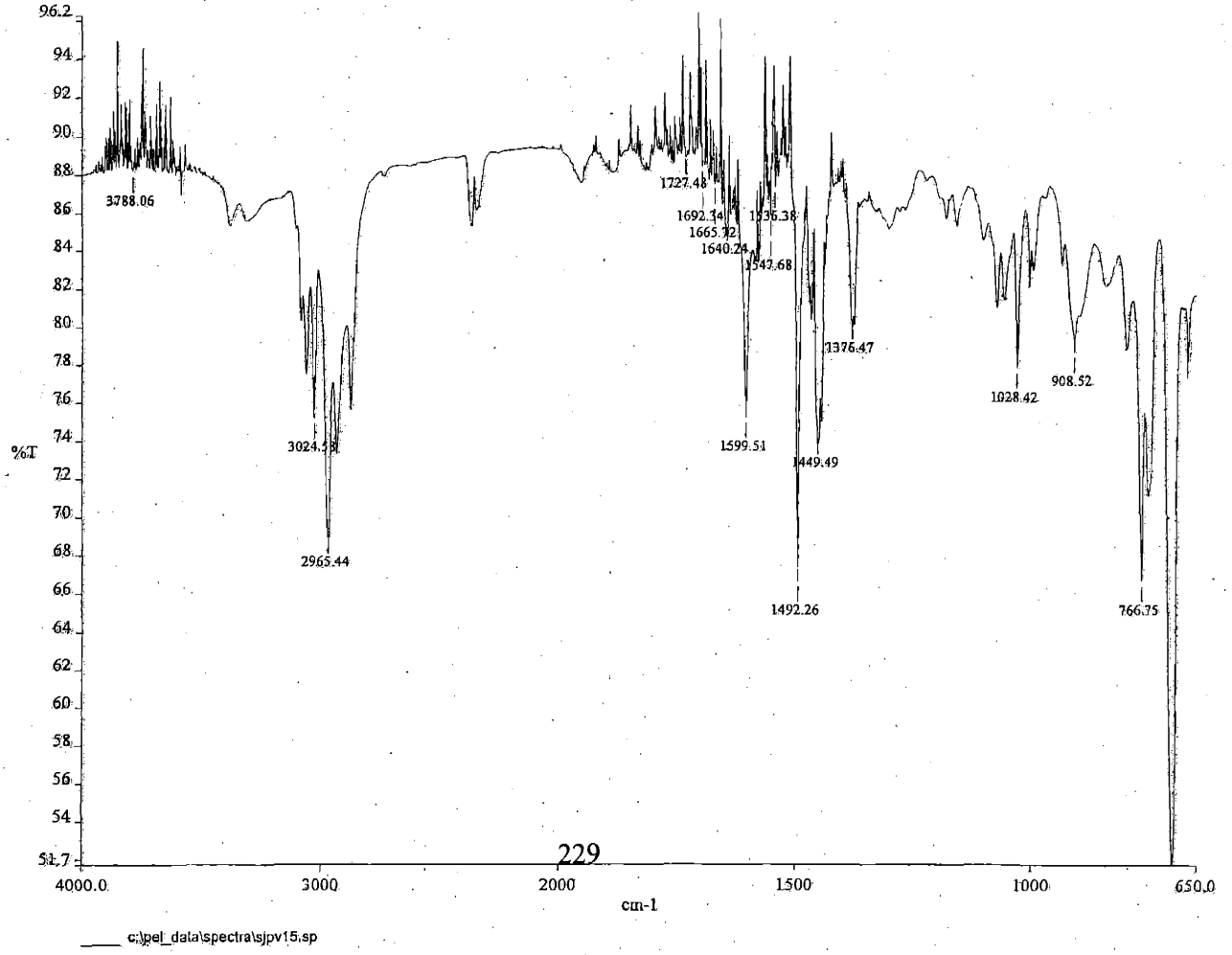
I-49

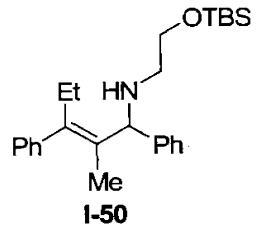

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.920
3.687
2.425
1.800
0.010
0.910
1.853
2.125
0.006
0.009
0.444
0.271
2.342


Et
NH2
Me

I-49

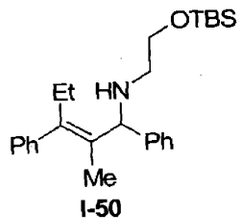
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3788.06
3024.58
2965.44
1727.48
1692.14
1665.12
1640.24
1599.51
1547.68
1536.38
1492.26
1449.49
1376.47
1028.42
908.52
766.75
4000.0
3000
2000
1500
1000
650.0
cm-1
c:\pel_data\spectra\sjpv15.sp

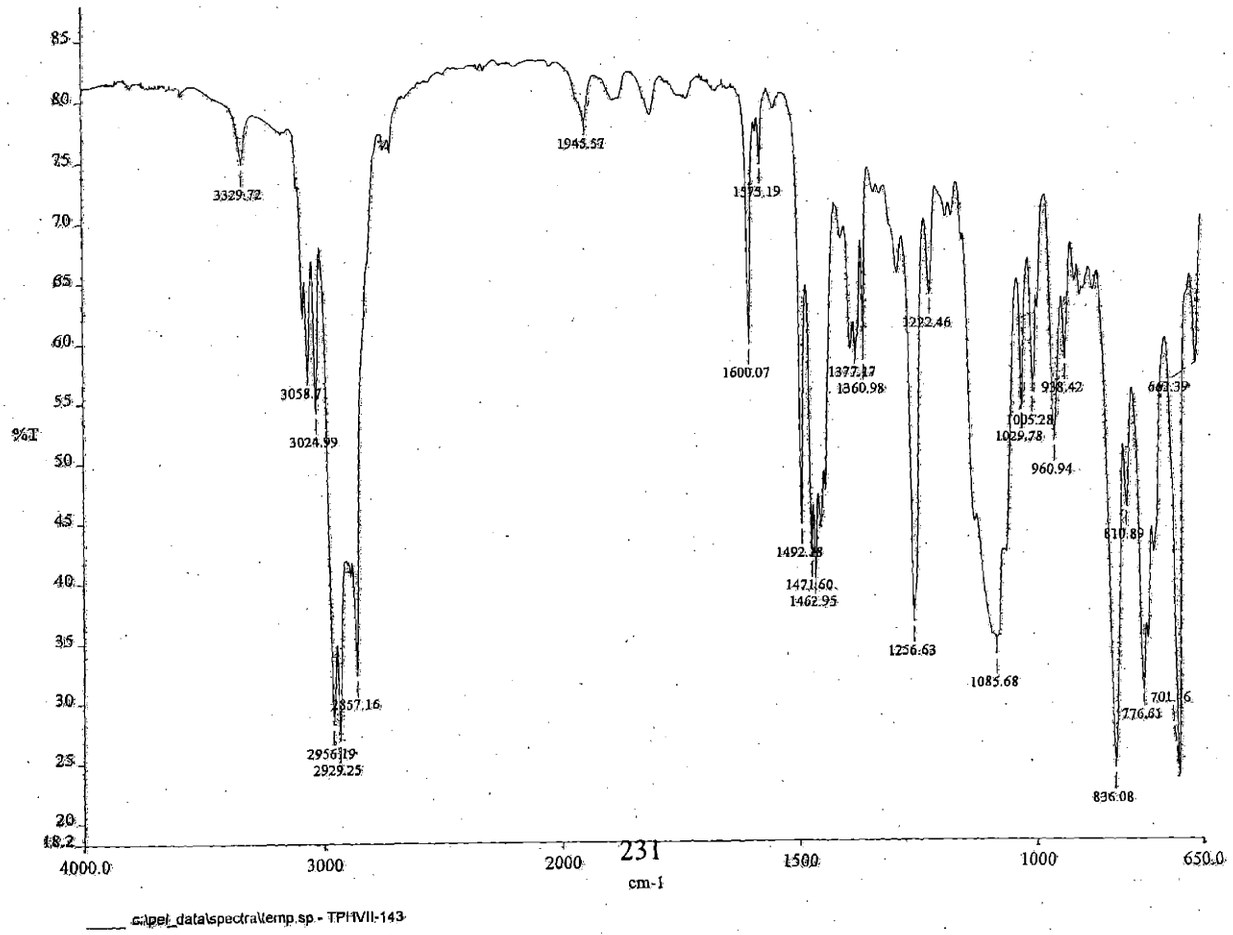

OTBS
Et
HN
Ph
Ph
Me

1-50

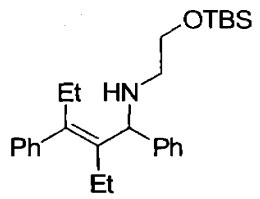
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.017
2.085
1.099
1.094
0.490
0.986
0.504
0.508
1.006
1.561
1.572
4.502
3.000



I-50

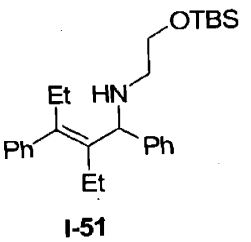


c:\pel_data\spectra\emp.sp - TPHVII-143


OTBS
Et
HN
Ph
Ph
Et

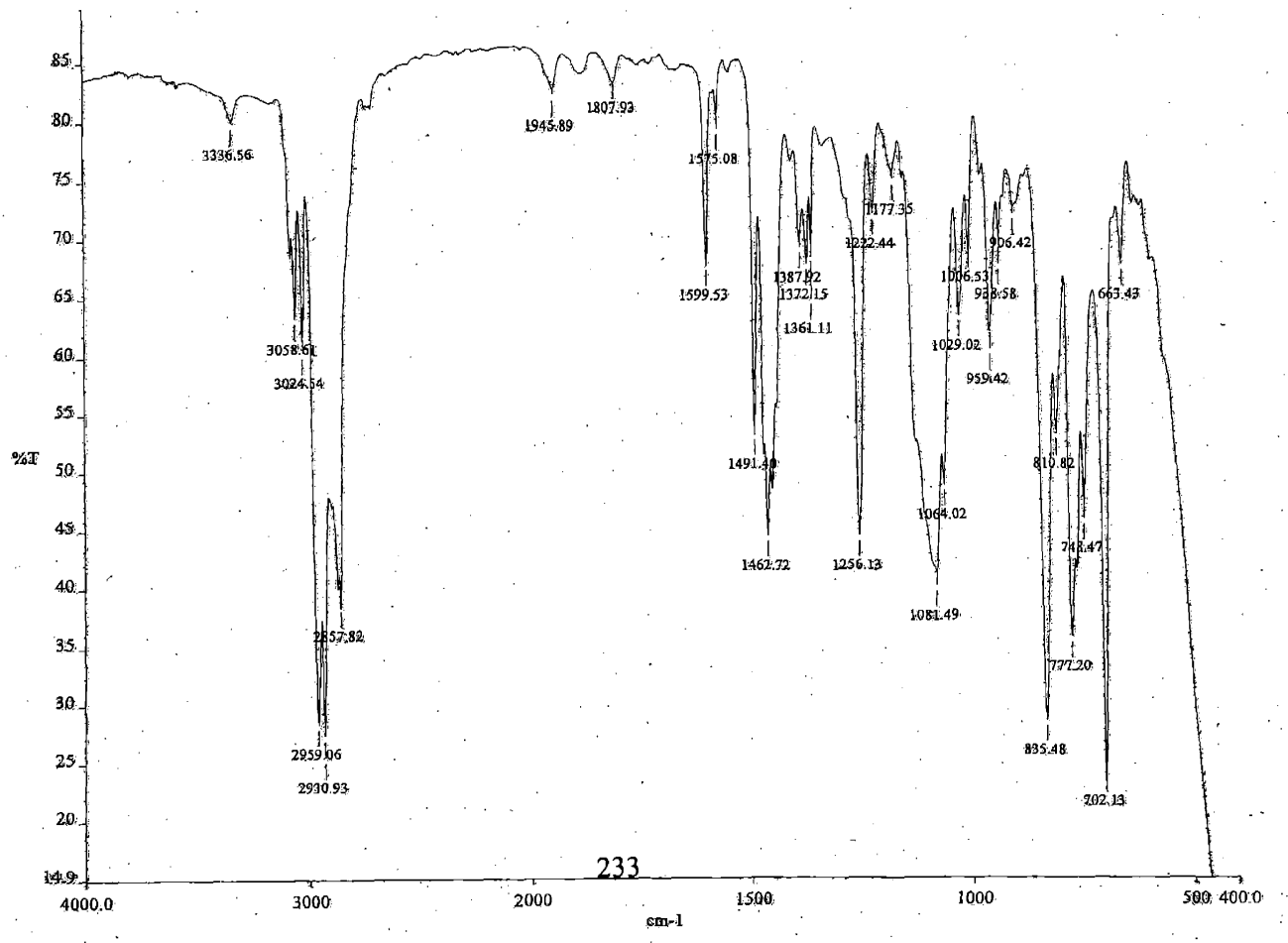
I-51

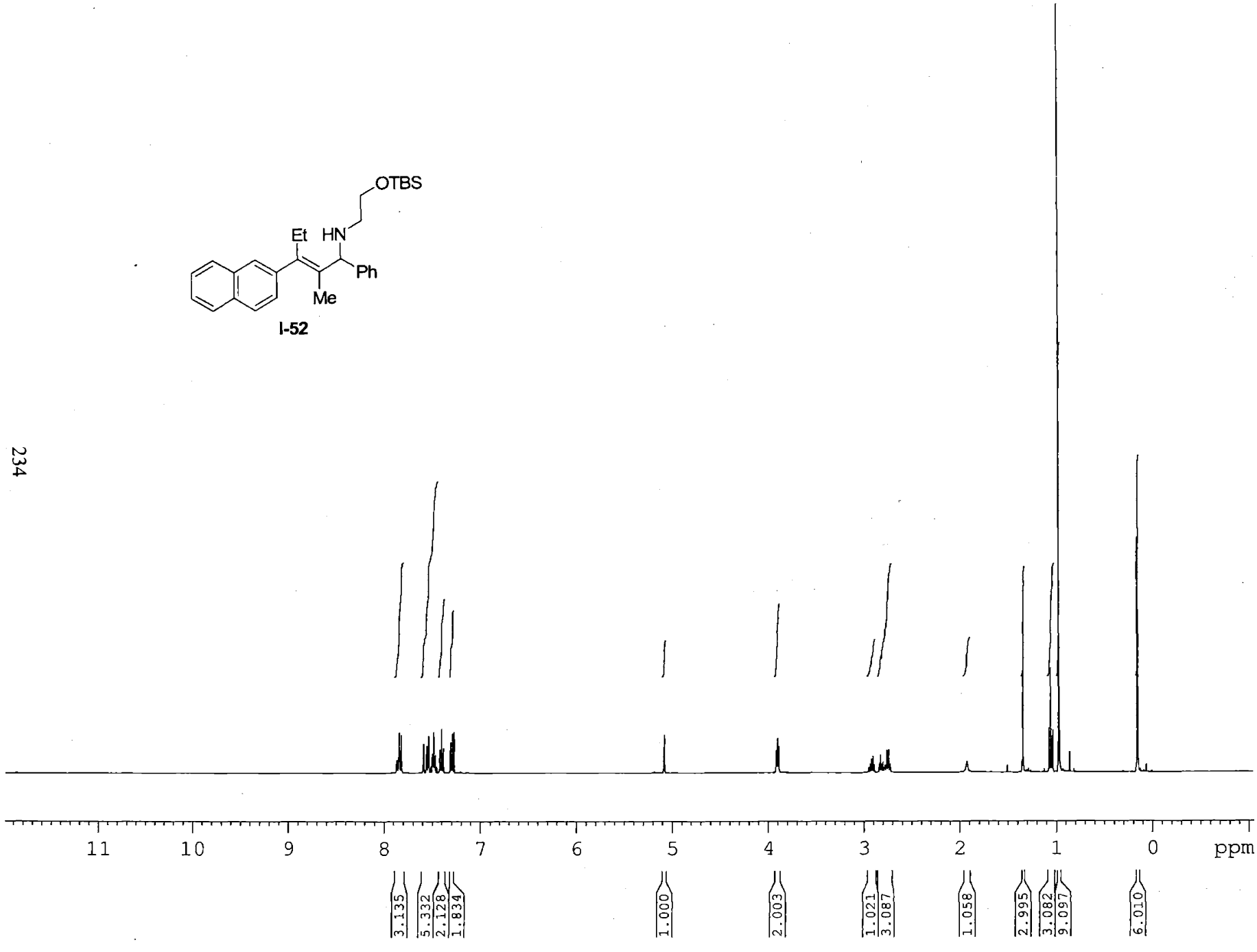
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.007
4.379
2.208
2.140
1.000
1.946
1.017
1.052
1.996
2.032
0.954
3.015
9.306
3.102
6.042

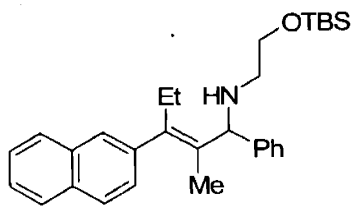

OTBS
Et
HN
Ph
Ph
Et

I-51

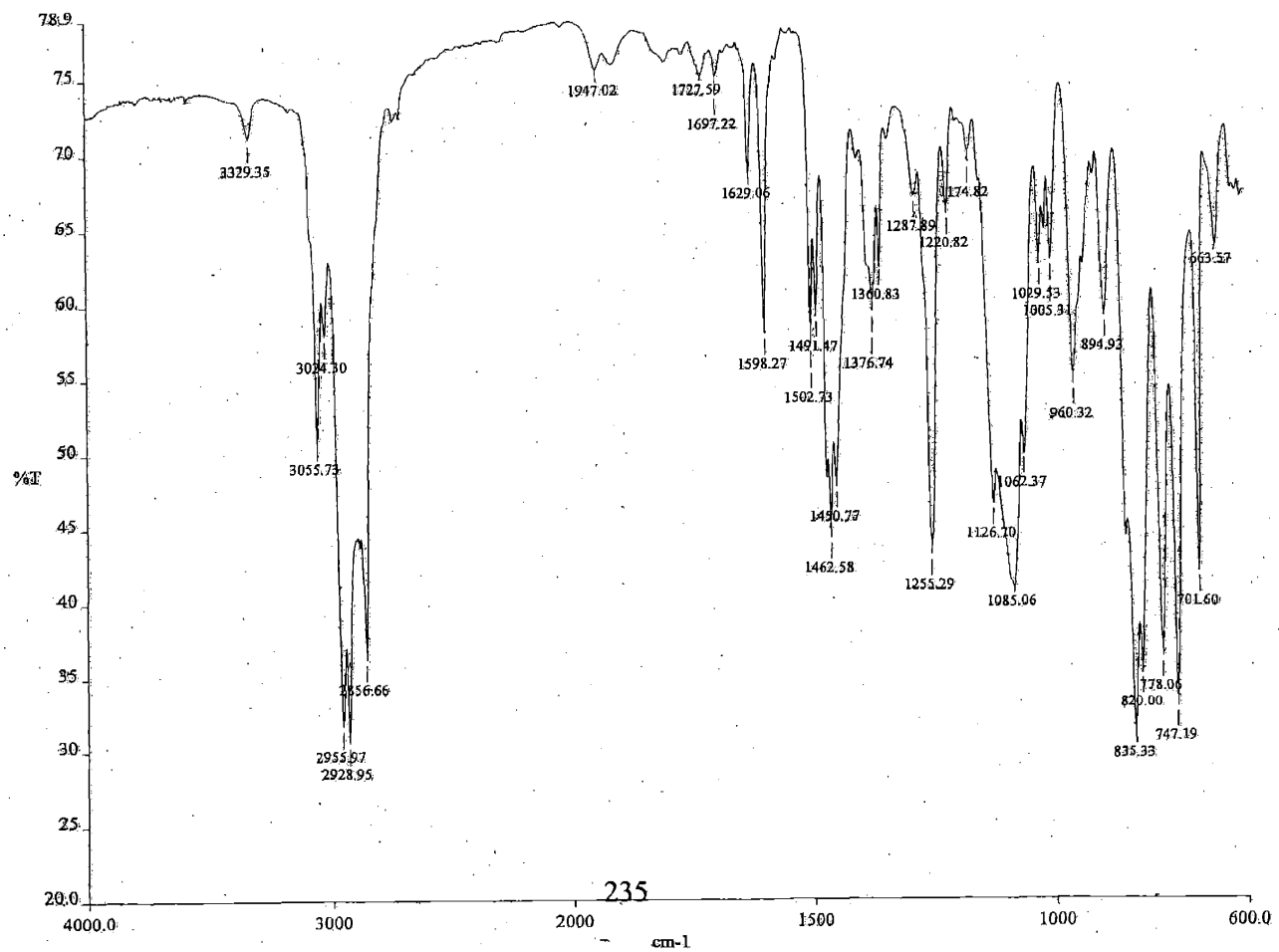
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3336.56
3058.61
3024.54
2957.82
2959.06
2930.93
1945.89
1807.93
1599.53
1575.08
1491.49
1462.72
1387.92
1372.15
1361.11
1256.13
1222.44
1177.35
1064.02
1081.49
1029.02
1006.53
955.42
906.42
928.58
810.82
748.47
777.20
835.48
702.13
663.43
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\sjpv137a.sp

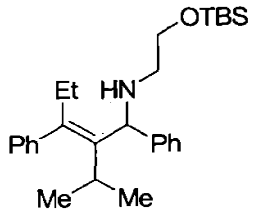

OTBS
Et
HN
Ph
Me
I-52
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.135
5.332
2.128
1.834
1.000
2.003
1.021
3.087
1.058
2.995
3.082
9.097
6.010



I-52

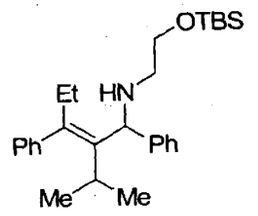


c:\pe_data\spectra\sjpv170.sp - SJPV170

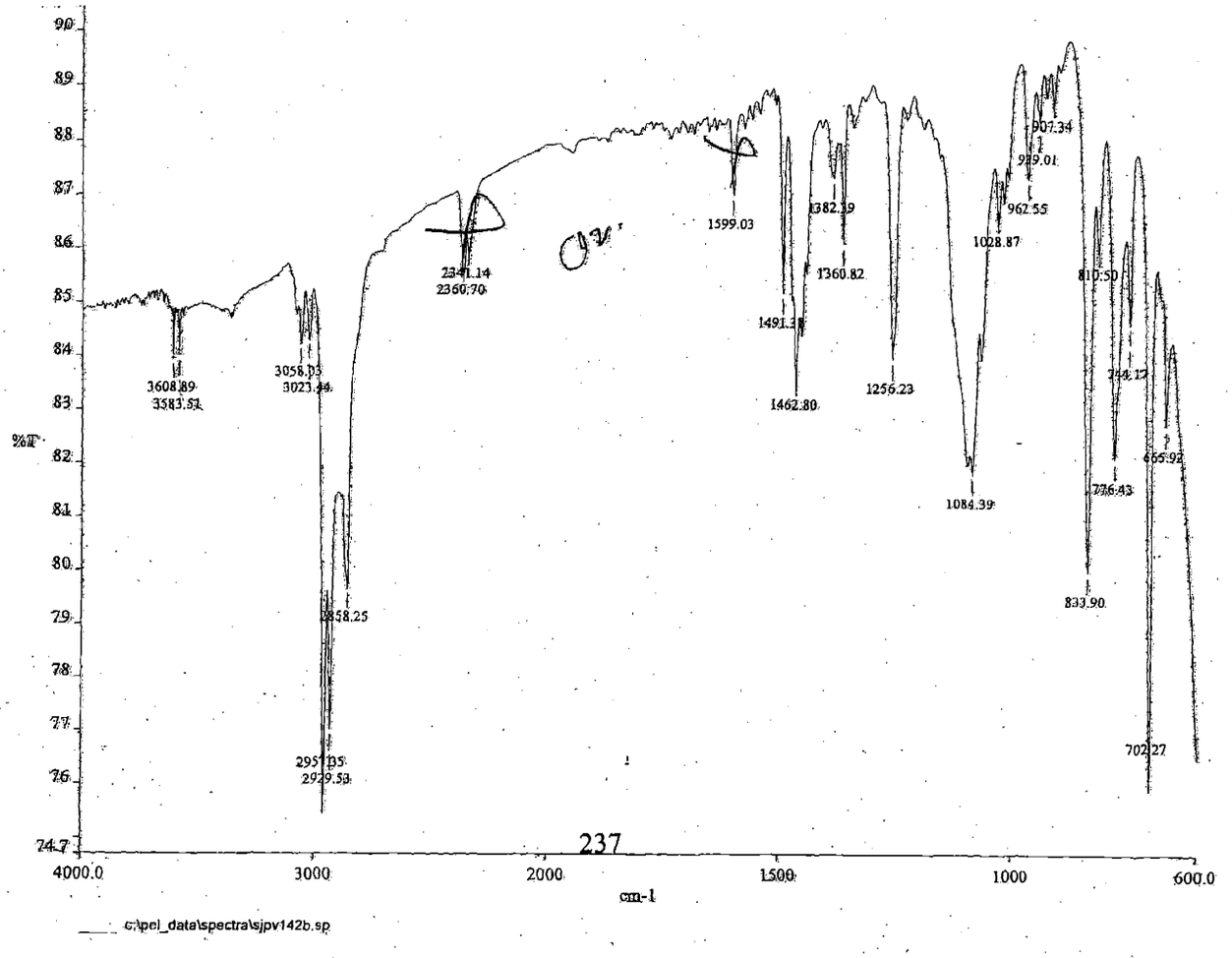

OTBS
Et
HN
Ph
Ph
Me
Me

I-53

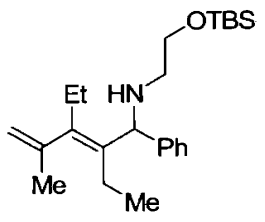
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.039
4.544
2.160
2.122
1.000
2.153
2.143
2.147
1.029
1.644
15.963
2.910
6.137



I-53

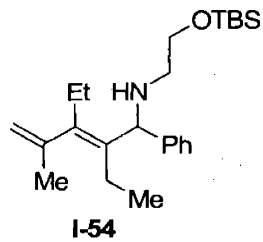


c:\pei_data\spectra\sjpv142b.sp


OTBS
Et
HN
Ph
Me
Me

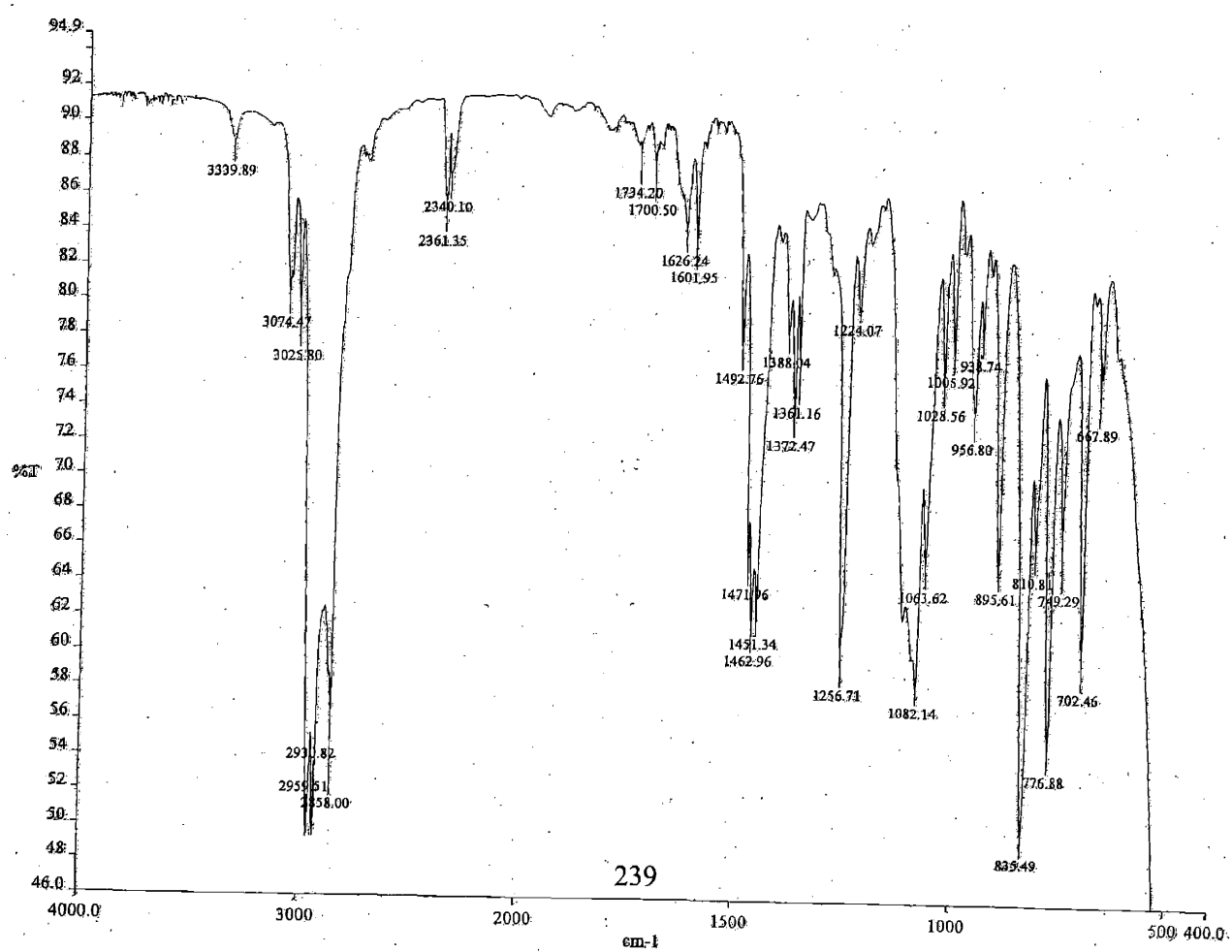
I-54

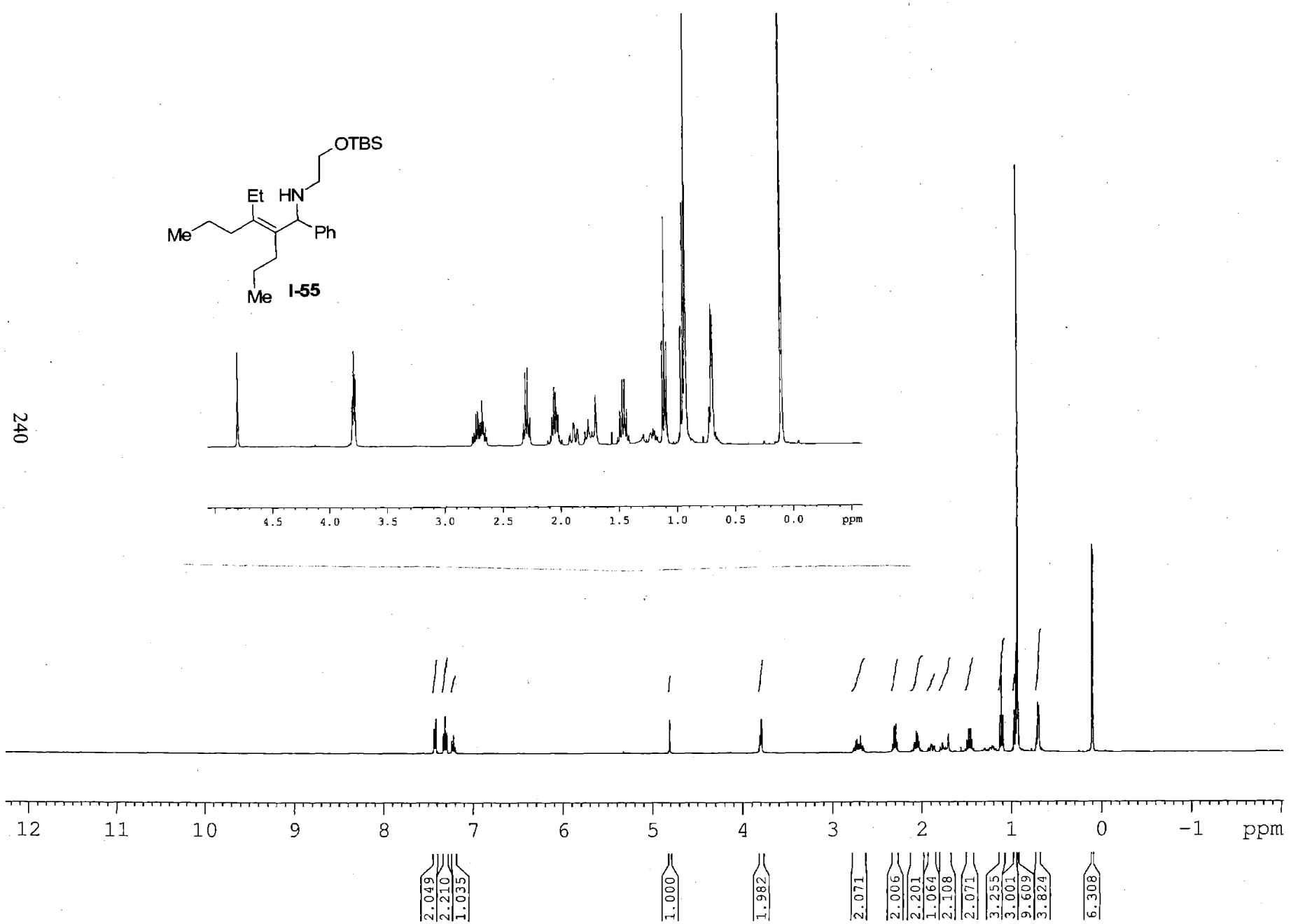
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.975
2.152
1.108
1.063
1.000
1.039
2.030
2.061
2.159
1.266
4.258
3.253
9.790
3.164
6.445

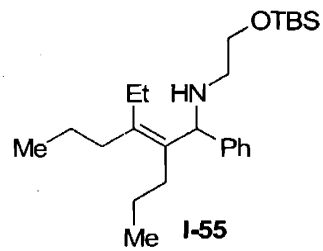

OTBS
Et
HN
Ph
Me
Me

I-54

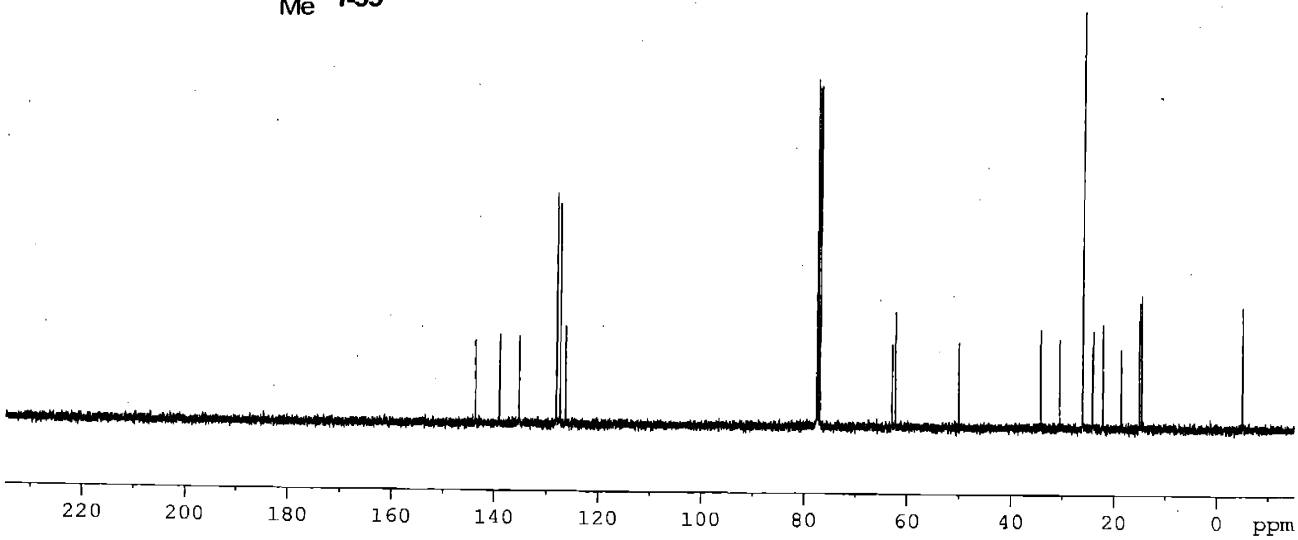
220
200
180
160
140
120
100
80
60
40
20
0
ppm

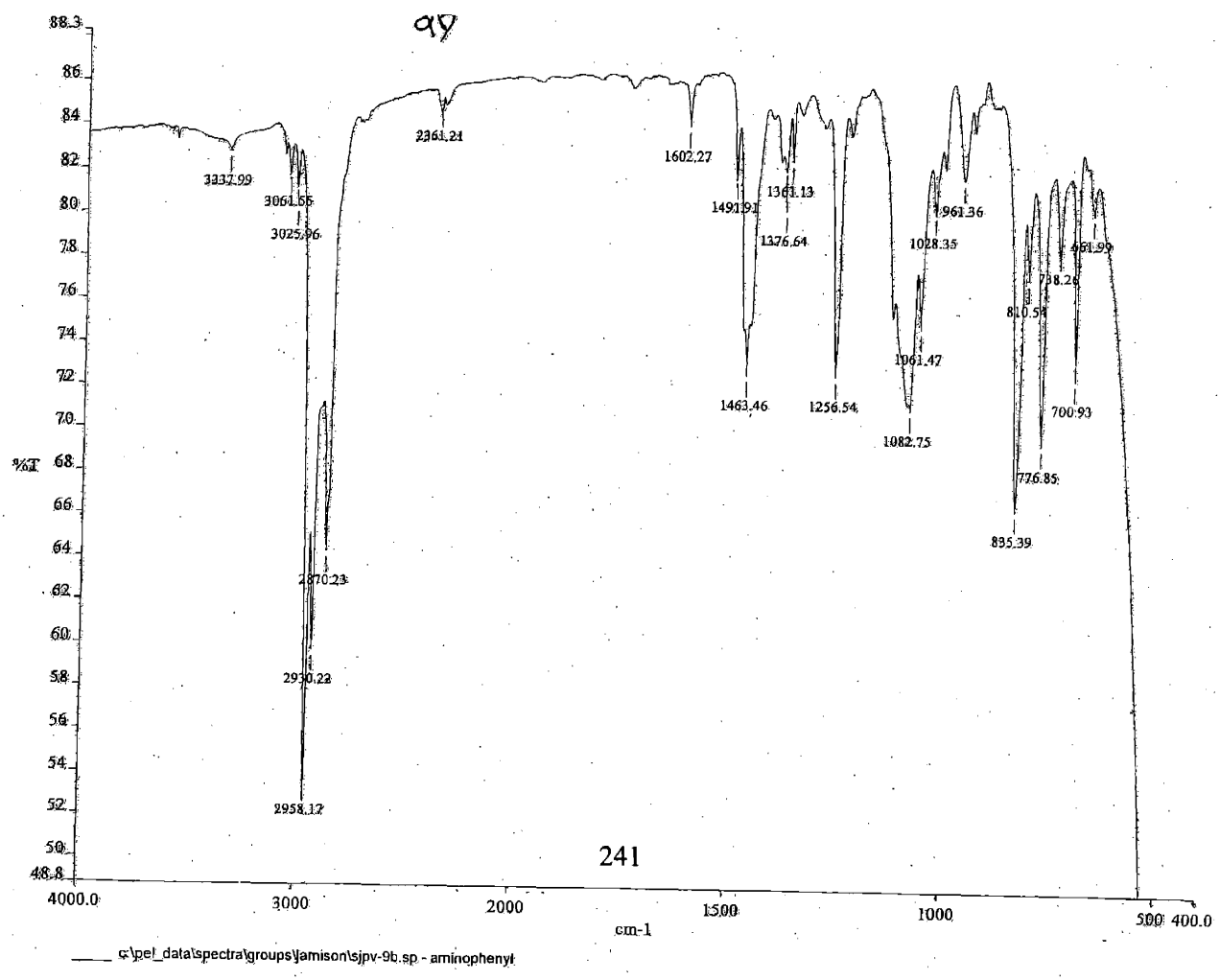

%T
3339.89
3074.47
3025.80
2340.10
2361.35
1734.20
1700.50
1626.24
1601.95
1492.76
1388.04
1361.16
1372.47
1224.07
1471.96
1451.34
1462.96
1256.71
1082.14
1063.62
1028.56
1005.92
938.74
956.80
895.61
810.81
749.29
667.89
776.88
702.46
839.49
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pet_data\spectra\sjpvi38.sp - SJPVI-38A

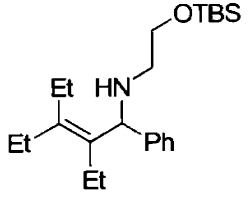

OTBS
Et HN
Me
Ph
Me
I-55
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
2.049 2.210 1.035 1.000 1.982 2.071 2.006 2.201 1.064 2.108 2.071 3.255 3.001 9.609 3.824 6.308


OTBS
Et
HN
Me
Ph
Me

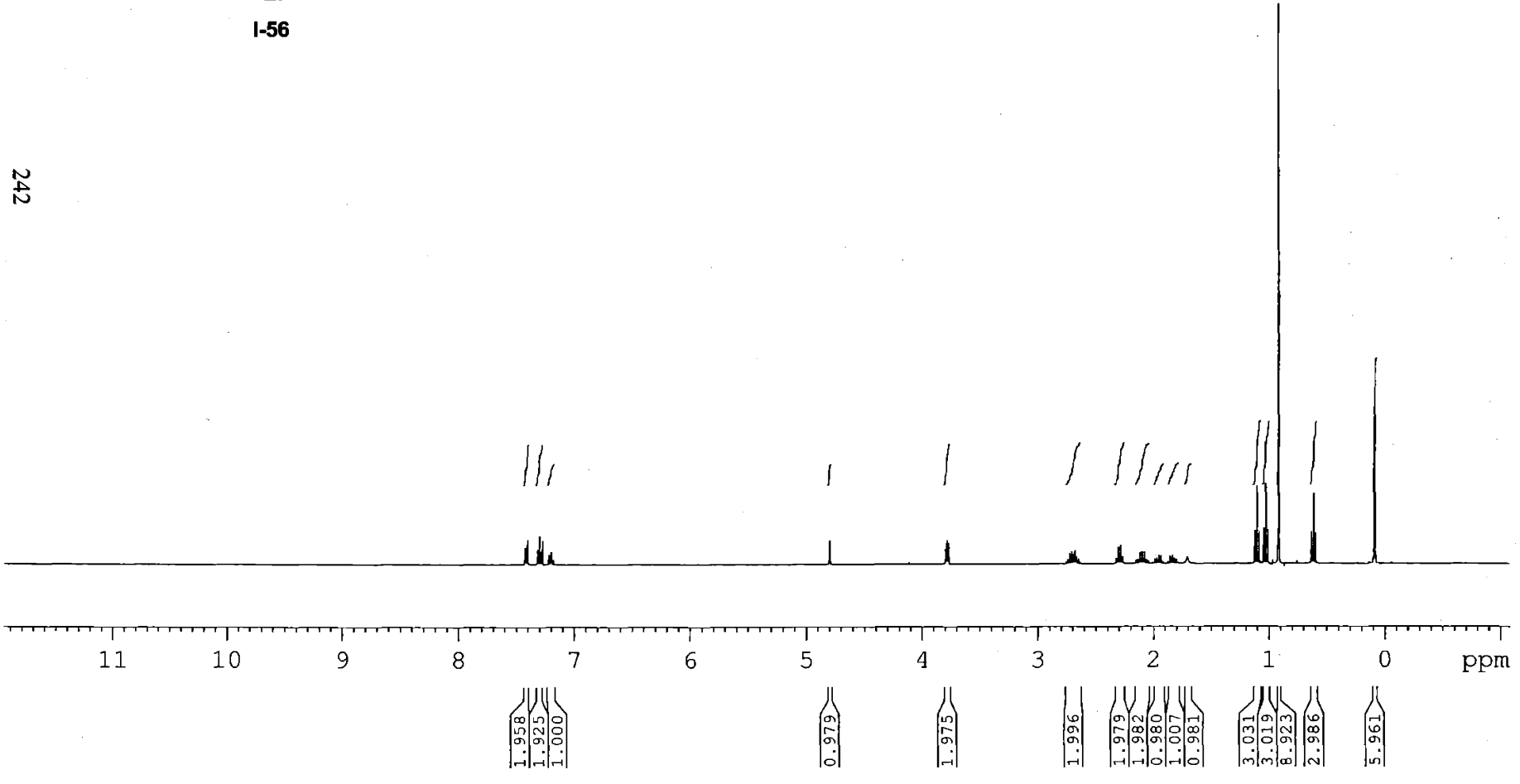
I-55

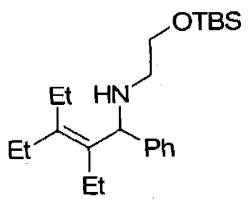

220
200
180
160
140
120
100
80
60
40
20
0
ppm


97
%T
3337.99
3061.55
3025.96
2361.21
1602.27
1491.91
1363.13
1376.64
1463.46
1256.54
1028.35
1961.36
1961.47
1082.75
810.58
758.26
751.99
700.93
776.85
835.39
2870.23
2930.22
2958.17
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\groups\jamison\sjpv-9b.sp - aminophenyl


OTBS
Et
HN
Et
Ph
Et

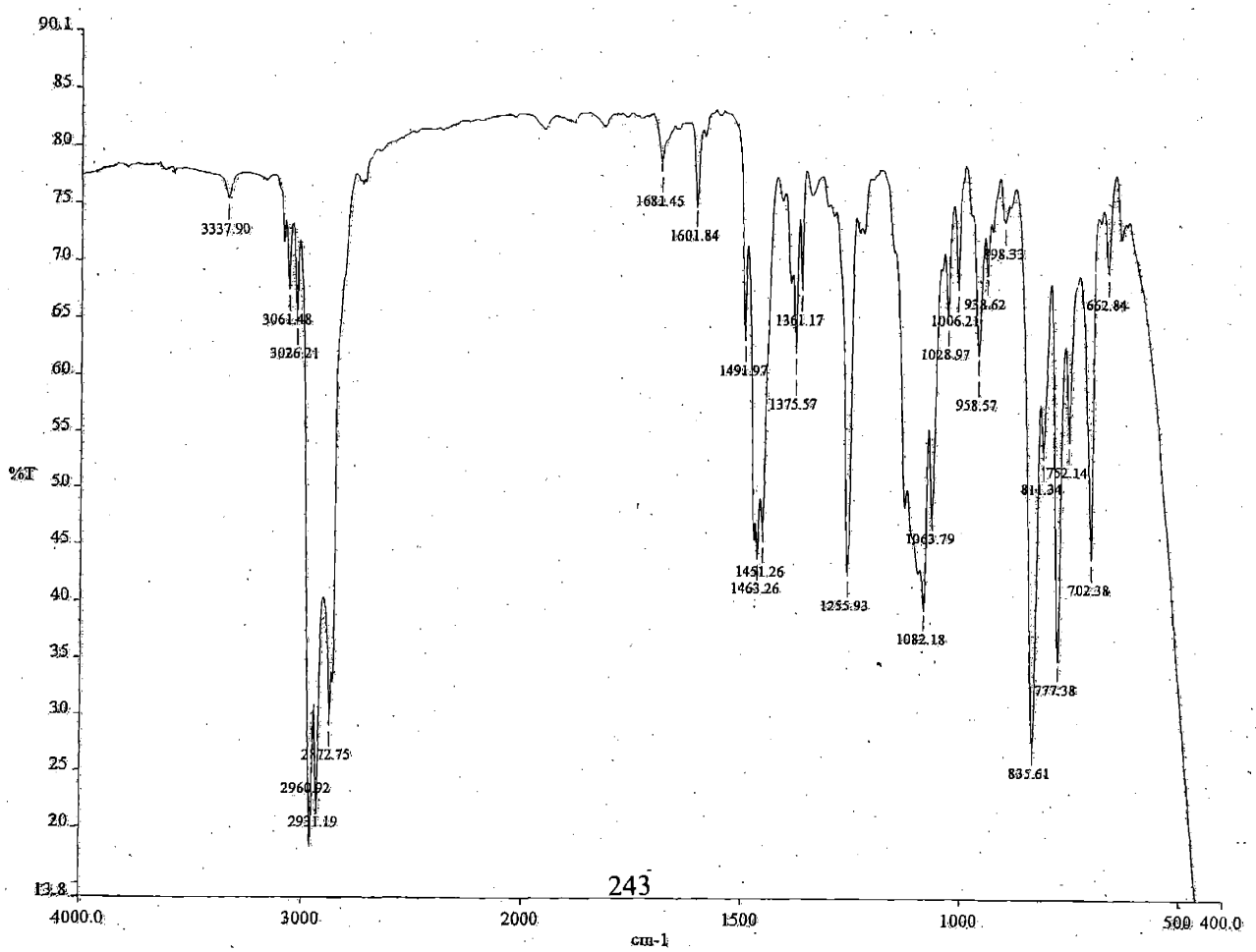
I-56

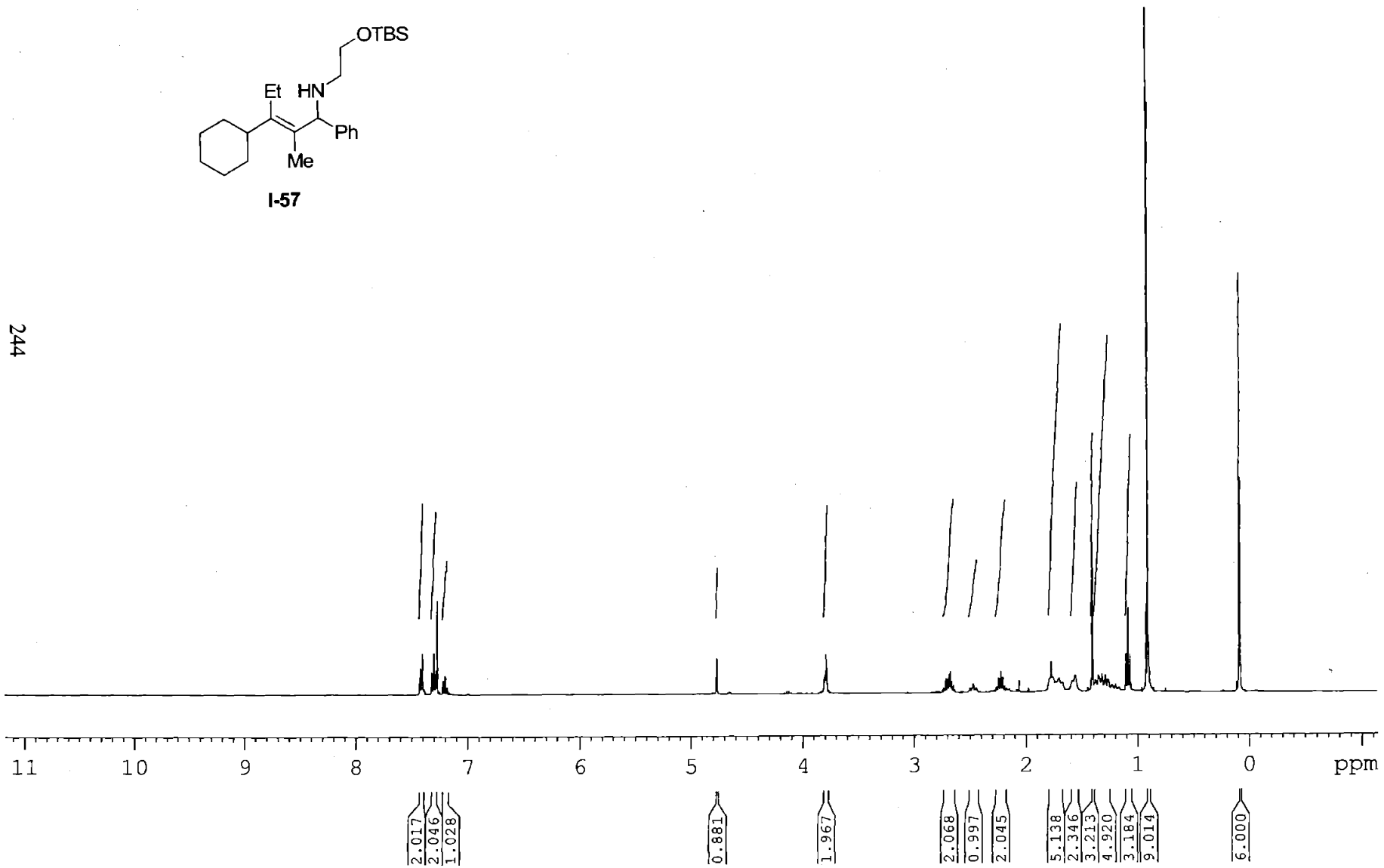

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.958
1.925
1.000
0.979
1.975
1.996
1.979
1.982
0.980
1.007
0.981
3.031
3.019
8.923
2.986
5.961

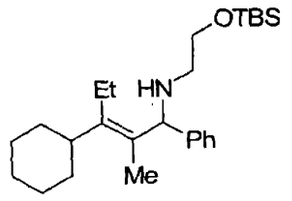

OTBS
Et
HN
Et
Ph
Et

I-56

220
200
180
160
140
120
100
80
60
40
20
0
ppm

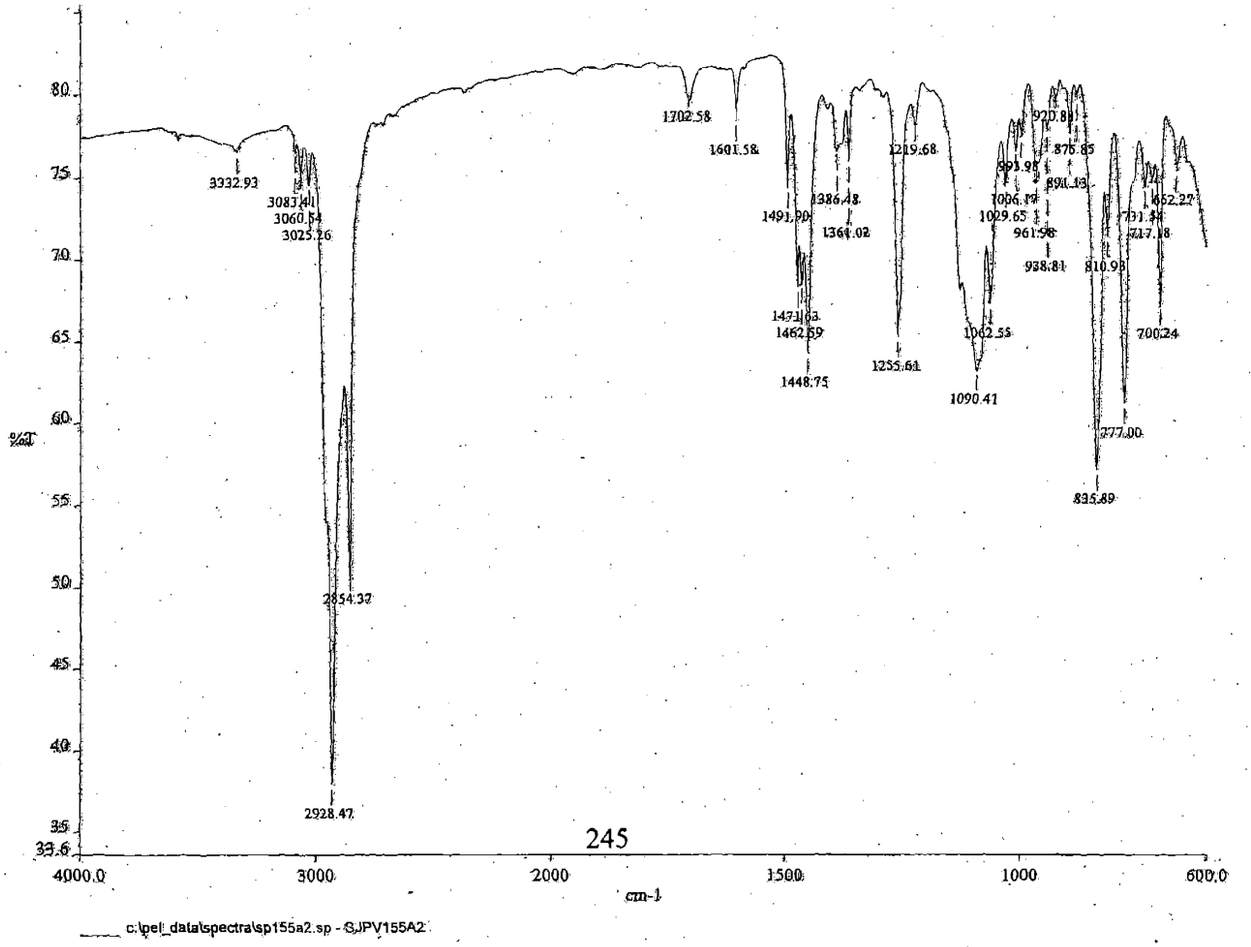

%T
3337.90
3061.48
3026.21
2972.75
2960.92
2931.19
1681.45
1601.84
1491.97
1451.26
1463.26
1375.57
1361.17
1255.93
1082.18
1028.97
1006.23
998.33
958.62
958.57
963.79
835.61
814.34
777.38
752.14
702.38
652.84
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv162.sp

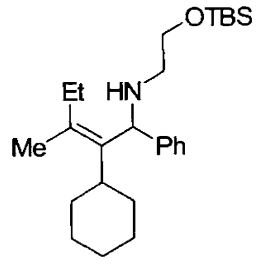

OTBS
Et
HN
Ph
Me
I-57
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.017
2.046
1.028
0.881
1.967
2.068
0.997
2.045
5.138
2.346
3.213
4.920
3.184
9.014
6.000


OTBS
Et
HN
Ph
Me

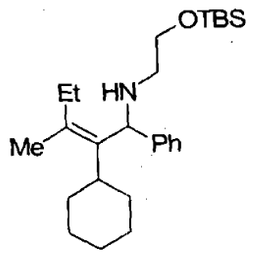
I-57

220
200
180
160
140
120
100
80
60
40
20
0
ppm

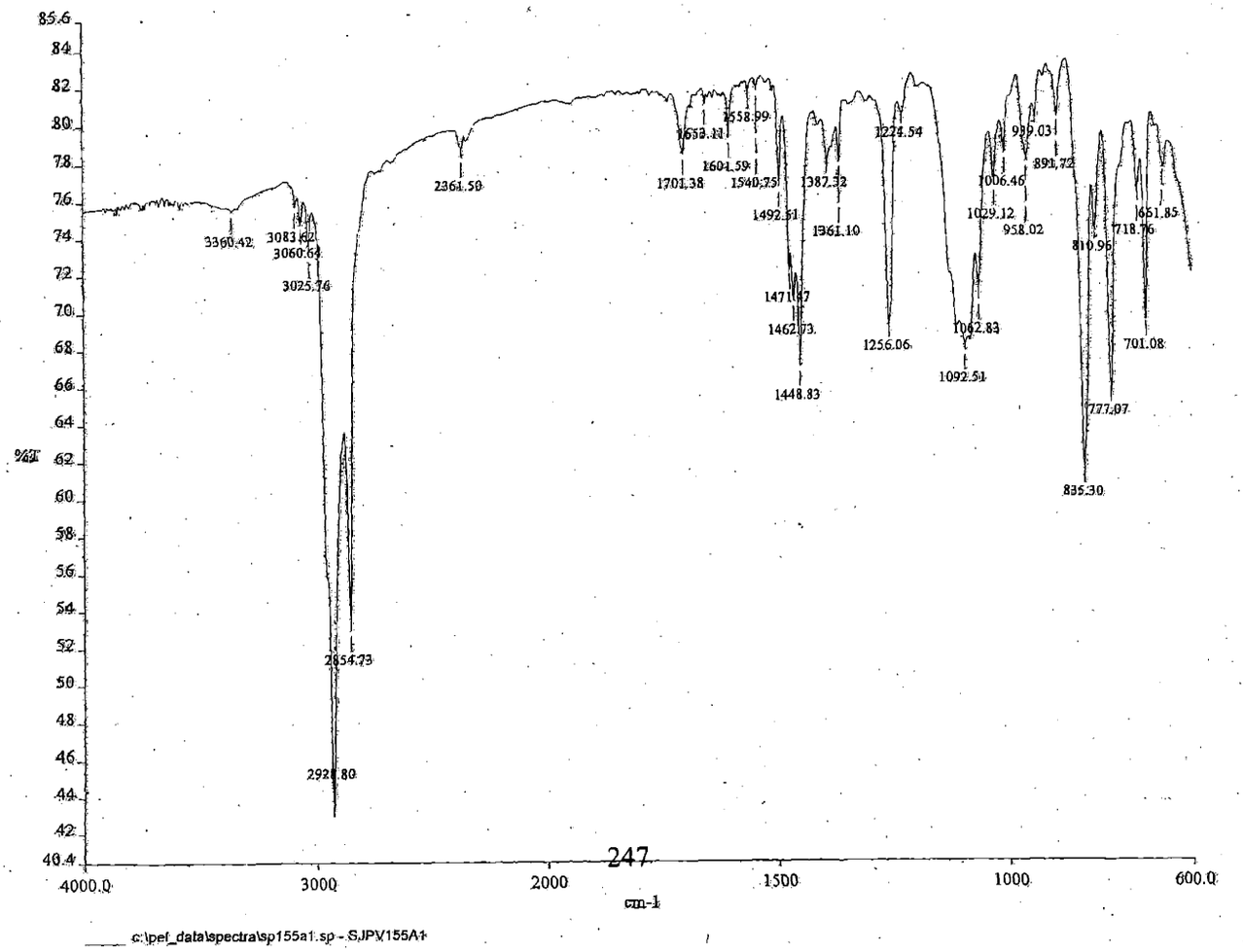

%T
80
75
70
65
60
55
50
45
40
35
33.6
3332.93
3083.41
3060.54
3025.26
2928.47
2854.37
1702.58
1601.58
1491.90
1473.63
1462.59
1448.75
1386.48
1364.02
1255.61
1219.68
1090.41
1062.55
1029.65
1006.11
993.95
961.98
938.81
920.89
891.43
876.85
835.89
810.93
777.00
731.34
717.18
700.24
652.27
4000.0
3000
2000
1500
1000
600.0
cm-1
c:\pel_data\spectra\sp155a2.sp - S_JPV155A2

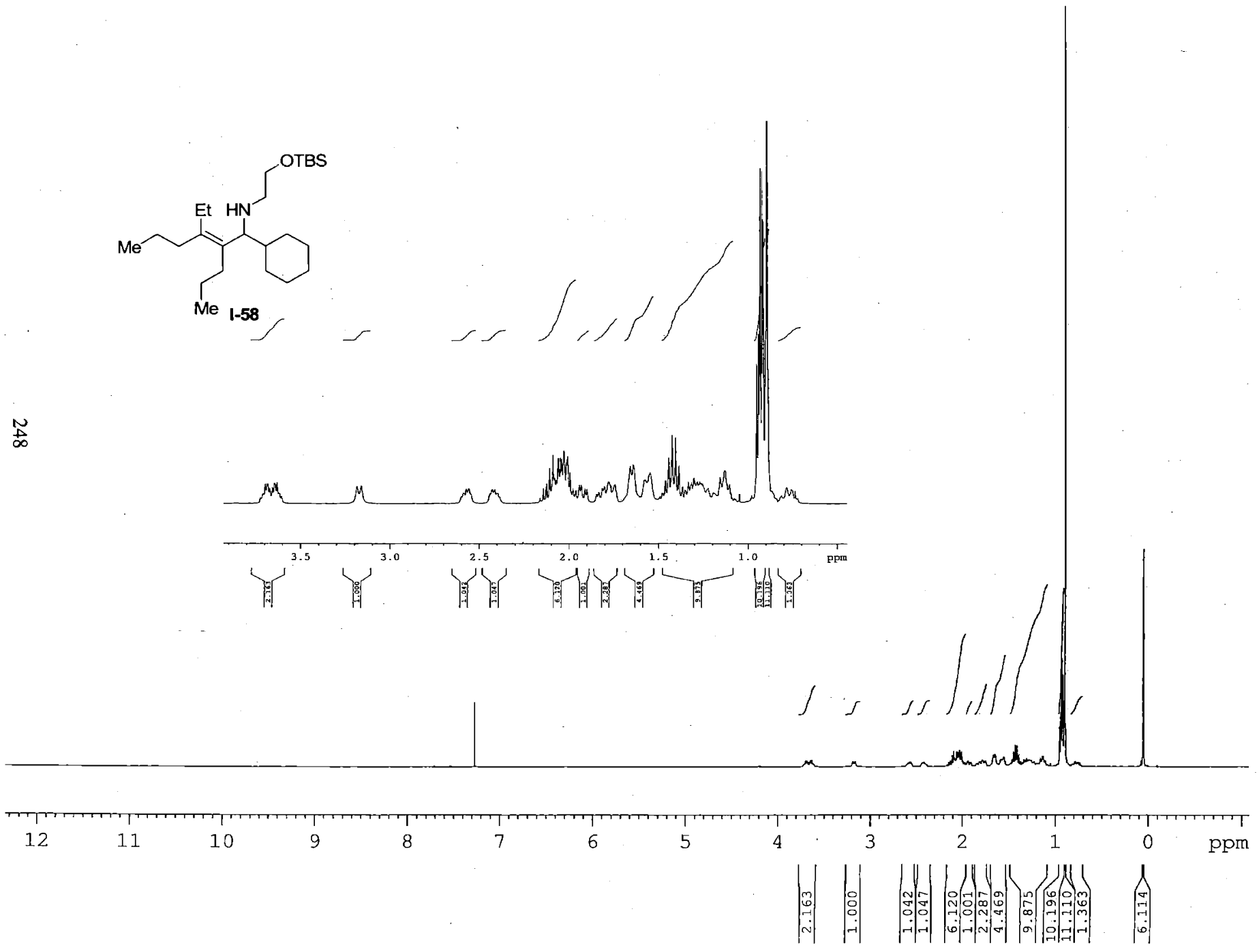


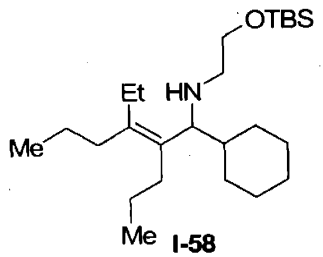
I-57 regioisomer



I-57 regioisomer

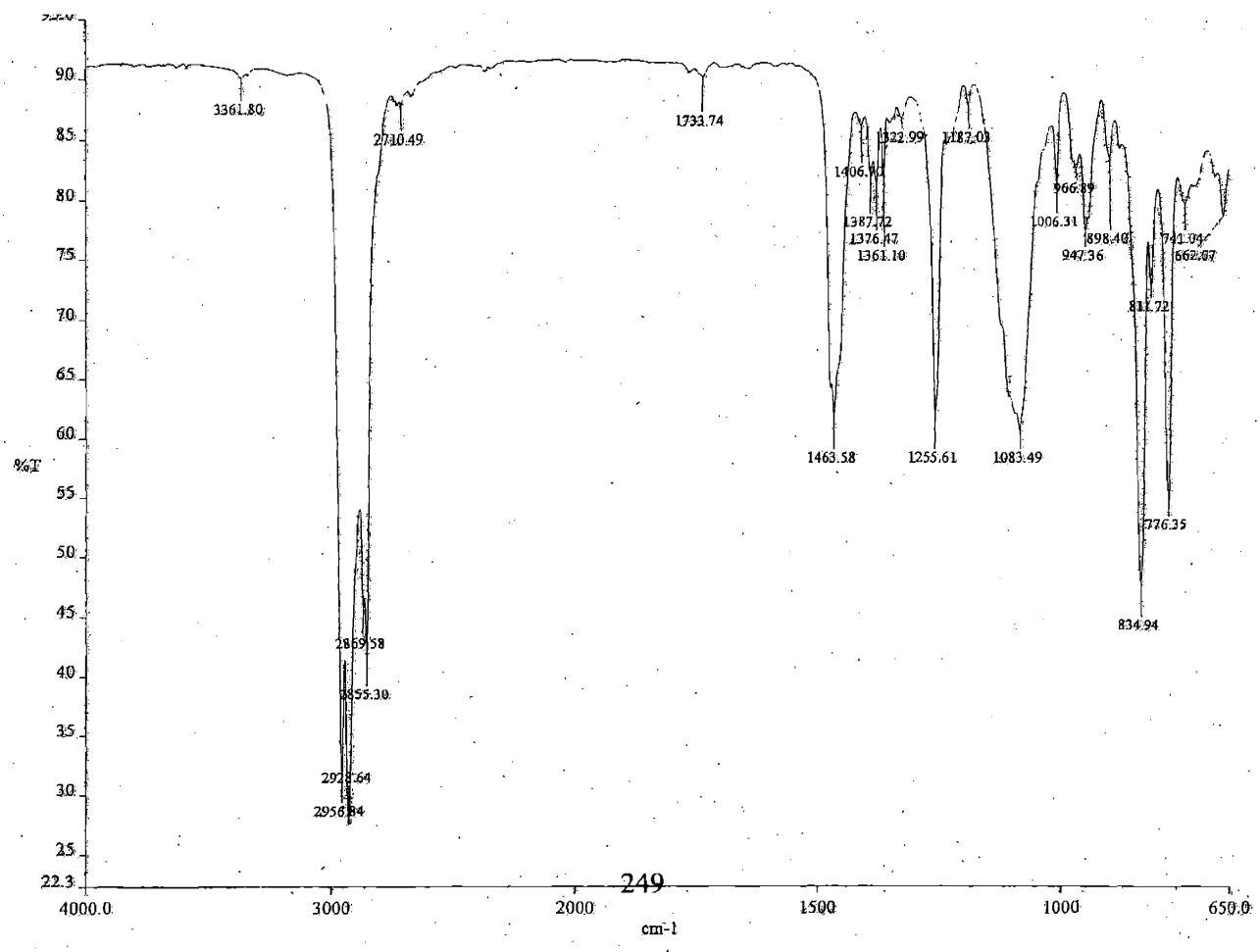


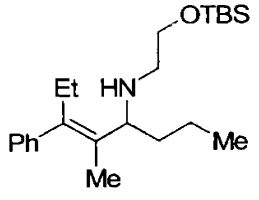

OTBS
Et HN
Me
Me
I-58
3.5
3.0
2.5
2.0
1.5
1.0
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.163
1.000
1.042
1.047
6.120
1.001
2.287
4.469
9.875
10.196
11.110
1.363
6.114


OTBS
Et
HN
Me
Me

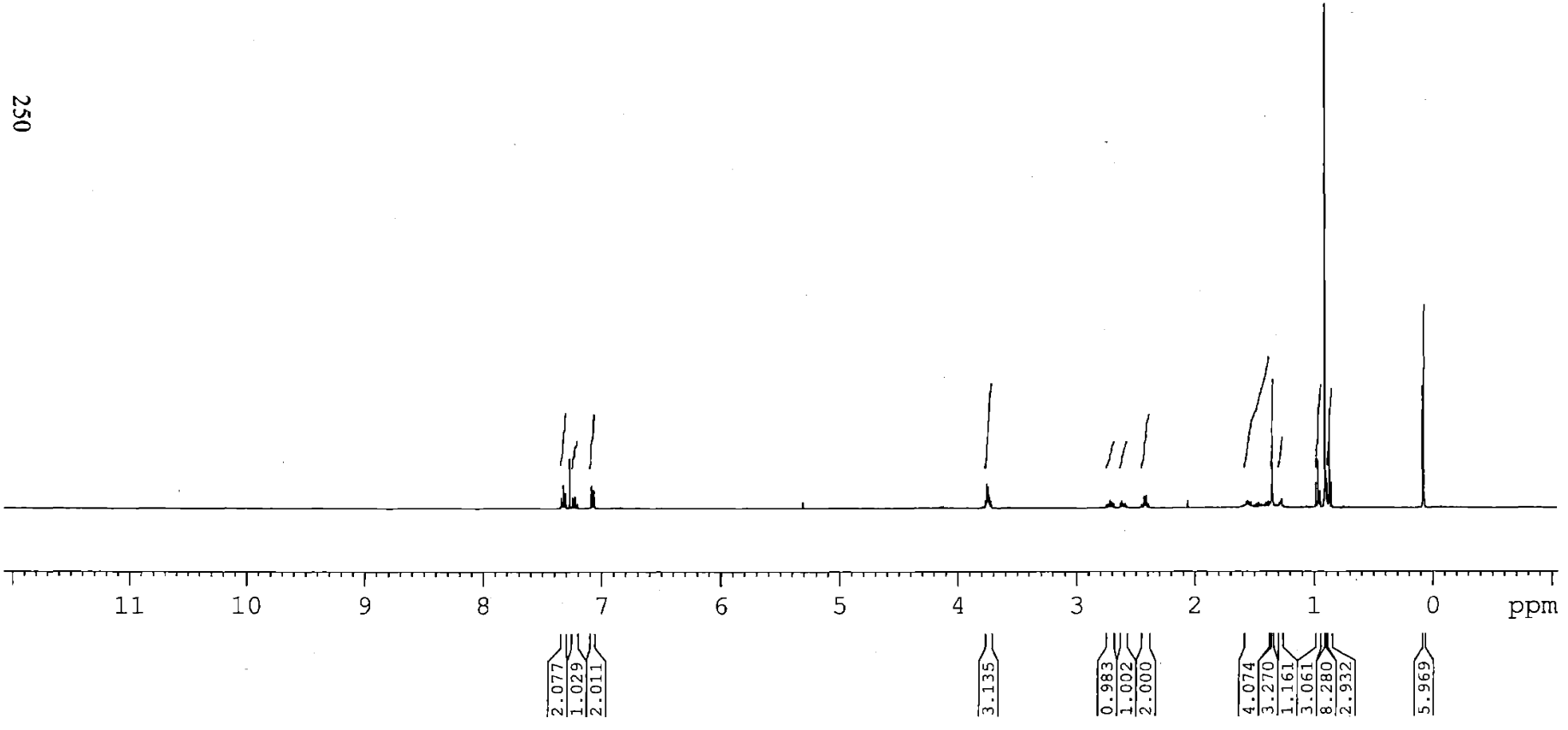
I-58

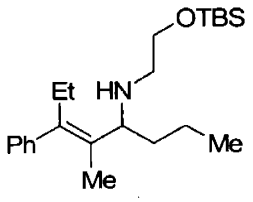
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3361.80
2710.49
1733.74
1406.90
1387.72
1376.47
1361.10
1322.99
1187.03
1463.58
1255.61
1083.49
1006.31
966.89
947.36
898.40
834.94
776.35
741.04
662.07
2869.58
2855.30
2956.84
4000.0
3000
2000
1500
1000
650.0
cm-1
c:\pel_data\spectra\sjpv298a.sp


OTBS
Et
HN
Ph
Me
Me

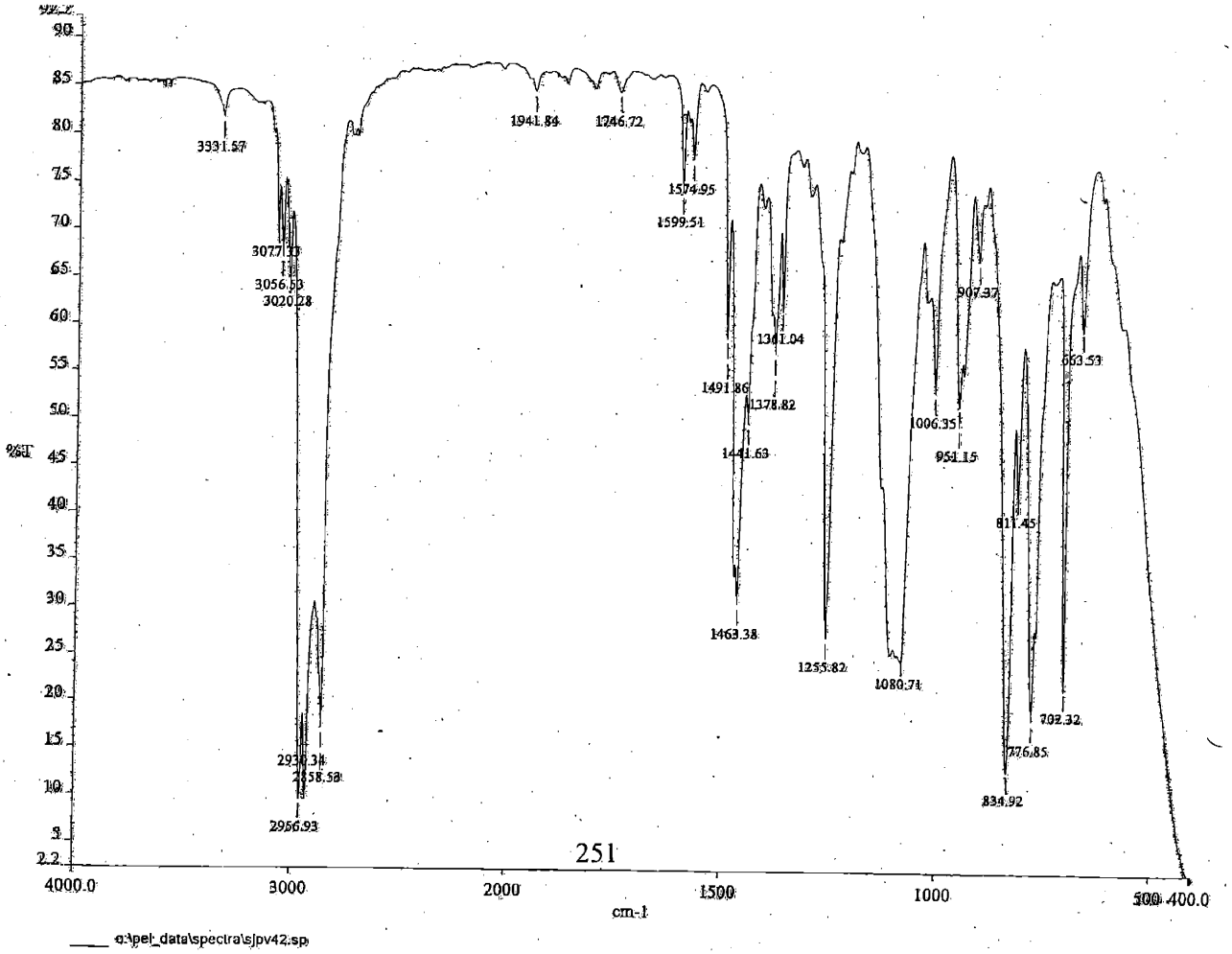
I-59

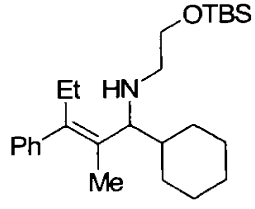

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.077
1.029
2.011
3.135
0.983
1.002
2.000
4.074
3.270
1.161
3.061
8.280
2.932
5.969


OTBS
Et
HN
Ph
Me
Me

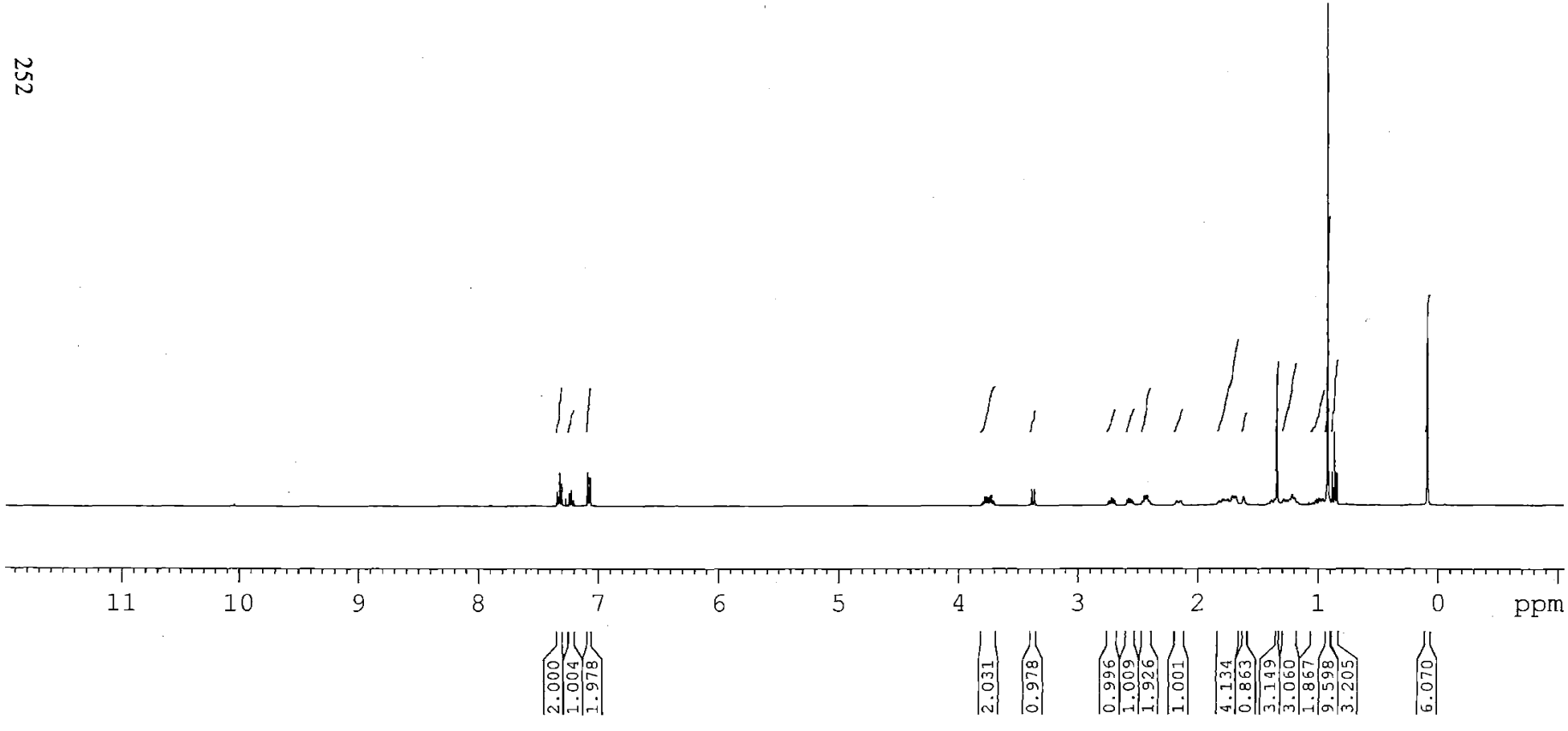
I-59

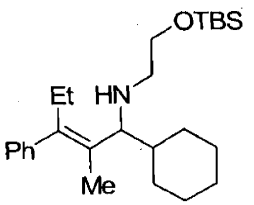
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3331.57
3077.23
3056.53
3020.28
2956.93
2936.38
2858.58
1941.84
1746.72
1574.95
1599.51
1491.86
1441.63
1378.82
1361.04
1463.38
1255.82
1080.71
1006.35
951.15
907.37
811.45
776.85
834.92
702.32
663.53
4000.0
3000
2000
1500
1000
500
400.0
cm-1
e:\pel_data\spectra\sjpv42.sp

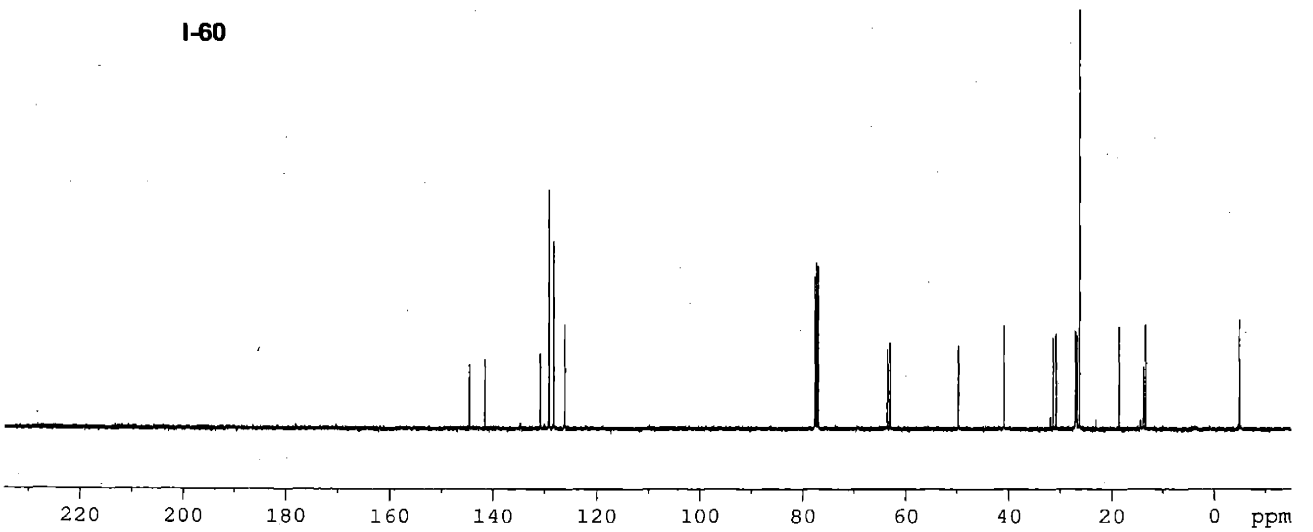

OTBS
Et
HN
Ph
Me

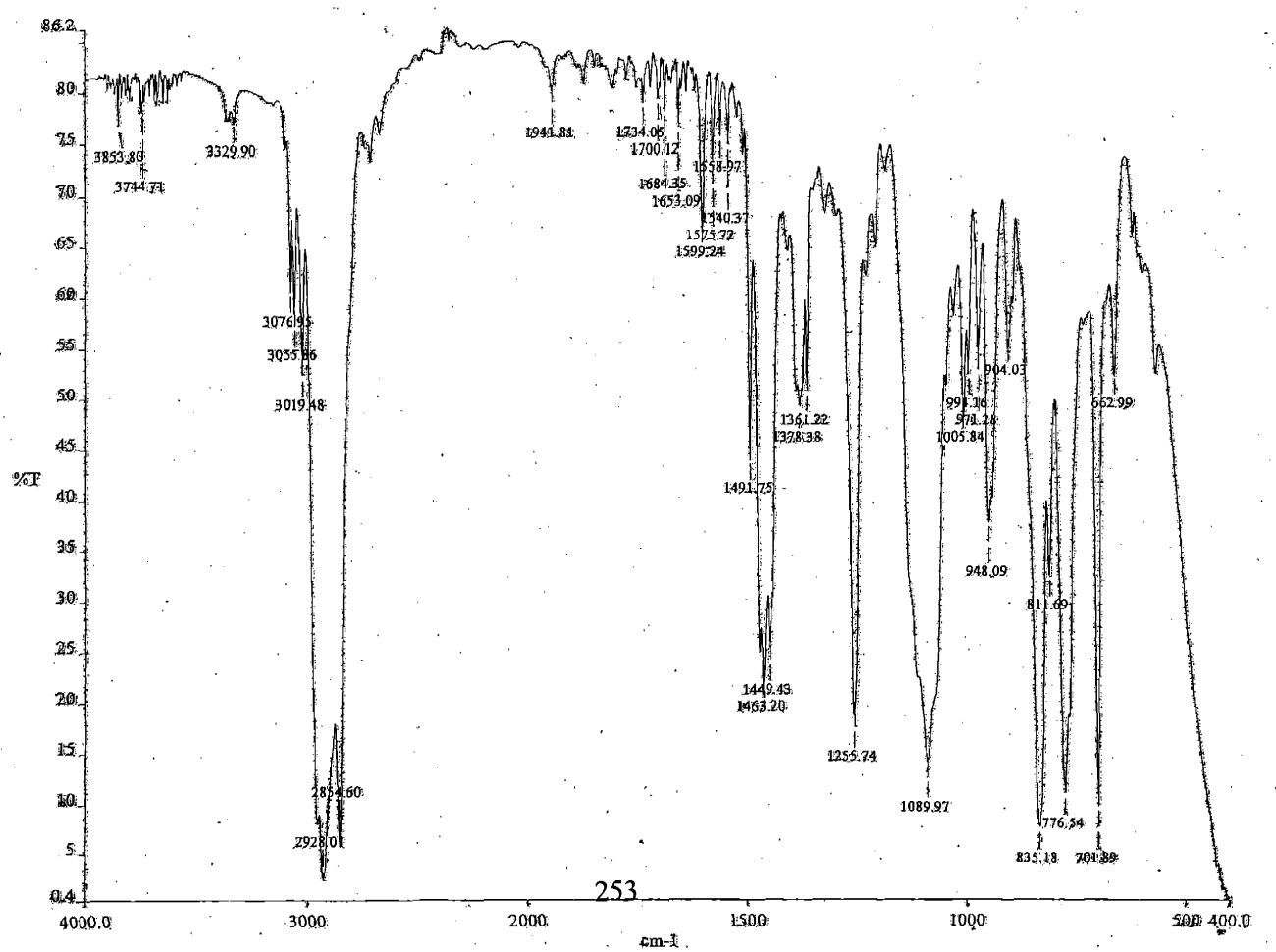
I-60

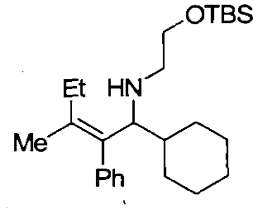

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.004
1.978
2.031
0.978
0.996
1.009
1.926
1.001
4.134
0.863
3.149
3.060
1.867
9.598
3.205
6.070


OTBS
Et
HN
Ph
Me

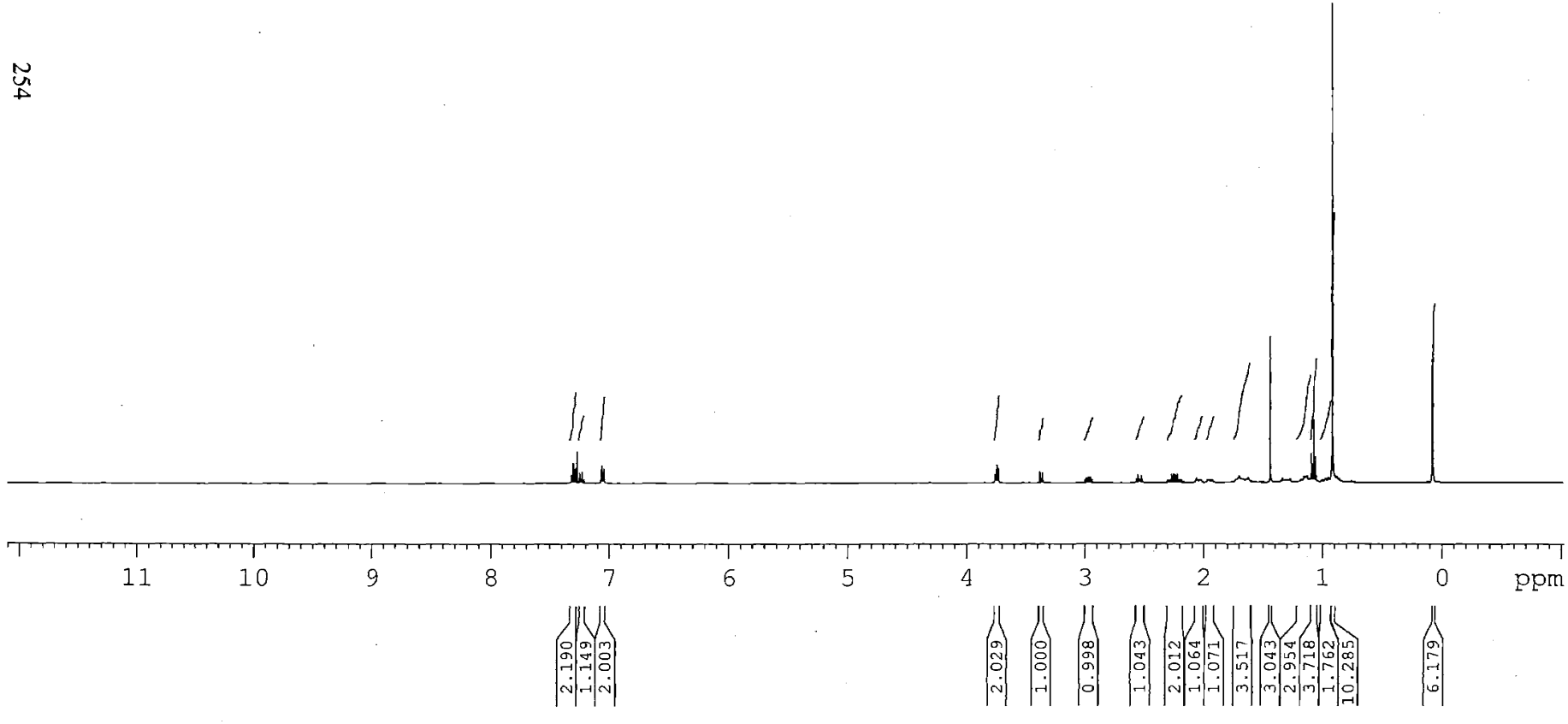
I-60

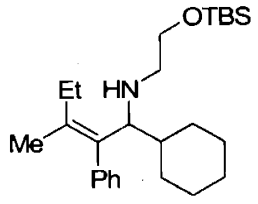

220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3853.80
3744.74
3329.90
3076.95
3055.86
3019.48
2928.01
2854.60
1941.81
1734.05
1700.12
1684.35
1653.09
1599.24
1491.75
1449.43
1463.20
1361.22
1327.38
1255.74
1089.97
1005.84
948.09
904.03
835.18
811.69
776.54
701.89
662.99
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv20.sp - sample

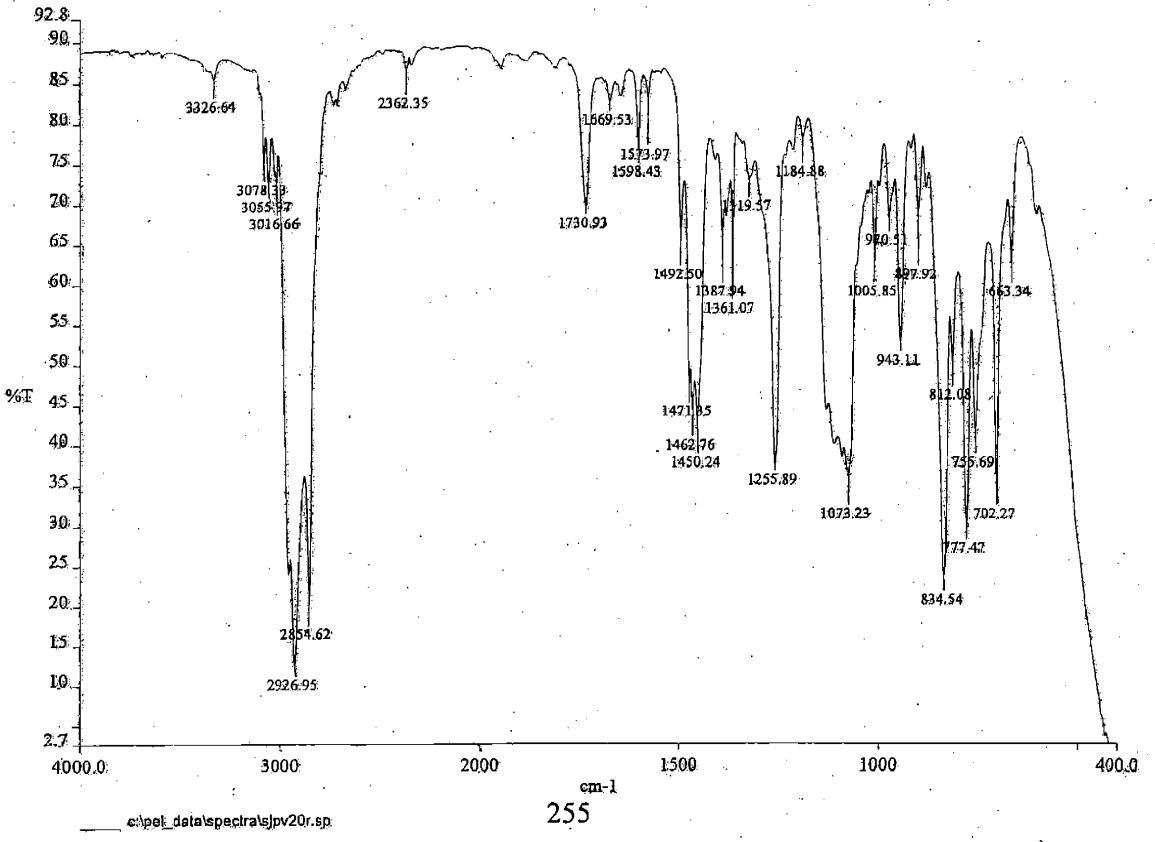


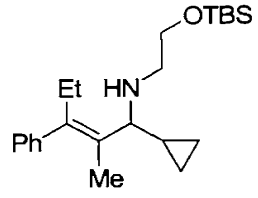
I-60 regioisomer



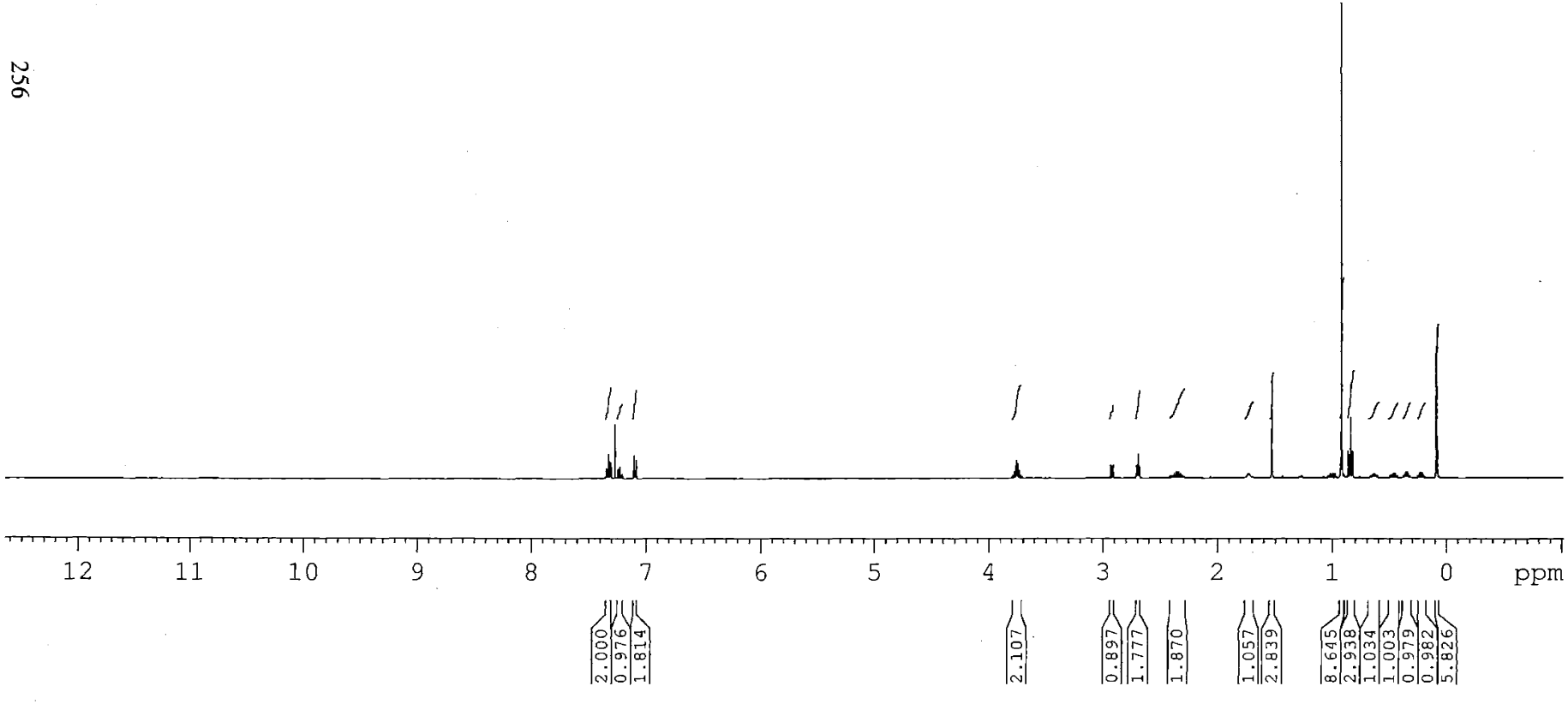


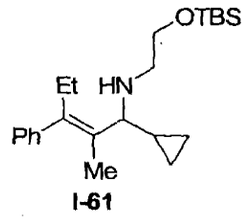
I-60 regioisomer




OTBS
Et
HN
Ph
Me

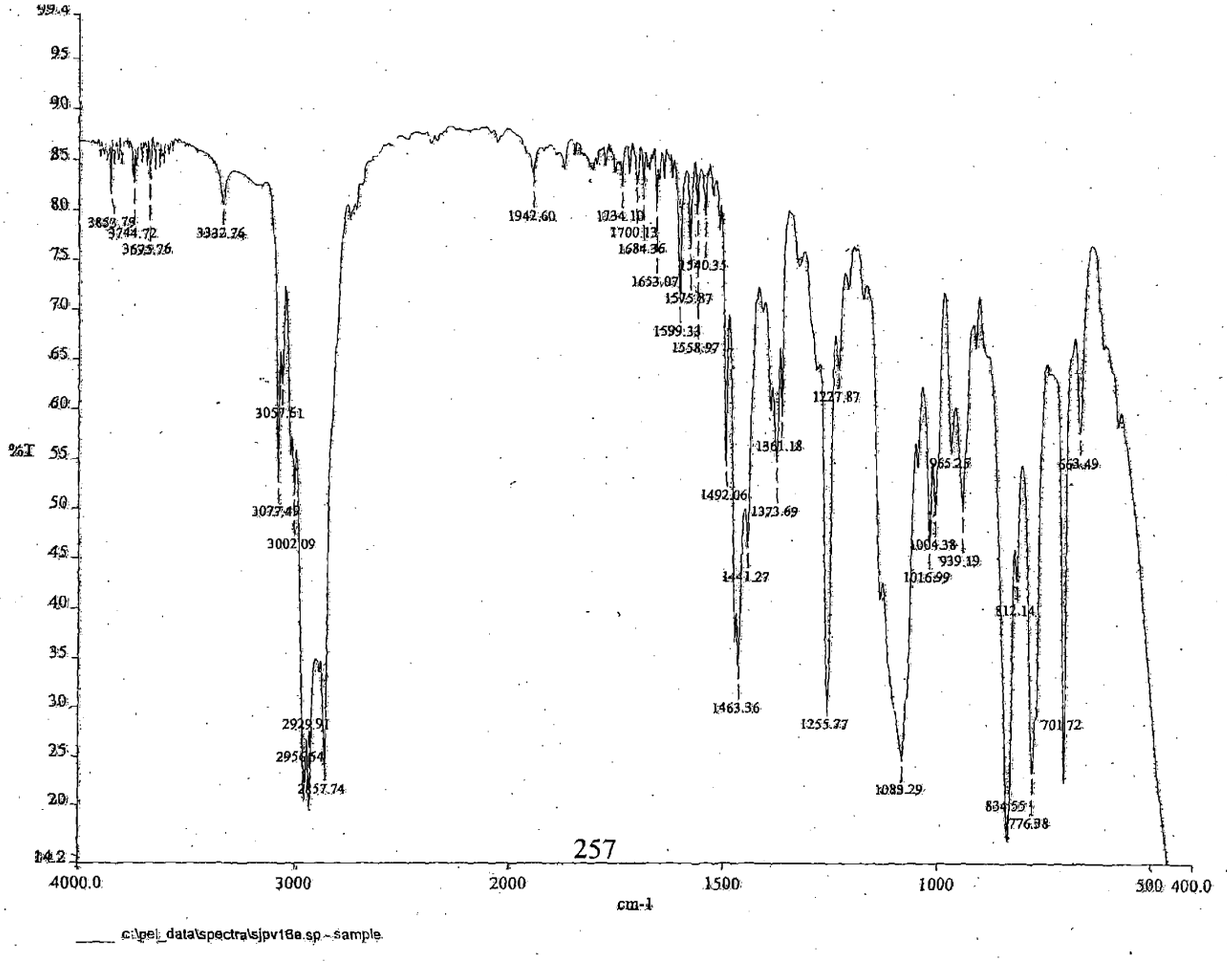
I-61

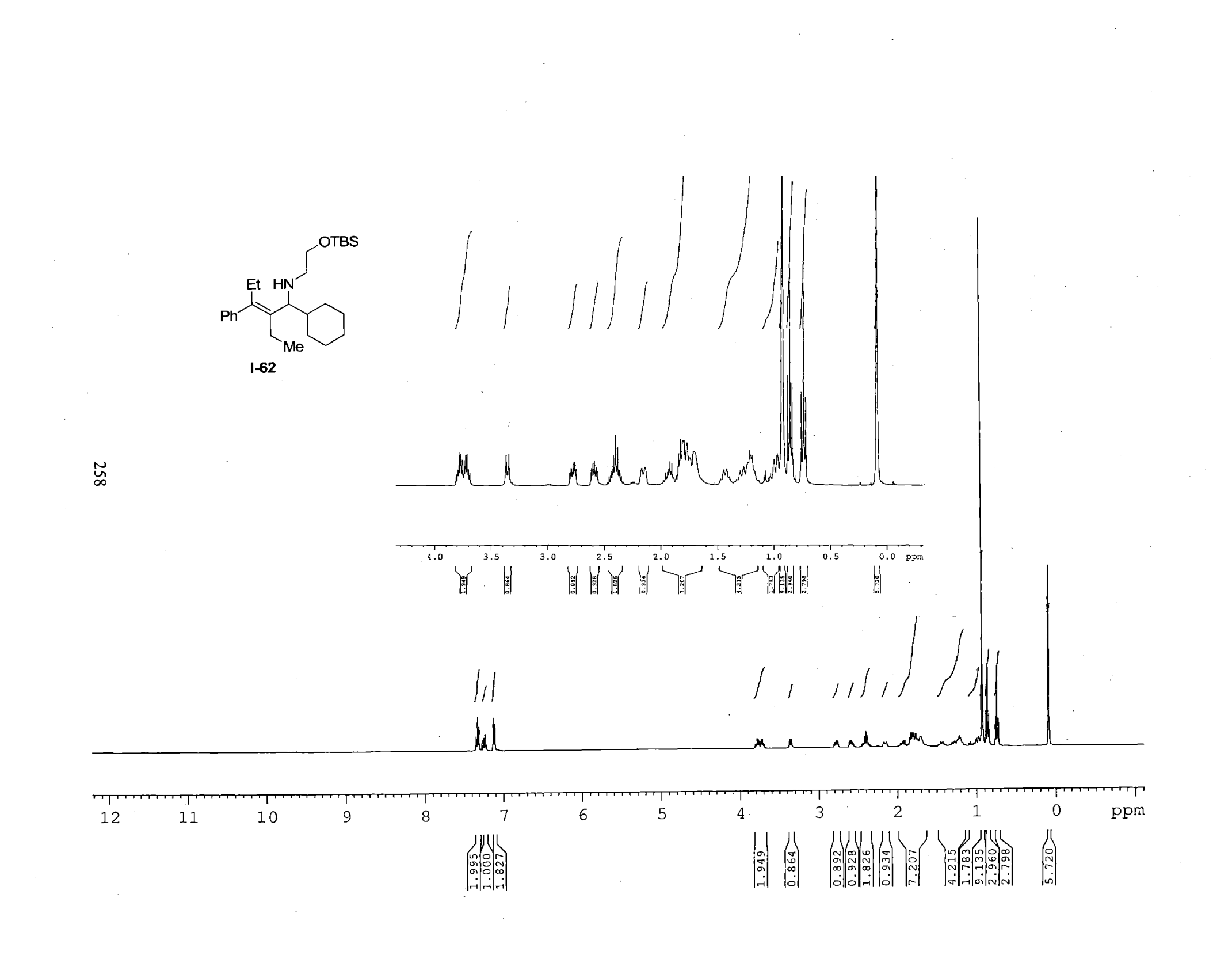

12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
0.976
1.814
2.107
0.897
1.777
1.870
1.057
2.839
8.645
2.938
1.034
1.003
0.979
0.982
5.826

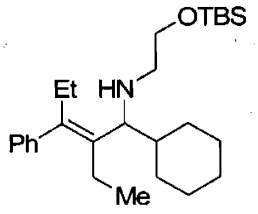

OTBS
Et
HN
Ph
Me

I-61

220
200
180
160
140
120
100
80
60
40
20
0
ppm

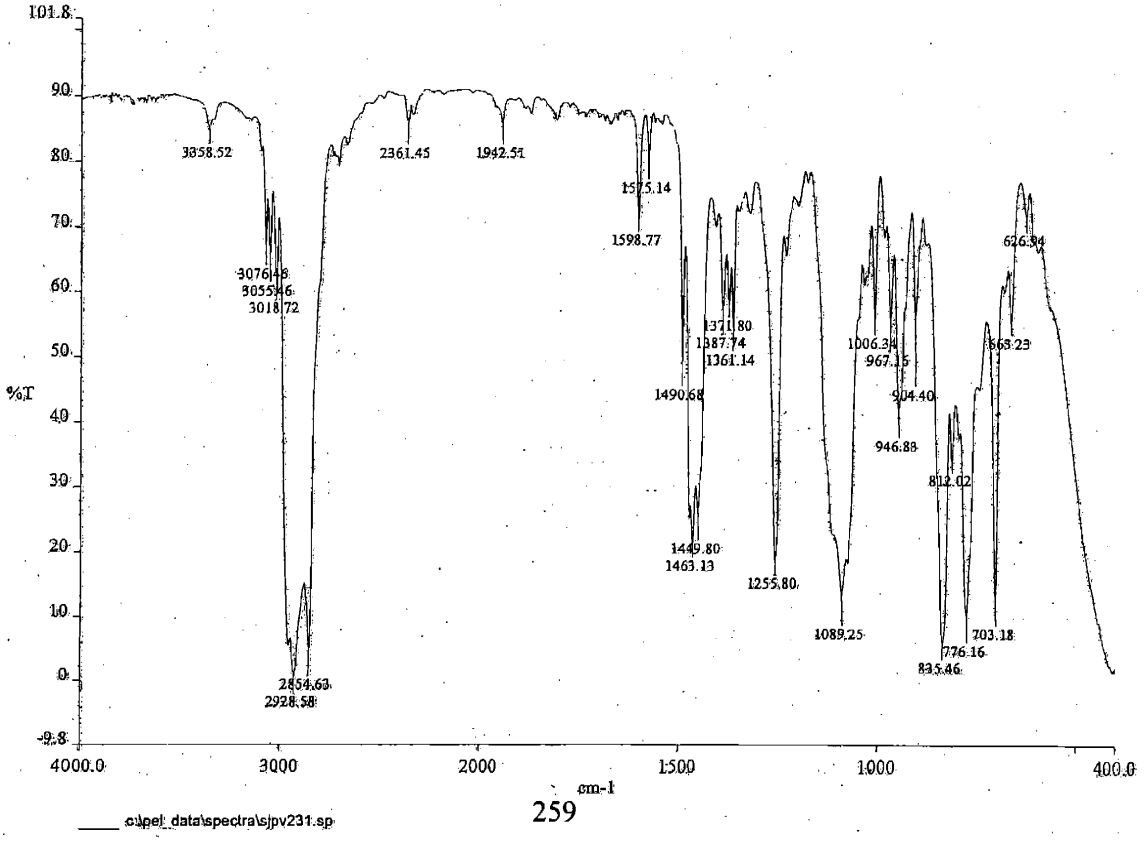

%T
3858.79
3744.72
3695.26
3382.74
3057.51
3077.48
3002.09
2929.91
2957.74
1942.60
1734.10
1700.13
1684.36
1653.07
1540.35
1575.87
1599.34
1558.97
1492.06
1463.36
1441.27
1373.69
1361.18
1227.87
1255.77
1089.29
1004.38
939.19
1016.99
965.28
912.14
834.55
776.98
701.72
563.49
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pei_data\spectra\sjpv16a.sp - sample

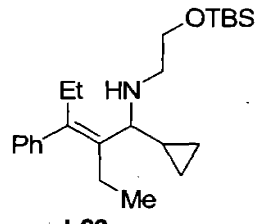

OTBS
Et HN
Ph
Me
I-62
4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.995 1.000 1.827
1.949 0.864 0.892 0.928 1.826 0.934 7.207 4.215 1.783 9.135 2.960 2.798 5.720


OTBS
Et
HN
Ph
Me

I-62

220
200
180
160
140
120
100
80
60
40
20
0
ppm

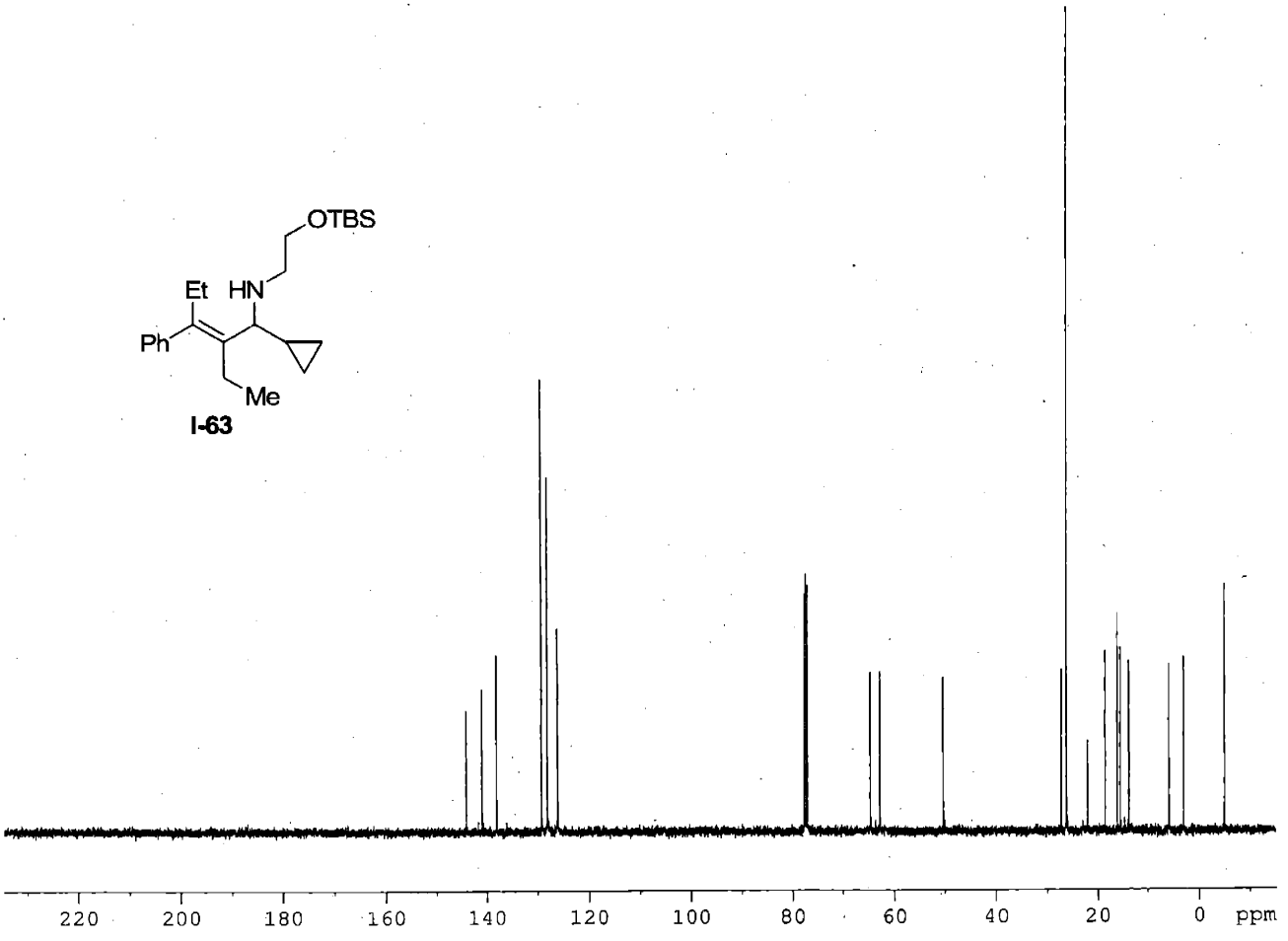

%T
3858.52
3076.48
3055.46
3018.72
2928.58
2854.63
2361.45
1942.51
1575.14
1598.77
1490.68
1449.80
1463.13
1371.80
1387.74
1361.14
1255.80
1089.25
1006.34
967.15
946.88
904.40
812.02
835.46
776.16
703.18
663.23
626.94
4000.0
3000
2000
1500
1000
400.0
cm-1
c:\pel_data\spectra\sjpv231.sp

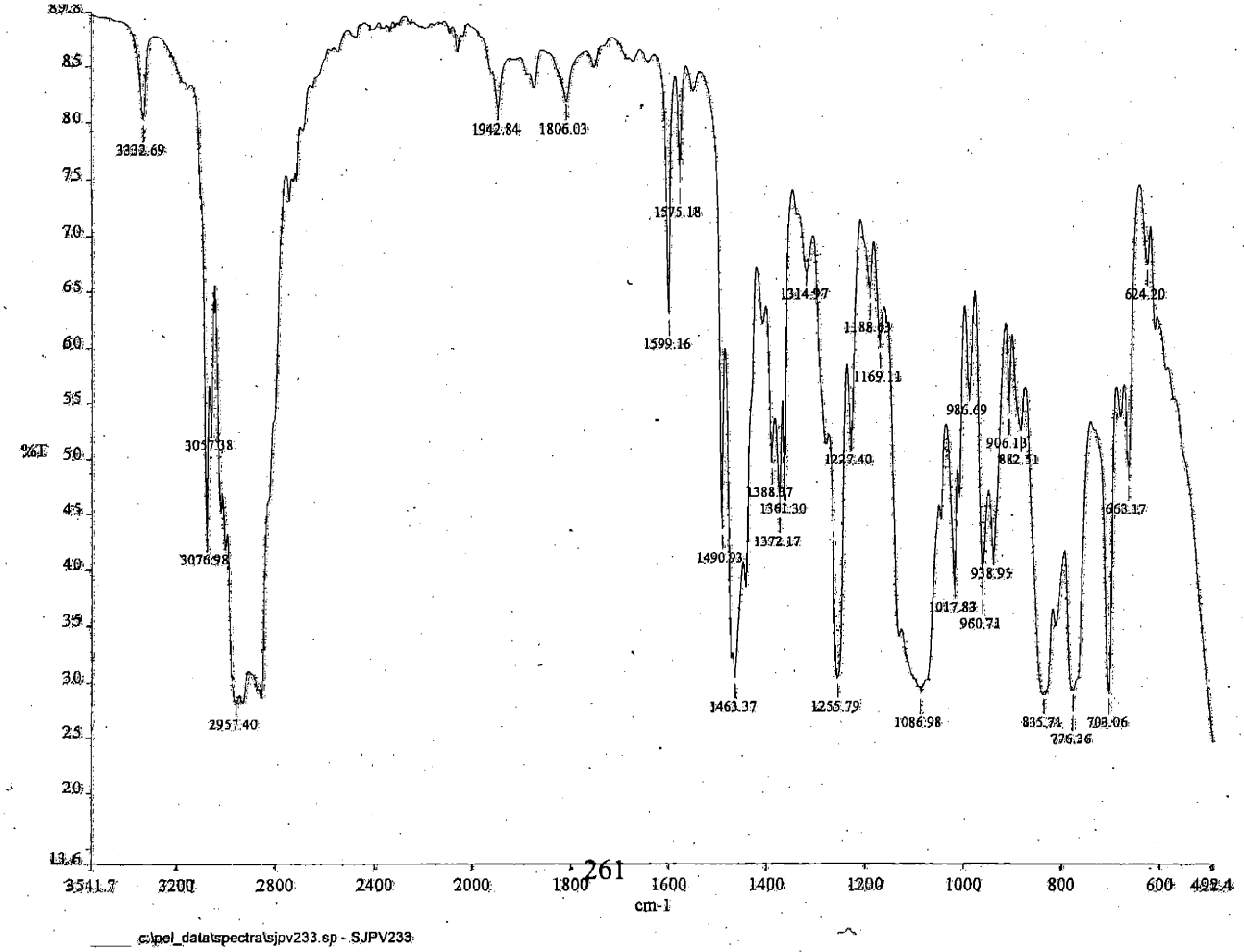

OTBS
Et
HN
Ph
Me

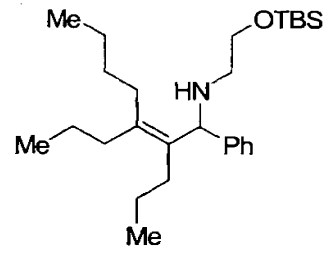
I-63

260

10
9
8
7
6
5
4
3
2
1
0
ppm
2.083
1.079
1.961
2.103
1.000
1.909
2.071
2.087
1.002
1.258
8.937
6.182
1.055
1.049
1.040
1.034
6.185

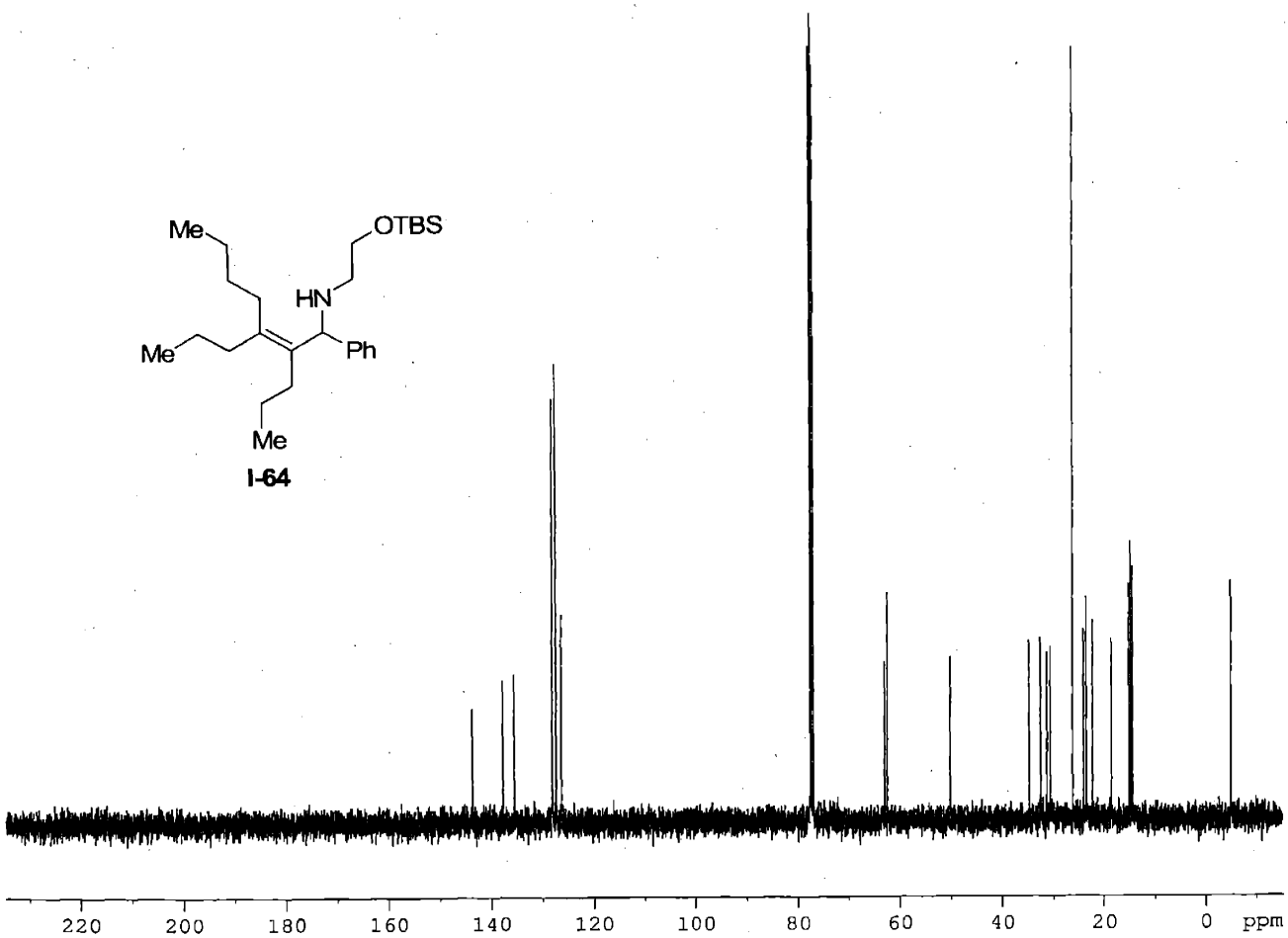

OTBS
Et
HN
Ph
Me
I-63
220
200
180
160
140
120
100
80
60
40
20
0
ppm


3332.69
3057.38
3076.98
2957.40
1942.84
1806.03
1575.18
1599.16
1490.93
1463.37
1314.97
1388.17
1361.30
1372.17
1255.79
1188.62
1169.11
1229.40
1086.98
1017.83
986.09
960.71
938.95
906.13
882.51
835.74
776.36
708.06
663.17
624.20
%T
cm-1
c:\pel_data\spectra\sjpv233.sp - SJPV233

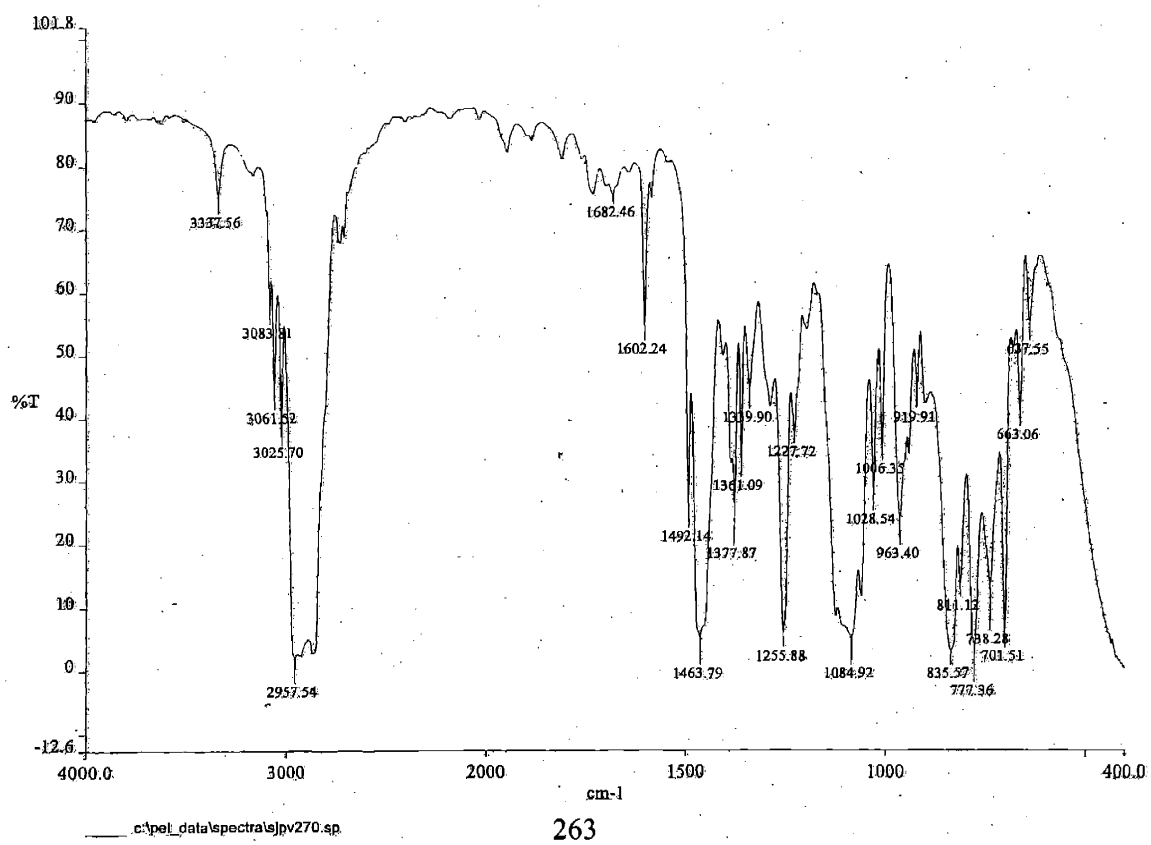

Me
OTBS
HN
Me
Ph
Me

I-64

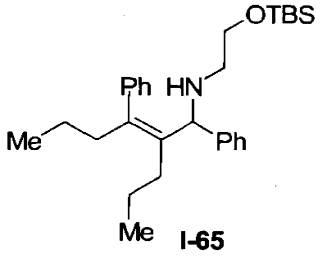
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.990
1.949
1.021
0.957
1.838
1.981
2.000
2.111
2.929
6.883
3.516
10.893
4.006
5.954



I-64

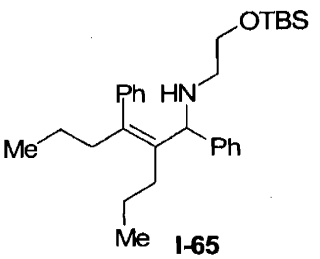


c:\pet_data\spectra\sjpv270.sp

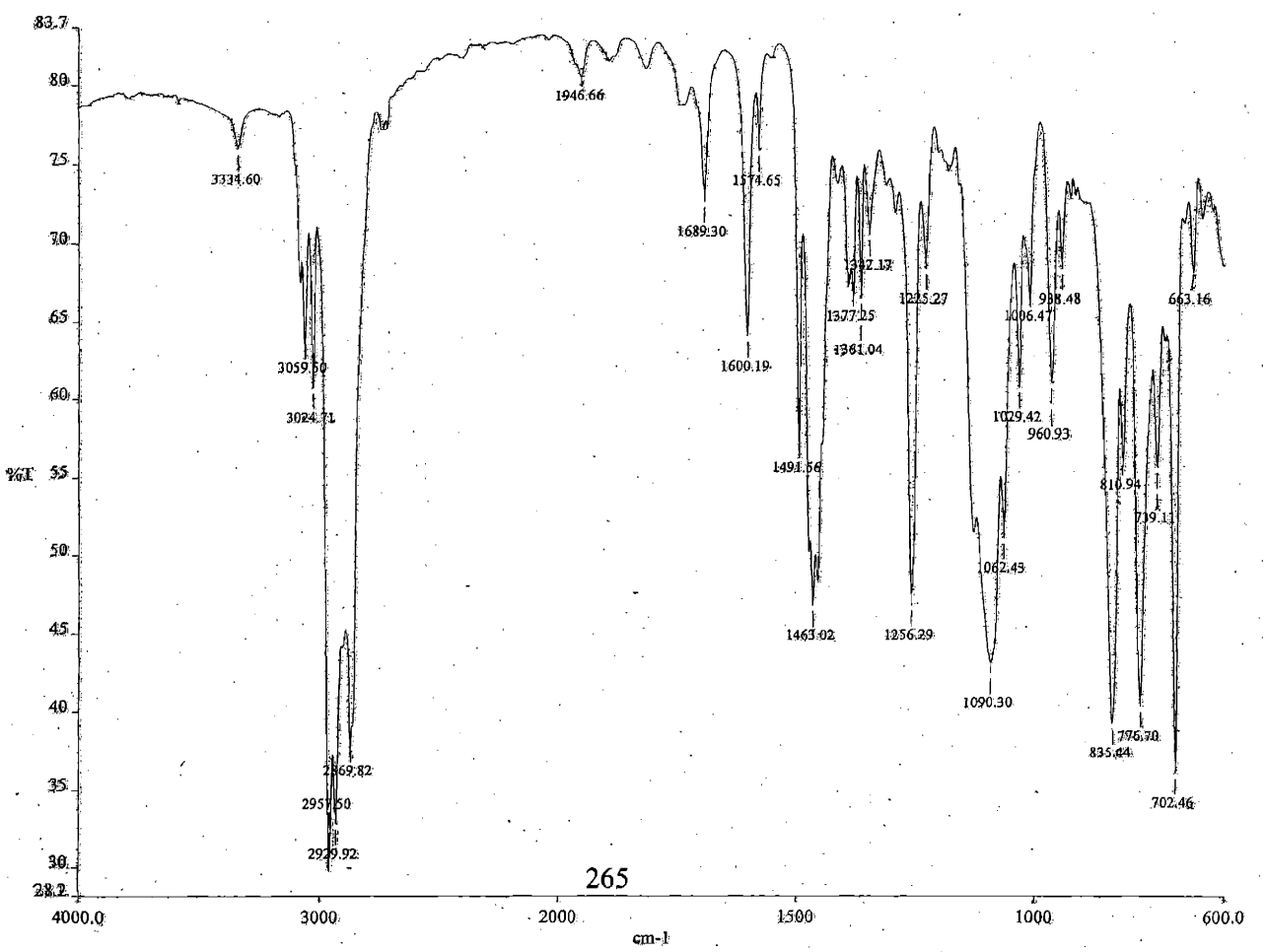

OTBS
Ph
HN
Me
Ph
Me

I-65

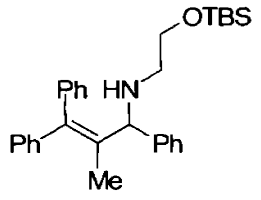
10
9
8
7
6
5
4
3
2
1
0
ppm
4.069
3.414
3.119
1.000
1.903
1.152
0.976
2.045
1.082
1.016
1.591
3.199
9.304
3.447
3.763
5.869



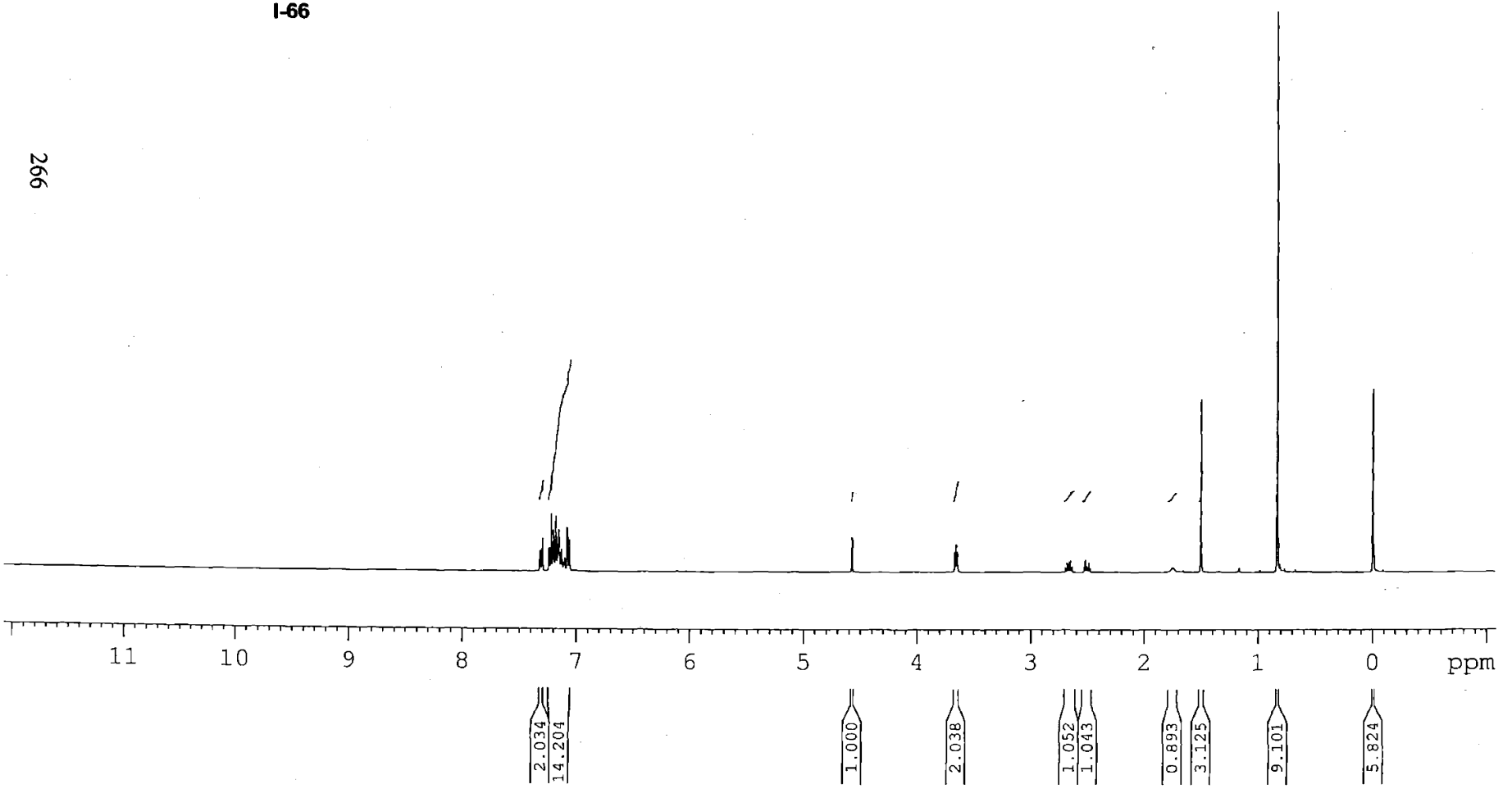
I-65

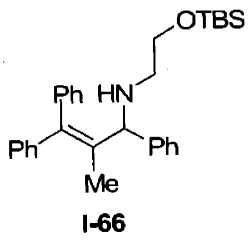


c:\pe_data\spectra\sjpv123.sp - SJPV123


OTBS
Ph
HN
Ph
Ph
Me

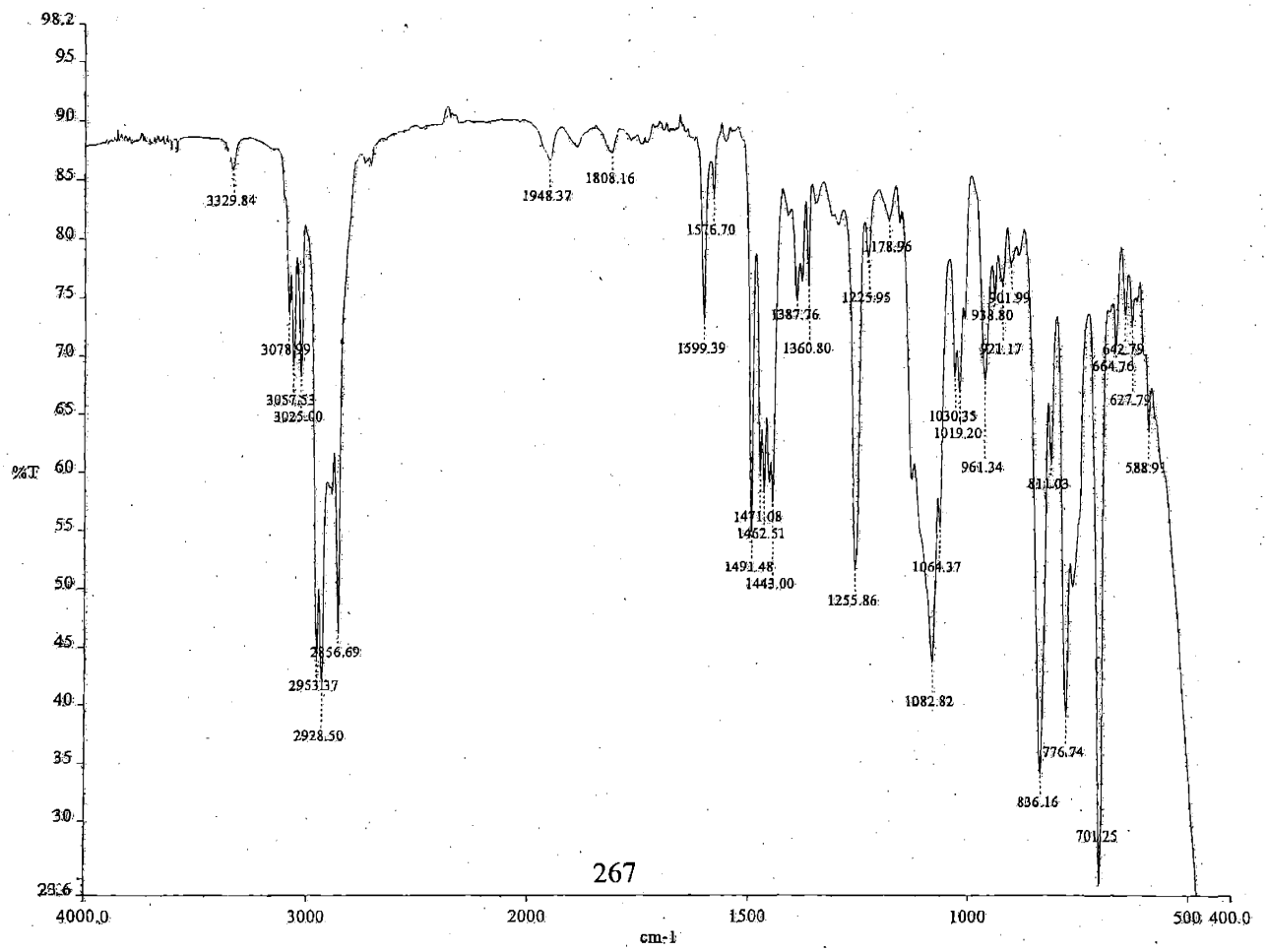
I-66

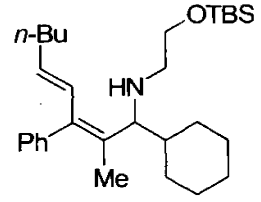

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.034
14.204
1.000
2.038
1.052
1.043
0.893
3.125
9.101
5.824


OTBS
Ph HN
Ph
Ph
Me

I-66

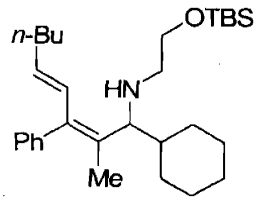
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
98.2
95
90
85
80
75
70
65
60
55
50
45
40
35
30
28.6
3329.84
3078.99
3057.53
3025.60
2956.69
2953.37
2928.50
1948.37
1808.16
1576.70
1599.39
1471.08
1462.51
1491.48
1443.00
1387.76
1360.80
1225.95
1178.96
1255.86
1082.82
1069.37
1030.35
1019.20
961.34
938.80
921.17
901.99
881.03
836.16
776.74
701.25
664.76
642.79
627.79
588.95
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\sjpv26.sp - SJPV26


n-Bu
OTBS
HN
Ph
Me

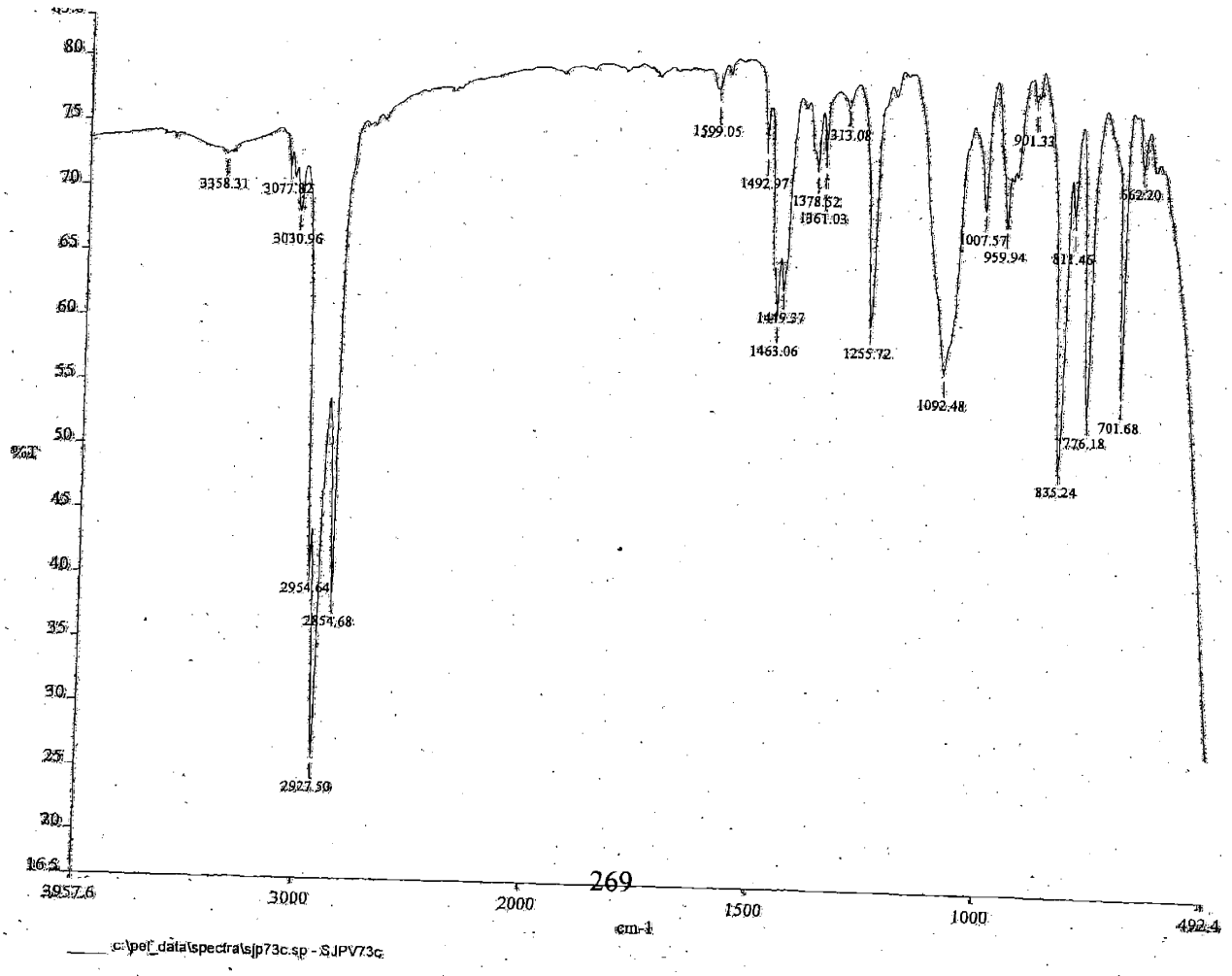
I-67

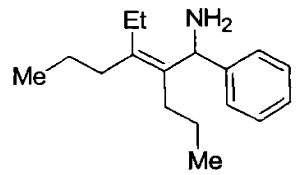
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
2.01 1.89
1.35 1.12
1.00
1.20
1.26
1.22
1.21 6.97
2.49
5.79 2.76
3.71 10.14
5.13


n-Bu
OTBS
HN
Ph
Me

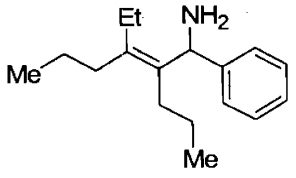
I-67

240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

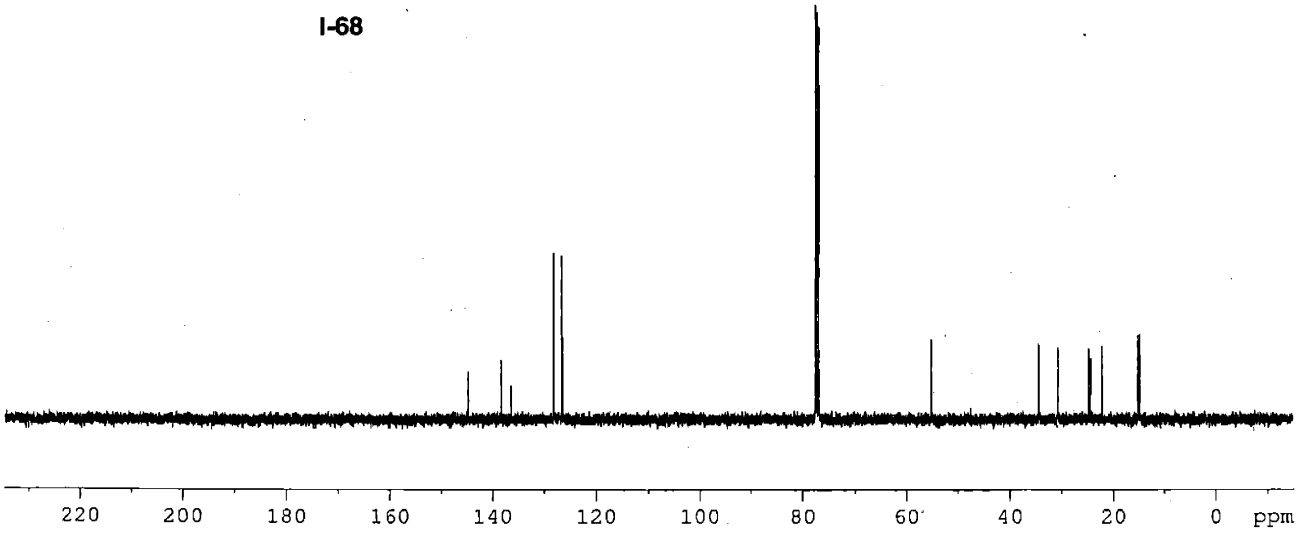

%T
3358.31
3077.82
3030.96
2954.64
2854.68
2927.50
1599.05
1492.97
1419.37
1463.06
1378.52
1361.03
1313.08
1255.72
1092.48
1007.57
959.94
901.33
835.24
776.18
701.68
562.20
3957.6
3000
2000
1500
1000
492.4
cm-1
c:\pe_data\spectra\sjp73c.sp - SJPV73c

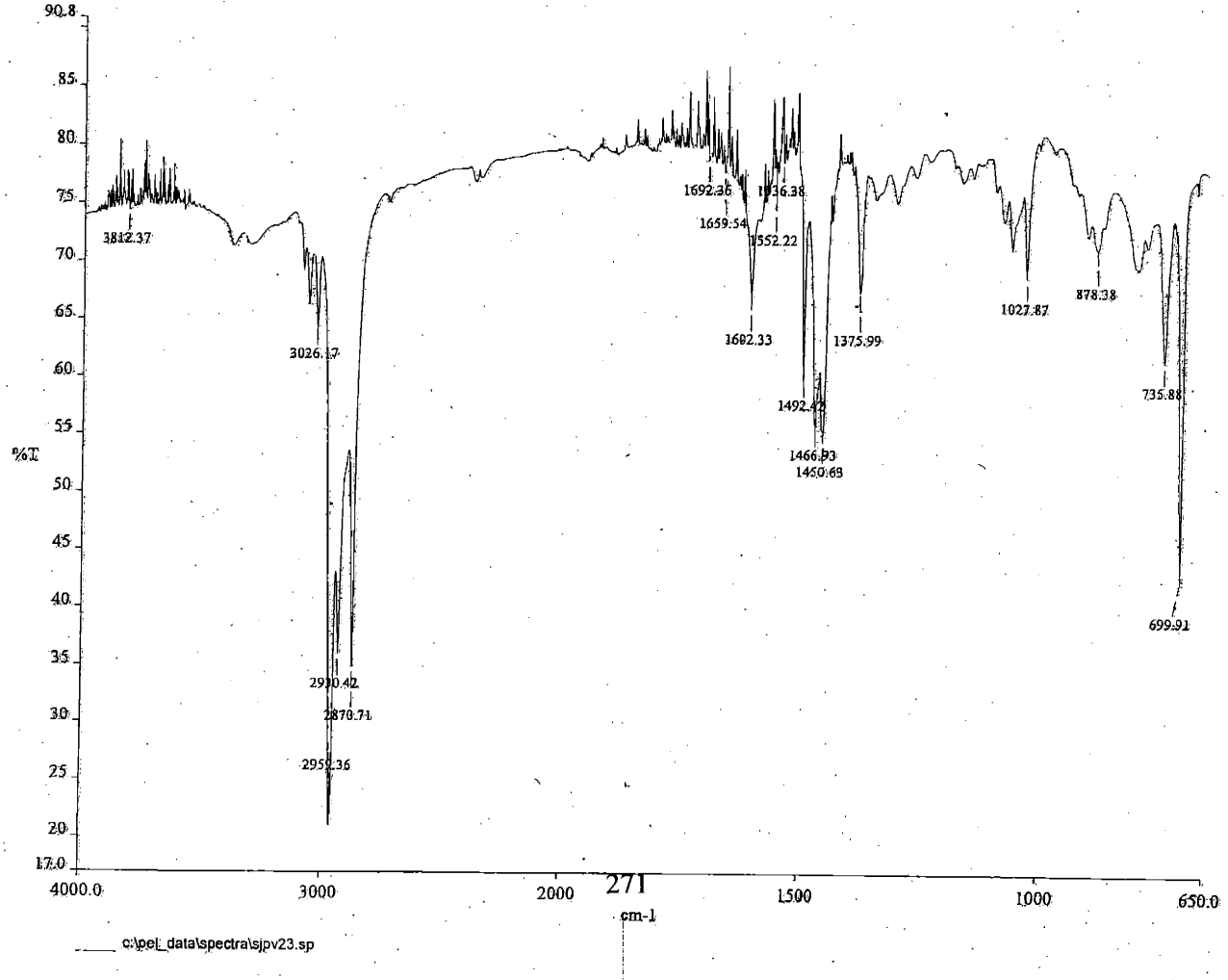


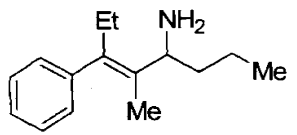
I-68


Et
NH2
Me
Me

I-68

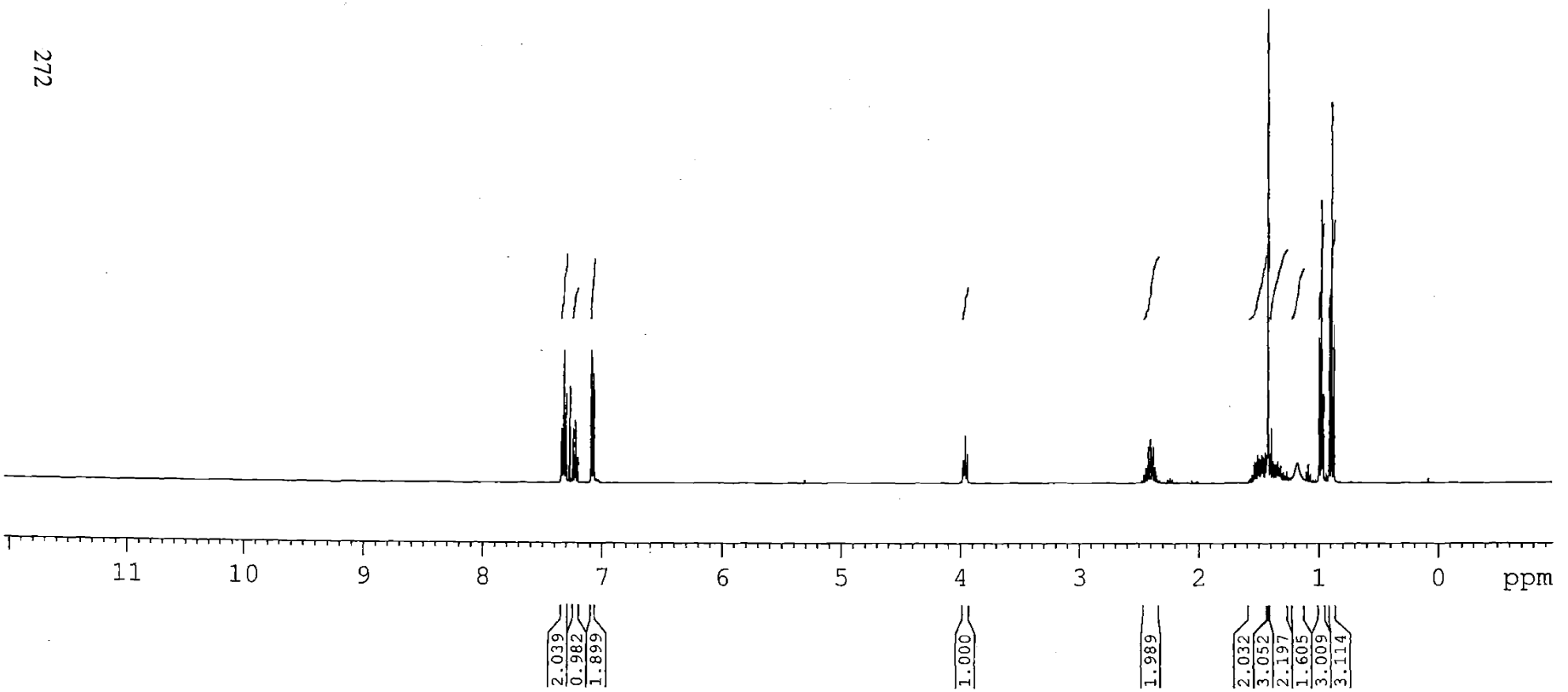

220
200
180
160
140
120
100
80
60
40
20
0
ppm

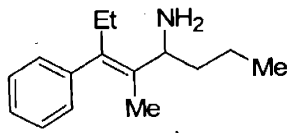

%T
3812.37
3026.17
2930.42
2870.71
2959.36
1692.36
1659.54
1636.38
1552.22
1602.33
1492.42
1466.93
1450.68
1375.99
1027.87
878.38
735.88
699.91
4000.0
3000
2000
1500
1000
650.0
cm-1
c:\pel_data\spectra\sjpv23.sp


Et
NH2
Me
Me

I-69

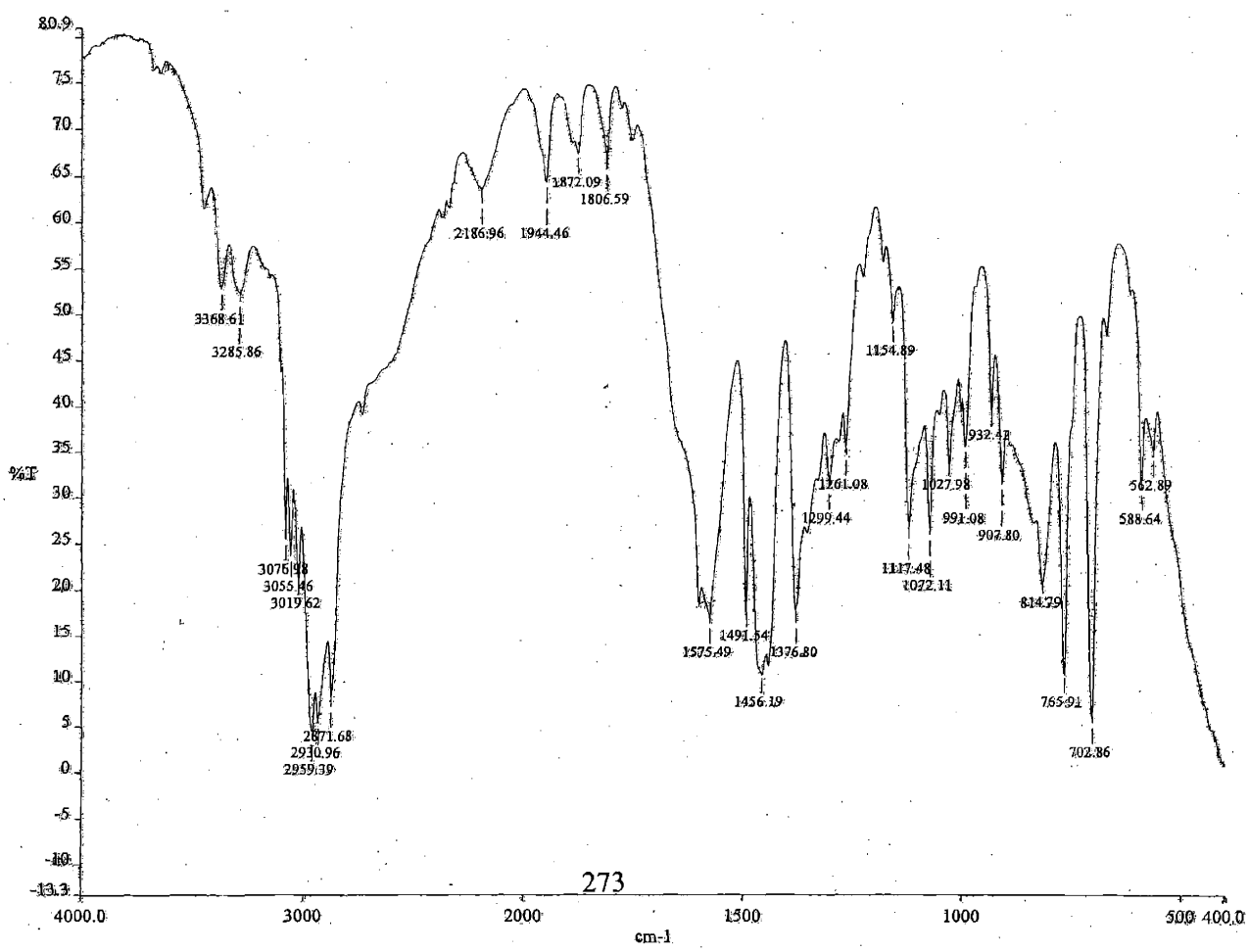
272

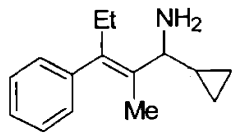

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.039
0.982
1.899
1.000
1.989
2.032
3.052
2.197
1.605
3.009
3.114


Et
NH2
Me
Me

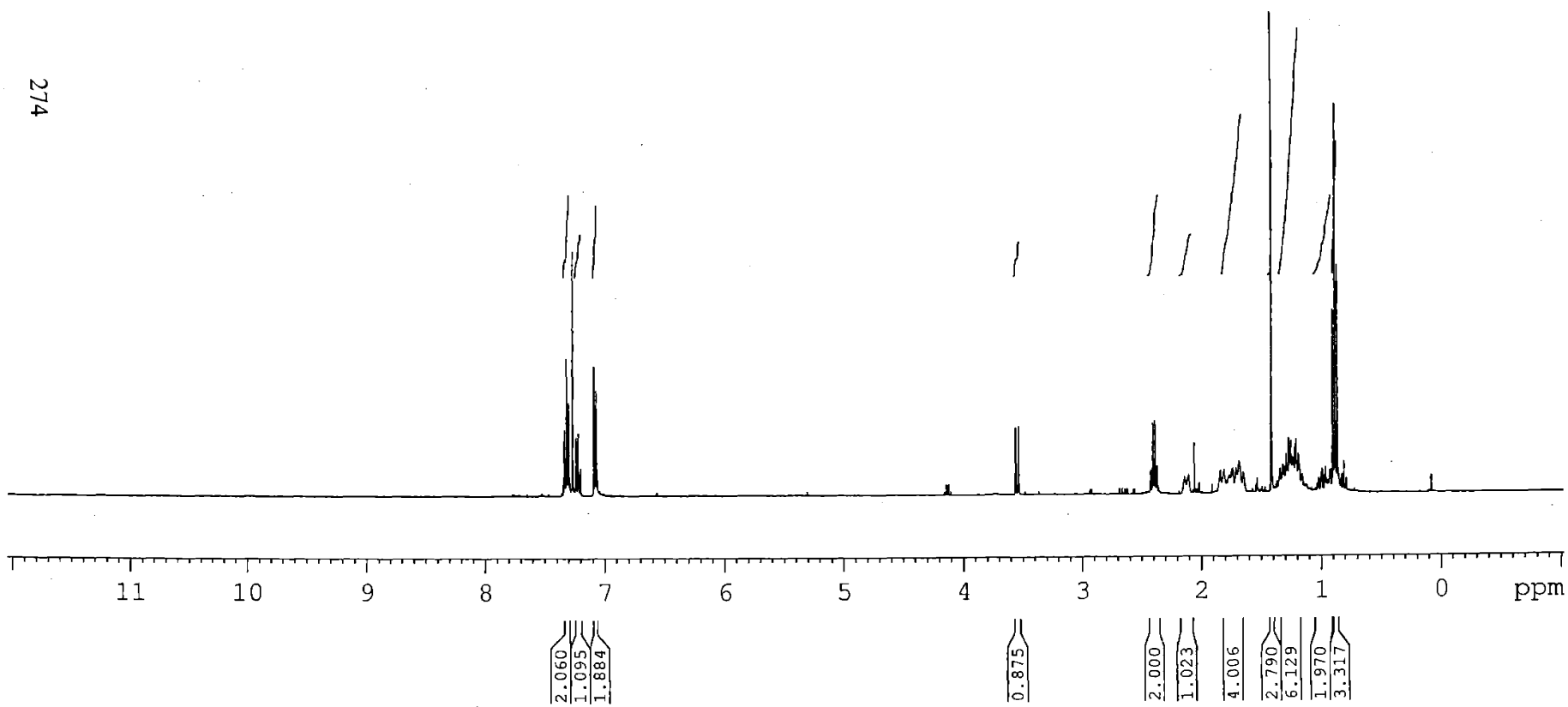
I-69

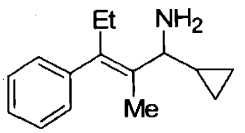
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
80.9
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-13.3
3368.61
3285.86
3076.98
3055.86
3019.62
2871.68
2930.96
2959.39
2186.96
1944.46
1872.09
1806.59
1575.49
1491.54
1456.19
1376.80
1299.44
1261.08
1154.89
1117.48
1072.11
1027.98
991.08
932.43
907.80
814.79
765.91
702.86
588.64
562.89
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe_data\spectra\sjpv49.sp


Et
NH2
Me

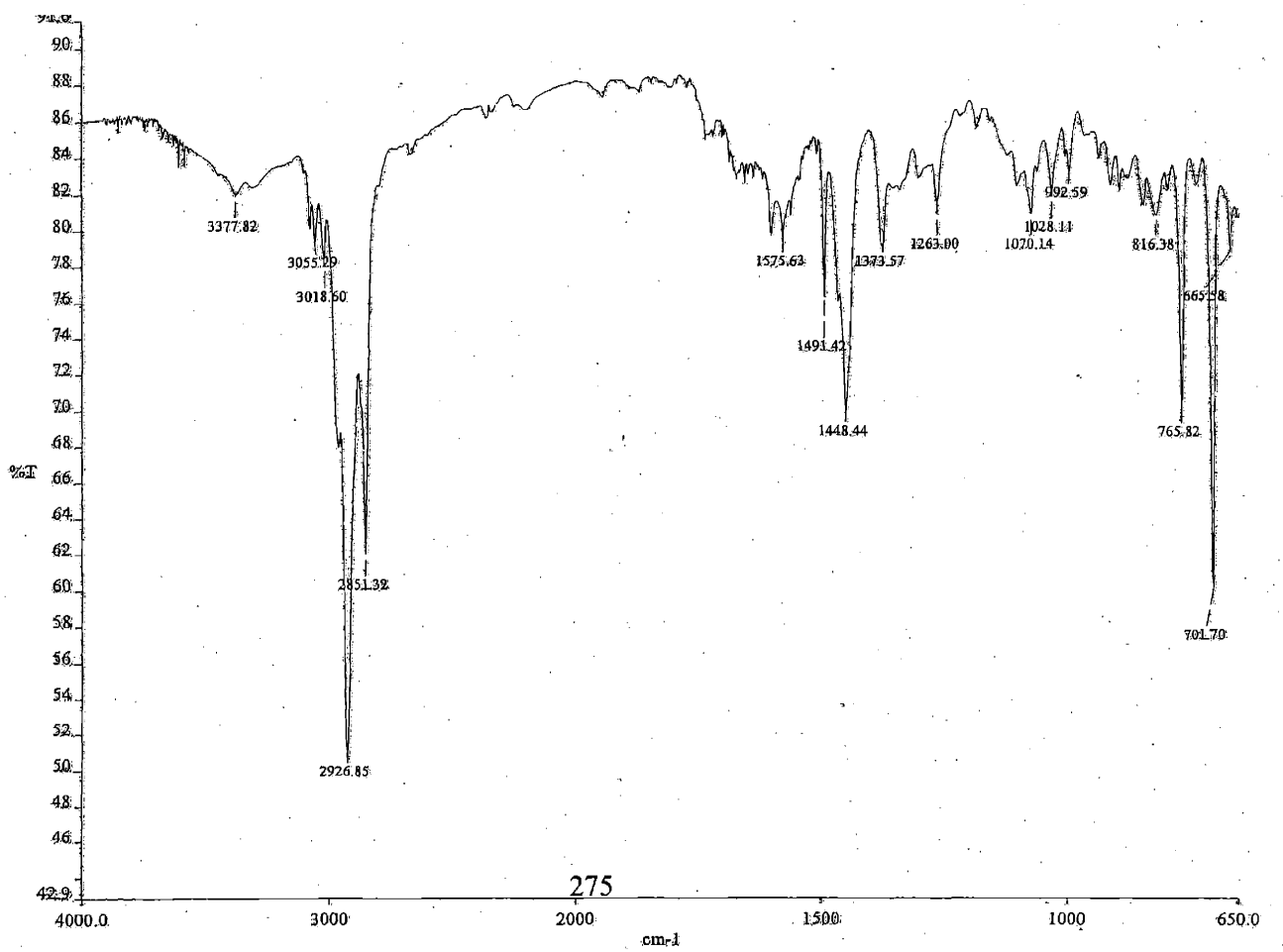
I-70

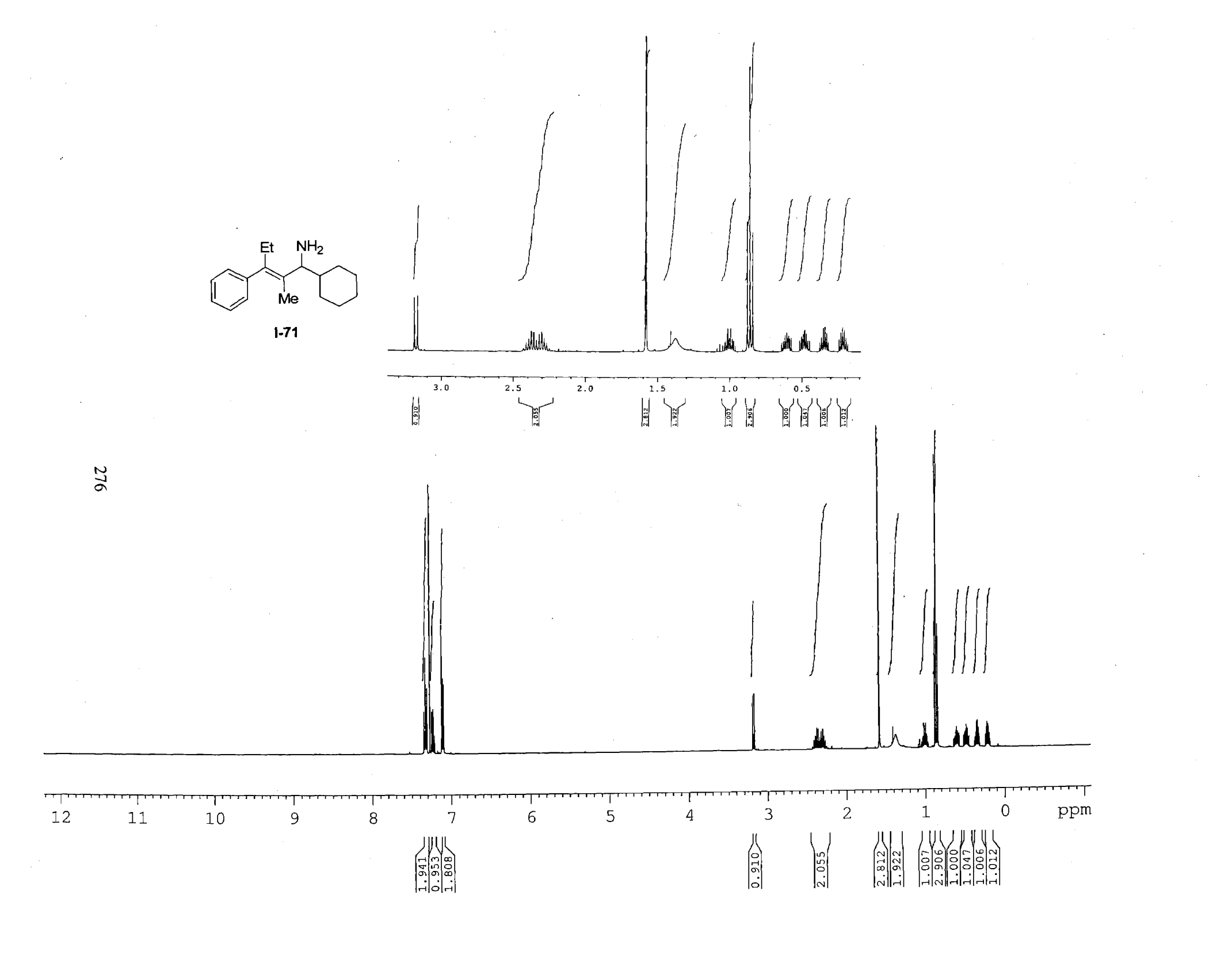

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.060
1.095
1.884
0.875
2.000
1.023
4.006
2.790
6.129
1.970
3.317

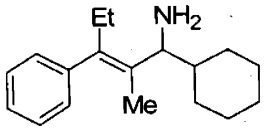

Et
NH2
Me

I-70

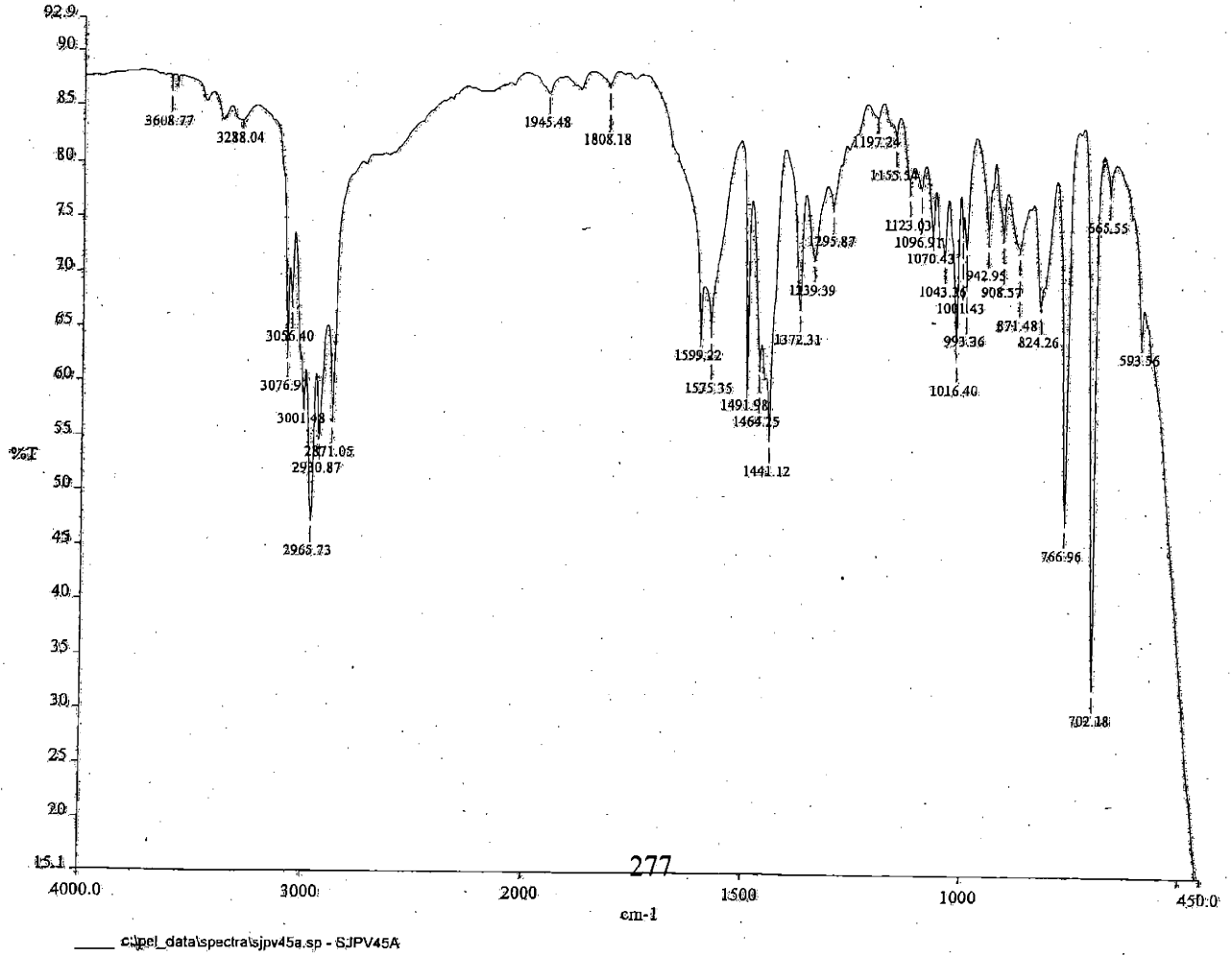
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3377.82
3055.29
3018.60
2926.85
2851.32
1575.63
1491.42
1448.44
1373.57
1263.00
1070.14
1028.11
992.59
816.38
765.82
701.70
4000.0
3000
2000
1500
1000
650.0
cm-1
c:\pe_data\spectra\sjpv48b1.sp - SJPV48B1

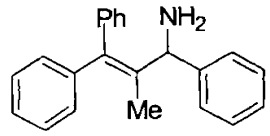

Et
NH2
Me
I-71
3.0
2.5
2.0
1.5
1.0
0.5
0.910
2.055
2.812
1.922
1.007
2.906
1.000
1.047
1.006
1.012
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.941
0.953
1.808
0.910
2.055
2.812
1.922
1.007
2.906
1.000
1.047
1.006
1.012



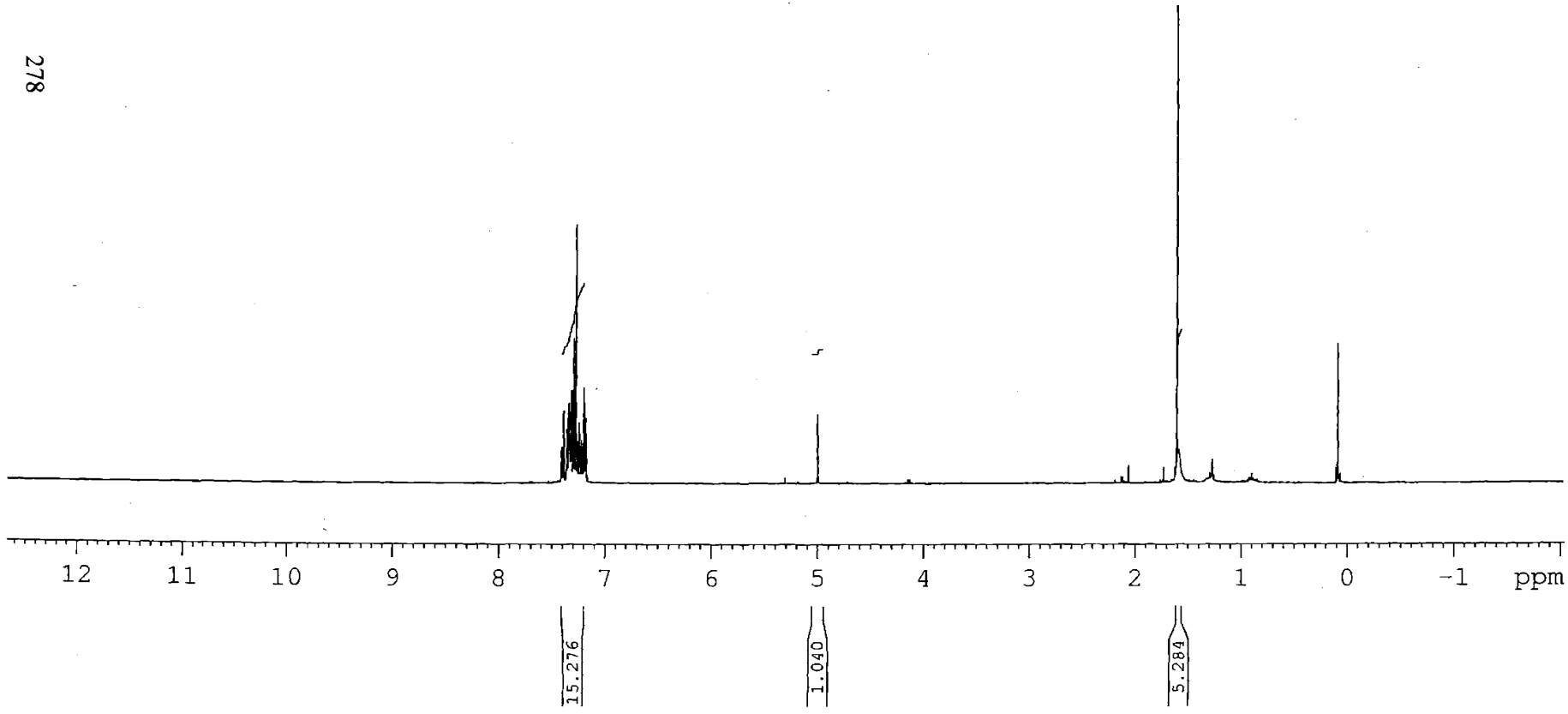
I-71

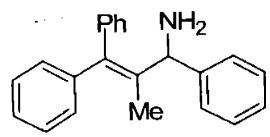


c:\pel_data\spectra\sjpv45a.sp - SJPV45A



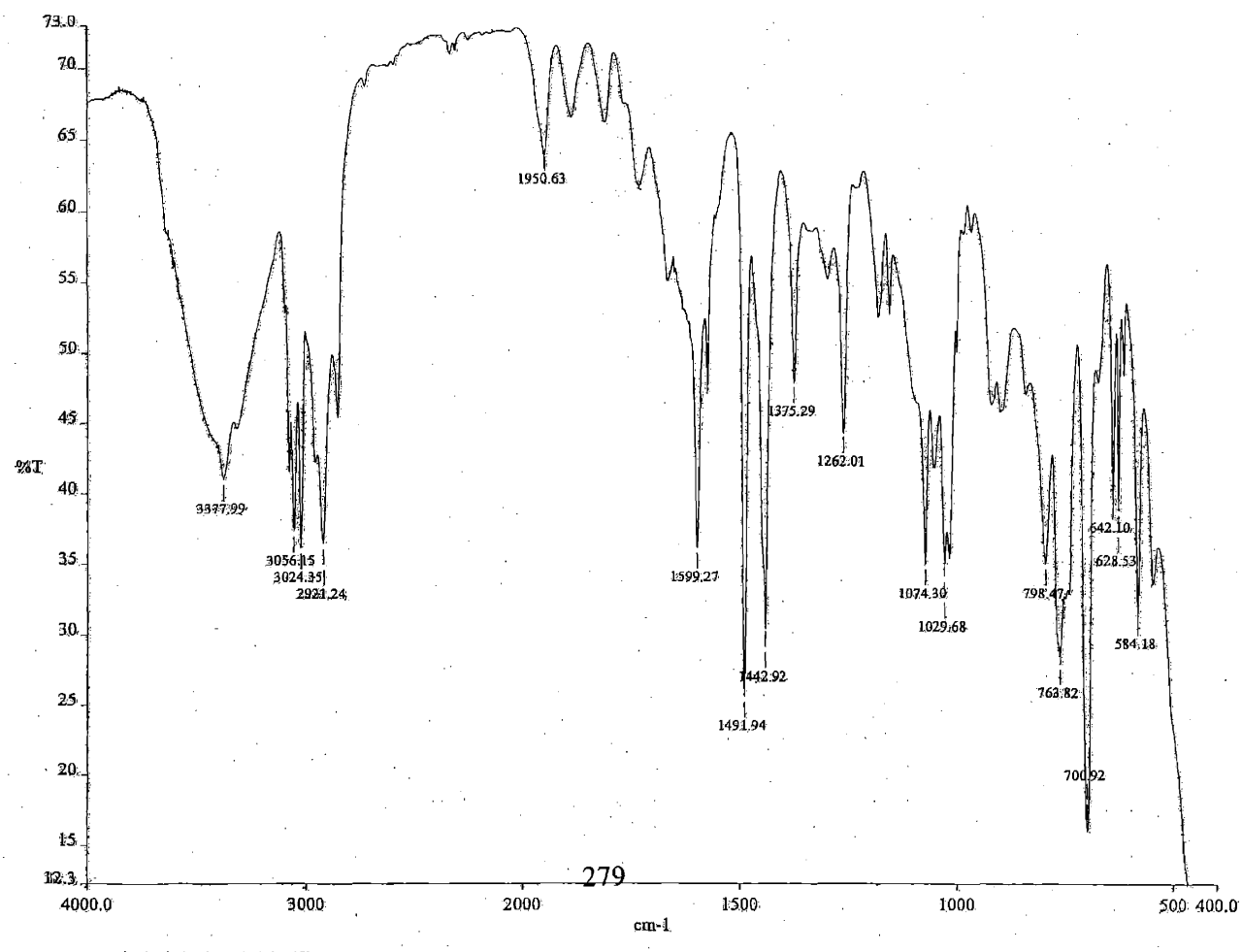
I-72

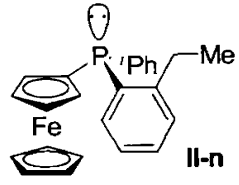



Ph
NH2
Me

I-72

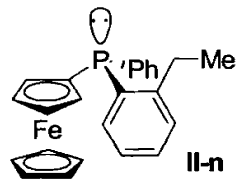
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3337.99
3056.15
3024.35
2921.24
1950.63
1599.27
1491.94
1442.92
1375.29
1262.01
1074.30
1029.68
798.47
763.82
700.92
642.10
628.53
584.18
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pe!_data\spectra\sjpv46b.sp


P
Ph
Me
Fe

II-n

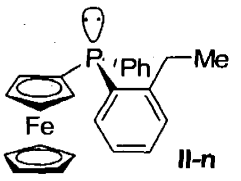
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.81 1.22 1.15
2.88 1.15 1.10
0.87 3.91
1.80 1.00
2.40
3.05



II-n

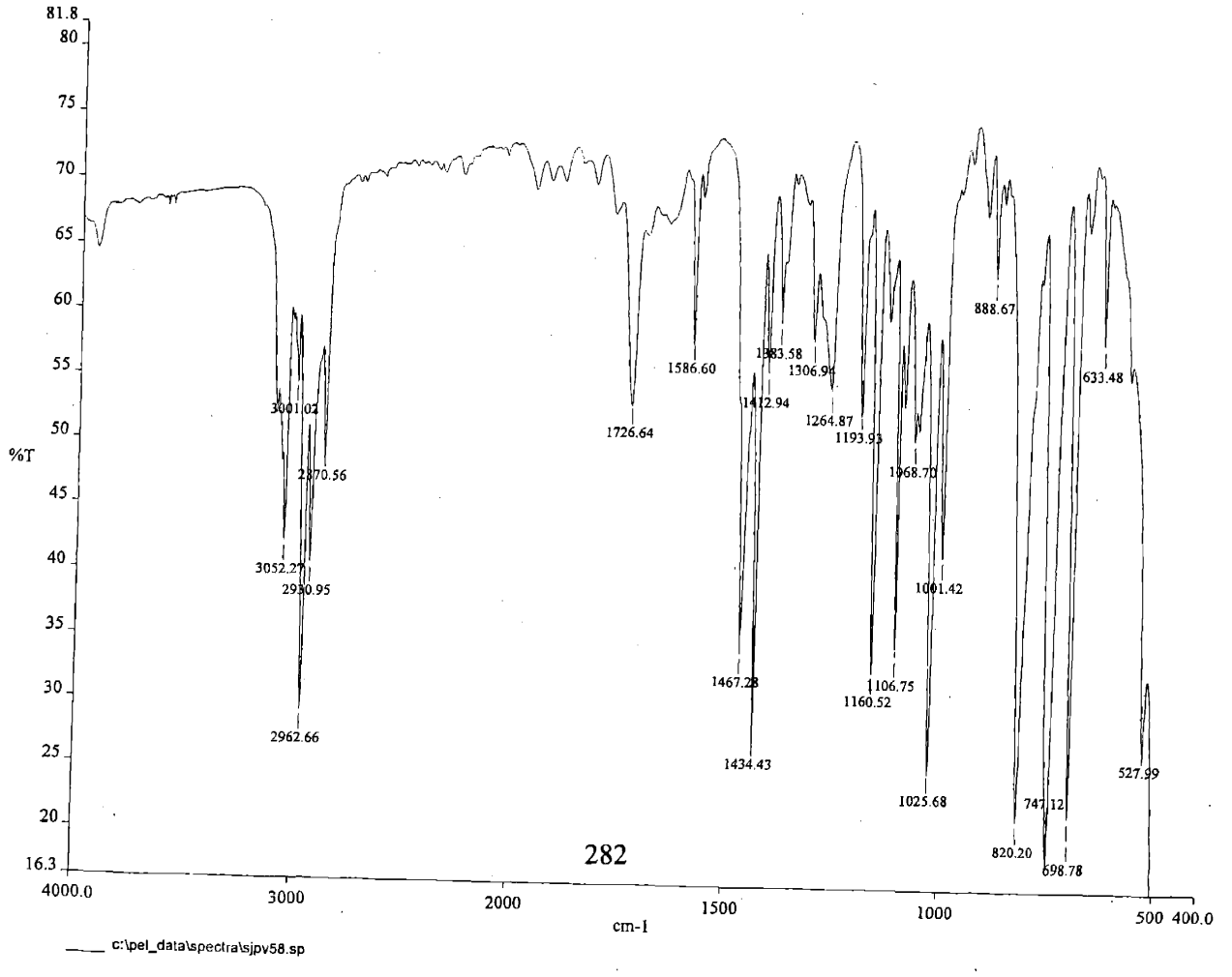
-25.535

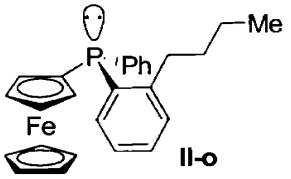
40 30 20 10 0 -10 -20 -30 ppm


P
Ph
Me
Fe

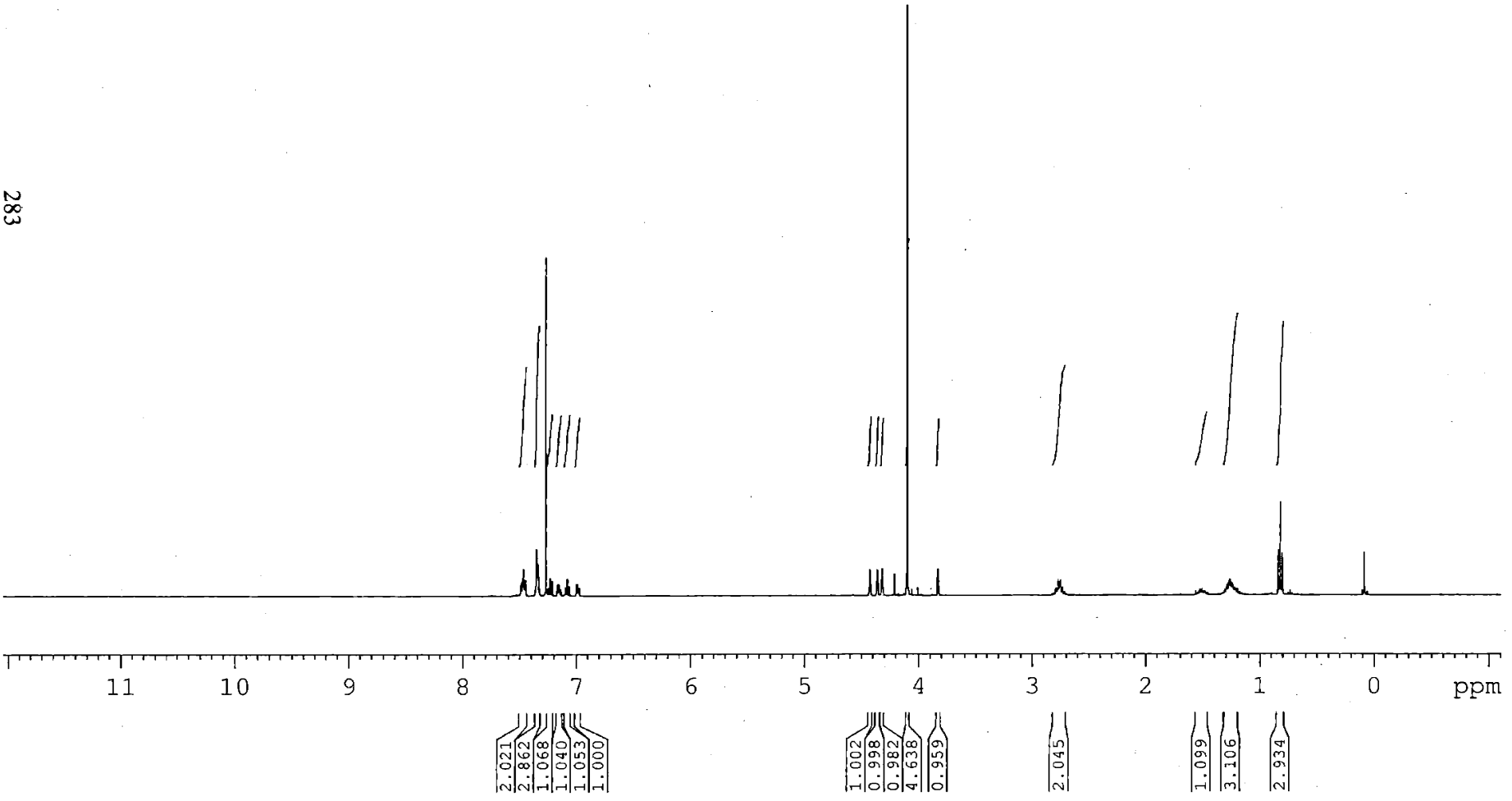
II-n

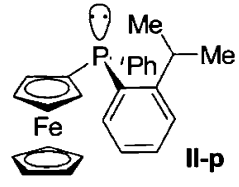
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm


%T
81.8
80
75
70
65
60
55
50
45
40
35
30
25
20
16.3
4000.0
3000
2000
1500
1000
500 400.0
cm-1
3001.02
2870.56
3052.27
2930.95
2962.66
1726.64
1586.60
1412.94
1383.58
1306.94
1264.87
1193.93
1106.75
1160.52
1467.28
1434.43
1025.68
1001.42
888.67
633.48
527.99
747.12
820.20
698.78
c:\pel_data\spectra\sjpv58.sp

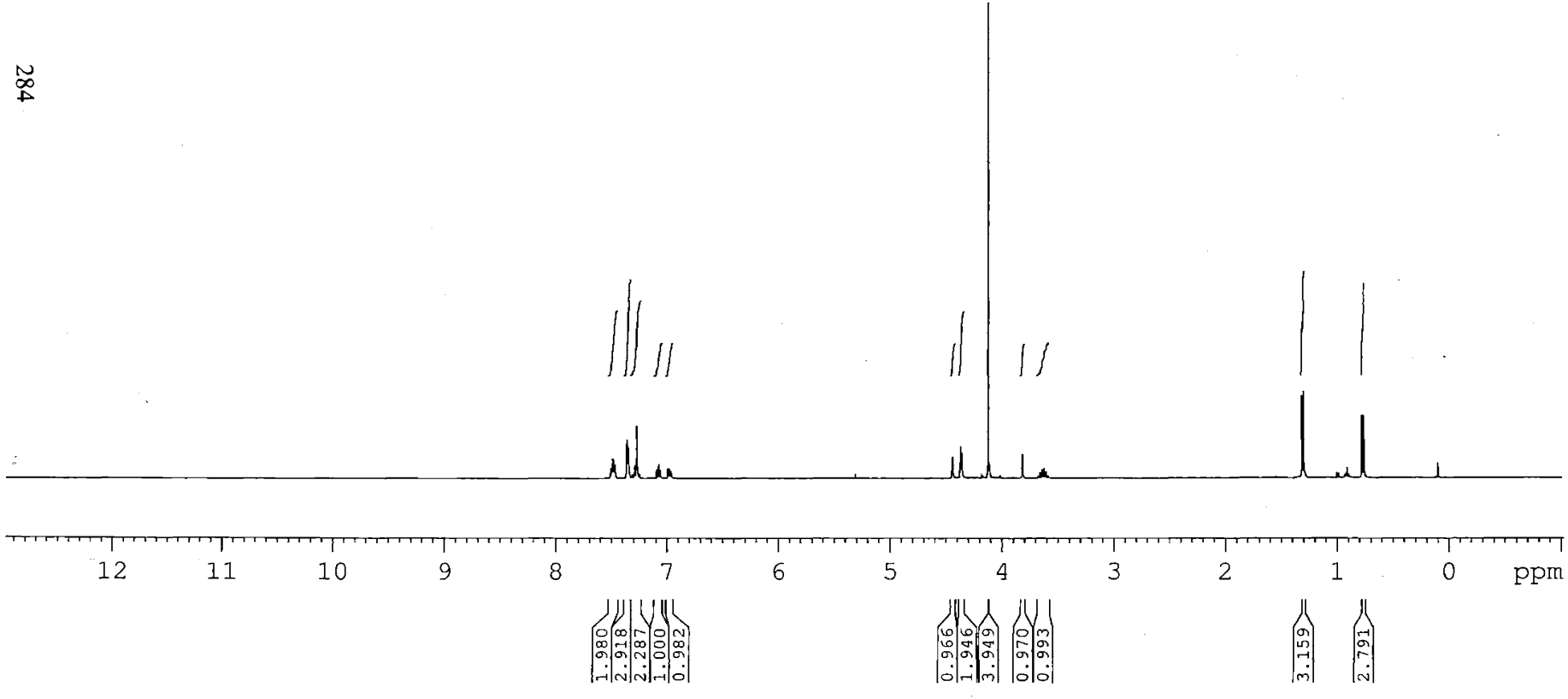

Me
P
Ph
Fe

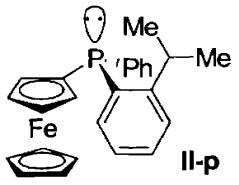
II-o


11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.021
2.862
1.068
1.040
1.053
1.000
1.002
0.998
0.982
4.638
0.959
2.045
1.099
3.106
2.934

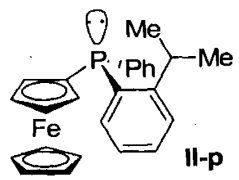

Me
P
Ph
Me
Fe

II-p


12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.980
2.918
2.287
1.000
0.982
0.966
1.946
3.949
0.970
0.993
3.159
2.791

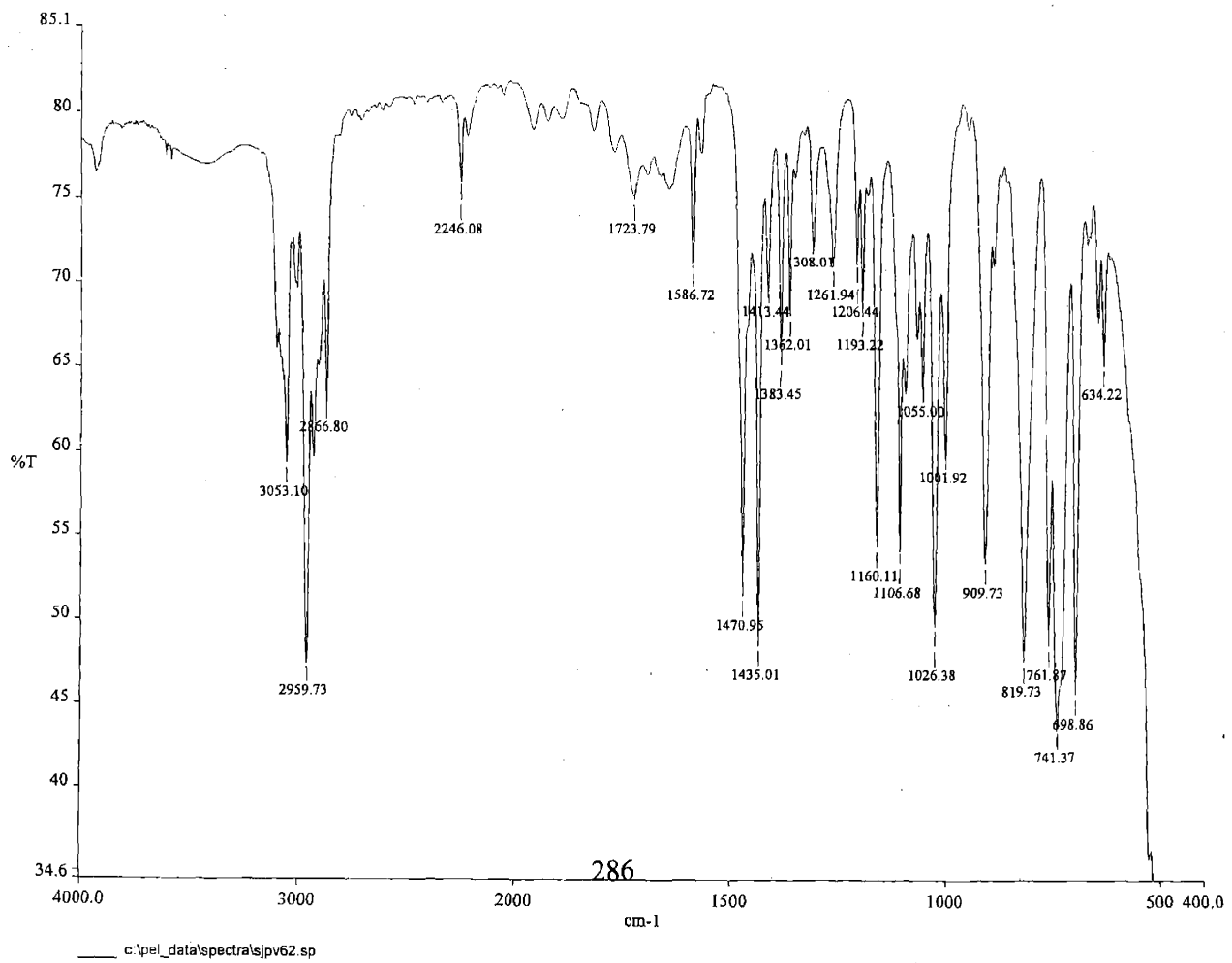


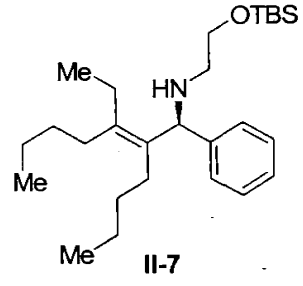
II-p


Me
P
iPh
Me
Fe

II-p

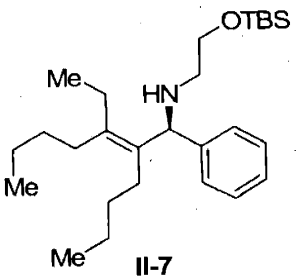
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
85.1
80
75
70
65
60
55
50
45
40
34.6
4000.0
3000
2000
1500
1000
500
400.0
cm-1
3053.10
2959.73
2866.80
2246.08
1723.79
1586.72
1470.95
1435.01
1413.44
1383.45
1362.01
1308.01
1261.94
1206.44
1193.22
1160.11
1106.68
1055.00
1026.38
1001.92
909.73
819.73
761.87
741.37
698.86
634.22
c:\pel_data\spectra\sjpv62.sp


OTBS
Me
HN
Me
Me

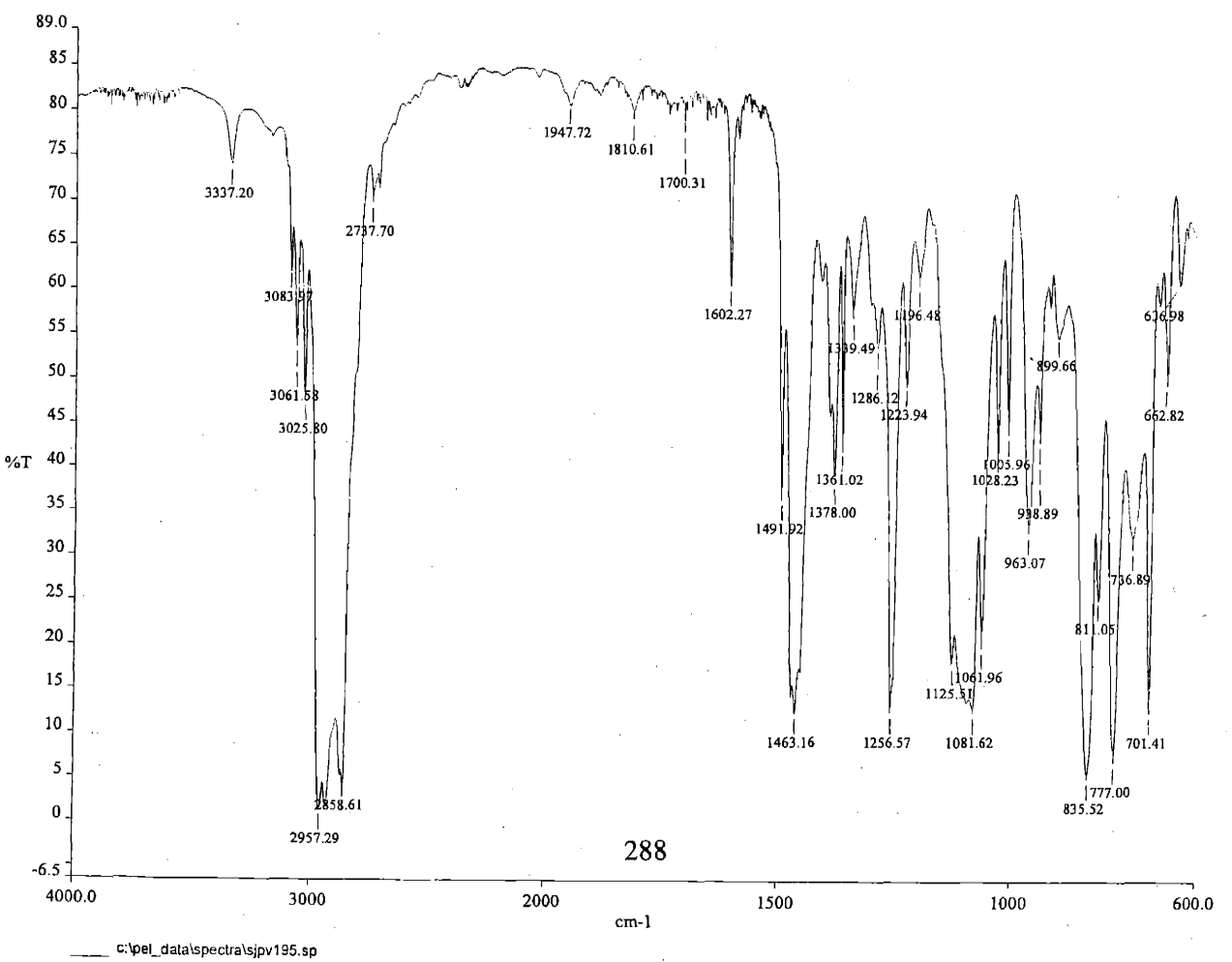
II-7

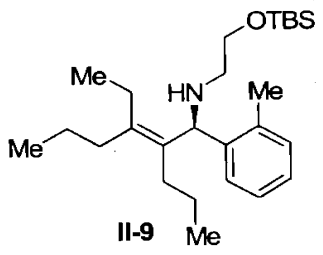
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.990
1.947
1.000
0.950
1.922
1.987
2.025
2.085
1.040
2.061
4.032
6.239
12.116
2.997
5.932


OTBS
HN
Me
Me
Me

II-7

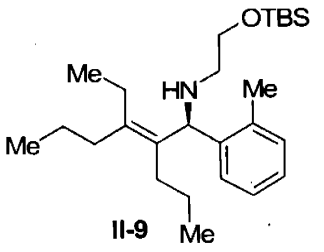
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
cm-1
4000.0
3000
2000
1500
1000
600.0
3337.20
3083.97
3061.68
3025.80
2957.29
2858.61
2737.70
1947.72
1810.61
1700.31
1602.27
1491.92
1463.16
1378.00
1361.02
1339.49
1286.12
1256.57
1223.94
1196.48
1125.51
1081.62
1061.96
1028.23
1005.96
963.07
938.89
899.66
835.52
811.05
777.00
736.89
701.41
662.82
616.98
c:\pel_data\spectra\sjpv195.sp


OTBS
Me
HN
Me
Me
Me

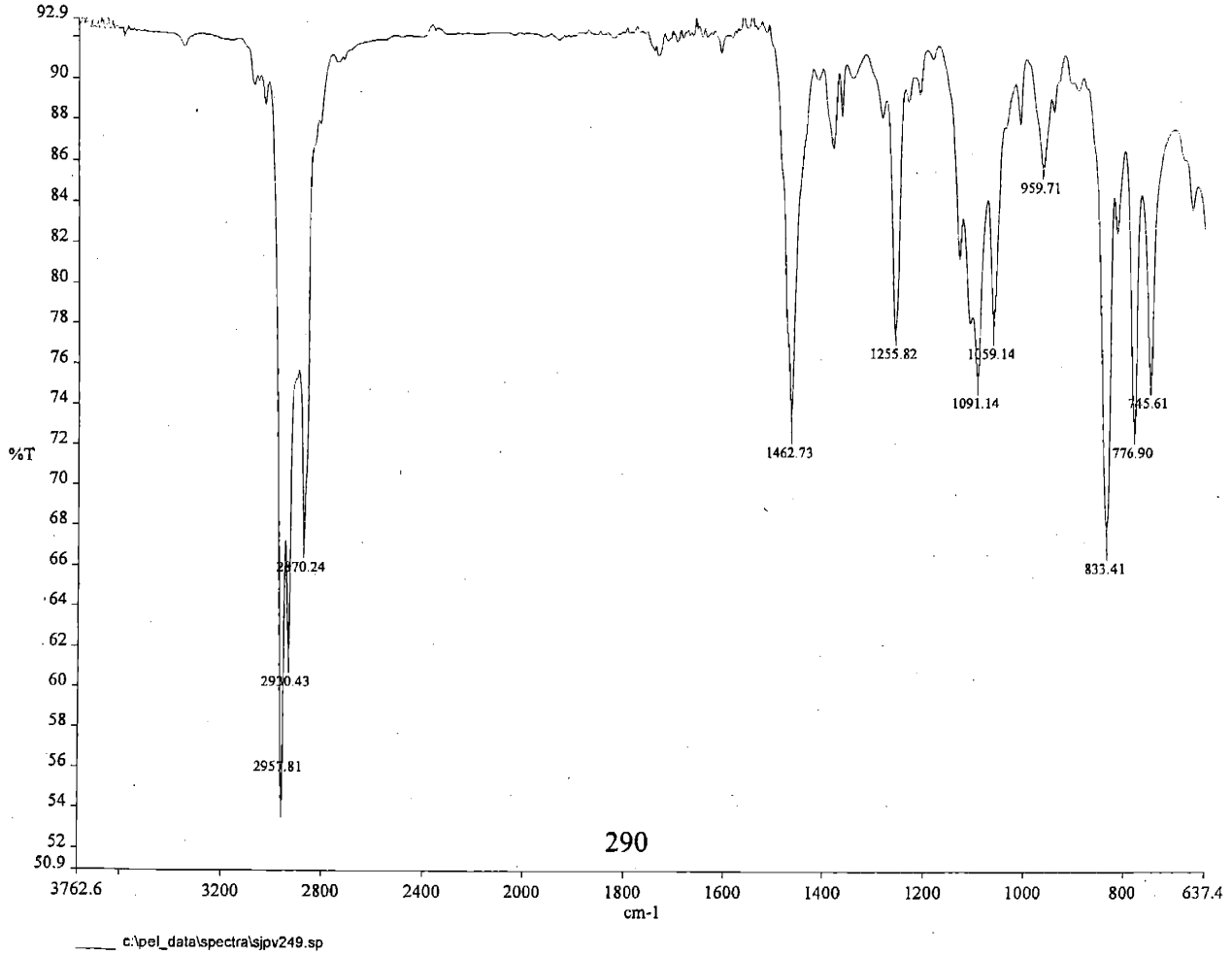
II-9

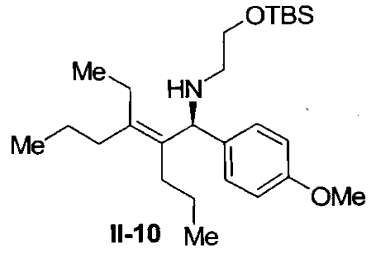
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.018
1.050
0.950
0.872
1.798
1.752
0.997
0.971
2.995
1.953
2.214
1.210
3.010
3.393
12.253
2.807
0.976
5.264


OTBS
Me
HN
Me
Me
Me

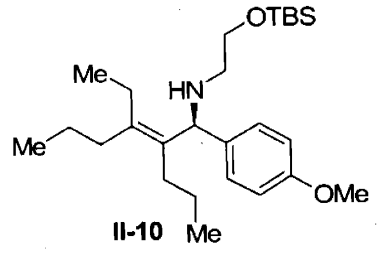
II-9

220
200
180
160
140
120
100
80
60
40
20
0
ppm


92.9
90
88
86
84
82
80
78
76
74
72
%T
70
68
66
64
62
60
58
56
54
52
50.9
2870.24
2930.43
2957.81
1462.73
1255.82
1159.14
1091.14
959.71
745.61
776.90
833.41
3762.6
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
637.4
cm-1
c:\pel_data\spectra\sjpv249.sp

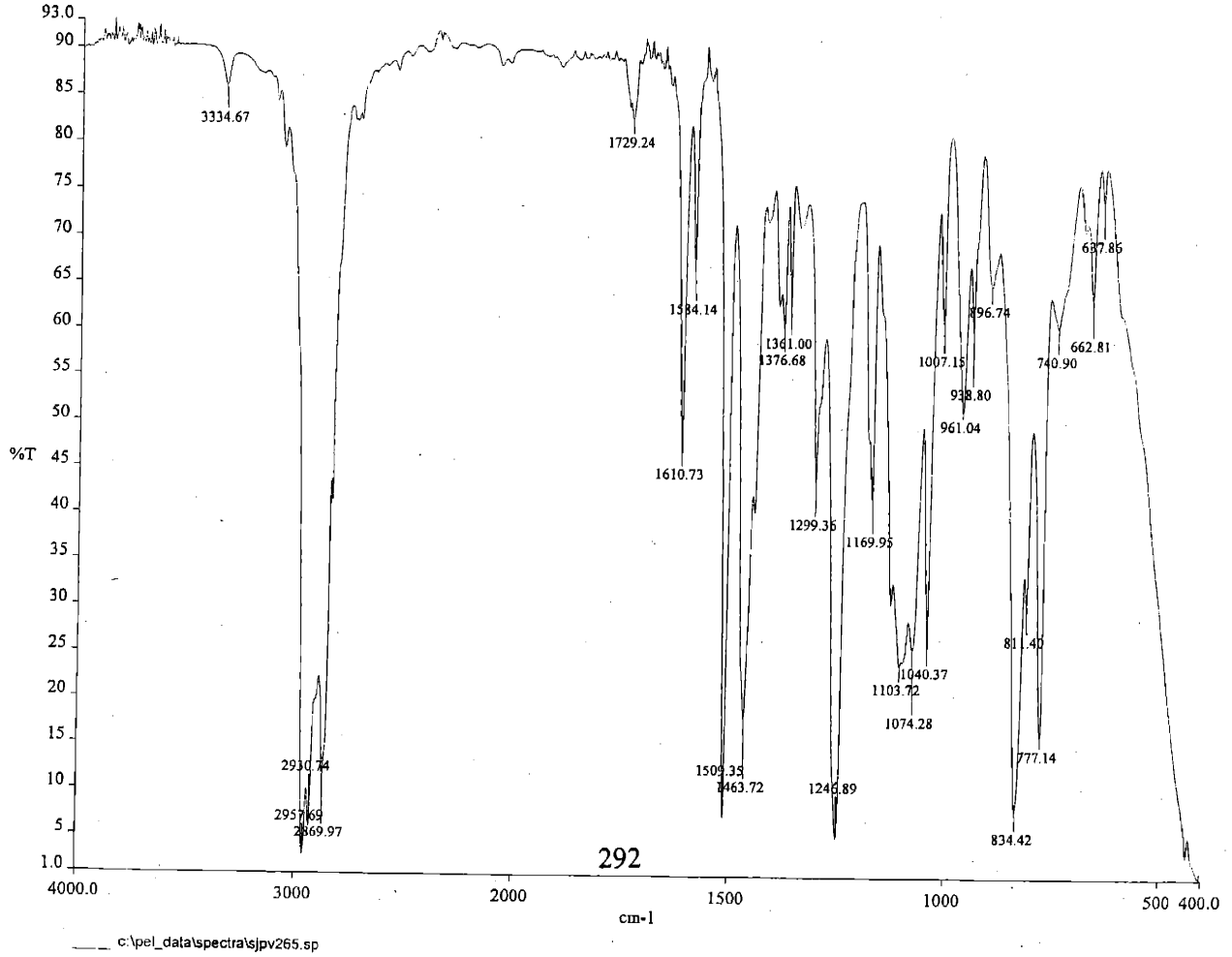

OTBS
Me
HN
Me
OMe
II-10
Me

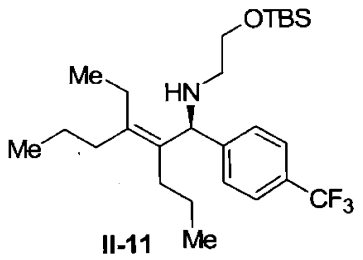
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.994
2.060
0.983
3.106
2.014
2.034
1.995
2.171
1.109
1.223
1.240
2.121
3.158
12.159
3.812
6.091


OTBS
Me
HN
Me
OMe
Me

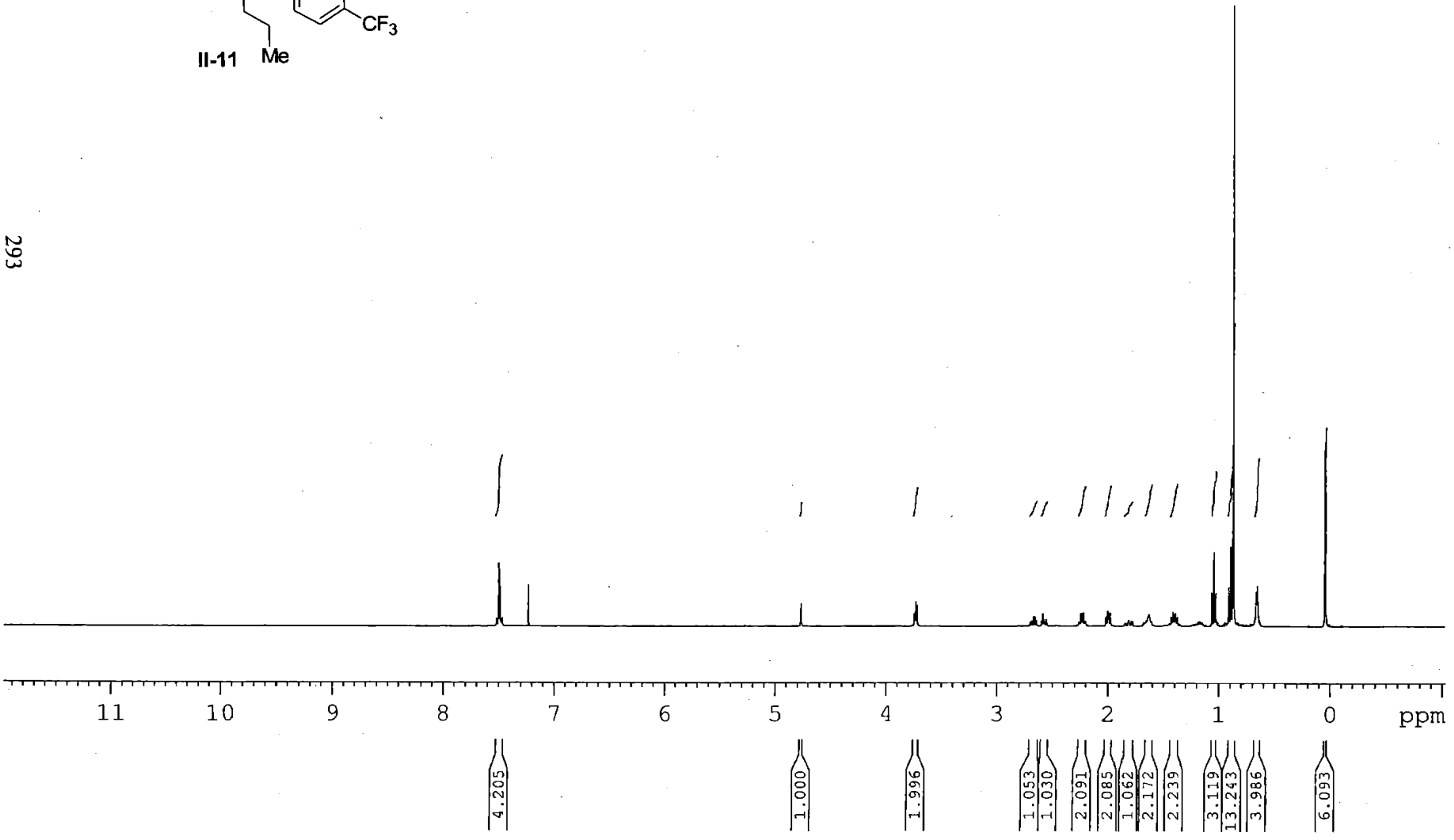
II-10

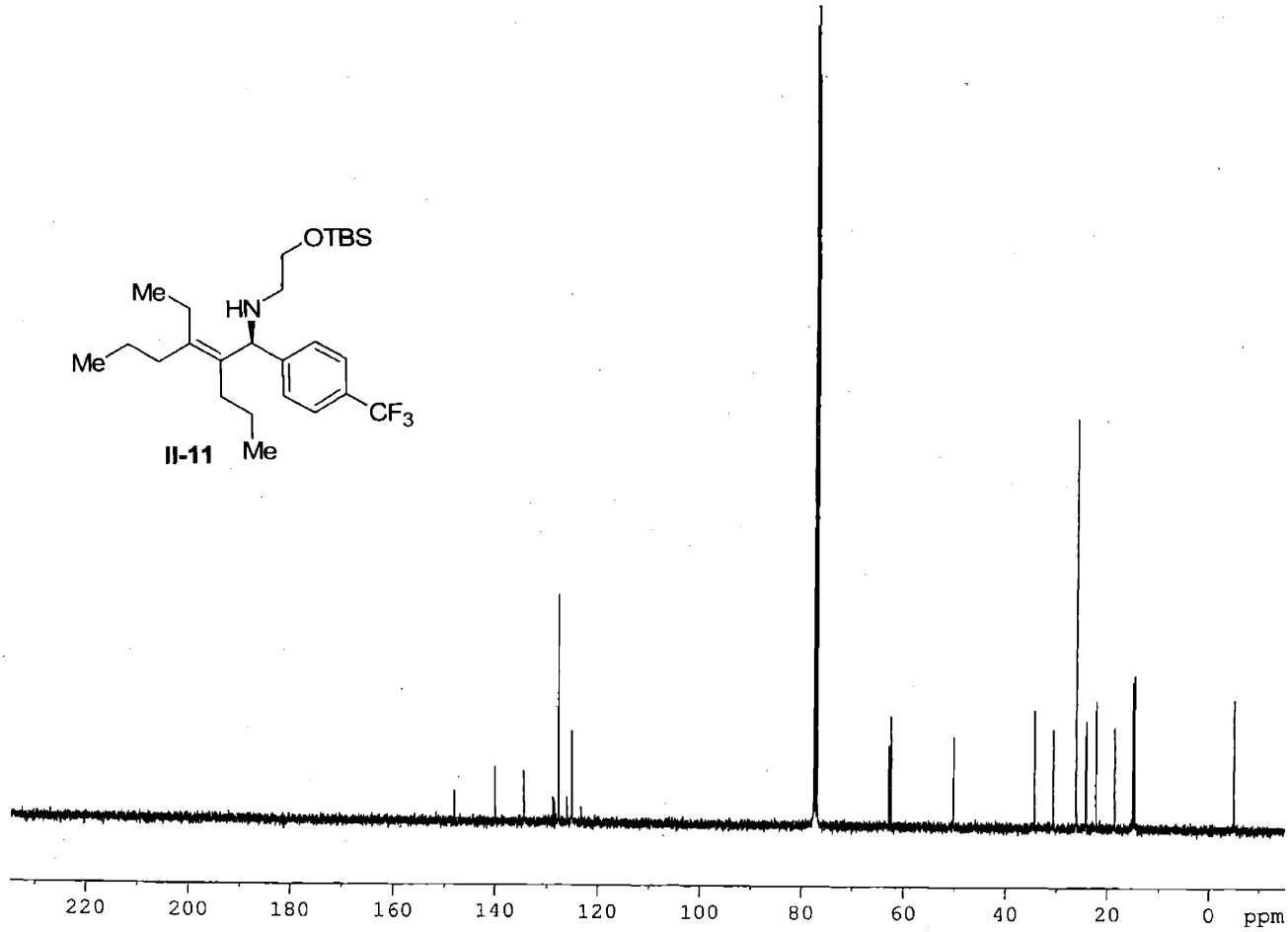
220
200
180
160
140
120
100
80
60
40
20
0
ppm

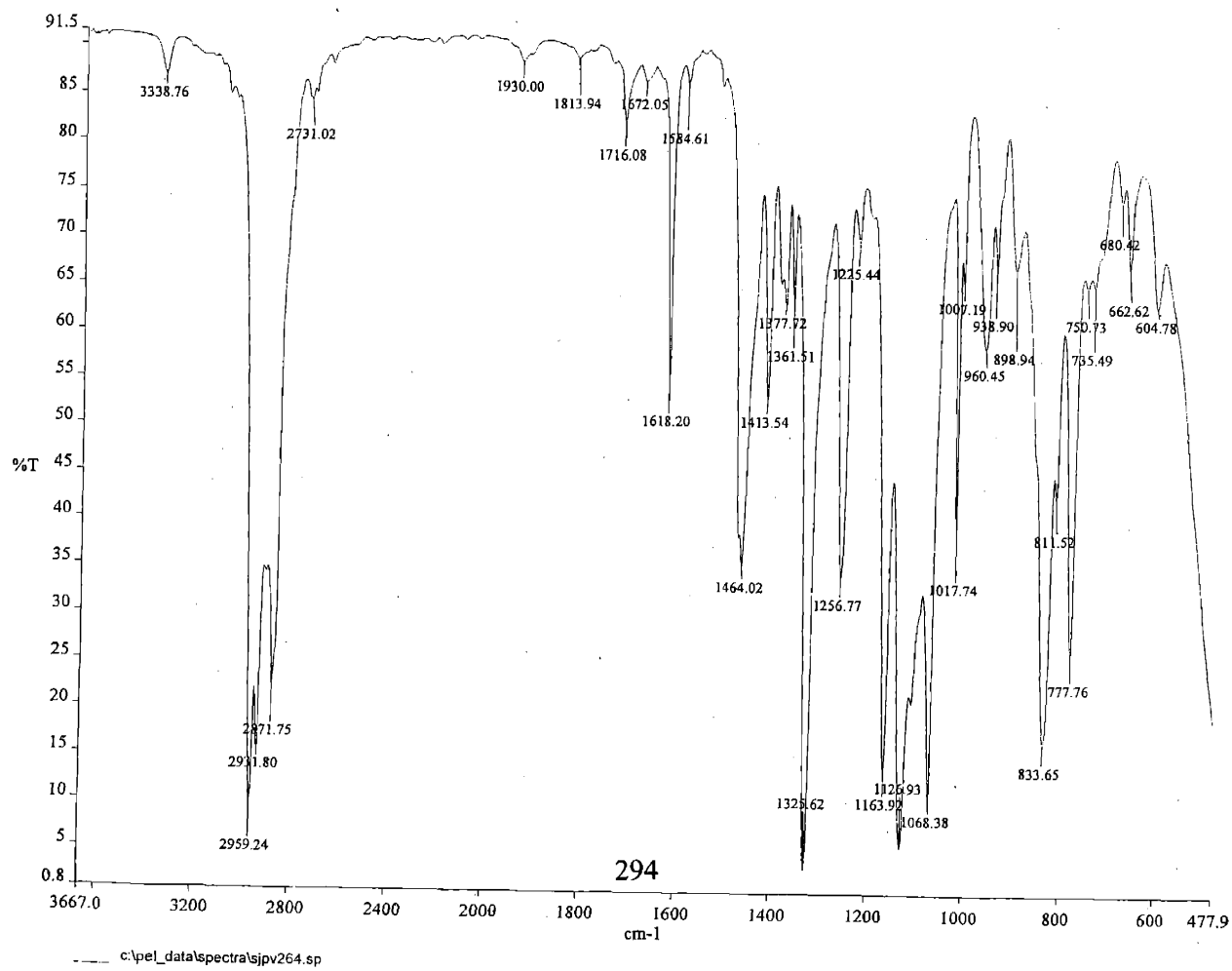

%T
93.0
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.0
3334.67
1729.24
1584.14
1610.73
1361.00
1376.68
1299.35
1169.95
1007.15
996.74
938.80
961.04
740.90
662.81
637.85
1040.37
1103.72
1074.28
811.42
777.14
834.42
1509.35
1463.72
1246.89
2930.74
2957.69
2869.97
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv265.sp

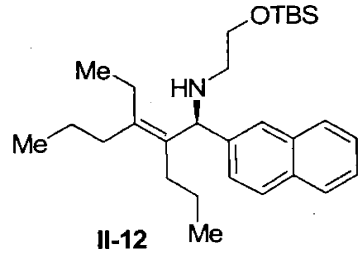

OTBS
Me
HN
Me
CF3
Me

II-11


11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.205
1.000
1.996
1.053
1.030
2.091
2.085
1.062
2.172
2.239
3.119
13.243
3.986
6.093

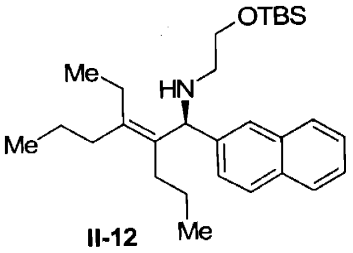

OTBS
Me
HN
Me
CF3
II-11
Me
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
cm-1
3338.76
2731.02
1930.00
1813.94
1672.05
1716.08
1584.61
1618.20
1464.02
1413.54
1377.72
1361.51
1325.62
1256.77
1225.44
1126.93
1163.92
1068.38
1017.74
1007.19
960.45
938.90
898.94
833.65
811.52
777.76
750.73
735.49
680.42
662.62
604.78
2959.24
2931.80
2871.75
3667.0
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
477.9
c:\pel_data\spectra\sjpv264.sp


OTBS
Me
HN
Me
Me

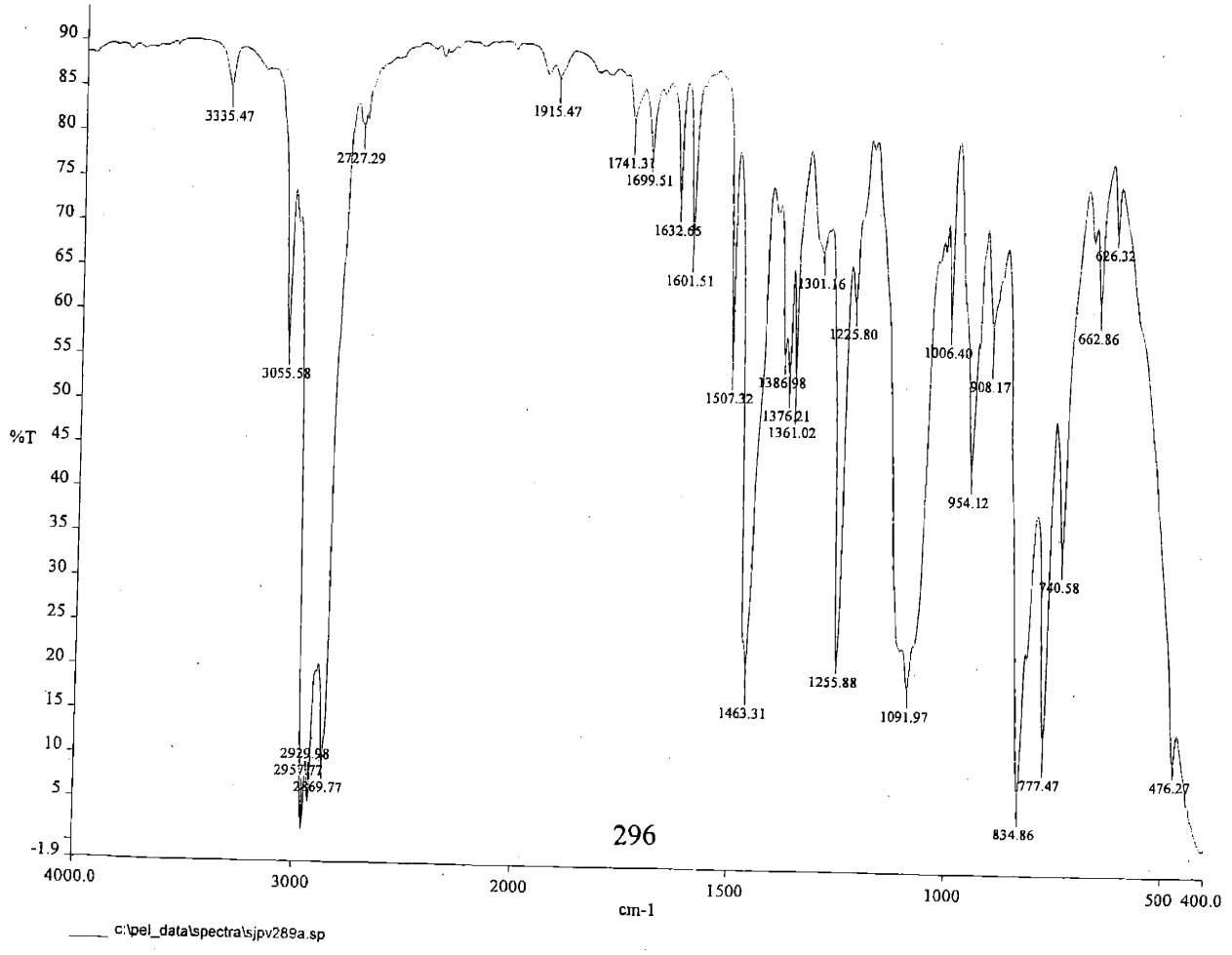
II-12

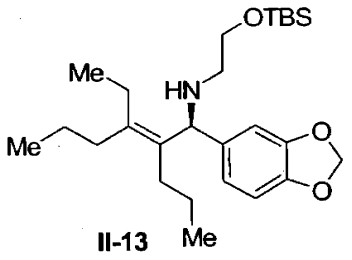
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.998
3.208
3.202
0.982
2.068
1.867
2.010
2.031
1.160
1.422
2.212
0.904
3.100
12.652
3.794
6.179


OTBS
Me
HN
Me
Me

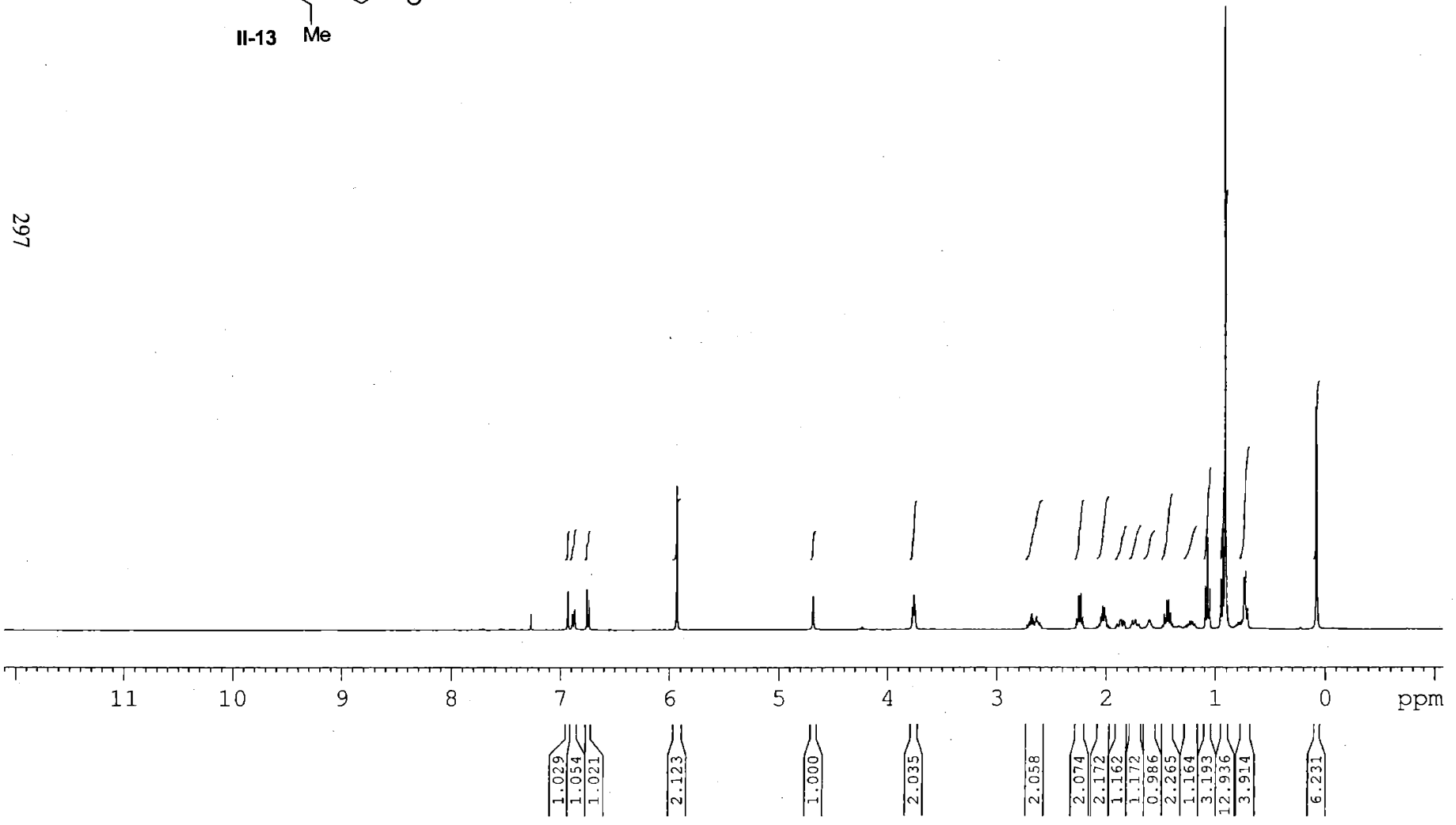
II-12

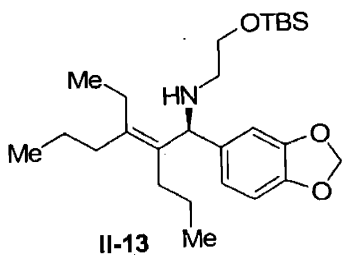
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3335.47
3055.58
2929.58
2957.77
2869.77
2727.29
1915.47
1741.31
1699.51
1632.65
1601.51
1507.32
1463.31
1386.98
1376.21
1361.02
1301.16
1255.88
1225.80
1091.97
1006.40
954.12
908.17
834.86
777.47
740.58
662.86
626.32
476.27
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv289a.sp


OTBS
HN
Me
Me
Me
O
O

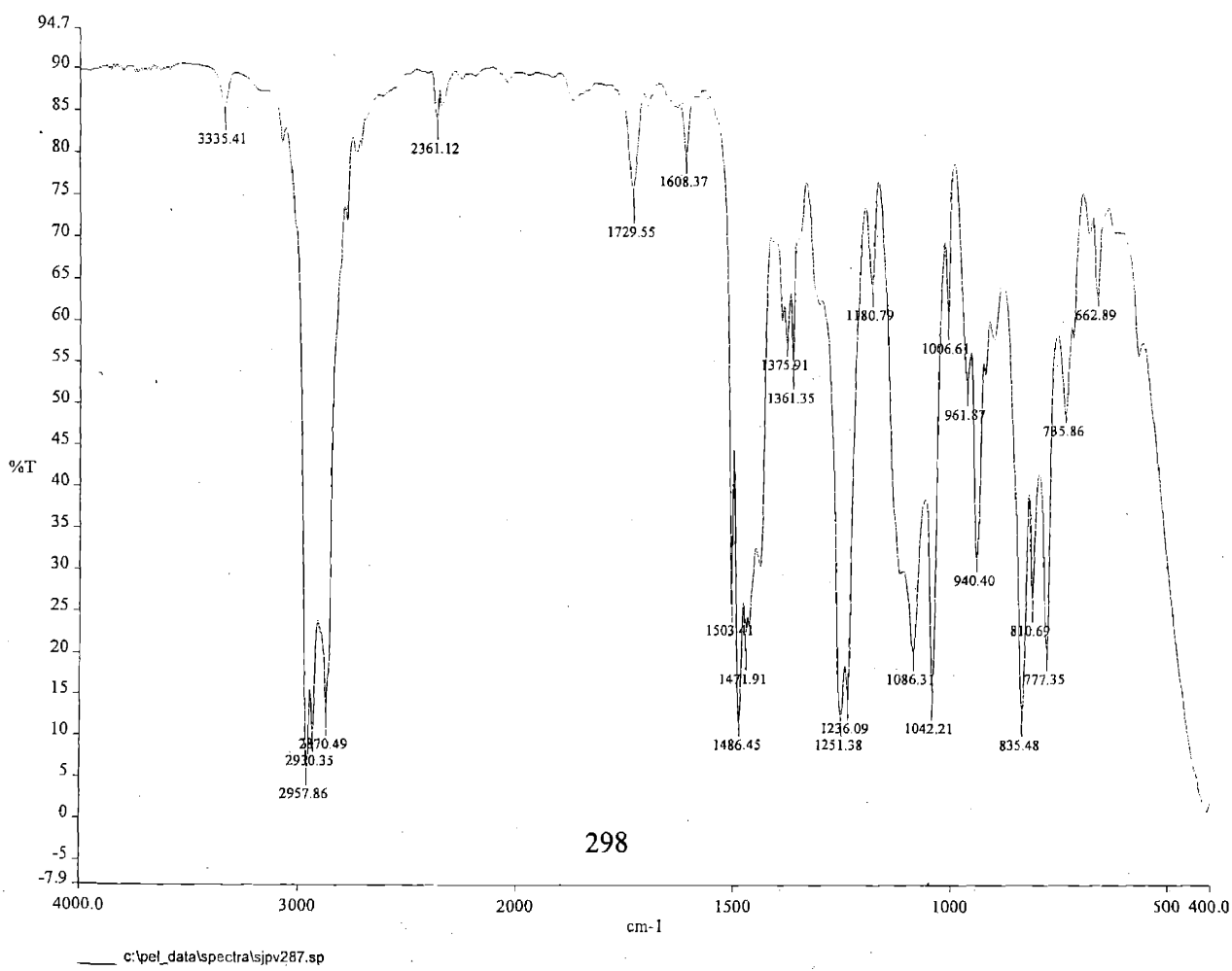
II-13

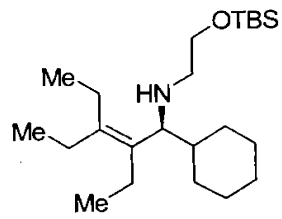

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.029
1.054
1.021
2.123
1.000
2.035
2.058
2.074
2.172
1.162
1.172
0.986
2.265
1.164
3.193
12.936
3.914
6.231


OTBS
HN
Me
Me
O
O
Me

II-13

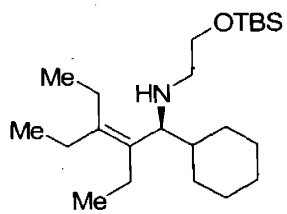
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3335.41
2361.12
1729.55
1608.37
1503.41
1471.91
1486.45
1375.91
1361.35
1180.79
1236.09
1251.38
1086.31
1042.21
1006.61
961.87
940.40
835.48
810.69
785.86
777.35
662.89
2870.49
2930.35
2957.86
4000.0
3000
2000
1500
1000
500
400.0
cm-1
c:\pel_data\spectra\sjpv287.sp


OTBS
HN
Me
Me
Me

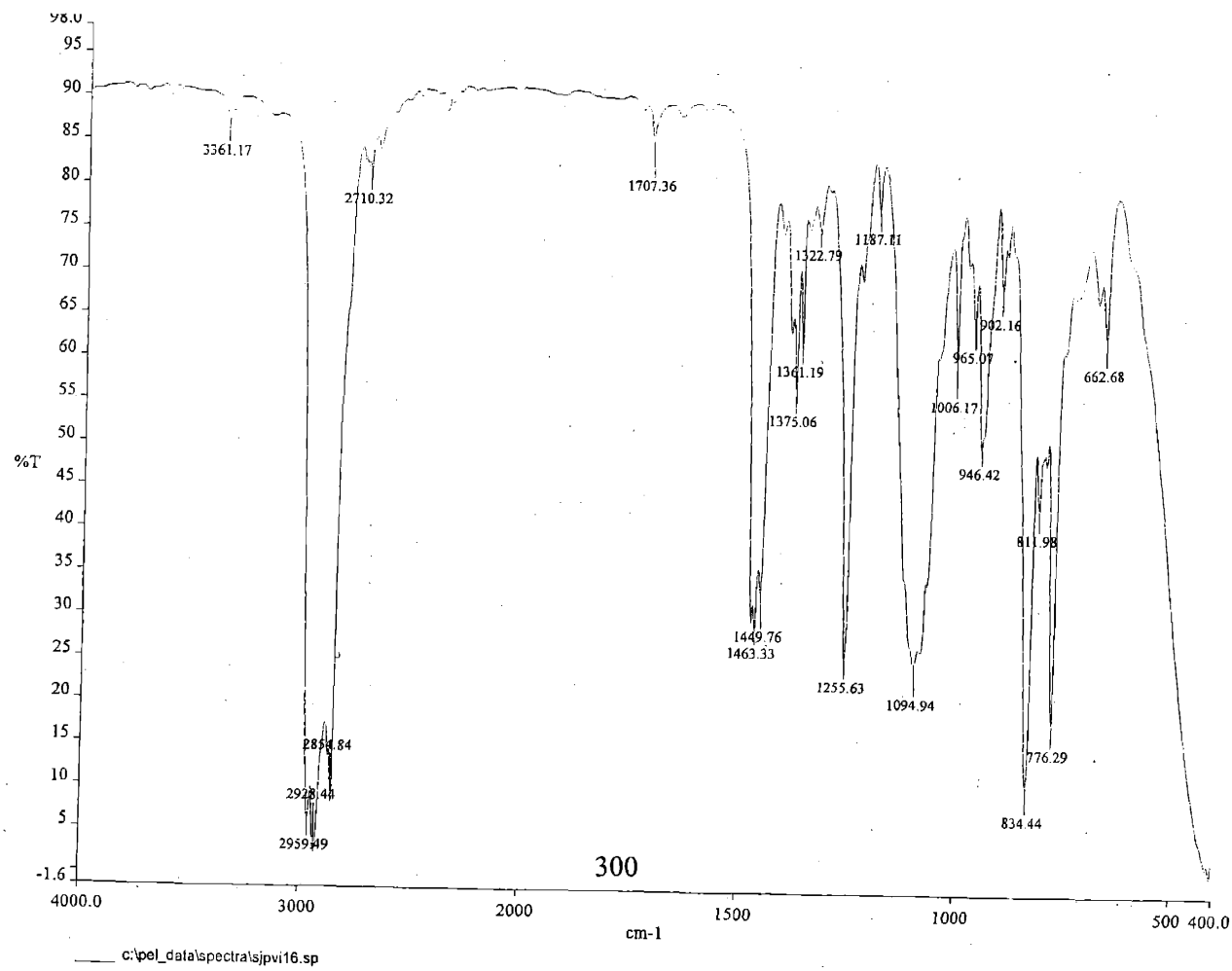
II-14

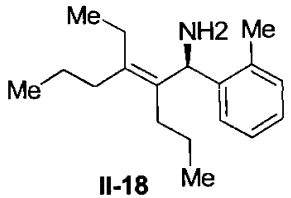
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.108
1.000
1.051
1.085
7.219
1.218
6.054
5.601
6.953
4.500
10.084
1.150
6.337


OTBS
HN
Me
Me
Me

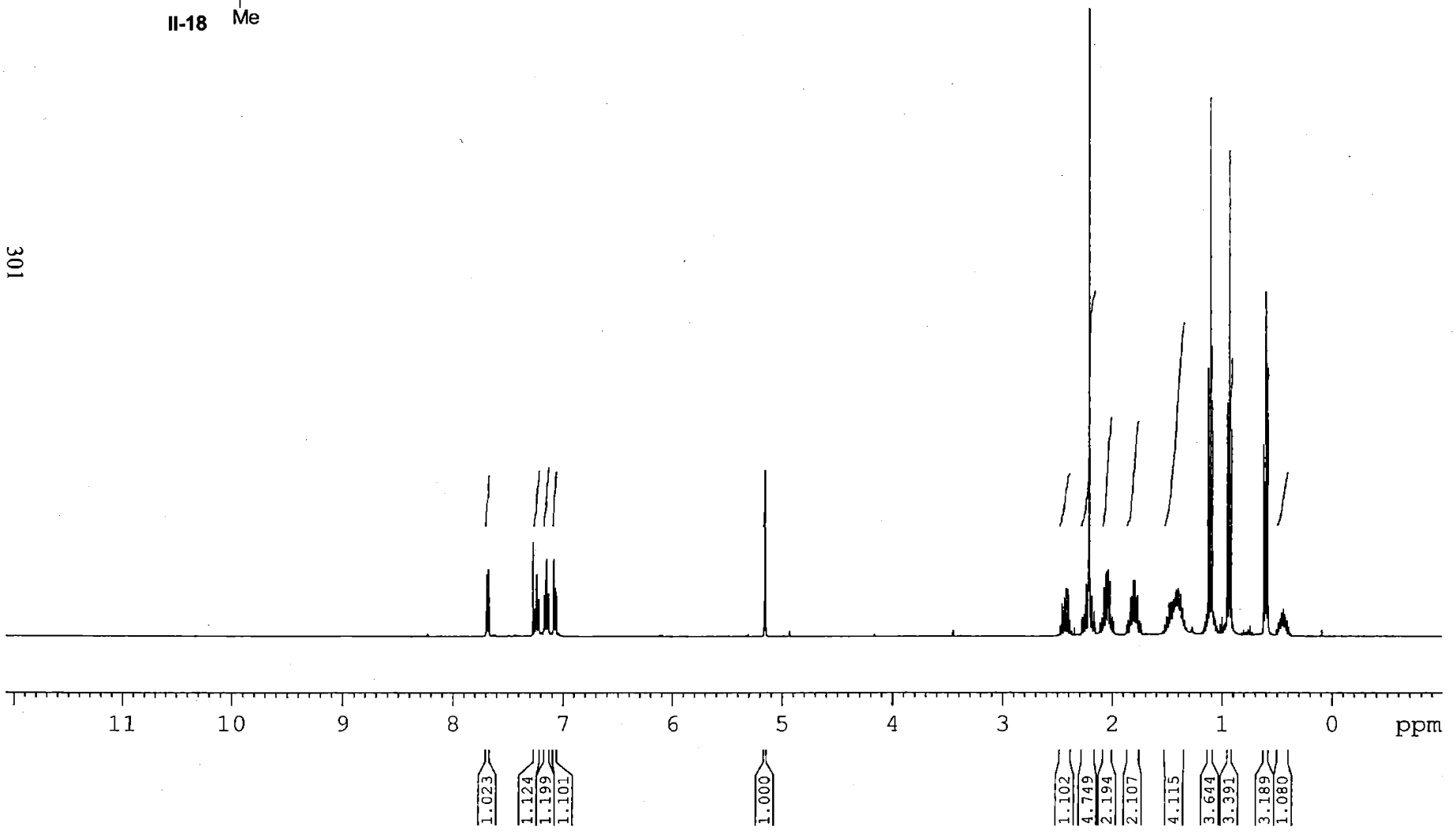
II-14

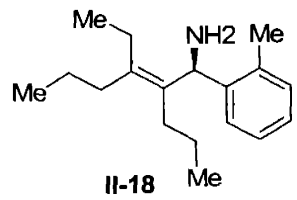
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
3361.17
2710.32
1707.36
1322.79
1187.11
1361.19
1375.06
902.16
965.07
1006.17
946.42
662.68
1449.76
1463.33
1255.63
1094.94
811.98
776.29
834.44
2928.44
2959.49
300
cm-1
4000.0
3000
2000
1500
1000
500
400.0
c:\pel_data\spectra\sjpvi16.sp


Me
NH2
Me
Me
Me

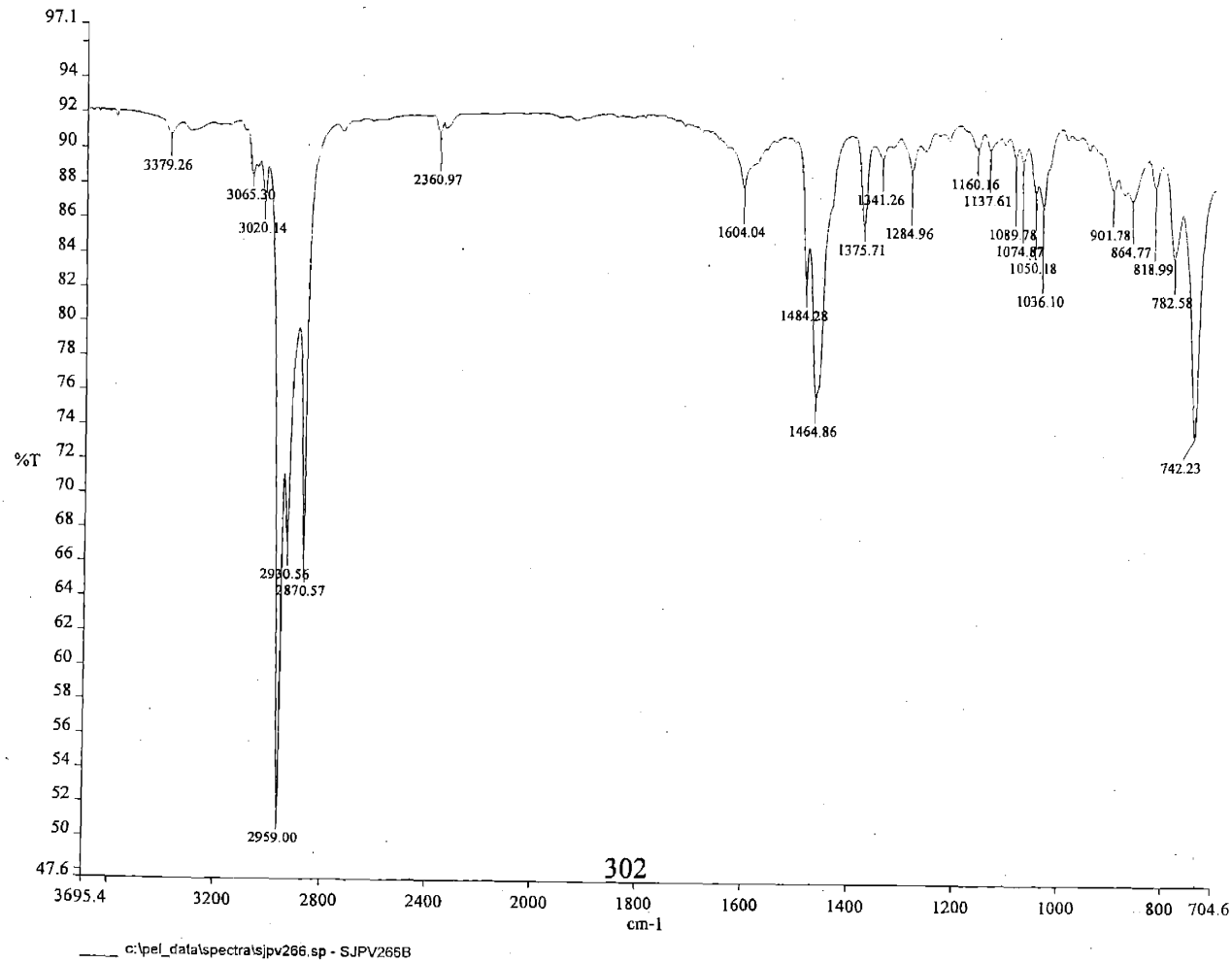
II-18

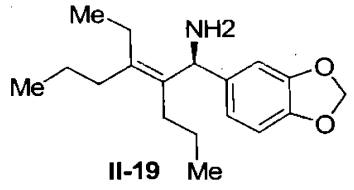

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.023
1.124
1.199
1.101
1.000
1.102
4.749
2.194
2.107
4.115
3.644
3.391
3.189
1.080

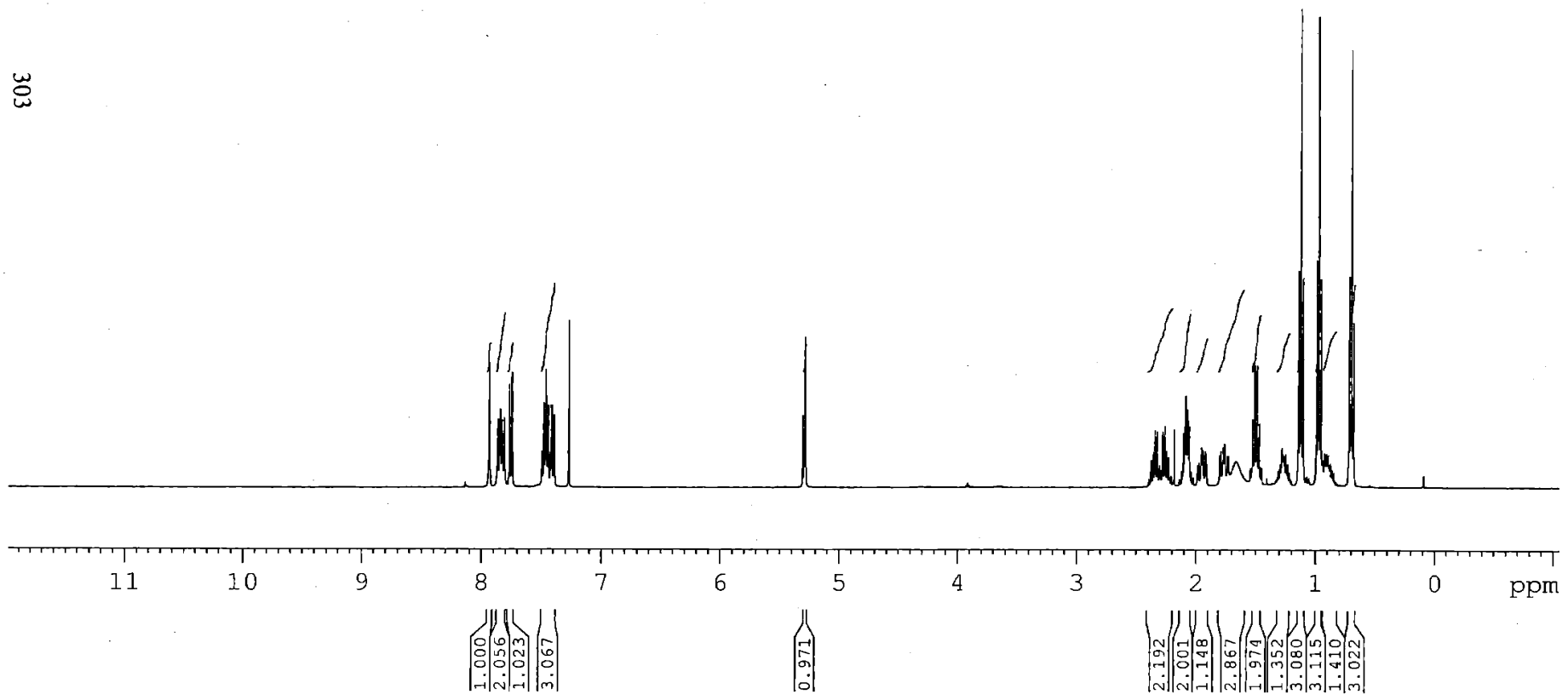

Me
NH2
Me
Me
Me

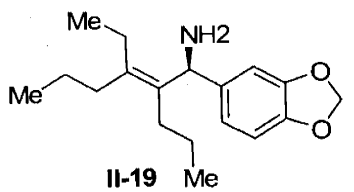
II-18

220
200
180
160
140
120
100
80
60
40
20
0
ppm

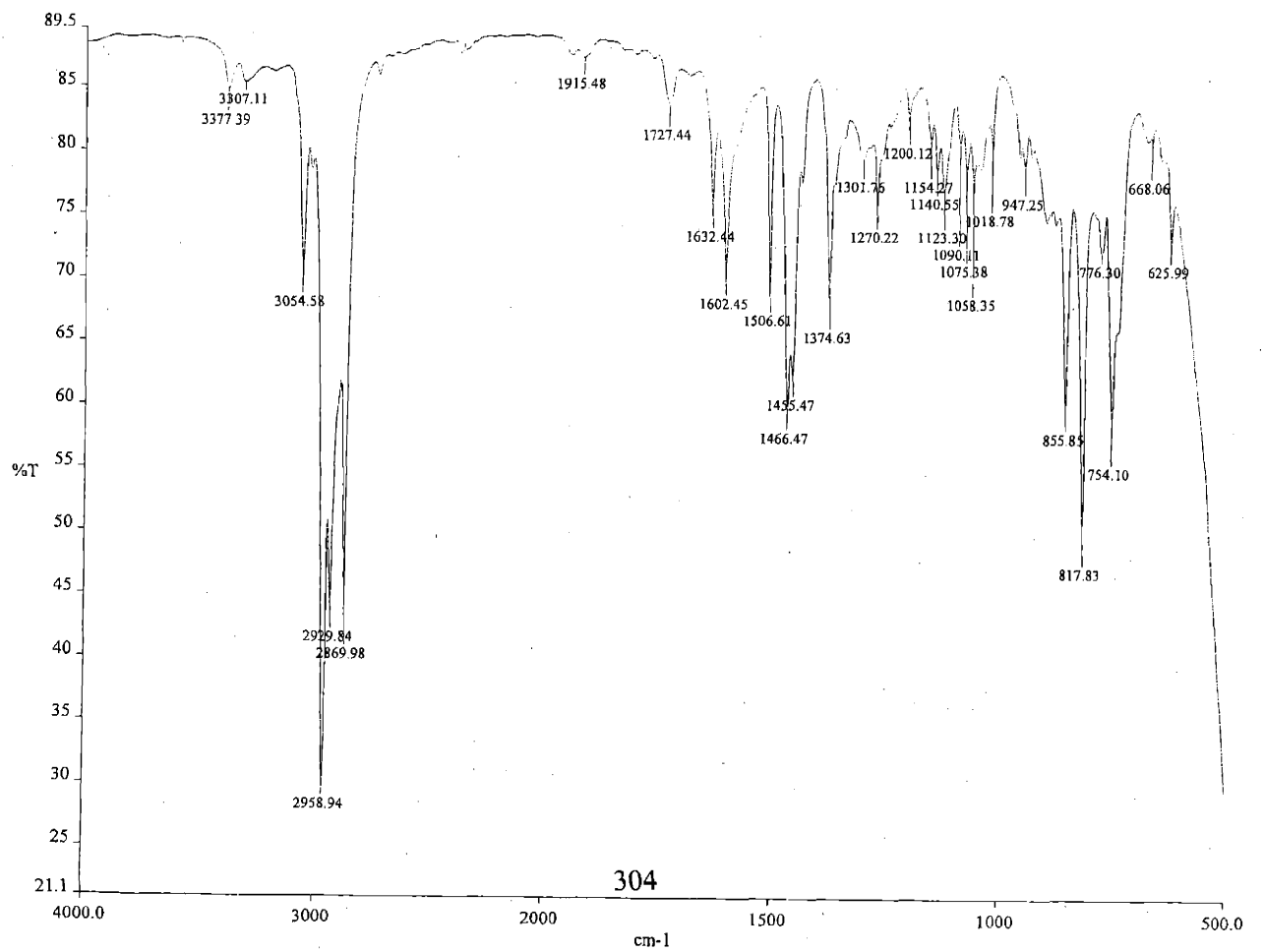

%T
97.1
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
47.6
3379.26
3065.30
3020.14
2959.00
2930.56
2870.57
2360.97
1604.04
1484.28
1464.86
1375.71
1341.26
1284.96
1160.16
1137.61
1089.78
1074.87
1050.18
1036.10
901.78
864.77
818.99
782.58
742.23
3695.4
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
704.6
cm-1
c:\pel_data\spectra\sjpv266.sp - SJPV265B


Me
NH2
Me
O
O
II-19
Me

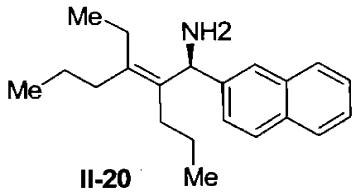

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.056
1.023
3.067
0.971
2.192
2.001
1.148
2.867
1.974
1.352
3.080
3.115
1.410
3.022



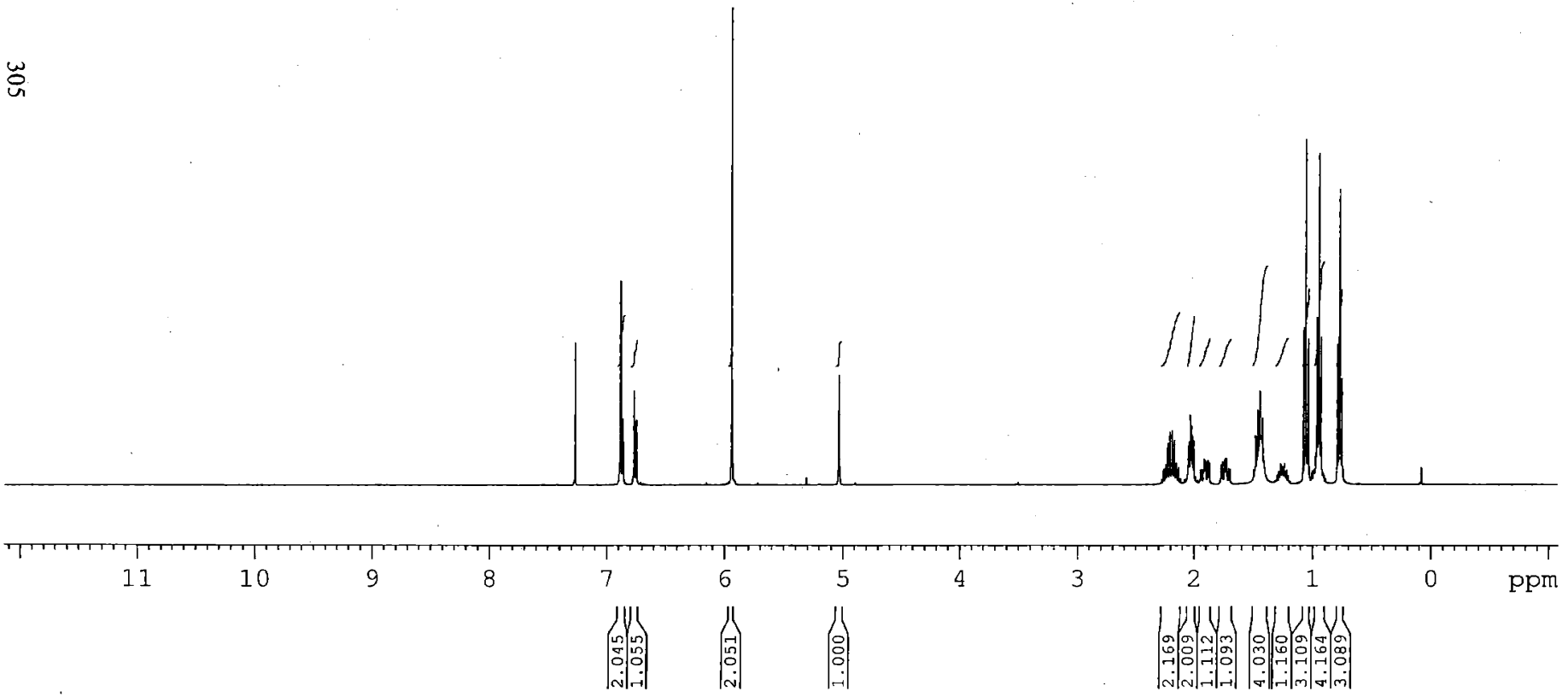
II-19 Me

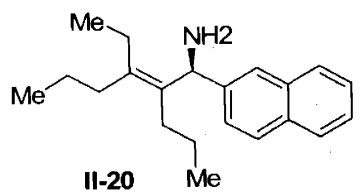


c:\pel_data\spectra\sjpvi37.sp - SJPVI-37


Me
NH2
Me
Me

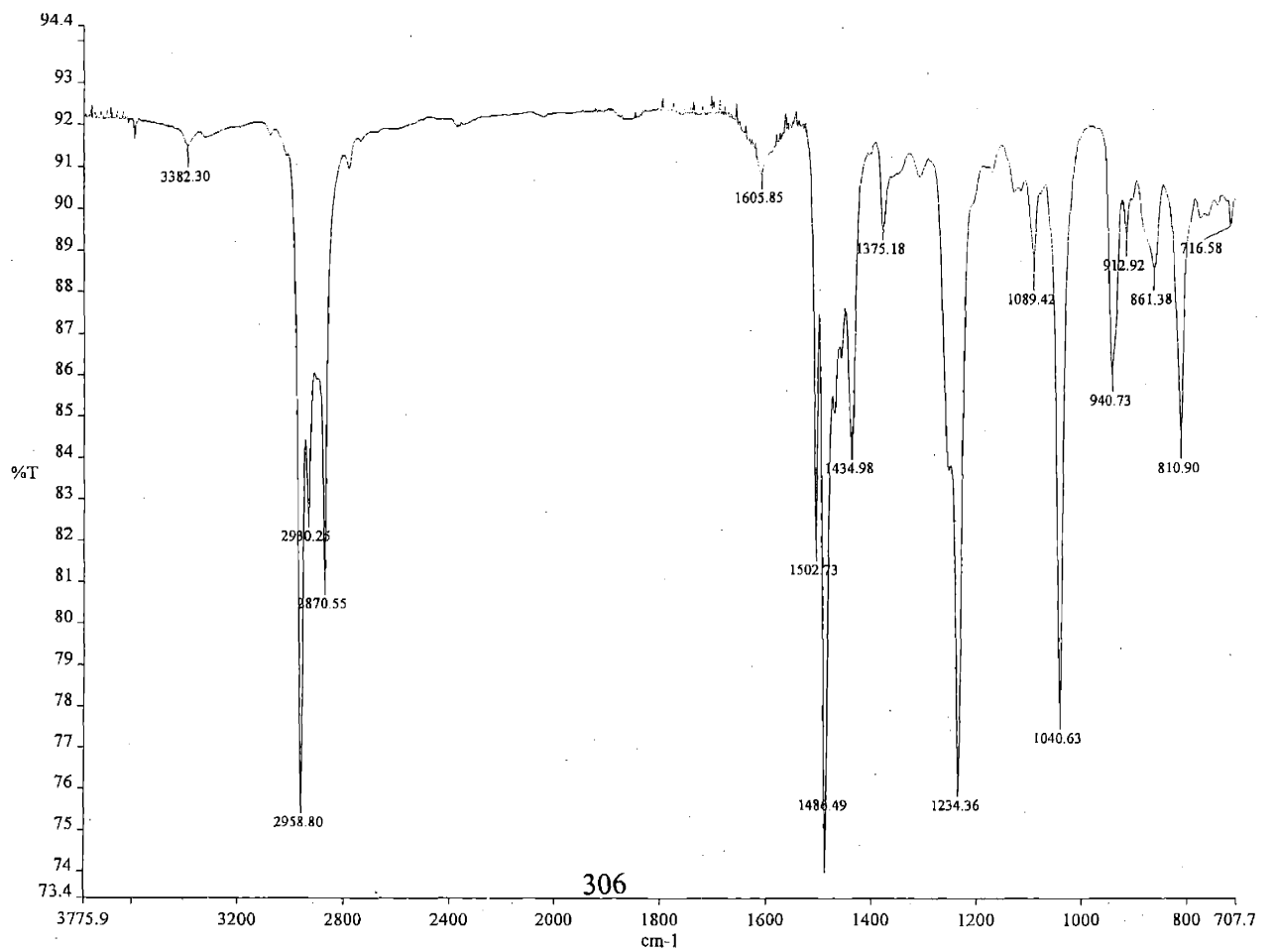
II-20

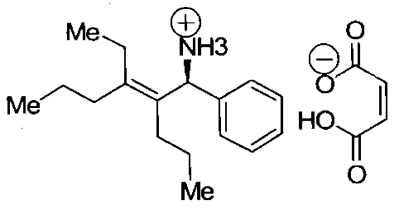

11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.045
1.055
2.051
1.000
2.169
2.009
1.112
1.093
4.030
1.160
3.109
4.164
3.089


Me
NH2
Me
Me

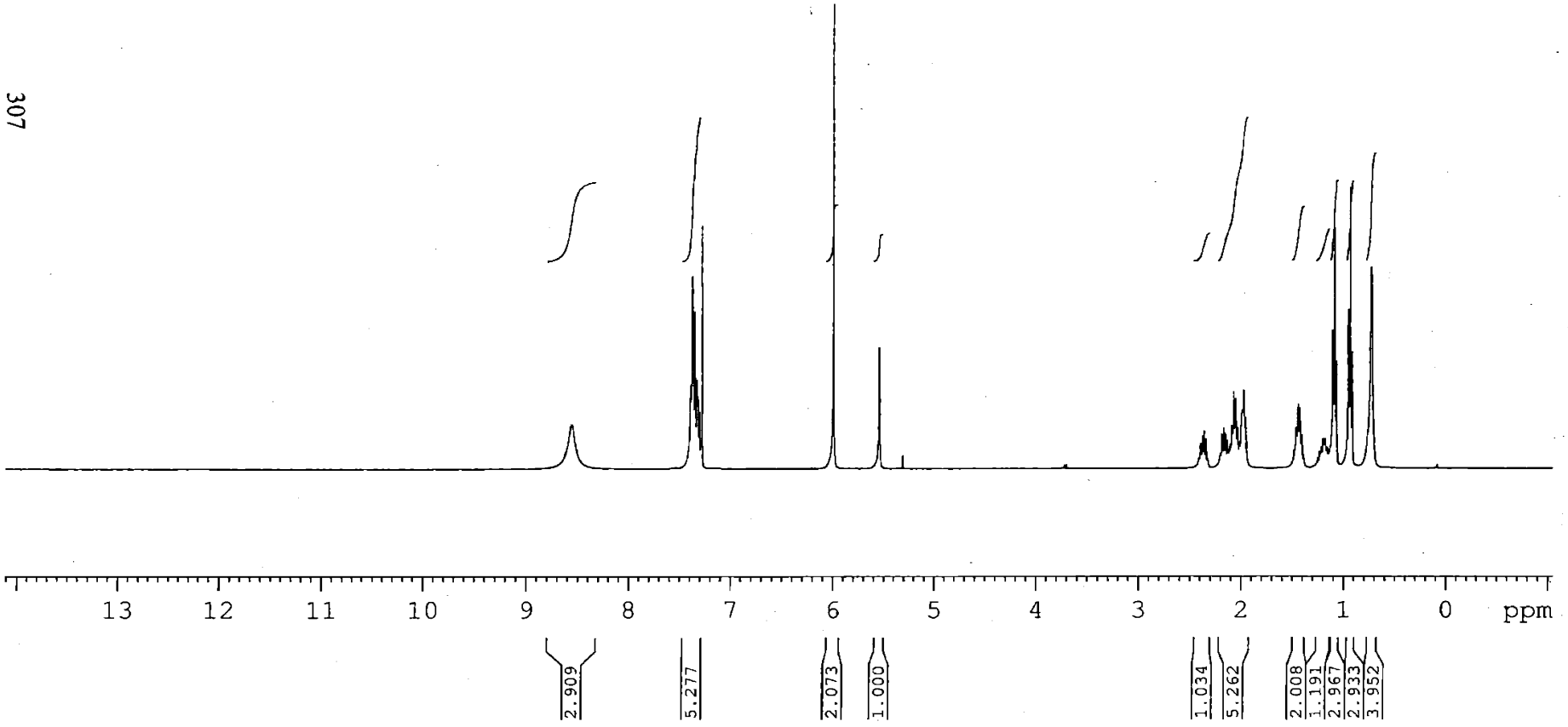
II-20

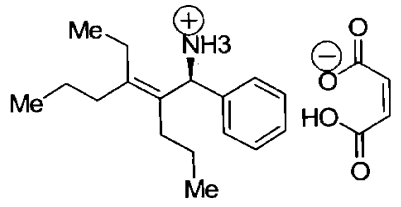
220
200
180
160
140
120
100
80
60
40
20
0
ppm


%T
94.4
93
92
91
90
89
88
87
86
85
84
83
82
81
80
79
78
77
76
75
74
73.4
3382.30
2930.26
2870.55
2958.80
1605.85
1502.73
1486.49
1434.98
1375.18
1234.36
1089.42
1040.63
940.73
912.92
861.38
810.90
716.58
3775.9
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
707.7
cm-1
c:\pei_data\spectra\sjpvi36.sp - SJPVI-36


Me
NH3
Me
O
O
HO
O
Me

II-22


13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.909
5.277
2.073
1.000
1.034
5.262
2.008
1.191
2.967
2.933
3.952



II-22

Appendix B X-ray Crystal Structure Data

Table 1. Crystal data and structure refinement for 03310t.

Identification code	03310t	
Empirical formula	$C_{25}H_{28}BFeP$	
Formula weight	426.10	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.886(3) Å	α= 90°.
	b = 9.014(3) Å	β= 99.520(19)°.
	c = 14.276(4) Å	γ = 90°.
Volume	1127.7(5) $Å^3$	
Z	2	
Density (calculated)	1.255 Mg/m^3	
Absorption coefficient	0.747 mm^{-1}	
F(000)	448	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.45 to 23.00°.	
Index ranges	-9<=h<=7, -9<=k<=9, -15<=l<=15	
Reflections collected	4937	
Independent reflections	2806 [R(int) = 0.0452]	
Completeness to theta = 23.00°	99.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2806 / 1 / 256	
Goodness-of-fit on F^2	1.194	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0956	
R indices (all data)	R1 = 0.0641, wR2 = 0.0995	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	0.423 and -0.286 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 03310t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe	-1296(1)	1447(1)	8010(1)	34(1)
P	1151(2)	4270(2)	7701(1)	27(1)
C(1)	624(7)	2690(7)	8356(4)	30(2)
C(2)	-284(7)	2742(8)	9082(5)	36(2)
C(3)	-412(7)	1280(9)	9421(4)	49(2)
C(4)	372(8)	320(8)	8894(5)	47(2)
C(5)	1023(6)	1168(7)	8224(4)	35(2)
C(6)	-2731(8)	2304(8)	6860(6)	51(2)
C(7)	-3468(8)	2131(11)	7657(7)	64(3)
C(8)	-3458(9)	617(12)	7912(6)	69(3)
C(9)	-2644(9)	-117(9)	7272(6)	60(2)
C(10)	-2225(9)	910(8)	6643(6)	58(2)
C(11)	1425(6)	3482(6)	6578(4)	26(1)
C(12)	411(7)	3738(6)	5756(5)	34(2)
C(13)	605(8)	3124(7)	4889(5)	44(2)
C(14)	1878(8)	2278(7)	4848(5)	47(2)
C(15)	2717(7)	2633(6)	6519(5)	35(2)
C(16)	2928(8)	2024(6)	5662(5)	47(2)
C(21)	3075(6)	4775(6)	8303(4)	29(2)
C(22)	3975(6)	5811(6)	7892(5)	37(2)
C(23)	5404(7)	6132(7)	8408(5)	43(2)
C(24)	5965(7)	5480(8)	9264(6)	51(2)
C(25)	5084(7)	4475(8)	9656(5)	50(2)
C(26)	3636(7)	4115(7)	9169(4)	39(2)
C(221)	3437(6)	6582(8)	6968(4)	44(2)
C(222)	3237(8)	8249(6)	7115(6)	68(2)
C(223)	4511(7)	6287(10)	6249(4)	63(2)
B	-295(8)	5871(7)	7658(6)	40(2)

Table 3. Bond lengths [Å] and angles [°] for 03310t.

Fe-C(7)	2.010(8)	C(6)-C(7)	1.412(11)
Fe-C(2)	2.014(7)	C(7)-C(8)	1.412(10)
Fe-C(1)	2.033(6)	C(8)-C(9)	1.419(11)
Fe-C(9)	2.029(7)	C(9)-C(10)	1.383(10)
Fe-C(3)	2.043(6)	C(11)-C(12)	1.375(8)
Fe-C(10)	2.048(8)	C(11)-C(15)	1.394(7)
Fe-C(8)	2.044(8)	C(12)-C(13)	1.393(8)
Fe-C(4)	2.050(7)	C(13)-C(14)	1.374(9)
Fe-C(5)	2.048(6)	C(14)-C(16)	1.384(9)
Fe-C(6)	2.056(8)	C(15)-C(16)	1.381(8)
P-C(1)	1.808(6)	C(21)-C(26)	1.387(8)
P-C(11)	1.807(6)	C(21)-C(22)	1.419(8)
P-C(21)	1.839(6)	C(22)-C(23)	1.389(8)
P-B	1.927(6)	C(22)-C(221)	1.498(8)
C(1)-C(2)	1.415(8)	C(23)-C(24)	1.374(9)
C(1)-C(5)	1.438(9)	C(24)-C(25)	1.376(8)
C(2)-C(3)	1.416(10)	C(25)-C(26)	1.396(8)
C(3)-C(4)	1.406(10)	C(221)-C(222)	1.532(9)
C(4)-C(5)	1.419(9)	C(221)-C(223)	1.535(8)
C(6)-C(10)	1.387(9)		

C(7)-Fe-C(2)	107.6(3)	C(3)-Fe-C(5)	68.3(3)
C(7)-Fe-C(1)	128.7(3)	C(10)-Fe-C(5)	110.5(3)
C(2)-Fe-C(1)	40.9(2)	C(8)-Fe-C(5)	151.2(3)
C(7)-Fe-C(9)	67.8(3)	C(4)-Fe-C(5)	40.5(3)
C(2)-Fe-C(9)	161.5(3)	C(7)-Fe-C(6)	40.6(3)
C(1)-Fe-C(9)	155.4(3)	C(2)-Fe-C(6)	121.9(3)
C(7)-Fe-C(3)	117.8(3)	C(1)-Fe-C(6)	111.8(3)
C(2)-Fe-C(3)	40.8(3)	C(9)-Fe-C(6)	67.1(3)
C(1)-Fe-C(3)	68.3(3)	C(3)-Fe-C(6)	154.4(3)
C(9)-Fe-C(3)	124.0(3)	C(10)-Fe-C(6)	39.5(3)
C(7)-Fe-C(10)	67.3(3)	C(8)-Fe-C(6)	68.3(3)
C(2)-Fe-C(10)	156.9(3)	C(4)-Fe-C(6)	165.3(3)
C(1)-Fe-C(10)	123.5(3)	C(5)-Fe-C(6)	129.9(3)
C(9)-Fe-C(10)	39.6(3)	C(1)-P-C(11)	103.5(3)
C(3)-Fe-C(10)	162.0(3)	C(1)-P-C(21)	104.7(3)
C(7)-Fe-C(8)	40.7(3)	C(11)-P-C(21)	105.1(3)
C(2)-Fe-C(8)	124.1(3)	C(1)-P-B	112.2(3)
C(1)-Fe-C(8)	163.7(3)	C(11)-P-B	117.0(3)
C(9)-Fe-C(8)	40.8(3)	C(21)-P-B	113.2(3)
C(3)-Fe-C(8)	104.2(3)	C(2)-C(1)-C(5)	108.1(6)
C(10)-Fe-C(8)	67.8(3)	C(2)-C(1)-P	125.5(5)
C(7)-Fe-C(4)	150.9(4)	C(5)-C(1)-P	126.4(5)
C(2)-Fe-C(4)	68.5(3)	C(2)-C(1)-Fe	68.8(4)
C(1)-Fe-C(4)	68.4(3)	C(5)-C(1)-Fe	70.0(4)
C(9)-Fe-C(4)	106.2(3)	P-C(1)-Fe	126.0(3)
C(3)-Fe-C(4)	40.2(3)	C(3)-C(2)-C(1)	107.9(6)
C(10)-Fe-C(4)	127.3(3)	C(3)-C(2)-Fe	70.7(4)
C(8)-Fe-C(4)	115.9(4)	C(1)-C(2)-Fe	70.2(4)
C(7)-Fe-C(5)	167.4(4)	C(4)-C(3)-C(2)	108.3(6)
C(2)-Fe-C(5)	69.3(3)	C(4)-C(3)-Fe	70.2(4)
C(1)-Fe-C(5)	41.3(3)	C(2)-C(3)-Fe	68.5(4)
C(9)-Fe-C(5)	119.0(3)	C(3)-C(4)-C(5)	108.8(6)

C(3)-C(4)-Fe	69.6(4)	C(12)-C(11)-P	121.7(5)
C(5)-C(4)-Fe	69.7(4)	C(15)-C(11)-P	120.2(5)
C(4)-C(5)-C(1)	106.8(6)	C(11)-C(12)-C(13)	122.1(6)
C(4)-C(5)-Fe	69.8(4)	C(14)-C(13)-C(12)	118.8(7)
C(1)-C(5)-Fe	68.8(3)	C(13)-C(14)-C(16)	120.2(6)
C(10)-C(6)-C(7)	106.9(8)	C(16)-C(15)-C(11)	120.4(6)
C(10)-C(6)-Fe	69.9(5)	C(15)-C(16)-C(14)	120.4(6)
C(7)-C(6)-Fe	67.9(5)	C(26)-C(21)-C(22)	120.4(6)
C(6)-C(7)-C(8)	109.3(8)	C(26)-C(21)-P	118.7(5)
C(6)-C(7)-Fe	71.4(4)	C(22)-C(21)-P	120.9(5)
C(8)-C(7)-Fe	70.9(6)	C(23)-C(22)-C(21)	116.5(6)
C(9)-C(8)-C(7)	105.5(8)	C(23)-C(22)-C(221)	120.1(6)
C(9)-C(8)-Fe	69.0(4)	C(21)-C(22)-C(221)	123.4(5)
C(7)-C(8)-Fe	68.3(5)	C(24)-C(23)-C(22)	123.2(6)
C(10)-C(9)-C(8)	109.0(8)	C(25)-C(24)-C(23)	119.8(6)
C(10)-C(9)-Fe	70.9(5)	C(24)-C(25)-C(26)	119.3(6)
C(8)-C(9)-Fe	70.2(4)	C(21)-C(26)-C(25)	120.7(6)
C(6)-C(10)-C(9)	109.3(8)	C(22)-C(221)-C(222)	111.2(6)
C(6)-C(10)-Fe	70.6(5)	C(22)-C(221)-C(223)	111.4(5)
C(9)-C(10)-Fe	69.5(5)	C(222)-C(221)-C(223)	111.1(6)
C(12)-C(11)-C(15)	118.1(6)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 03310t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe	30(1)	33(1)	38(1)	-4(1)	5(1)	-7(1)
P	23(1)	27(1)	32(1)	-3(1)	3(1)	-3(1)
C(1)	20(3)	46(4)	20(4)	6(3)	-3(3)	5(3)
C(2)	38(4)	44(4)	27(4)	-1(3)	8(3)	1(3)
C(3)	53(4)	59(5)	34(4)	13(5)	6(3)	-10(5)
C(4)	56(5)	40(4)	42(6)	18(4)	4(4)	4(4)
C(5)	29(3)	32(4)	46(4)	3(3)	7(3)	2(3)
C(6)	43(5)	48(5)	54(6)	3(4)	-18(4)	-12(4)
C(7)	26(5)	82(7)	83(8)	-46(6)	2(5)	-8(4)
C(8)	43(6)	112(9)	56(7)	-12(6)	19(5)	-46(5)
C(9)	75(6)	50(5)	50(6)	-18(4)	-1(5)	-22(4)
C(10)	50(5)	55(5)	65(6)	-17(4)	1(4)	-8(4)
C(11)	25(3)	18(3)	37(4)	6(3)	7(3)	-2(3)
C(12)	34(4)	35(3)	34(4)	4(3)	8(3)	2(3)
C(13)	50(5)	57(5)	23(5)	-3(4)	5(3)	-11(4)
C(14)	58(5)	49(4)	41(5)	-11(4)	28(4)	-5(4)
C(15)	29(4)	45(4)	31(4)	1(3)	2(3)	-3(3)
C(16)	49(5)	37(4)	56(6)	-4(4)	16(4)	6(3)
C(21)	26(4)	30(3)	33(4)	-13(3)	12(3)	-2(3)
C(22)	21(4)	31(3)	59(5)	-13(3)	9(3)	-4(3)
C(23)	33(4)	30(4)	66(5)	-10(4)	5(3)	-5(3)
C(24)	21(4)	66(5)	64(6)	-15(4)	2(4)	-8(4)
C(25)	39(4)	73(5)	35(5)	-13(4)	-4(4)	8(4)
C(26)	32(4)	47(4)	38(4)	-1(4)	4(3)	2(3)
C(221)	34(3)	27(3)	70(5)	12(4)	10(3)	-8(4)
C(222)	56(5)	25(4)	117(8)	-5(4)	-6(5)	-15(3)
C(223)	53(4)	78(5)	62(5)	15(5)	18(4)	-17(5)
B	29(4)	38(4)	56(6)	7(4)	13(4)	7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 03310t.

	x	y	z	U(eq)
H(2)	-729	3606	9302	43
H(3)	-939	996	9920	59
H(4)	453	-725	8972	56
H(5)	1610	800	7776	43
H(6)	-2605	3203	6534	62
H(7)	-3904	2910	7971	77
H(8)	-3901	182	8407	83
H(9)	-2423	-1149	7275	72
H(10)	-1676	694	6142	69
H(12)	-449	4354	5781	41
H(13)	-131	3288	4335	52
H(14)	2038	1867	4260	56
H(15)	3457	2471	7071	42
H(16)	3800	1427	5631	56
H(23)	6023	6838	8156	52
H(24)	6959	5722	9584	61
H(25)	5457	4030	10253	60
H(26)	3029	3412	9432	47
H(221)	2414	6166	6697	52
H(22A)	2572	8406	7589	102
H(22B)	2777	8707	6513	102
H(22C)	4235	8701	7338	102
H(22D)	5559	6533	6537	95
H(22E)	4204	6902	5684	95
H(22F)	4454	5237	6068	95
H(0A)	-1292	5542	7323	61
H(0B)	58	6718	7323	61
H(0C)	-388	6166	8307	61