



The asymmetric Rh(I) catalyzed [4+2] cycloisomerization reaction : new homochiral bisphosphine ligands
by Lydia McKinstry

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
© Copyright by Lydia McKinstry (1994)

Abstract:

Intramolecular [4+2] cycloisomerization of ene-dienes and dien-ynes was effected with novel Rh(I) templates. The efficiency of cyclization was affected by steric and electronic influences within the ligand sphere. Asymmetric [4+2] cycloisomerization was mediated by Rh(I) complexes modified by ligands. Highly flexible and general procedures for the synthesis of new homochiral bisphosphine ligands have been developed. These new methods were used in the preparation of two generations of carbon-based homochiral bisphosphines. Additionally, a rational approach to the synthesis of a class of homochiral ferrocenyl ligands bearing chirality at phosphorus was introduced.

THE ASYMMETRIC Rh(I) CATALYZED [4+2]
CYCLOISOMERIZATION REACTION: NEW
HOMOCHIRAL BISPHOSPHINE LIGANDS

by

Lydia McKinstry

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

July, 1994

DB78
M2169

ii

APPROVAL
of a thesis submitted by
Lydia McKinstry

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

July 21, 1994
Date

Tom Ripley
Chairperson, Graduate Committee

Approved for the Major Department

July 20, 1994
Date

David M. Orley
Head, Major Department

Approved for the College of Graduate Studies

7/25/94
Date

RA Brown
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute my dissertation for sale in and from microfilm^{orm} or electronic format, along with the right to reproduce and distribute ^{my} by abstract in any format in whole or in part."

Signature Lychia McKusky
Date July 21, 1994

To Katherine A. and David A. McKinstry
and Constantine C. Gober

ACKNOWLEDGEMENTS

For his encouragement, patience and friendship, Professor Tom Livinghouse deserves special thanks. His wisdom and skill have made our collaboration exciting and challenging. Professors Arnold Craig, Brad Mundy and Lee Spangler provided invaluable guidance throughout the course of this endeavor. The skills and services of Miss Susan Clark, Mr. Lee David and Dr. Joe Sears are also appreciated. Former and present graduate students Dr. Steve Dunham, Mr. Klark Hanson, Dr. Scott Harring, Mr. Rich Hughes and Dr. Paul McGrane deserve thanks for their inspiration and expertise. Mr. Derek Sheehan not only conspired to make a portion of this research a success but was always available for discussion. Financial support was provided by: The Petroleum Research Fund; The Alfred P. Sloan Foundation; The National Science Foundation; and The National Institutes of Health. In addition, the Johnson Matthey Corporation is acknowledged for providing a discounted sample of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. The preparation of this manuscript was not possible without the word processing skills and patience of Mrs. Barb Hamblet. Most importantly, the ever present generosity, inspiration, tolerance and faith of my family and friends are the unrelenting well-springs of my strengths. Thank you all and God bless you forever.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
BACKGROUND	4
Chiral Phosphine Ligands	5
Monophosphines	5
Diphosphines	16
Transition Metal Complexes as Catalysts in Asymmetric Synthesis	26
Hydrogenation	28
Carbon-Carbon Bond Formation	29
Simple Isomerization	30
Olefin Dimerization	33
Olefin Cycloisomerization	34
Intramolecular [4+2] Cycloisomerization	37
RESULTS AND DISCUSSION	43
Rh(I) Catalyzed [4+2] Cycloisomerization	43
Asymmetric Rh(I) Catalyzed [4+2] Cyclo- isomerization	45
Electronic and Torsional Derivatives of (+)-DIOP	47
Enantioselective [4+2] Cycloisomerization	49
Homochiral Bisphosphino Hexane and Pentane Ligands	54
Phosphine-Borane Decomplexation with $\text{HBF}_3 \cdot \text{OMe}_2$	55
Electron Rich Homochiral Bisphosphines	58
Design of Phosphorus-Centered Homochiral Bisphosphino Ferrocene Ligands	62

TABLE OF CONTENTS--Continued

	Page
CONCLUSION	70
EXPERIMENTAL	71
Ligand Synthesis -- Phosphine Substituents	74
Bis(2-trifluoromethylphenyl)phosphine Oxide (4a)	74
Bis(2-trifluoromethylphenyl)phos- phine (5a)	75
Bis(2-methylphenyl)phosphine Oxide (4b)	76
Bis(2-methylphenyl)phosphine (5b)	76
Bis[3,5-bis(trifluoromethyl)phenyl]phos- phine Oxide (4c)	76
Bis[3,5-bis(trifluoromethyl)phenyl]phos- phine (5c)	77
Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d)	77
Bis(4-methoxy-2-methylphenyl)phosphine (5d)	78
Boronato-dicyclohexyl phosphine (27a)	78
Boronato-diphenyl phosphine (27b)	79
4-Lithio-3-methylanisole	79
Bis(4-methoxy-2-methylphenyl)-N,N- dimethylaminophosphine (31)	80
Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)	81
Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)	82

TABLE OF CONTENTS--Continued

	Page
Ligand Synthesis-Tartaric Acid Series	
(1,4-diphosphines)	82
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2,2-dimethyl- 1,3-dioxolane (100a)	82
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2,2-dimethyl- 1,3-dioxolane (101a)	83
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2,2- dimethyl-1,3-dioxolane (6a)	84
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethyl- phenyl) phosphino]methyl]-2,2-dimethyl- 1,3-dioxolane (3f)	85
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3- dioxolane (3e)	86
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis[3,5-bis(trifluoro- methyl) phenyl]phosphino]methyl]-2,2- dimethyl-1,3-dioxolane (3d)	87
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(4-methoxy-2- methylphenyl)phosphino]methyl]-2,2- dimethyl-1,3-dioxolane (3h)	88
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(boronatodicyclohexyl phosphino)methyl]-2,2-dimethyl-1,3- dioxolane (33)	88
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(dicyclohexylphosphino) methyl]-2,2-dimethyl-1,3-dioxolane (32)	89
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2-methyl- 2-phenyl-1,3-dioxolane (100b)	90
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2-methyl- 2-phenyl-1,3-dioxolane (101b)	90
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2- methyl-2-phenyl-1,3-dioxolane (6b)	91
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-	

TABLE OF CONTENTS--Continued

	Page
2-methyl-2-phenyl-1,3-dioxolane (3b)	92
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethyl phenyl)phosphino]methyl]-2-methyl-2- phenyl-1,3-dioxolane (3g)	93
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2- <i>t</i> - butyl-1,3-dioxolane (100c)	94
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2- <i>t</i> -butyl- 1,3-dioxolane (101c)	95
(4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2- <i>t</i> - butyl-1,3-dioxolane (6c)	95
(4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino) methyl]-2- <i>t</i> -Butyl-1,3-dioxolane (3c)	96
Ligand Synthesis--Hexane Series (1,4-diphosphines) .	97
(2 <i>S</i> ,5 <i>S</i>)-2,5-Hexandiol (102)	97
(2 <i>S</i> ,5 <i>S</i>)-2,5-Bis-(<i>p</i> -tosyloxy)hexane (30)	97
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(diphenylphosphino)hexane (21b) .	98
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(2-trifluoromethyl- phenyl) phosphino]hexane (15a)	99
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato-diphenylphos- phino)hexane (26b)	100
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato dicyclohexyl- phosphino)hexane (26a)	101
(2 <i>R</i> ,2 <i>R</i>)-2,5-Bis[boronato-Bis(4-methoxy -2-methylphenyl)phosphino]hexane (26c)	102
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(diphenylphosphino)hexane (21b)	103
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(dicyclohexylphosphino) hexane (21a)	104
(2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(4-methoxy-2-methyl-	

TABLE OF CONTENTS--Continued

	Page
phenyl)phosphino] hexane (21c)	104
Ligand Synthesis--Cyclohexane (1,4-diphosphine) .	105
(1 <i>S</i> ,2 <i>S</i>)-1,2-Bis[(boronato-dicyclohexyl- phosphino)methyl] cyclohexane (25a)	105
Ligand Synthesis--Pentane Series (1,3-diphosphines)	106
(2 <i>R</i> ,4 <i>R</i>)-2,4-Bis([bis(2-trifluoro- methylphenyl)phosphino] pentane (16a)	106
(2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(boronato-dicyclohexyl- phosphino)pentane (24)	107
(2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(dicyclohexylphosphino) pentane (19)	108
Substrate Synthesis-Ene-dienes and Dien-ynes . . .	108
Ethyl-4-methyl-2(E),4-pentadienoate (103) . .	108
4-Methyl-2(E),4-pentadien-1-ol (104)	109
8-Methyl-4-oxo-1,6(E),8-nonatriene (7a) . . .	110
8-Methyl-4-oxo-6(E),8-nonadien-1-yne (105) .	112
8-Methyl-4-oxo-1-(trimethylsilyl)-6(E), 8-nonadien-1-yne (10)	112
4-Oxo-1,6(E),8(E)-decatriene (7c)	113
4-Oxo-6(E),8(E)-decadien-1-yne (1)	115
4-Oxo-1-(trimethylsilyl)-6(E),8(E)- decadien-1-yne (106)	115
1-Chloro-4-methyl-2(E),4-pentadiene (107) . .	116
4,4-Bis(carboethoxy)-8-methyl-1,6(E),8- nonatriene (108)	117
4,4-Bis(hydroxymethyl)-8-methyl-1,6(E), 8-nonatriene (109)	118

TABLE OF CONTENTS--Continued

	Page
4,4-Bis(methoxymethyl)-8-methyl-1,6(E), 8-nonatriene (7b)	119
Rh(I) Mediated Alkene Cycloisomerizations	121
1,3,5 α ,7a β -Tetrahydro-5-methyl-4- (trimethylsilyl)-isobenzofuran (110)	121
1,3,3a β ,6,7,7a β -hexahydro-5-methylisobenzo- furan (8a)	122
[4+2] cycloisomerization of 7a with homochiral bisphosphine ligands	123
3a β ,6,7,7a β -Tetrahydro-2,2-bis(methoxy- methyl)-5-methylindan (8b)	124
[4+2] cycloisomerization of with homo- chiral bisphosphine ligands	125
1,3,5,7a β -Tetrahydro-6-methyl-4-(tri- methylsilyl) isobenzofuran (11)	126
[4+2] cycloisomerization reaction of 10 with homochiral bisphosphine ligands	127
1,3,3a β ,4,5 α ,7a β -hexahydro-5-methyliso- benzofuran (8c)	127
[4+2] cycloisomerization of 7c with homochiral bisphosphine ligands	128
1,3,3a β ,4 α ,5 β ,6,7,7a β -Octahydro-4-hydroxy- 5-methylisobenzofuran (9a)	128
3a β ,4 α ,5 β ,6,7,7a β -Hexahydro-4-hydroxy-2, 2-bis(methoxymethyl)-5-methylindan (9b)	129
1,3,3a β ,4 α ,5 β ,6-Hexahydro-4-hydroxy-5- methyl-7-(trimethylsilyl)isobenzofuran (12)	130
1,3,3a β ,4 α ,5 α ,6 β ,7,7a β -Octahydro-4,5- bis(hydroxy)-6-methylisobenzofuran (9c)	131

TABLE OF CONTENTS--Continued

	Page
Preparation of Esters of (R)- α -Methoxy- α -trifluoromethylphenylacetic Acid	132
Ferrocene Ligand Synthesis	133
Bis(dimethylamino)-4-methoxyphenyl phosphine (39a)	134
Bis(dimethylamino)-2-trifluoromethylphenyl phosphine (39b)	134
Bis(dimethylamino)-phenyl phosphine (39c)	135
Chloro-(dimethylamino)-4-methoxyphenyl phosphine (40a)	135
Chloro-(dimethylamino)-2-trifluoromethyl- phenyl phosphine (40b)	135
Chloro-(dimethylamino)-phenyl phosphine (40c)	135
(2R,4S,5R)-2-(4-methoxyphenyl)-3,4- dimethyl-5-phenyl-1,3,2-oxazaphospholidine- 2-borane (38a)	136
(2R,4S,5R)-2-(2-Trifluoromethylphenyl)-3, 4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine- 2-borane (38b)	137
(2R,4S,5R)-3,4-Dimethyl-2,5-diphenyl- 1,3,2-oxazaphospholidine-2-borane (38c)	137
1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(Rp)-N-methyl, N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl)) amino-boronato-(4-methoxyphenyl)phosphino] ferrocene (42a)	138
1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(Rp)-N-Methyl, N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl)) amino-boronato-(2-trifluoromethyl- phenyl)phosphino]ferrocene (42b)	139
1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(Rp)-N-Methyl, N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl)) amino-boronatophenylphosphino]ferrocene (42c)	140

TABLE OF CONTENTS--Continued

	Page
1,1'-Bis[(Rp)-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxyphenyl)phosphino]ferrocene (37a)	140
1,1'-Bis[(Rp)-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-trifluoromethylphenyl)phosphino]ferrocene (37b)	142
1,1'-Bis[(Rp)-N-methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenyl-phosphine]ferrocene (37c)	142
1,1'-Bis[boronato-fluoro-(4-methoxyphenyl)phosphino]ferrocene (36a)	142
1,1'-Bis[boronato-fluoro-(2-trifluoromethylphenyl)phosphino]ferrocene (36b)	143
1,1'-Bis[boronato-methyl-(4-methoxyphenyl)phosphino]ferrocene (35a)	144
1,1'-Bis[boronato-methyl-(2-trifluoromethylphenyl)phosphino]ferrocene (35b)	145
APPENDIX	146
REFERENCES	342

LIST OF TABLES

Table		Page
1	Solvent Effects on Catalysis	39
2	Monodentate Phosphite Ligands	40
3	Rh(I)-Catalyzed [4+2] Cycloisomeri- zations	41
4	Monodentate Phosphine Ligands	44
5	Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations Mediated by Homochiral Bisphosphines	52
6	Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 7a	124
7	Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 7b	125
8	Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 10	127
9	Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 7c	128

LIST OF FIGURES

Figure		Page
1	Examples of Three Types of Chiral Monophosphines	6
2	Ferrocenyl Monophosphine Ligands	8
3	Examples of Three Types of Chiral Diphosphines	17
4	(4 <i>R</i> ,5 <i>R</i>) DIOP Ligands	19
5	Chiral Ferrocenyl Phosphines	21
6	Axially Dissymmetric Bisphosphines	23
7	(<i>S</i>)-DOPA	23
8	The Chiral Conformations of a Saturated Five-Membered Chelate Ring	29
9	Asymmetric Olefin Dimerization	33
10	Asymmetric Intramolecular [2+2+2] Cycloisomerization	35
11	Internal Diastereoselectivity in the Rh(I) Catalyzed [4+2] Cycloisomerization of Olefins	42
12	Commercial Homochiral Bisphosphines	45
13	Annular Dependency of Cyclization	46
14	Homochiral Bisphosphines Derived from (L)-Tartaric Acid	47
15	Ene-Diene and Diene-Yne Substrates	50
16	Absolute Configuration of Cycloadducts	51
17	Electron Deficient Bisphosphines Derived from (2 <i>S</i> ,5 <i>S</i>)-2,5-dihydroxyhexane and (2 <i>S</i> ,4 <i>S</i>)-2,4-Dihydroxypentane	55
18	Decomplexation of Bisphosphine-Borane Adducts	57

LIST OF FIGURES--Continued

Figure		Page
19	Electron Rich Homochiral Bisphosphine-Boranes	58
20	^1H NMR Spectrum of Bis(2-trifluoromethylphenyl)phosphine Oxide (4a) . . .	147
21	^{13}C NMR Spectrum of Bis(2-trifluoromethylphenyl)phosphine Oxide (4a) . .	148
22	^{31}P NMR Spectrum of Bis(2-trifluoromethylphenyl)phosphine Oxide (4a) . . .	149
23	^1H NMR Spectrum of Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c) . . .	150
24	^{13}C NMR Spectrum of Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c) . . .	151
25	^{31}P NMR Spectrum of Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c) . . .	152
26	^1H NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d) . . .	153
27	^{31}P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d) . . .	154
28	^{31}P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine (5d)	155
29	^1H NMR Spectrum of Boronato-dicyclohexyl phosphine (27a)	156
30	^{13}C NMR Spectrum of Boronato-dicyclohexyl phosphine (27a)	157
31	^{31}P NMR Spectrum of Boronato-dicyclohexyl phosphine (27a)	158
32	^1H NMR Spectrum of Boronato-diphenyl phosphine (27b)	159
33	^{13}C NMR Spectrum of Boronato-diphenyl phosphine (27b)	160

LIST OF FIGURES--Continued

Figure		Page
34	³¹ P NMR Spectrum of Boronato-diphenyl phosphine (27b)	161
35	¹ H NMR Spectrum of 4-Bromo-3-methylanisole	162
36	¹³ C NMR Spectrum of 4-Bromo-3-methylanisole	163
37	¹ H NMR Spectrum of Bis(4-methoxy-2-methylphenyl)-N,N-dimethylamino-phosphine (31)	164
38	³¹ P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)-N,N-dimethylamino-phosphine (31)	165
39	¹ H NMR Spectrum of Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)	166
40	¹³ C NMR Spectrum of Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)	167
41	³¹ P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)	168
42	¹ H NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2,2-dimethyl-1,3-dioxolane (100a)	169
43	¹³ C NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2,2-dimethyl-1,3-dioxolane (100a)	170
44	¹ H NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (101a)	171
45	¹³ C NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (101a)	172

LIST OF FIGURES--Continued

Figure		Page
46	¹ H NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (6a)	173
47	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (6a)	174
48	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)	175
49	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)	176
50	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)	177
51	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)	178
52	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)	179
53	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)	180
54	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis[3,5-bis(trifluoromethyl) phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)	181

LIST OF FIGURES--Continued

Figure		Page
55	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis[3,5-bis(trifluoromethyl) phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)	182
56	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis[3,5-bis(trifluoromethyl) phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)	183
57	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(4-methoxy-2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3h)	184
58	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(4-methoxy-2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3h)	185
59	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(4-methoxy-2-methylphenyl) phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3h)	186
60	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(boronatodicyclohexyl phosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33)	187
61	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(boronatodicyclohexyl phosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33)	188
62	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(boronatodicyclohexyl phosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33)	189
63	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(dicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (32)	190

LIST OF FIGURES--Continued

Figure		Page
64	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(dicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (32)	191
65	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2-methyl-2-phenyl-1,3-dioxolane (100b)	192
66	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2-methyl-2-phenyl-1,3-dioxolane (100b)	193
67	¹ H NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)	194
68	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)	195
69	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)	196
70	¹ H NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2-methyl-2-phenyl-1,3-dioxolane (6b)	197
71	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2-methyl-2-phenyl-1,3-dioxolane (6b)	198
72	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2-methyl-2-phenyl-1,3-dioxolane (3b)	199
73	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2-methyl-2-phenyl-1,3-dioxolane (3b)	200
74	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2-methyl-2-phenyl-1,3-dioxolane (3b)	201

LIST OF FIGURES--Continued

Figure		Page
75	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethyl phenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g) . . .	202
76	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethyl phenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g) . . .	203
77	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[[bis(2-trifluoromethyl phenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g) . . .	204
78	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2- <i>t</i> -butyl-1,3-dioxolane (100c)	205
79	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis(carbomethoxy)-2- <i>t</i> -butyl-1,3-dioxolane (100c)	206
80	¹ H NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2- <i>t</i> -butyl-1,3-dioxolane (101c)	207
81	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis(hydroxymethyl)-2- <i>t</i> -butyl-1,3-dioxolane (101c)	208
82	¹ H NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2- <i>t</i> -butyl-1,3-dioxolane (6c)	209
83	¹³ C NMR Spectrum of (4 <i>S</i> ,5 <i>S</i>)-4,5-Bis[(<i>p</i> -tosyloxy)methyl]-2- <i>t</i> -butyl-1,3-dioxolane (6c)	210
84	¹ H NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2- <i>t</i> -Butyl-1,3-dioxolane (3c)	211

LIST OF FIGURES--Continued

Figure		Page
85	¹³ C NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2- <i>t</i> -Butyl-1,3-dioxolane (3c)	212
86	³¹ P NMR Spectrum of (4 <i>R</i> ,5 <i>R</i>)-4,5-Bis[(diphenylphosphino)methyl]-2- <i>t</i> -Butyl-1,3-dioxolane (3c)	213
87	¹ H NMR Spectrum of (2 <i>S</i> ,5 <i>S</i>)-2,5-Hexandiol (102)	214
88	¹³ C NMR Spectrum of (2 <i>S</i> ,5 <i>S</i>)-2,5-Hexandiol (102)	215
89	¹ H NMR Spectrum of (2 <i>S</i> ,5 <i>S</i>)-2,5-Bis-(<i>p</i> -tosyloxy)hexane (30)	216
90	¹³ C NMR Spectrum of (2 <i>S</i> ,5 <i>S</i>)-2,5-Bis-(<i>p</i> -tosyloxy)hexane (30)	217
91	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(diphenylphosphino)hexane (21b)	218
92	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(diphenylphosphino)hexane (21b)	219
93	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(diphenylphosphino)hexane (21b)	220
94	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(2-trifluoromethyl-phenyl) phosphino]hexane (15a)	221
95	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(2-trifluoromethyl-phenyl) phosphino]hexane (15a)	222
96	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(2-trifluoromethyl-phenyl) phosphino]hexane (15a)	223
97	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato-diphenylphosphino)hexane (26b)	224

LIST OF FIGURES--Continued

Figure		Page
98	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato-diphenylphosphino)hexane (26b)	225
99	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato-diphenylphosphino)hexane (26b)	226
100	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato dicyclohexylphosphino)hexane (26a)	227
101	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato dicyclohexylphosphino)hexane (26a)	228
102	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(boronato dicyclohexylphosphino)hexane (26a)	229
103	¹ H NMR Spectrum of (2 <i>R</i> ,2 <i>R</i>)-2,5-Bis[boronato-Bis(4-methoxy-2-methylphenyl)phosphino]hexane (26c) .	230
104	³¹ P NMR Spectrum of (2 <i>R</i> ,2 <i>R</i>)-2,5-Bis[boronato-Bis(4-methoxy-2-methylphenyl)phosphino]hexane (26c) .	231
105	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(dicyclohexylphosphino)hexane (21a)	232
106	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(dicyclohexylphosphino)hexane (21a)	233
107	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis(dicyclohexylphosphino)hexane (21a)	234
108	¹ H NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino] hexane (21c)	235

LIST OF FIGURES--Continued

Figure		Page
109	¹³ C NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino] hexane (21c)	236
110	³¹ P NMR Spectrum of (2 <i>R</i> ,5 <i>R</i>)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino] hexane (21c)	237
111	¹ H NMR Spectrum of (1 <i>S</i> ,2 <i>S</i>)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl] cyclohexane (25a)	238
112	¹³ C NMR Spectrum of (1 <i>S</i> ,2 <i>S</i>)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl] cyclohexane (25a)	239
113	³¹ P NMR Spectrum of (1 <i>S</i> ,2 <i>S</i>)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl] cyclohexane (25a)	240
114	³¹ P NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis([bis(2-trifluoromethylphenyl)phosphino] pentane (16a)	241
115	¹ H NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24)	242
116	¹³ C NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24)	243
117	³¹ P NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24)	244
118	¹ H NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(dicyclohexylphosphino)pentane (19)	245
119	³¹ P NMR Spectrum of (2 <i>R</i> ,4 <i>R</i>)-2,4-Bis(dicyclohexylphosphino)pentane (19)	246

LIST OF FIGURES--Continued

Figure		Page
120	¹ H NMR Spectrum of Ethyl-4-methyl-2(E),4-pentadienoate (103)	247
121	¹³ C NMR Spectrum of Ethyl-4-methyl-2(E),4-pentadienoate (103)	248
122	¹ H NMR Spectrum of 4-Methyl-2(E),4-pentadien-1-ol (104)	249
123	¹³ C NMR Spectrum of 4-Methyl-2(E),4-pentadien-1-ol (104)	250
124	¹ H NMR Spectrum of 8-Methyl-4-oxo-1,6(E),8-nonatriene (7a)	251
125	¹³ C NMR Spectrum of 8-Methyl-4-oxo-1,6(E),8-nonatriene (7a)	252
126	¹ H NMR Spectrum of 8-Methyl-4-oxo-6(E),8-nonadien-1-yne (105)	253
127	¹³ C NMR Spectrum of 8-Methyl-4-oxo-6(E),8-nonadien-1-yne (105)	254
128	¹ H NMR Spectrum of 8-Methyl-4-oxo-1-(trimethylsilyl)-6(E),8-nonadien-1-yne (10)	255
129	¹³ C NMR Spectrum of 8-Methyl-4-oxo-1-(trimethylsilyl)-6(E),8-nonadien-1-yne (10)	256
130	¹ H NMR Spectrum of 4-Oxo-1,6(E),8(E)-decatriene (7c)	257
131	¹³ C NMR Spectrum of 4-Oxo-1,6(E),8(E)-decatriene (7c)	258
132	¹ H NMR Spectrum of 4-Oxo-6(E),8(E)-decadien-1-yne (1)	259
133	¹³ C NMR Spectrum of 4-Oxo-6(E),8(E)-decadien-1-yne (1)	260

LIST OF FIGURES--Continued

Figure		Page
134	¹ H NMR Spectrum of 4-Oxo-1-(trimethylsilyl)-6(E),8(E)-decadien-1-yne (106)	261
135	¹³ C NMR Spectrum of 4-Oxo-1-(trimethylsilyl)-6(E),8(E)-decadien-1-yne (106)	262
136	¹ H NMR Spectrum of 1-Chloro-4-methyl-2(E),4-pentadiene (107)	263
137	¹³ C NMR Spectrum of 1-Chloro-4-methyl-2(E),4-pentadiene (107)	264
138	¹ H NMR Spectrum of 4,4-Bis(carboethoxy)-8-methyl-1,6(E),8-nonatriene (108)	265
139	¹³ C NMR Spectrum of 4,4-Bis(carboethoxy)-8-methyl-1,6(E),8-nonatriene (108)	266
140	¹ H NMR Spectrum of 4,4-Bis(hydroxymethyl)-8-methyl-1,6(E),8-nonatriene (109)	267
141	¹³ C NMR Spectrum of 4,4-Bis(hydroxymethyl)-8-methyl-1,6(E),8-nonatriene (109)	268
142	¹ H NMR Spectrum of 4,4-Bis(methoxymethyl)-8-methyl-1,6(E),8-nonatriene (7b)	269
143	¹³ C NMR Spectrum of 4,4-Bis(methoxymethyl)-8-methyl-1,6(E),8-nonatriene (7b)	270
144	¹ H NMR Spectrum of 1,3,5 α ,7 $\alpha\beta$ -Tetrahydro-5-methyl-4-(trimethylsilyl)-isobenzofuran (110)	271
145	¹³ C NMR Spectrum of 1,3,5 α ,7 $\alpha\beta$ -Tetrahydro-5-methyl-4-(trimethylsilyl)-isobenzofuran (110)	272

LIST OF FIGURES--Continued

Figure		Page
146	¹ H NMR Spectrum of 1,3,3a β ,6,7,7a β -hexahydro-5-methylisobenzofuran (8a)	273
147	¹³ C NMR Spectrum of 1,3,3a β ,6,7,7a β -hexahydro-5-methylisobenzofuran (8a)	274
148	¹ H NMR Spectrum of 3a β ,6,7,7a β -Tetrahydro-2,2-bis(methoxymethyl)-5-methylindan (8b)	275
149	¹³ C NMR Spectrum of 3a β ,6,7,7a β -Tetrahydro-2,2-bis(methoxymethyl)-5-methylindan (8b)	276
150	¹ H NMR Spectrum of 1,3,5,7a β -Tetrahydro-6-methyl-4-(trimethylsilyl) isobenzofuran (11)	277
151	¹³ C NMR Spectrum of 1,3,5,7a β -Tetrahydro-6-methyl-4-(trimethylsilyl) isobenzofuran (11)	278
152	¹ H NMR Spectrum of 1,3,3a β ,4,5 α ,7a β -hexahydro-5-methylisobenzofuran (8c)	279
153	¹³ C NMR Spectrum of 1,3,3a β ,4,5 α ,7a β -hexahydro-5-methylisobenzofuran (8c)	280
154	¹ H NMR Spectrum of 7a β -Octahydro-4-hydroxy-5-methylisobenzofuran (9a)	281
155	¹³ C NMR Spectrum of 7a β -Octahydro-4-hydroxy-5-methylisobenzofuran (9a)	282
156	¹ H NMR Spectrum of 3a β ,4 α ,5 β ,6,7,7a β -Hexahydro-4-hydroxy-2,2-bis(methoxymethyl)-5-methylindan (9b)	283

LIST OF FIGURES--Continued

Figure		Page
157	¹³ C NMR Spectrum of 3a β ,4 α ,5 β ,6,7,7a β -Hexahydro-4-hydroxy-2,2-bis(methoxy-methyl)-5-methylindan (9b)	284
158	¹ H NMR Spectrum of 1,3,3a β ,4 α ,5 β ,6-Hexahydro-4-hydroxy-5-methyl-7-(trimethylsilyl)isobenzofuran (12)	285
159	¹³ C NMR Spectrum of 1,3,3a β ,4 α ,5 β ,6-Hexahydro-4-hydroxy-5-methyl-7-(trimethylsilyl)isobenzofuran (12)	286
160	¹ H NMR Spectrum of 1,3,3a β ,4 α ,5 α ,6 β ,7,7a β -Octahydro-4,5-bis(hydroxy)-6-methylisobenzofuran (9c)	287
161	¹³ C NMR Spectrum of 1,3,3a β ,4 α ,5 α ,6 β ,7,7a β -Octahydro-4,5-bis(hydroxy)-6-methylisobenzofuran (9c)	288
162	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Racemate)	289
163	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3a)	290
164	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3b)	291
165	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3c)	292
166	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3d)	293
167	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3e)	294
168	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3f)	295
169	¹ H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3g)	296

LIST OF FIGURES--Continued

Figure		Page
170	¹ H NMR Spectrum of MTPA Derivatives (<i>R</i>) and (<i>S</i>) of 13a (Ligand 21b)	297
171	¹ H NMR Spectrum of MTPA Derivatives (<i>R</i>) and (<i>S</i>) of 13b (Racemate)	298
172	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13b (Ligand 3a)	299
173	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13b (Ligand 3e)	300
174	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13b (Ligand 3f)	301
175	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13c (Racemate)	302
176	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13c (Ligand 3a)	303
177	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13c (Ligand 3b)	304
178	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13c (Ligand 3c)	305
179	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 13c (Ligand 3d)	306
180	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Racemate)	307
181	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Ligand 3a)	308
182	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Ligand 3b)	309
183	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Ligand 3e)	310
184	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Ligand 3f)	311

LIST OF FIGURES--Continued

Figure		Page
185	¹ H NMR Spectrum of MTPA derivatives (<i>R</i>) and (<i>S</i>) of 14 (Ligand 3g)	312
186	¹ H NMR Spectrum of Bis(dimethylamino) -4-methoxyphenyl phosphine (39a)	313
187	¹³ C NMR Spectrum of Bis(dimethylamino) -4-methoxyphenyl phosphine (39a)	314
188	¹ H NMR Spectrum of Bis(dimethylamino)- phenyl phosphine (39c)	315
189	¹ H NMR Spectrum of Chloro-(dimethyl- amino)-4-methoxyphenyl phosphine (40a) .	316
190	¹³ C NMR Spectrum of Chloro-(dimethyl- amino)-4-methoxyphenyl phosphine (40a) .	317
191	¹ H NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(4- methoxyphenyl)-3,4-dimethyl-5-phenyl- 1,3,2-oxazaphospholidine-2-borane (38a)	318
192	¹³ C NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(4- methoxyphenyl)-3,4-dimethyl-5-phenyl- 1,3,2-oxazaphospholidine-2-borane (38a)	319
193	³¹ P NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(4- methoxyphenyl)-3,4-dimethyl-5-phenyl- 1,3,2-oxazaphospholidine-2-borane (38a)	320
194	¹ H NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(2- Trifluoromethylphenyl)-3,4-dimethyl- 5-phenyl-1,3,2-oxazaphospholidine- 2-borane (38b)	321
195	¹³ C NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(2- Trifluoromethylphenyl)-3,4-dimethyl- 5-phenyl-1,3,2-oxazaphospholidine- 2-borane (38b)	322
196	³¹ P NMR Spectrum of (2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i>)-2-(2- Trifluoromethylphenyl)-3,4-dimethyl- 5-phenyl-1,3,2-oxazaphospholidine- 2-borane (38b)	323

LIST OF FIGURES--Continued

Figure		Page
197	¹ H NMR Spectrum of 1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxy-phenyl)phosphino]ferrocene (42a)	324
198	³¹ P NMR Spectrum of 1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxy-phenyl)phosphino]ferrocene (42a)	325
199	¹ H NMR Spectrum of 1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -Methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-tri-fluoromethylphenyl)phosphino]ferrocene (42b)	326
200	³¹ P NMR Spectrum of 1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -Methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-tri-fluoromethylphenyl)phosphino]ferrocene (42b)	327
201	¹ H NMR Spectrum of 1-(Tri- <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -Methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphino]ferrocene (42c)	328
202	³¹ P NMR Spectrum of <i>n</i> -butylstannyl)-1 ¹ -[(<i>Rp</i>)- <i>N</i> -Methyl, <i>N</i> -((1 <i>R</i> ,2 <i>S</i>)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphino]ferrocene (42c)	329

LIST OF FIGURES--Continued

Figure		Page
203	^1H NMR Spectrum of $^1\text{-Bis}[(\text{Rp})\text{-N-Methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-(4-methoxy-phenyl)phosphino}] \text{ferrocene (37a)}$	330
204	^{13}C NMR Spectrum of $^1\text{-Bis}[(\text{Rp})\text{-N-Methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-(4-methoxy-phenyl)phosphino}] \text{ferrocene (37a)}$	331
205	^{31}P NMR Spectrum of $^1\text{-Bis}[(\text{Rp})\text{-N-Methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-(4-methoxy-phenyl)phosphino}] \text{ferrocene (37a)}$	332
206	^1H NMR Spectrum of $1,1'\text{-Bis}[(\text{Rp})\text{-N-Methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-(2-tri-fluoromethylphenyl)phosphino}] \text{ferrocene (37b)}$	333
207	^{31}P NMR Spectrum of $1,1'\text{-Bis}[(\text{Rp})\text{-N-Methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-(2-tri-fluoromethylphenyl)phosphino}] \text{ferrocene (37b)}$	334
208	^{31}P NMR Spectrum of $1,1'\text{-Bis}[(\text{Rp})\text{-N-methyl,N-}((1\text{R},2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl}))\text{amino-boronato-phenyl-phosphine}] \text{ferrocene (37c)}$	335
209	^1H NMR Spectrum of $1,1'\text{-Bis}[\text{boronato-fluoro-(4-methoxyphenyl)phosphino}] \text{ferrocene (36a)}$	336
210	^{31}P NMR Spectrum of $1,1'\text{-Bis}[\text{boronato-fluoro-(4-methoxyphenyl)phosphino}] \text{ferrocene (36a)}$	337

LIST OF FIGURES--Continued

Figure		Page
211	¹ H NMR Spectrum of 1,1'-Bis[boronato-fluoro-(2-trifluoromethyl-phenyl)phospino]ferrocene (36b)	338
212	³¹ P NMR Spectrum of 1,1'-Bis[boronato-fluoro-(2-trifluoromethyl-phenyl)phospino]ferrocene (36b)	339
213	¹ H NMR Spectrum of 1,1'-Bis[boronato-methyl-(2-trifluoromethyl-phenyl)phosphino]ferrocene (35b)	340
214	³¹ P NMR Spectrum of 1,1'-Bis[boronato-methyl-(2-trifluoromethyl-phenyl)phosphino]ferrocene (35b)	341

Abstract

Intramolecular [4+2] cycloisomerization of ene-dienes and dien-ynes was effected with novel Rh(I) templates. The efficiency of cyclization was affected by steric and electronic influences within the ligand sphere. Asymmetric [4+2] cycloisomerization was mediated by Rh(I) complexes modified by ligands. Highly flexible and general procedures for the synthesis of new homochiral bisphosphine ligands have been developed. These new methods were used in the preparation of two generations of carbon-based homochiral bisphosphines. Additionally, a rational approach to the synthesis of a class of homochiral ferrocenyl ligands bearing chirality at phosphorus was introduced.

INTRODUCTION

Current demand for highly enantioenriched biologically active substances, such as pharmaceuticals and pesticides, is exceedingly high. As a result, the demand for efficient synthetic methodologies which can invoke asymmetric selection in chemical transformations is also very high. Presently there are numerous techniques in practice which utilize chiral compounds, as mediators or auxiliaries, to effect such chemical selection. The most common method involves the use of a stoichiometric quantity of a given reagent, for instance a chiral resolving agent. Although this technique has made a significant impact on asymmetric synthesis, it is often disadvantageous because reclamation of the chiral reagent can be both time consuming and costly. Additionally, chiral resolution of a racemic mixture involves the preparation and consumption of *both* the desired and the unwanted enantiomers, rendering the overall process 50% efficient at best. In contrast, the distinguishing feature of a catalyst is the *in situ* reusability of a single molecule. Hence, a single chiral molecule (or a substoichiometric quantity) can generate thousands of chiral products. It is the potential low cost and high efficiency associated with chiral catalysis that has made this methodology particularly attractive for study.

For over three decades, synthetic chemists have participated in the development of homogeneous catalyst

systems that consist of transition metal complexes. The well known Wilkinson's catalyst $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, discovered in 1966, is perhaps the most important of these reagents.¹ First used as a homogeneous catalyst for the hydrogenation of olefins, today it is used extensively in many chemical transformations including hydrosilylation, hydroboration, oxidation and double bond isomerization.² In order to further the potential of such "Wilkinson-like" complexes, the rhodium center was quickly modified by other alkyl and aryl phosphorus ligands. In fact, the discovery of Wilkinson's reagent initiated extensive research into the catalysis of chemical processes with transition metal-phosphorus complexes.

More importantly, research concerning transition metal catalysts bearing *chiral* phosphine ligands became increasingly widespread. These catalyst systems were designed to effect the stereo- and regiochemical outcome of a wide range of organic reactions. At the forefront of this research was the use of Rh(I)-monophosphine and Rh(I)-bisphosphine catalysts to effect the asymmetric hydrogenation of β -substituted α -acylaminoacrylic acid derivatives.³ The successful synthesis of optically pure α -amino acids constitutes a powerful example of how chiral transition metal complexes could be used as catalysts to generate chiral products.³

Popular throughout the last two decades have been investigations of the utility of a vast selection of newly synthesized chiral molecules as ligands for transition metal mediated asymmetric reactions. Much of the current research focuses on the importance of ligand-metal interactions to the efficiency of asymmetric selectivity. These studies should lead to the design of new ligand systems specifically tailored to effect stereocontrol in selected chemical transformations.

Due to our interest in transition metal catalyzed enantioselective processes,⁴ the object of the following research was the development of highly flexible and general procedures for the synthesis of three generations of homochiral bisphosphine ligands of determinate structural variation. It was also our goal to determine how ligand structure might influence the efficiency of Rh(I) catalyzed *intramolecular* [4+2] cycloisomerization reactions. In addition, our interest in such ligand-metal interactions led us to an investigation of the stereoinductive strength of several novel homochiral bisphosphine ligands in the Rh(I) catalyzed *asymmetric* [4+2] cycloisomerization of olefins.

BACKGROUND

A substantial portion of all asymmetric synthesis currently draws upon catalysis with chiral transition metal templates. The employment of this process has become so widespread that it would not be practical to discuss it here in its entirety. The application of asymmetric catalysis to hydrogenation³ and hydroformylation⁷ reactions no longer constitutes the bulk of research into this methodology. In fact, examples of reactions that have more recently been successfully catalyzed by chiral transition metal complexes include hydroboration,⁵ double-bond migration,⁶ hydrosilylation,⁷ hydrocyanation,⁸ olefin codimerization,⁹ carbon-carbon cross-coupling,¹⁰ cyclopropanation,¹¹ and epoxidation.¹² As the number of new catalyst systems increases, it is likely that the application of this methodology will continue to expand.

The majority of all the transition metal complexes used in homogeneous catalysis contain manganese, nickel, cobalt, copper, rhodium, ruthenium, palladium or platinum. In addition, although chiral phosphorus ligands are prevalent in these complexes, there are many cases in which amines, amides, alcohols and sulfoxides have proven to be good chiral ligands as well.¹³

Chiral Phosphine Ligands

The first instance of an optically active phosphorus compound was in 1911, in which Meisenheimer and Lichtenstadt were investigating the bonding properties and stereochemistry of Phosphorus-III, -IV and -V compounds.¹⁴ Despite this early report, it was not until the 1960s that chemists were able to efficiently synthesize compounds containing asymmetric phosphorus atoms.¹⁵ As a result, research into methods for preparing such chiral compounds has increased dramatically over the past two decades.

Chiral phosphines can be divided into three major categories: monophosphines, diphosphines, and polyphosphines. The third category is the youngest of the three and consists mainly of chiral triphosphines, although there have been a few reports on cyclic tetraphosphines.¹⁶ The latter category is omitted from the following discussion.

Monophosphines

According to Kagan, a chiral monophosphine can contain either a chiral organic unit in the vicinity of an achiral phosphorus (Type I), a chiral phosphorus unit (Type II), or both (Type III) (Figure 1).¹³

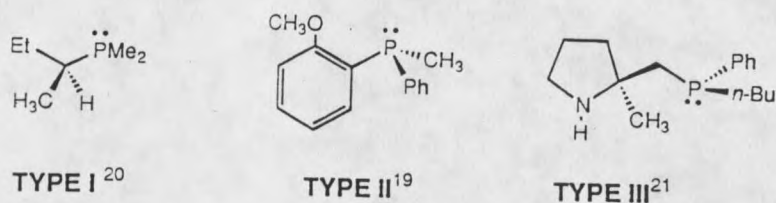
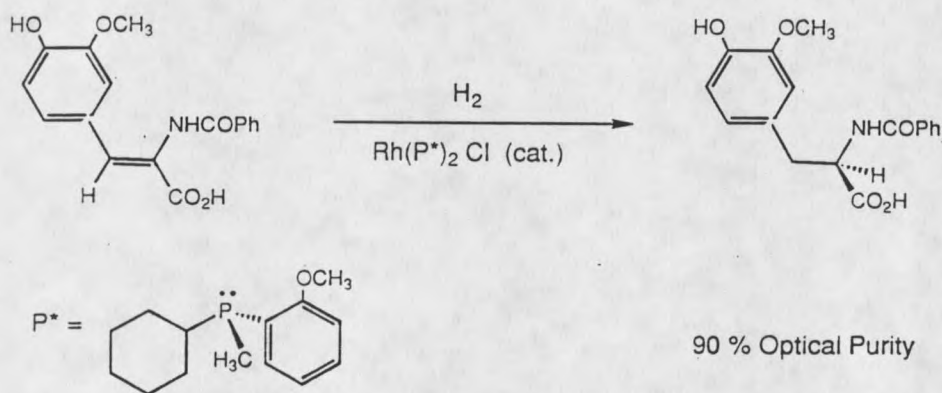


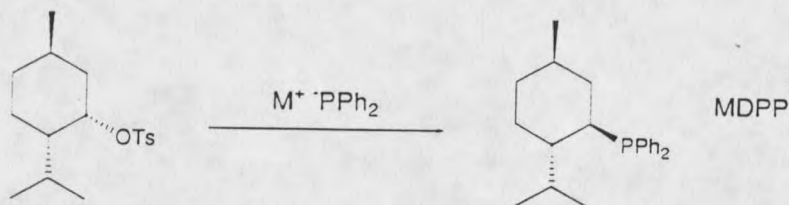
Figure 1. Examples of Three Types of Chiral Monophosphines

Many of the chiral monophosphorus compounds such as Type I and Type II were first designed to be used as ligands in the Rh(I) catalyzed asymmetric hydrogenation of α -acylamino-acrylic acids (Eq. 1).^{3c}



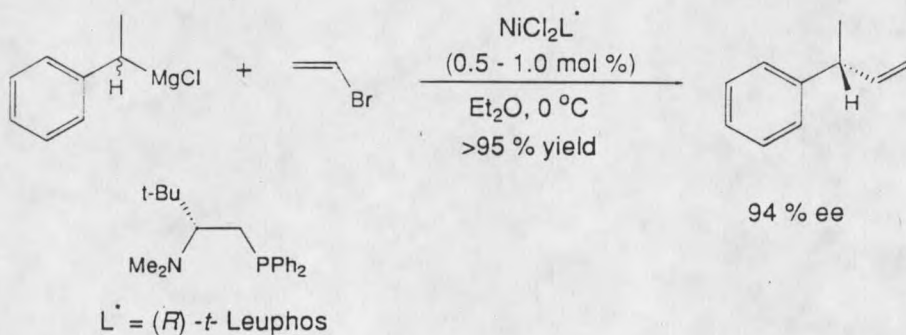
Eq. 1

The most common method employed for the synthesis of Type I monophosphines involves nucleophilic substitution of a *p*-tosyloxy (or halide) derivative of a commercially available chiral compound with the desired metallophosphide (Eq. 2).¹⁷



Eq. 2

Many Type I and Type III monophosphines were designed with a second ligating function (i.e. amine or alcohol) incorporated into one or more of the organic substituents. These difunctionalized monophosphines could then serve as *bidentate* chiral ligands in such reactions as the nickel-catalyzed asymmetric Grignard cross-coupling reaction (Eq. 3).¹⁰



Eq. 3

In the presence of such nickel-phosphine catalysts the reaction of 1-phenylethylmagnesium chloride with vinyl bromide has been shown to proceed in high yield with high enantiomeric excess.²¹

Two important chelating monophosphines, also used in nickel (or palladium) catalyzed Grignard cross-coupling reactions, are (*S*)-FePN and (*R*)-(*R*)-PPFA (Figure 2).^{22,23}

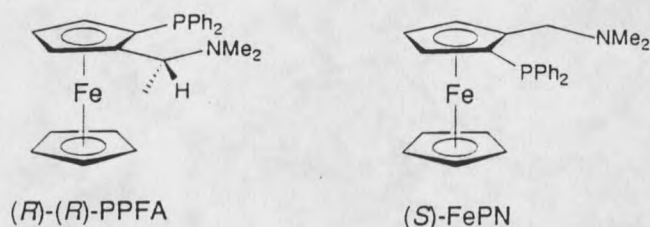
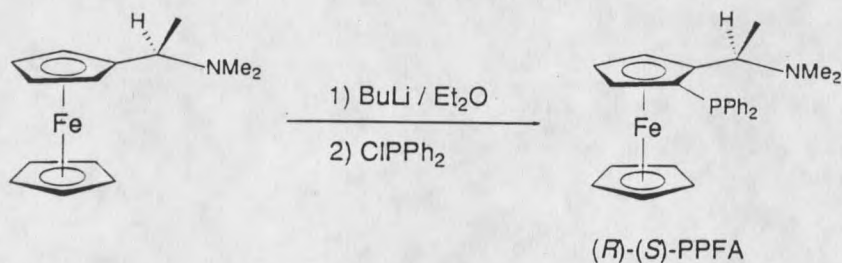


Figure 2. Ferrocenyl Monophosphine Ligands

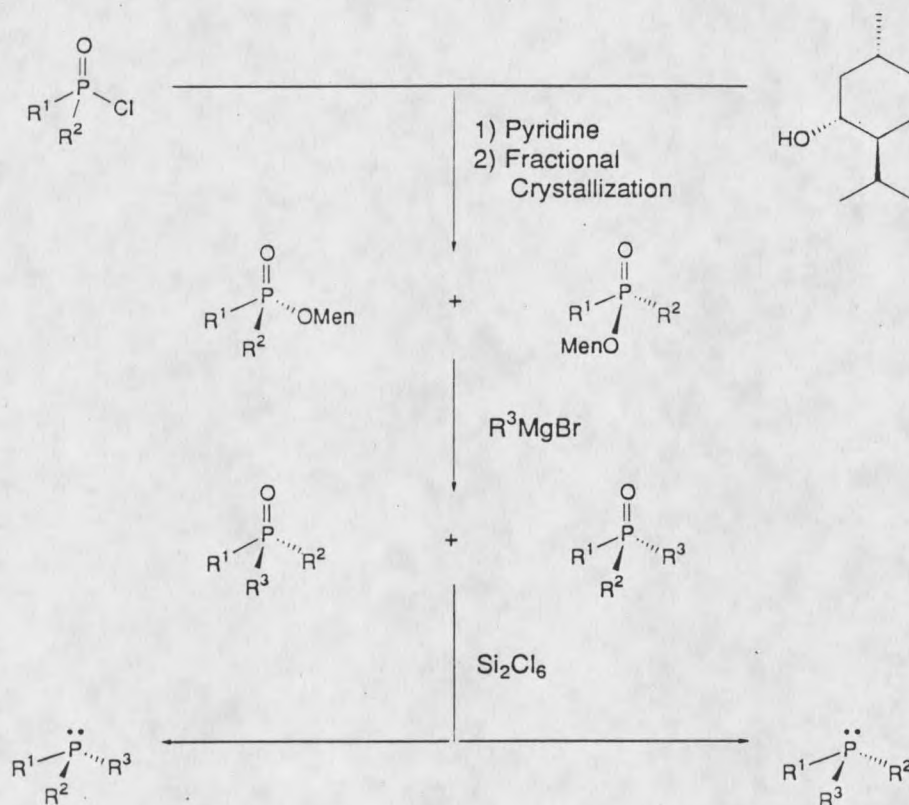
These were the first ferrocenyl phosphine ligands (Type I), and were synthesized by an alternate method consisting of the reaction of ferrocenyl lithium with the desired phosphine chloride (Eq. 4).



Eq. 4

The first method for preparing Type II chiral monophosphines was advanced by Mislow.²⁴ This approach combined the separation of diastereomeric menthyl

phosphinates (via fractional crystallization) with stereoselective phosphine oxide reduction (Scheme 1).

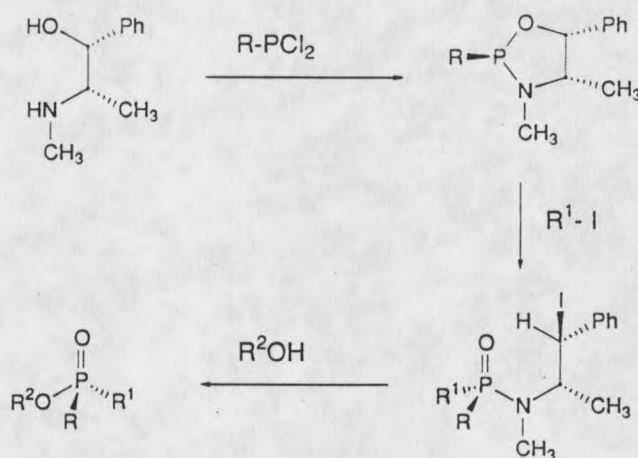


Scheme 1

Mislow demonstrated that acyclic alkyl phosphinates can be converted to phosphine oxides, with high stereoselectivity, upon reaction with alkyl and aryl Grignard reagents.^{24,25}

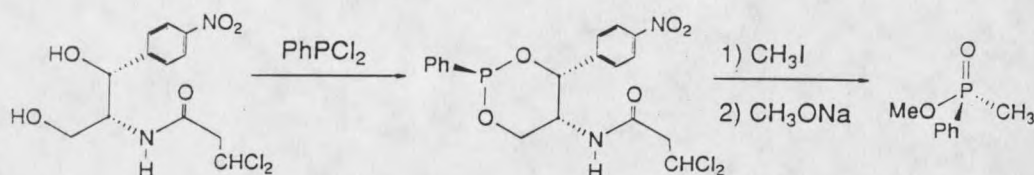
Horner and Balzer reported that the reduction of a phosphine oxide with trichlorosilane ($HSiCl_3$) proceeds with overall retention of configuration.²⁶ However, by combining this reagent with a strongly basic tertiary amine, such as Et_3N , both inversion and retention products are formed due

to competing inter- and intramolecular reduction processes.²⁷ Inversion of configuration was attributed to the intermolecular reduction of the phosphine oxide by a trichlorosilylanion formed in the presence of a basic tertiary amine. In light of this, Mislow demonstrated that the reduction proceeded with *complete* inversion of configuration with hexachlorodisilane (Si_2Cl_6).²⁸



Scheme 2

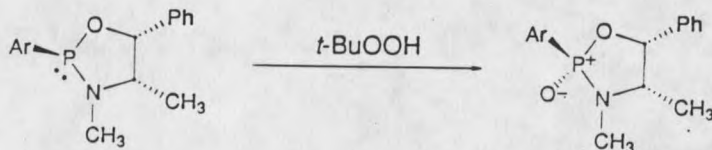
Several more recent methods have been described for the synthesis of Type II chiral monophosphines which also rely upon stereoselective phosphine oxide reduction. These methods utilize enantiopure chiral pool molecules to form 1,3,2-oxazaphospholidines (Scheme 2),²⁵ or cyclic phosphinites (Scheme 3).²⁹



Scheme 3

In both of these early methods, the phosphorus heterocycles were treated with alkyl halides via an Arbusov-like reaction. This transformation occurred with an overall retention of configuration at phosphorus.^{25a} In the former case (Scheme 2), removal of the chiral auxiliary was accomplished by a well documented acid catalyzed alcoholysis reaction to form the corresponding alkyl phosphinate in high enantiomeric purity.^{25a,30c,31}

In contrast to Mislow's acyclic phosphinates, Brown and co-workers prepared *cyclic* phosphinates by treating 1,3,2-oxazaphospholidines with *t*-butylhydroperoxide (Eq. 5).³²

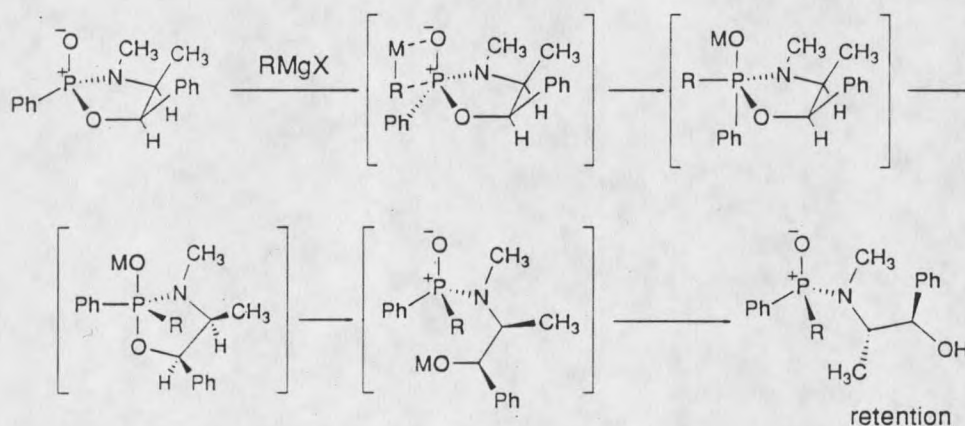


Eq. 5

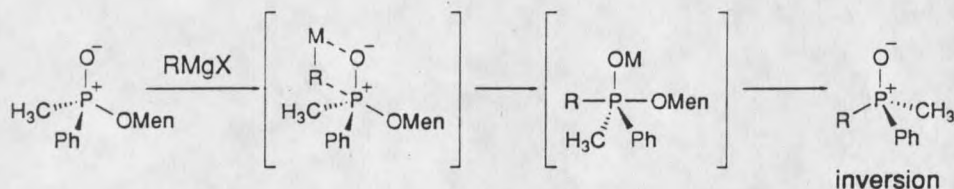
These authors determined that the reaction of cyclic phosphinates with aryl Grignard reagents resulted in the formation of phosphine oxides with an overall retention of configuration at phosphorus. According to Brown, approach of the Grignard reagent *trans*-axially to the P-O bond of the

oxazaphospholidine ring is disfavored in cyclic phosphinates vs. acyclic phosphinates, due to non-bonded interactions with the amino-methyl group. In addition, there is a limited number of possible positions for the electronegative substituents around the phosphorus center during transition state formation. These limitations govern the stereofacial approach of the incoming aryl Grignard nucleophile (Scheme 4).³²

Cyclic Phosphinates



Acyclic Phosphinates

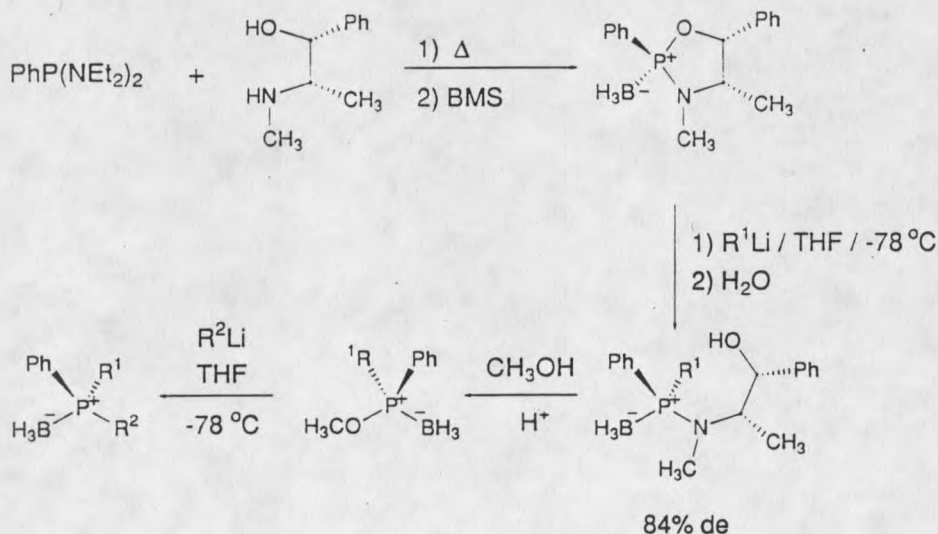


Scheme 4

Furthermore, a pseudorotation within the penta-coordinate transition state is favored by the 5-membered oxazaphospholidine ring which results in a net retention of

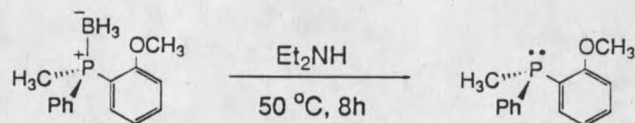
configuration at phosphorus. Brown also observed that smaller carbon nucleophiles (e.g., CH_3MgCl) resulted in the formation of some inversion products.³² According to the above interpretation, these reagents are not as susceptible to steric approach control. Therefore, the nucleophile can attack both *trans*-axially to the P-N bond and *trans*-axially to the P-O bond of the oxazaphospholidine ring, resulting in both retention and inversion products, respectively.³³ Stereochemical control is also lower for organolithium reagents which, according to Brown, can be attributed to a lower Lewis-acidity of the Li^+ counterion.³²

Juge and Brown have utilized a thermal condensation reaction between (-)-ephedrine and bis(diethylamino)phenyl phosphine, followed by treatment with $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (BMS) *in situ* to form the 1,3,2-oxazaphospholidine-borane (Scheme 5).^{32,34}



Scheme 5

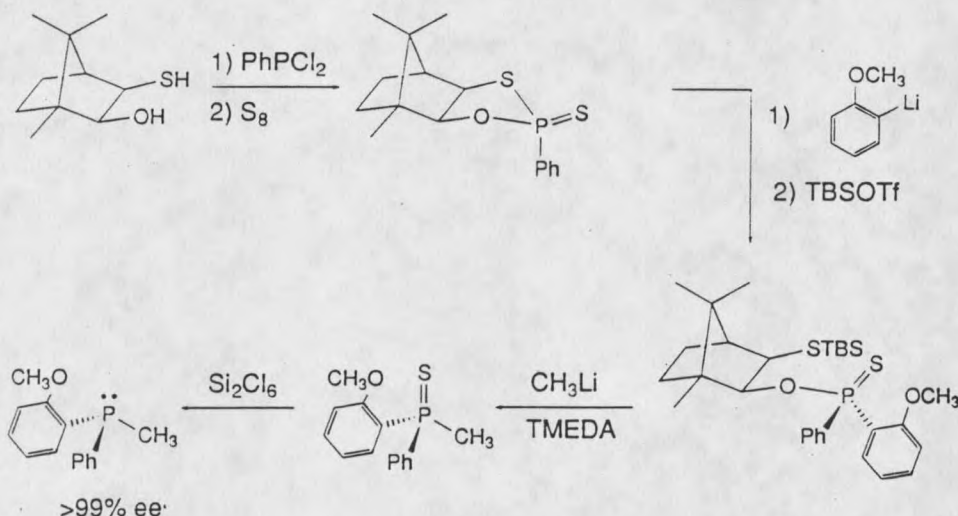
Cleavage of the P-O bond with an organolithium reagent gives rise to the corresponding amino phosphine-borane in high diastereomeric excess. The explanation for this observed retention of configuration is similar to that described for cyclic phosphinate ring-opening reactions with Grignard reagents. In this case, retention of configuration has been attributed to both steric approach control and the strong affinity the lithium ion has for the negative BH₃ of the phosphorus-boron dipole.³² Acid methanolysis results in the formation of a phosphinite-borane which can be converted to a phosphine-borane, with complete inversion of configuration, upon treatment with an organolithium reagent. Rather than utilizing a reduction step to obtain the free phosphine, Imamoto, Ward and LeCorre have demonstrated that removal of the boronate moiety from tertiary phosphine boranes occurs with retention of configuration in the presence of excess secondary or tertiary amines such as morpholine, diethylamine or DABCO (Eq. 6).^{35,36,37}



Eq. 6

In 1993, Corey provided a new route to chiral monophosphines via phosphine sulfides.³⁸ This method is reminiscent of that reported by Juge³⁴ in that a camphor

derivative (chiral pool) is condensed with dichlorophenyl phosphine, followed by treatment with S_8 *in situ* to give a 1,3,2-oxathiaphospholidine (Scheme 6).



Scheme 6

Corey reported that the reaction of 1,3,2-oxathiaphospholidines with organolithium reagents forming the corresponding acyclic thiophosphinates, proceeds with nearly complete *retention* of configuration. This observation is in accordance with the findings of Inch and co-workers, who demonstrated that the conversion of a cyclic thiophosphinate to an acyclic thiophosphinate by cleavage with organolithium reagents occurs with retention of configuration at phosphorus.³³ Treatment of the acyclic thiophosphinates (Scheme 6) with methyllithium gives rise to the corresponding methylphosphine sulfides in very high yield with complete inversion of configuration. Subsequent

reduction with Si_2Cl_6 proceeds with *retention* of configuration to yield the free phosphine in >99% enantiomeric excess. This result is in contrast to that observed for the reduction of phosphine oxides with Si_2Cl_6 . Mislow and Zon have suggested that the regioselective attack on sulfur vs. phosphorus by the trichlorosilyl anion is favored by the formation of a transition state that is stabilized by ($p\pi-d\pi$) bonding.³⁹

Two other methods for preparing monophosphines with asymmetric phosphorus atoms have been reported. Both require a resolution step and either (1) a displacement reaction on chiral phosphinites with organometallic reagents,³⁰ or (2) the electrolytic reduction of a benzyl phosphonium salt.⁴⁰

Diphosphines

Although not formally defined, the classification scheme for diphosphines is generally the same as that for monophosphines. There are two *major* categories:

(1) diphosphines consisting of two achiral phosphorus centers connected by a chiral organic backbone (Type A, e.g. DIOP); and (2) diphosphines which contain one or two asymmetric phosphorus centers (Type B, E.G. biPAMP). A third category of diphosphines includes those which consist of one or two asymmetric phosphorus centers connected by a chiral organic skeleton (Type C) (Figure 3).

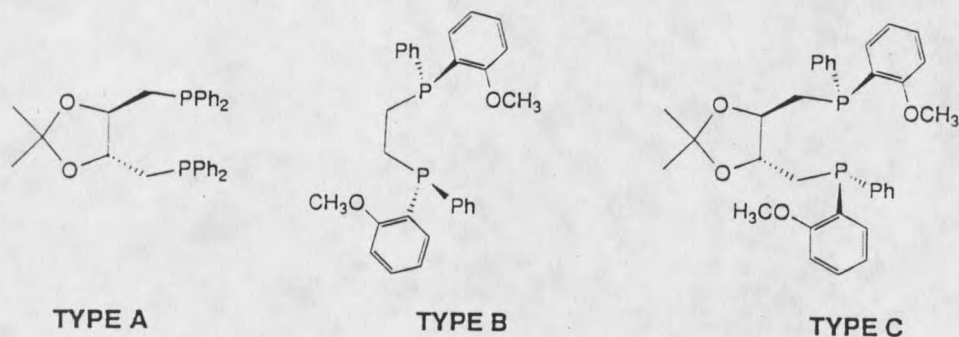
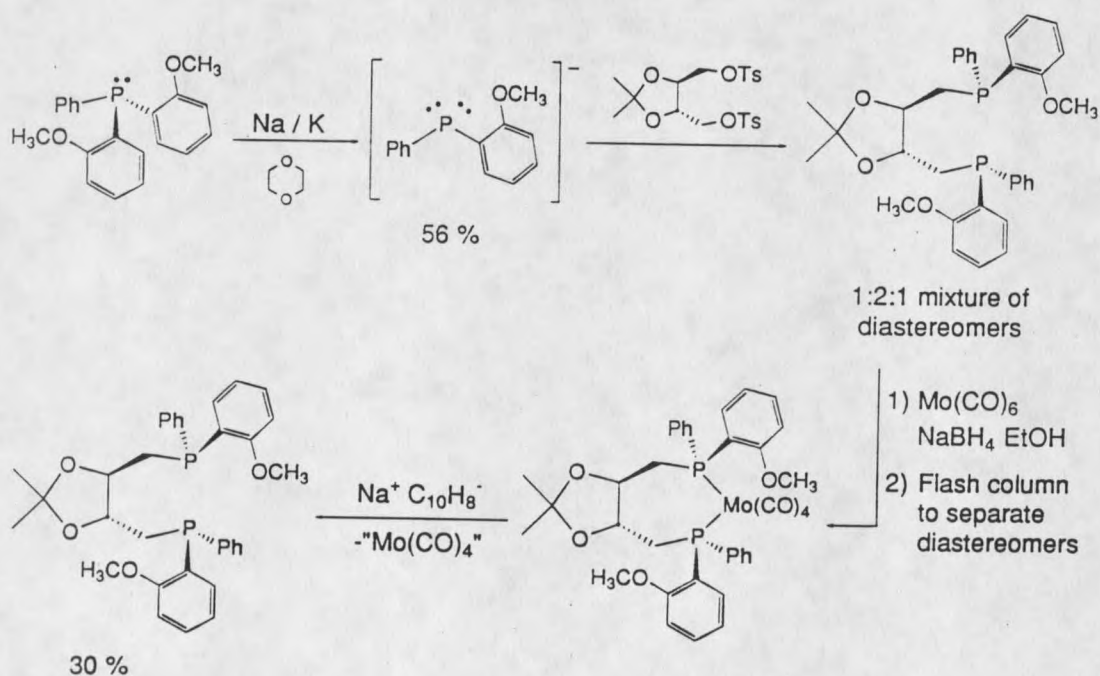


Figure 3. Examples of Three Types of Chiral Diphosphines

Over the past three decades, very few of the Type C diphosphines have been reported. In 1992 Burgess and co-workers synthesized a few of these "DIOP-DIPAMP hybrids" by the methodology depicted in Scheme 7.⁴¹ Arylphenylphosphide



Scheme 7

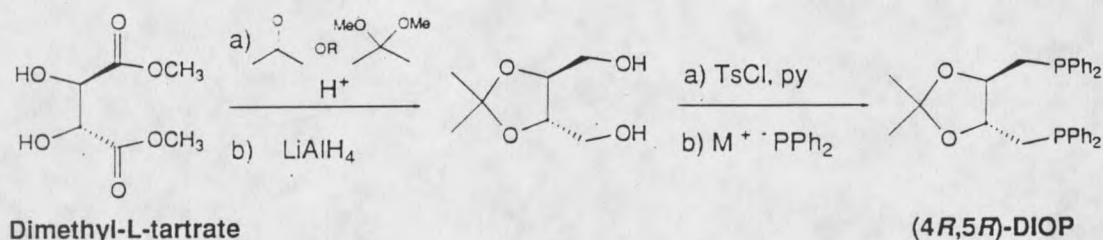
anions were prepared by the reduction of diarylphenylphosphines with sodium/potassium alloy. Burgess demonstrated that the aryl group bearing ortho substituents (e.g., OMe) was cleaved chemoselectively. Furthermore, if such an aryl group were absent, chemoselective cleavage of the least electron rich aryl group would then occur.

Reaction of the resulting arylphenylphosphide anions with (4*R*,5*R*)-*trans*-4,5-bis[(*p*-tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane formed the Type C diphosphines in statistical diastereomeric ratios. The separation of diastereomers, in most cases, was accomplished by chromatographic separation of the corresponding molybdenum tetracarbonyl adducts.

Burgess examined the ability of these hybrid ligands to induce asymmetric selection in several transition metal mediated reactions. Their findings were interesting but predictable. Constructive and destructive interference between the phosphorus and carbon stereocenters was observed. Moreover, they found that in some instances the chirality at phosphorus was not the most influential of the two forces, despite its proximity to the metal center.

In 1971 Kagan and Dang developed the Type A diphosphine DIOP (Figure 3).^{3d} An explosion of research into the synthesis of 1,2-, 1,3- and 1,4-diphosphines quickly followed. These efforts intensified because of the high degree of asymmetric induction observed when such ligands were utilized in transition metal catalyzed processes.³

The most common method for the synthesis of these types of diphosphines is based on the double displacement of a chiral ditosylate (or dihalide), available from chiral pool molecules (e.g., tartaric acid), with a disubstituted metallophosphide. Examples of this include the preparation of DIOP (Scheme 8) and various derivatives (Figure 4).^{3d,42,43,60,61} By this general method, several



Scheme 8

$\text{Ar}' = \text{Ar}'' = 2\text{-CH}_3\text{C}_6\text{H}_4$; $3\text{-CH}_3\text{C}_6\text{H}_4$; $4\text{-CH}_3\text{C}_6\text{H}_4$;
 $3,5\text{-(CH}_3)_2\text{-C}_6\text{H}_3$ (ref. 43)

$\text{Ar}' = \text{Ar}'' = 2\text{-OCH}_3\text{C}_6\text{H}_4$; $3\text{-OCH}_3\text{C}_6\text{H}_4$ (ref. 60)

$\text{Ar}' = \text{Ar}'' = 1\text{-C}_{10}\text{H}_7$; $2\text{-C}_{10}\text{H}_7$ (ref. 61)

$\text{Ar}' = \text{Ar}'' = 4\text{-NMe}_2\text{C}_6\text{H}_4$ (ref. 42a)

$\text{Ar}' = \text{Ar}'' = 3,5\text{-(CH}_3)_2\text{-4-OCH}_3\text{C}_6\text{H}_2$ (ref. 42b)

$\text{Ar}' = \text{Ar}'' = \text{Et}$; $i\text{-Pr}$; $c\text{-C}_6\text{H}_{11}$ (ref. 42c and 42e)

$\text{Ar}' = 4\text{-NMe}_2\text{C}_6\text{H}_4$, $\text{Ar}'' = 4\text{-ClC}_6\text{H}_4$; Ph (ref. 42f)

$\text{Ar}' = \text{Ph}$, $\text{Ar}'' = 2\text{-OCH}_3\text{C}_6\text{H}_4$; $4\text{-OCH}_3\text{C}_6\text{H}_4$;
 $4\text{-CH}_3\text{C}_6\text{H}_4$; $c\text{-C}_6\text{H}_{11}$ (ref. 42g and 42h)

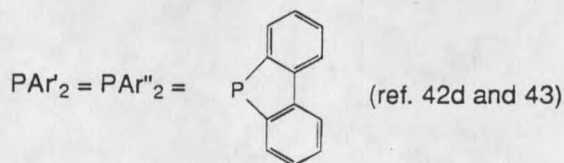
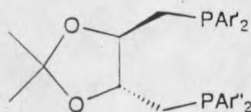
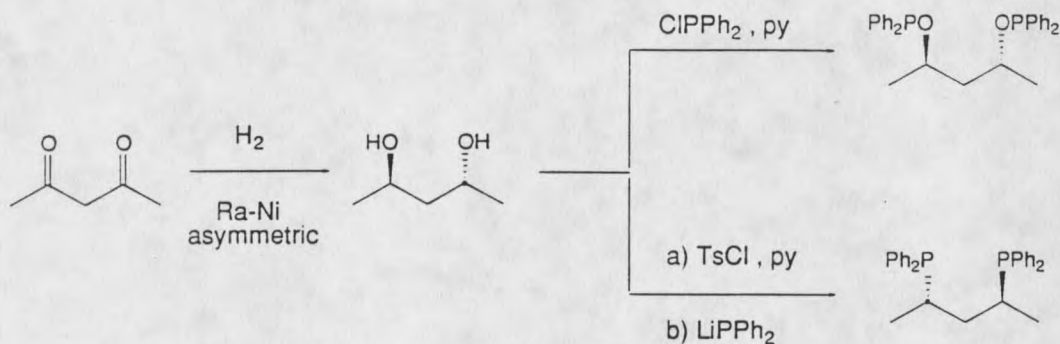
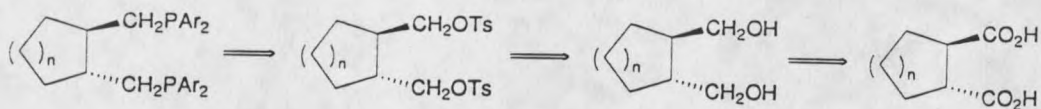


Figure 4. (4*R*,5*R*) DIOP Ligands

1,2-, 1,3- and 1,4-diphosphines have been synthesized. Bakos prepared the chiral 1,3-diphosphines (2*R*,4*R*)- and (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane from the corresponding chiral 1,3-diols (Scheme 9).⁴⁴ In a like manner, many carbocyclic 1,4-diphosphines have been synthesized from cyclic *trans*-dicarboxylic acids (Scheme 10).^{43,45}



Scheme 9

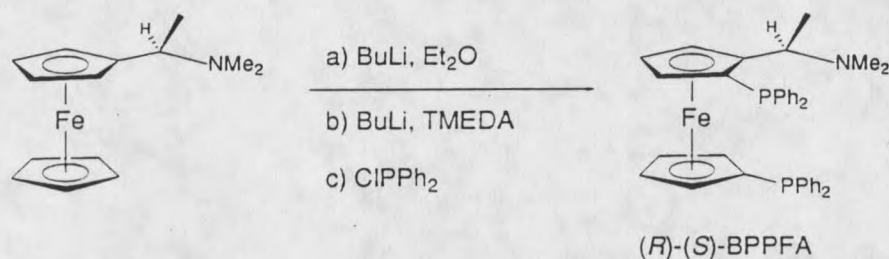


Scheme 10

Brunner and Kagan used dienes derived from commercially available terpenes in a Diels-Alder reaction with 1(E),2-Bis(diphenylthiophosphino)ethylene to synthesize similar chiral 1,2-diphosphines.^{46,47}

An interesting family of ligands are the ferrocenyl diphosphines. These compounds are considered to be

1,4-diphosphines and display both planar chirality, imparted by the ferrocene, and carbon chirality. Hayashi and Kumada have prepared many of these ligands (both mono- and diphosphine) from a commercially available chiral ferrocenylamine (Eq. 7).^{23, 48, 49, 50}



Eq. 7

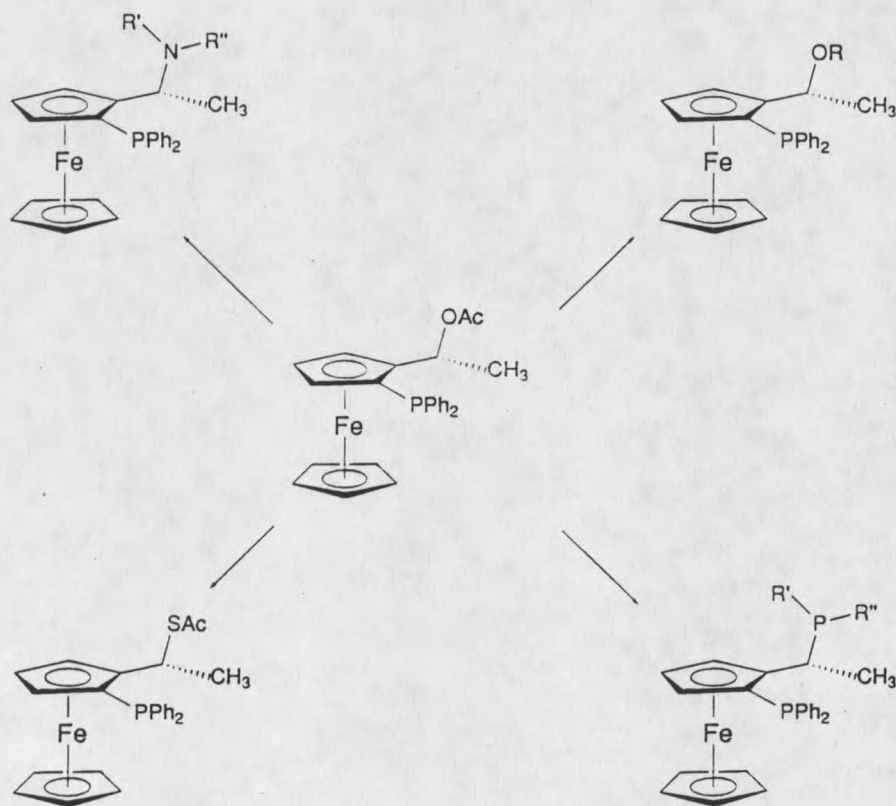


Figure 5. Chiral Ferrocenyl Phosphines

Recently, several derivatives have been prepared in which various carbon sidechains are attached via a nucleophilic displacement at the "pseudo-benzylic" position (Figure 5).⁵¹ These ligands have been found to impart enantioselectivity in palladium and nickel catalyzed coupling reactions¹¹ as well as in rhodium catalyzed hydrogenation and hydroboration reactions.⁵¹

The axially dissymmetric diphosphine, BINAP, (Figure 6) has been shown to be an unusually effective ligand in rhodium catalyzed asymmetric hydrogenation (99% ee), and double bond migration (95% ee) reactions.^{52a,53} Noyori originally synthesized BINAP by forming 2,2'-dilithio-1,1'-binaphthyl and quenching the dianion with ClPPh₂. Optical resolution of the resulting racemate was accomplished with (-)-Bis(μ -chloro)bis[(S)-N,N-dimethyl-1-phenylethylamine-2C,N]dipalladium(II).⁵⁴ Later, Noyori⁵⁵ prepared optically pure BINAP, as well as several derivatives, by optical resolution of a racemic bisphosphine oxide with chiral organic acids such as camphorsulfonic acid¹⁴ and dibenzoyl tartaric acid.⁴⁶ This resolution method, originally developed by Meisenheimer and Lichtenstadt,¹⁴ has also been utilized in the synthesis of several novel biphenyl diphosphine ligands (Figure 6).⁵⁶

Synthesized by Knowles⁵⁷ in 1974, (R,R)-DIPAMP (Figure 3) was one of the first Type B diphosphines to be

employed in transition metal catalyzed asymmetric hydrogenations.³ In fact, since its development, the

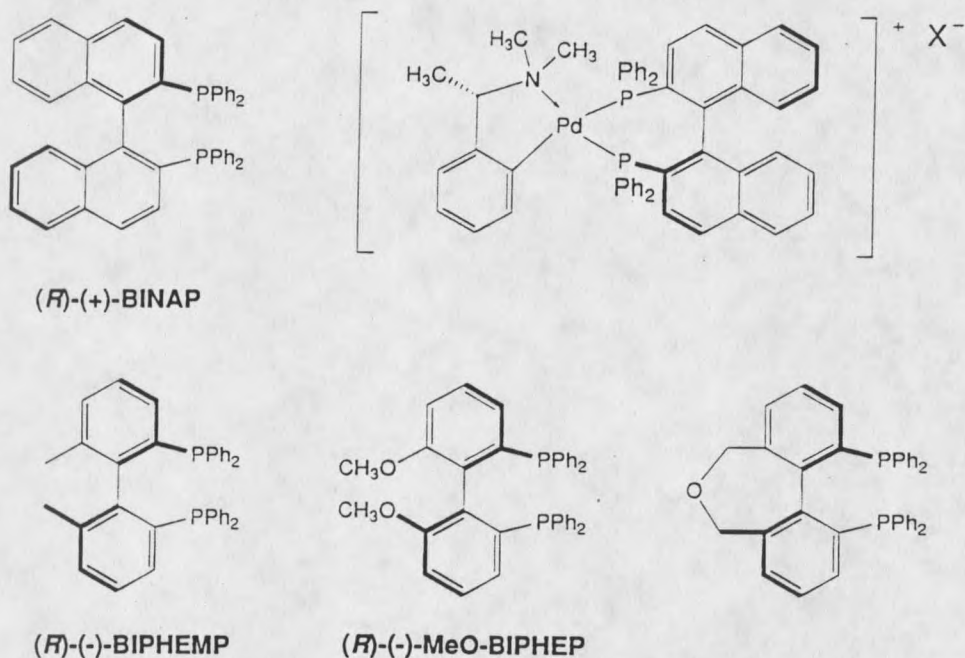


Figure 6. Axially Dissymmetric Bisphosphines

Monsanto Corporation has utilized a rhodium-DIPAMP catalyst in the commercial preparation of

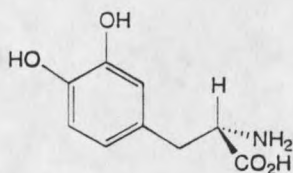
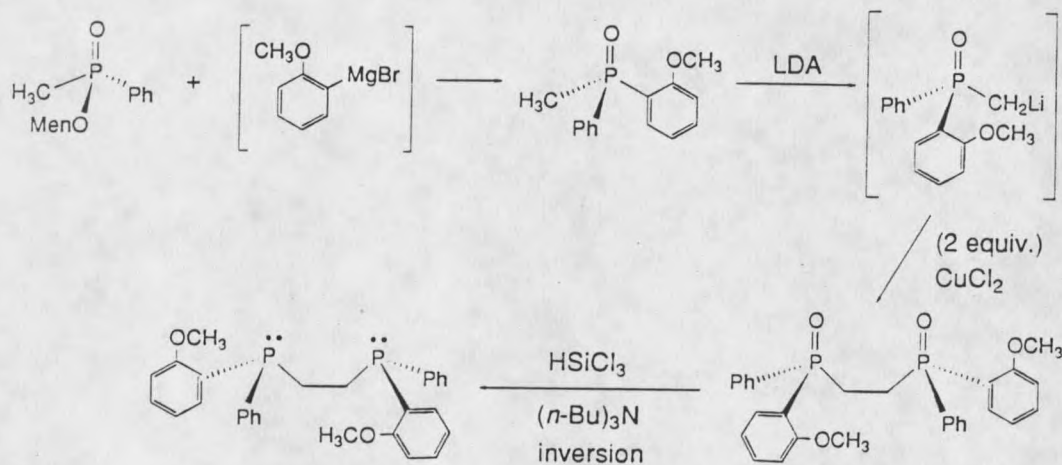


Figure 7. (S)-DOPA

(S)-3,4-dihydroxyphenylalanine ((S)-DOPA), a drug used in the treatment of Parkinson's disease.

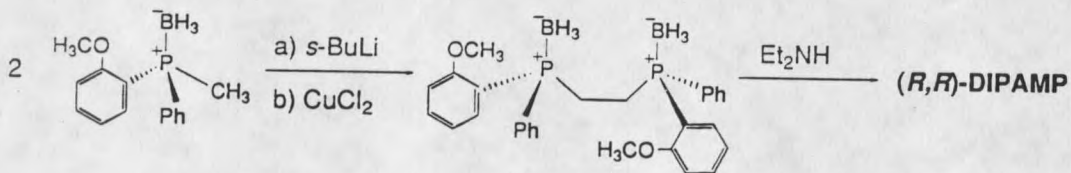
One synthesis of (R,R)-DIPAMP consists of an oxidative coupling of two o-anisylmethylphenylphosphine oxide

residues, followed by reduction to the diphosphine
(Scheme 11).^{57,58} Imamoto has synthesized several new

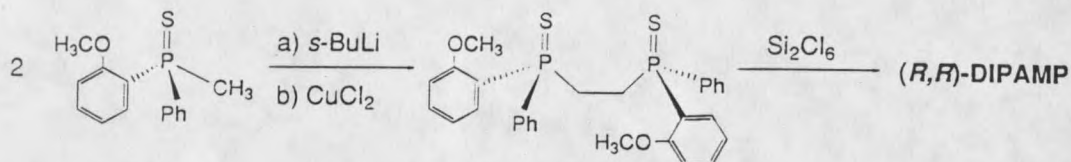


Scheme 11

homochiral bisphosphines, as well as (*R,R*)-DIPAMP, by coupling two analogous phosphine-borane precursors (Scheme 12).³⁵ Likewise, Corey demonstrated the generality of Cu (II) catalyzed oxidative coupling when he prepared (*R,R*)-DIPAMP from two phosphine-sulfide monomers (Scheme 13).³⁸

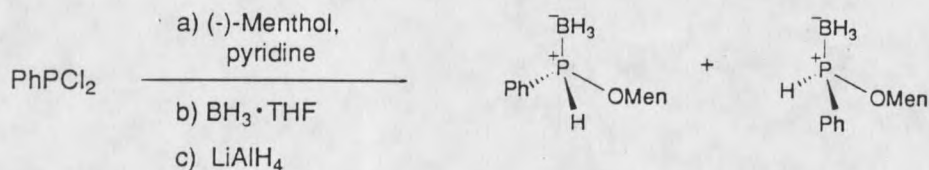


Scheme 12



Scheme 13

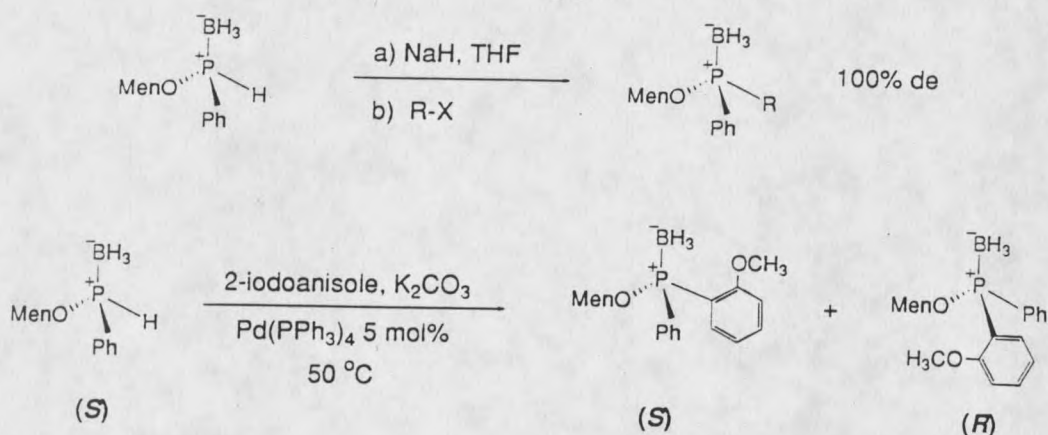
Imamoto has prepared optically pure secondary phosphine-borane monomers by the reduction of secondary phosphine chlorides with LiAlH_4 in the presence of BH_3 (Eq. 8).^{35b}



Eq. 8

The resulting menthyloxyphosphine-boranes could be separated by fractional crystallization and used either in (1) nucleophilic substitution reactions (as metallophosphides) which were found to proceed with complete retention of configuration,^{35b} or (2) palladium catalyzed cross-coupling reactions with alkyl or aryl iodides (Scheme 14).⁵⁹ The stereoselectivity of the palladium catalyzed cross-coupling reaction is highly dependent on solvent polarity and base strength.

Displacement of the menthyloxy group can be effected with an organolithium reagent (inversion) in a manner



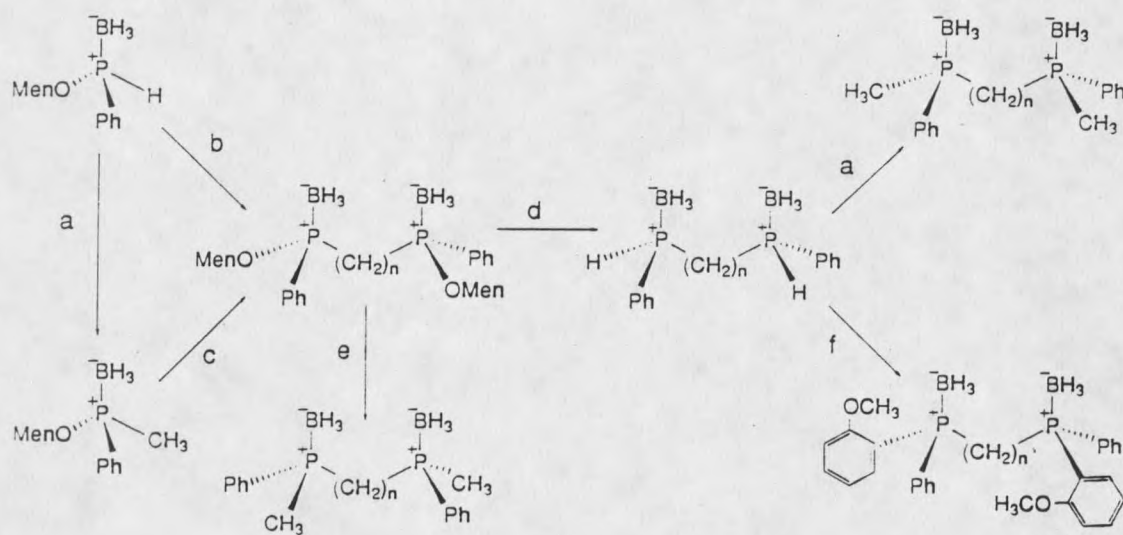
Solvent	Time (h)	Yield (%)	(S) : (R)
CH ₃ CN	16	98	100 : 0
THF	48	67	4 : 96

Scheme 14

analogous to that described by Juge.³⁴ Alternatively, Imamoto demonstrated a reductive removal of the menthyloxy group using lithium naphthalenide or Li/NH₃, with retention of configuration at phosphorus.⁵⁹ By combining these new methods with the copper promoted oxidative coupling reaction, Imamoto has synthesized a variety of new homochiral mono- and bisphosphine ligands (Scheme 15).⁵⁹ It is the aforementioned methodologies put forth by Juge,³⁴ Brown³² and Imamoto⁵⁹ that dominate the current research in this area of ligand synthesis.

Transition Metal Complexes as Catalysts in Asymmetric Synthesis

There are a great number of useful synthetic transformations catalyzed by transition metal complexes. Of



- a) NaH, CH_3I ; b) NaH, $\text{I}-(\text{CH}_2)_n-\text{I}$; c) i. *s*-BuLi ii. CuCl_2 ; d) $\text{Li}^+ \text{C}_{10}\text{H}_8^-$; e) CH_3Li ;
f) 2-I-1-(OCH_3) C_6H_4 , $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 .

Scheme 15

these, homogeneous catalysis of hydrogenation, hydroformylation and oxidation⁶³ reactions have been studied most extensively. Much of the work concerning transition metal mediated hydrogenation has set precedence for the investigation of carbon-carbon bond forming processes such as olefin cycloisomerization.^{64,65} Many of these reactions may be made stereoselective through a modification of the active catalytic center via coordination of an appropriate chiral ligand. For instance in hydrogenation and hydroformylation reactions, rhodium complexes containing chiral mono- and bisphosphine ligands have been utilized to induce asymmetric product formation^{3,7}.

Hydrogenation

Soluble transition metal catalyst systems which consist of rhodium-phosphine complexes have been used extensively for the asymmetric hydrogenation of olefins and other unsaturated molecules.⁶⁶ Initial work in this area of homogeneous catalysis focused on the use of neutral Rh(I) species modified by chiral monophosphine ligands such as neomenthyldiphenylphosphine (NMDPP)⁶⁷ and methylpropylphenylphosphine.^{15b,28,68} Hydrogenations mediated by Wilkinson type complexes ($[L_3RhCl]$) resulted in the formation of product mixtures which were slightly enriched in one enantiomer. Uniquely high enantioselectivities were observed in the hydrogenation of α -acetamidocinnamic acids when the chiral monophosphine *o*-anisylcyclohexylmethylphosphine was used.^{3c,18b,69} The high degree of stereoselectivity observed in this case has been rationalized as having resulted from a rigid chelation between the *o*-methoxyphenyl substituent on a bound ligand and an uncoordinated metal site.^{3c,18b} The notion that structural rigidity within the ligand-metal complex is responsible for high degrees of stereoinduction was confirmed by numerous reports⁷⁰ in which chiral chelating *bisphosphines* coordinated to rhodium gave rise to high enantiomeric excesses. Most of the monophosphine complexes

did not display the "structural rigidity" necessary for a high degree of asymmetric induction.

It is well documented that in the five-membered chelate rings of CHIRAPHOS,⁷⁰ PROPHOS⁷¹ and NORPHOS⁷² the carbon substitution one center away from phosphorus (absent in DIPHOS⁷³) prevents the rapid interconversion from one chiral conformation to the other (Figure 8).⁷⁴ The substituents at the asymmetric carbon atoms tend to occupy the equatorial

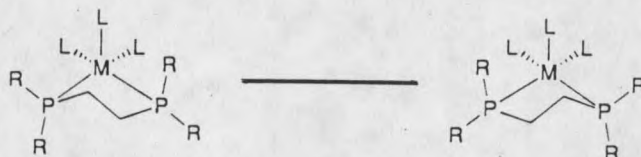


Figure 8. The Chiral Conformations of a Saturated Five-Membered Chelate Ring

positions around the chelate ring resulting in a *fixed* conformation. The aryl substituents on each phosphorus atom are therefore differentiated in quasi-axial and quasi-equatorial arrangements. For many asymmetric processes the conformational array of aryl substituents governs the facial approach and subsequent binding of the prochiral substrate, resulting in enantiomerically enriched product mixtures.

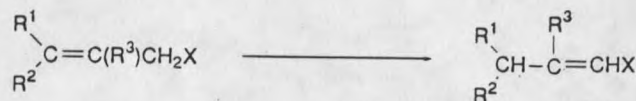
Carbon-Carbon Bond Formation

Some very promising synthetic transformations involve transition metal catalyzed carbon-carbon bond forming reactions. In addition to rhodium-mediated hydrogenation, carbon-carbon bond formation in hydroformylation,

hydrocyanation and cyclopropanation reactions has also been studied quite extensively with respect to transition-metal catalyzed asymmetric synthesis. The asymmetric cross-coupling reaction of alkenyl or aryl halides and allylic compounds, with organometallic reagents, catalyzed by nickel or palladium complexes have also received extensive investigation throughout the past decade. In contrast, the asymmetric catalysis of olefin isomerization, particularly cycloisomerization, has been examined to a lesser degree. In the realm of homogeneous catalysis, iron, cobalt, nickel, ruthenium, rhodium and iridium have been used in conjunction with various ligand systems as chiral templates for asymmetric olefin isomerization.⁶

Simple Isomerization

Asymmetric double-bond migration in prochiral allylic alcohols and amines (and derivatives) catalyzed by transition-metal complexes is interesting for two major reasons (Eq. 9): (1) the process is potentially

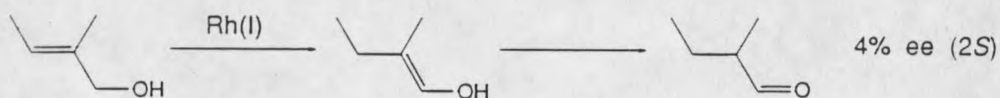


Eq. 9

very useful because functionality at the terminus can be converted to more reactive moieties (i.e. aldehydes, enamines, etc.) and (2) the use of prochiral olefins prompts

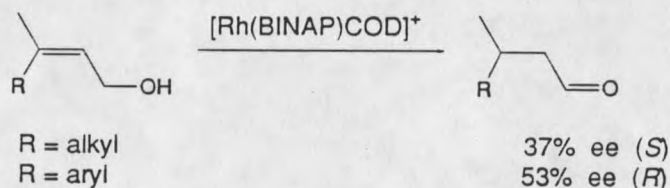
the design and generation of *tailored* chiral catalyst systems which can induce asymmetry in the products as well as govern the formation of the various structural isomers (i.e. cis and trans).

Botteghi utilized a Rh(I)-(-)-DIOP complex for the catalysis of asymmetric isomerization in simple allylic alcohols (Eq. 10).⁷⁵ Although their optical yields were



Eq. 10

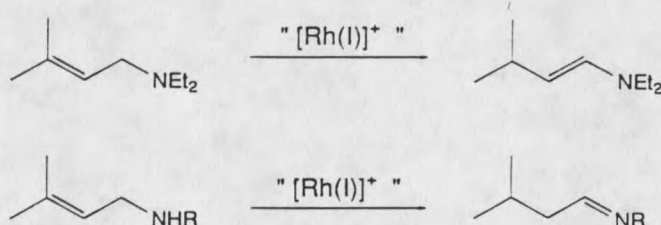
very low, these authors demonstrated that asymmetric induction by the catalyst was occurring to a small degree during the enol tautomerization step.⁷⁵ Cationic Rh(I)-BINAP complexes effected moderate levels of asymmetric induction in the isomerization of 3,3-disubstituted allylic alcohols (Eq. 11).⁶



Eq. 11

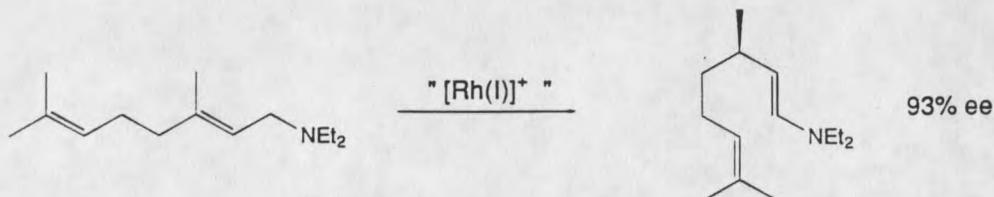
Cationic Rh(I) complexes such as [Rh-BINAP(diene)]⁺ (diene=1,5 cyclooctadiene, norbornadiene) have more

effectively been used to isomerize tertiary and secondary allylic amines to *trans* enamines and imines respectively (Eq. 12).⁷⁶ Several rhodium and ruthenium complexes have



Eq. 12

also been employed for the isomerization of cyclic and acyclic allylamides.⁷⁷ Chiral Co(II)-diphosphine complexes have been commonly used for asymmetric isomerization of allylic amines.⁶ The best results, however, have been obtained with the cationic complex [Rh-(BINAP)(COD)]⁺ClO₄ (Eq. 13).⁷⁸ This enantioselective isomerization is currently being used in the commercial production of menthol (Eq. 14).⁷⁹



Eq. 13



Eq. 14

Olefin Dimerization

Utilizing a nickel catalyst prepared from $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$, $[(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3]$ and a chiral monophosphine, Bogdanovic and co-workers established a mechanism for the asymmetric hydrovinylation of various olefins. Moderate to good ee's were obtained with a nickel-aluminum complex modified by (-)-isopropylidimethylphosphine, for the reaction

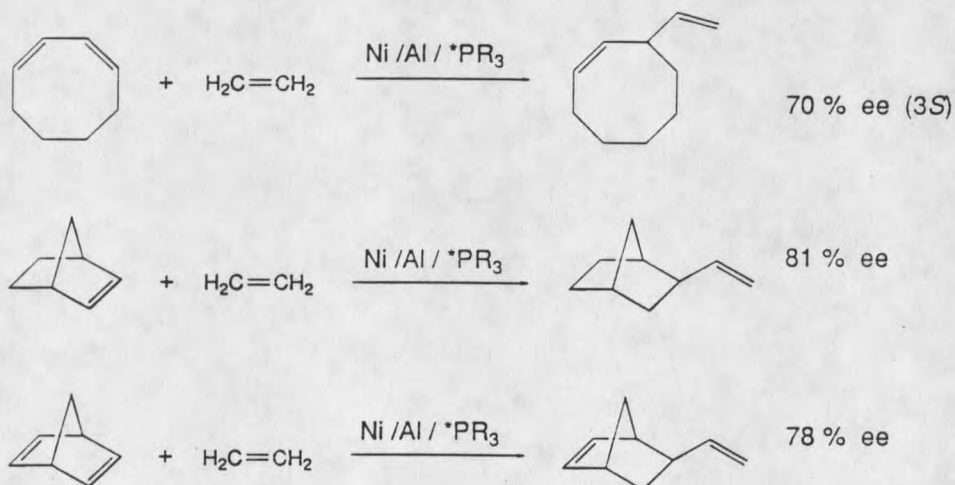


Figure 9. Asymmetric Olefin Dimerization

of 1,3-cyclooctadiene, norbornene and norbornadiene with ethylene (Figure 9).⁹

Olefin Cycloisomerizations

In addition to rhodium, complexes containing transition metals such as palladium, nickel, cobalt, chromium, iron and titanium have also been used in the catalysis of inter- and intramolecular olefin cycloisomerizations.⁸⁰ The trimerization of alkynes and nitriles,⁸¹ in the presence of metal catalysts, are of interest primarily because of their utility in benzenoid and steroid synthesis.⁸² The inter- and intramolecular [2+2+2] cycloisomerization of acetylenes has been effected with high chemoselectivity using Wilkinson's catalyst.⁸³ An asymmetric intermolecular [2+2+2] cycloisomerization has also been reported in which the reaction of norbornadiene and monosubstituted acetylenes is mediated by a chiral cobalt-bisphosphine catalyst (Figure 10).⁸⁴ Lautens obtained high enantioselectivities (78-91% ee) in this process, by utilizing *S,S*-CHIRAPHOS and *R*-PROPHOS as chiral modifiers for the metal center.⁸⁴

Since acid and base catalysts are widely utilized to accelerate organic reactions, a great deal of effort has been devoted to the development of chiral Lewis acids for asymmetric olefin *cycloaddition* reactions. Usually

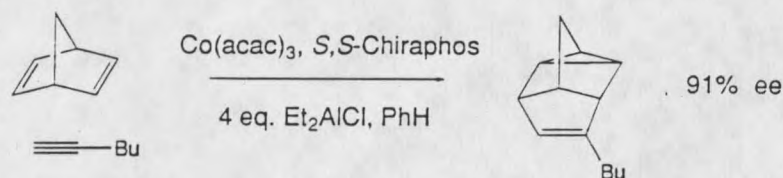
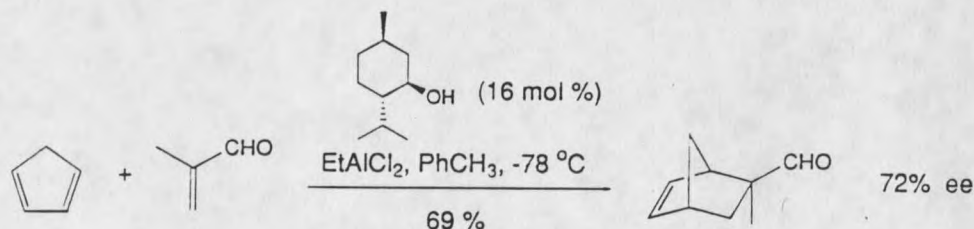


Figure 10. Asymmetric Intramolecular [2+2+2] Cycloisomerization

generated *in situ* from a Lewis acid and a chiral auxiliary, these reagents have been used to promote various asymmetric reactions including the Diels-Alder and the [2+2] cycloaddition reactions.⁸⁵

The earliest work involved catalysis of the Diels-Alder reaction with chiral aluminum and europium reagents (Eq. 15).^{86,87} The importance of this early work was that it



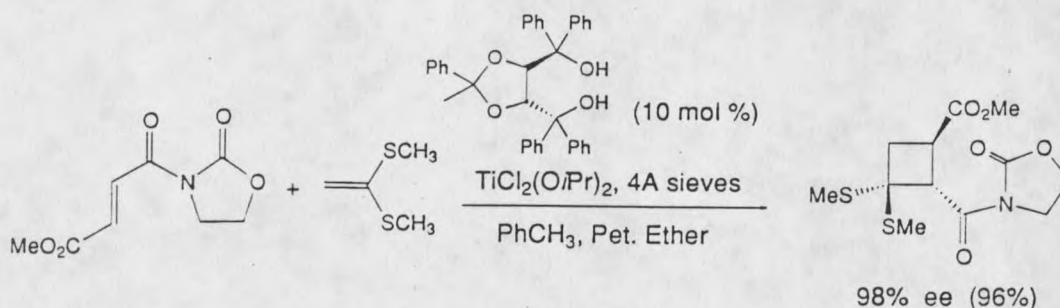
Eq. 15

established precedence for the development of chiral auxiliaries which could interact with Lewis acids in such a manner as to invoke high levels of asymmetric induction.

In addition to aluminum, several chiral titanium, boron and ruthenium reagents were derived from homochiral organic moieties such as tartaric acid and binaphthol.^{88,89,90,92}

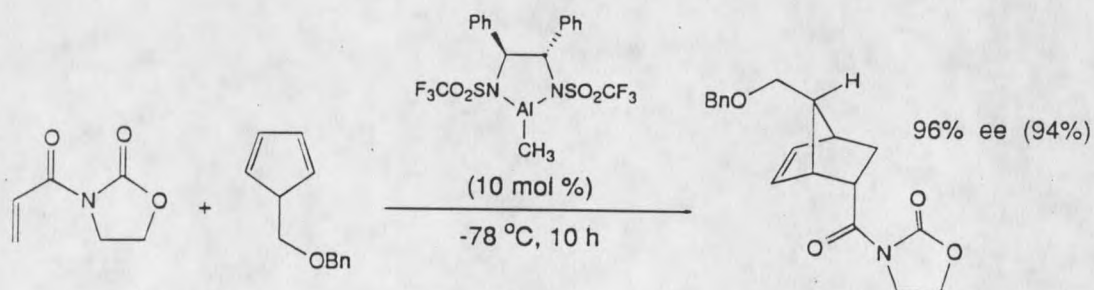
Asymmetric intermolecular [2+2] cycloisomerization between

oxazolidin-2-one derivatives of α,β -unsaturated acids and ketene dithioacetals, have been catalyzed by such chiral titanium reagents and result in very high enantiomeric excesses (Eq. 16).^{91a} Vinyl sulfides and alkynyl sulfides have also been used in this reaction, and in the latter case almost complete asymmetric induction is observed.^{91b} Some of the highest reported enantiomeric excesses for the Lewis



Eq. 16

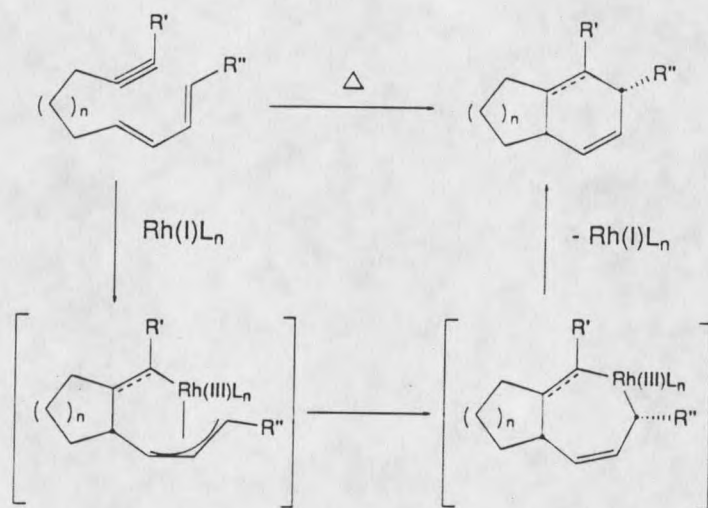
acid catalyzed asymmetric Diels-Alder reaction have resulted from the use of chiral titanium⁸⁸ (Eq. 17) and aluminum reagents.⁹²



Eq. 17

Intramolecular [4+2] Cycloisomerization

Our interest in the Rh(I) catalyzed [4+2] cycloisomerization reaction was initiated in early 1990 when we discovered that certain Rh(I) complexes could accelerate an *intramolecular* [4+2] cycloisomerization reaction (at low temperatures) between *electronically similar* components (Scheme 16).⁴ There have been few reports concerning



Scheme 16

transition metal catalyzed *intermolecular* [4+2] cycloisomerization,⁹³ and only one regarding the intramolecular variation.⁹⁴ These reports include the use of complexes with titanium, iron, nickel and rhodium as catalysts for such reactions.

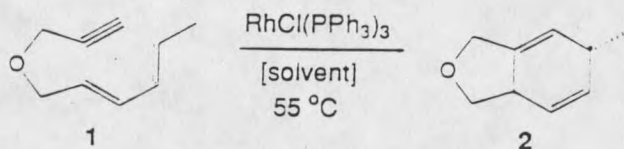
In 1989, Wender reported the catalysis of intramolecular [4+2] cycloaddition of dien-yne with Ni(0)

complexes.⁹⁴ The Ni(0) catalyzed reaction, however, was limited. Wender found that this metal complex could not effect the cyclization of substrates bearing enedienes as precycloaddends nor could they achieve high levels of diastereocontrol in the reaction. In contrast to systems containing Fe(0) and Ni(0), the Rh(I) catalyst systems developed in these laboratories do not display polymerization products from substrates containing non-terminal alkyne functionality. These Rh(I) complexes can also be utilized as catalysts in the cyclization of *both* ene-diene and dien-yne precyclic substrates. More importantly, this process has been shown to be highly stereoselective.

Preliminary investigations included a survey of the influences of solvent polarity and temperature on the Rh(I) catalyzed, intramolecular [4+2] cycloisomerization of 1-(2-propynyloxy)-2,4-hexadiene (1). Upon warming (55 °C) a solution (THF) of 1 in the presence of 10 mol % of commercial (Ph₃P)₃RhCl, under argon, the desired cycloadduct 2 was formed.⁴ An increase in solvent polarity (2,2,2-trifluoroethanol over THF or ethanol) resulted in a significant enhancement of the rate and efficiency of cyclization (Table 1).

There have been numerous reports concerned with the enhancement of both the rate and selectivity of transition metal catalyzed processes by electronic and/or steric

Table 1. Solvent Effects on Catalysis



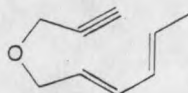
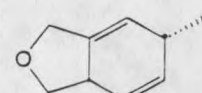
<u>Solvent</u>	<u>Result</u>
Toluene	N.R.
Tetrahydrofuran	2-3 hours
Ethanol	2-3 hours
Trifluoroethanol	15 minutes
Glacial Acetic Acid	N.R.*

* Intercepts reactive rhodium intermediate.

perturbations on the ligand sphere.⁹⁵ In an effort to further enhance the efficiency of [4+2] cyclization, through ligand modification, several new Rh(I) complexes were generated in situ. A variety of tertiary phosphites were initially employed as monodentate ligands in order to elucidate the electronic and steric parameters of the reaction. The desired catalytic complexes were formed in situ by the addition of the ligands (2 equiv)⁹⁶ to a solution of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ in CH_2Cl_2 (or THF), followed by dilution with 2,2,2-trifluoroethanol (TFE) and subsequent addition of the precyclic substrate. In consonance with the findings of van Leeuwen and Roobeek,^{65,97} it was demonstrated that through the coordination of electron deficient phosphite ligands the rate and efficiency of cyclization were

greatly enhanced (Table 2). Of particular significance was the highly active complex $[i\text{-C}_3\text{F}_6\text{HO})_3\text{P}]_2\text{RhCl}$, which was found to be effective in THF solutions at temperatures as low as

Table 2. Monodentate Phosphite Ligands

 $\xrightarrow[\text{THF, TFE, } 55^\circ\text{C}]{\text{RhCl}[\text{phosphite}]_2}$  1 2			
<u>Phosphite</u>	<u>χ</u>	<u>θ</u>	<u>Result</u>
$(\text{CF}_3\text{CH}_2\text{O})_3\text{P:}$	39	110	N.R.
$(i\text{-C}_3\text{F}_6\text{HO})_3\text{P:}$	51	130	fast
$(i\text{-C}_3\text{F}_6\text{HO})_2(i\text{C}_3\text{H}_7\text{O})\text{P:}$	41	130	slow
$(i\text{-C}_3\text{F}_6\text{HO})_2(\text{Ph})\text{P:}$	39	135	slow

in THF solutions at temperatures as low as 25°C . The parameters χ and θ refer to the electronic and steric properties, respectively, of the phosphite ligands. The "cone angle," θ , describes the limit of the van der Waals radii of atoms on the ligand. As determined by van Leeuwen and Roobeek,⁶⁵ the electron donating phosphites have low χ values, while electron withdrawing phosphites have high χ values. As shown in Table 2, the combined effect of "cone angle" and electronic index is crucial to rate enhancement.

In research pursued concurrently with that presented in this thesis, Derek Sheehan, of our laboratories, determined the generality of the rhodium-catalyzed intramolecular [4+2] cycloisomerization reaction for the preparation of 5/6 and

6/6 ring systems. A summary of these results appears in Table 3.

Table 3. Rh(I)-Catalyzed [4+2] Cycloisomerizations

Substrate	Product	(Yield %)	Reaction Conditions
		(96 %)	(Ph ₃ P) ₃ RhCl - TFE 55 °C, 15 min
		(90 %)	[(<i>i</i> -C ₃ F ₆ HO) ₃ P] ₂ RhCl THF, 55 °C, 15 min
		(93 %)	(Ph ₃ P) ₃ RhCl-TFE 55 °C, 45 min
		(87 %)	[(<i>i</i> -C ₃ F ₆ HO) ₃ P] ₂ Rh ⁺ THF, 55 °C, 15 min
		(78 %)	(Ph ₃ P) ₃ RhCl-TFE 55 °C, 45 min
		(96 %)	[(<i>i</i> -C ₃ F ₆ HO) ₃ P] ₂ Rh ⁺ THF, 55 °C, 15 min
		(96 %)	[(<i>i</i> -C ₃ F ₆ HO) ₃ P] ₂ RhCl THF, 55 °C, 15 min
		(89 %)	[(<i>i</i> -C ₃ F ₆ HO) ₃ P] ₂ RhCl THF, 55 °C, 18 hr

Another major focus of Sheehan's research was an examination of the internal diastereoselectivity of the cyclization process. He demonstrated that the Rh(I) catalyzed [4+2] cycloisomerization of various 4-substituted ene-dienes and dien-yne proceeds with excellent to complete diastereocontrol (Fig. 11).⁹⁸

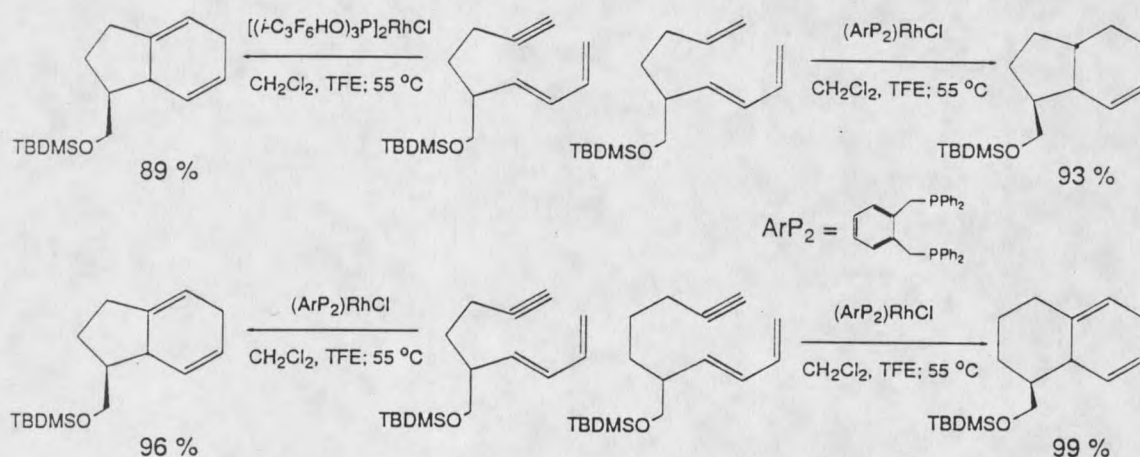


Figure 11.

Internal Diastereoselectivity in the Rh(I) Catalyzed [4+2]Cycloisomerization of Olefins

RESULTS AND DISCUSSION

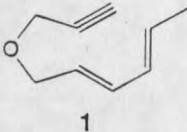
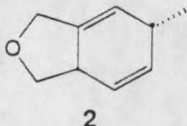
The object of this research was to determine the influences of bisphosphine ligand structure on the stereochemical outcome of Rh(I) catalyzed intramolecular [4+2] cycloisomerizations. It was also our goal to design highly flexible methods for the preparation of three structurally varied families of homochiral bisphosphine ligands.

Rh(I) Catalyzed [4+2] Cycloisomerization

Elucidation of the electronic and steric parameters of the Rh(I) catalyzed [4+2] cycloisomerization reaction with regard to monophosphine ligands was conducted in a preliminary study. Accordingly, several Rh(I) complexes were generated *in situ* by the addition of various monodentate trisubstituted phosphines (2 equiv.) to a solution of $[\text{RhCl}(\text{C}_6\text{H}_{14})_2]_2$ in CH_2Cl_2 (or THF), followed by dilution with TFE and subsequent addition of substrate. A summary of these results appears in Table 4. The overall trend is similar to that found with the phosphite ligands: coordination of the metal to electron deficient phosphines results in rapid cyclization of precycloadducts. Although it is difficult to separate the steric and electronic effects of phosphine substitution, the observed enhancement

with $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$: (Table 4, entry 2) vs. $(4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$: (entry 4), suggests that a favorable conformation exists

Table 4. Monodentate Phosphine Ligands

 1 $\xrightarrow[\text{TFE, 55 } ^\circ\text{C}]{\text{RhCl}(\text{Ar}_3\text{P})_2}$ 2 hr  2		
Entry	Ar	Conversion (%)
1	C_6F_5	87%
2	$2\text{-CF}_3\text{C}_6\text{H}_4$	36%
3	$2\text{-CH}_3\text{C}_6\text{H}_4$	17%
4	$4\text{-CF}_3\text{C}_6\text{H}_4$	16%
5	$n\text{-C}_4\text{H}_9$	14%
6	$2\text{-(OCH}_3\text{)C}_6\text{H}_4$	9%
7	$4\text{-(OCH}_3\text{)C}_6\text{H}_4$	80%

with the 2-trifluoromethylphenyl, contributing to the rate increase. Since a quantitative analysis of the electronic and steric parameters (χ and θ) of these ligands has not been conducted, it is difficult to interpret the rate enhancement observed with the electron rich tris(4-methoxyphenyl)phosphine (Table 4, entry 7).

In general, electron donating ligands enhance the oxidative addition of a substrate to the transition-metal center. Shaw reported that both the size and basicity of phosphine ligands affect oxidative addition of substrate to $\text{IrL}_2\text{Cl}(\text{CO})$ complexes.¹⁰⁰ These researchers found that the rate of oxidative addition can be increased with increasing

phosphine basicity, and decreased with increasing ligand size.^{100b} Our result obtained with the highly basic (n-Bu)₃P: (Table 4, entry 5), in which [4+2] cycloisomerization was sluggish, suggests that the rate enhancement may be occurring primarily at the *reductive elimination* step of the catalytic cycle (Scheme 16).

Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerization

Previously observed diastereocontrol in cycloisomerizations catalyzed by *achiral* bisphosphine-rhodium complexes (Figure 11) demonstrated the possibility

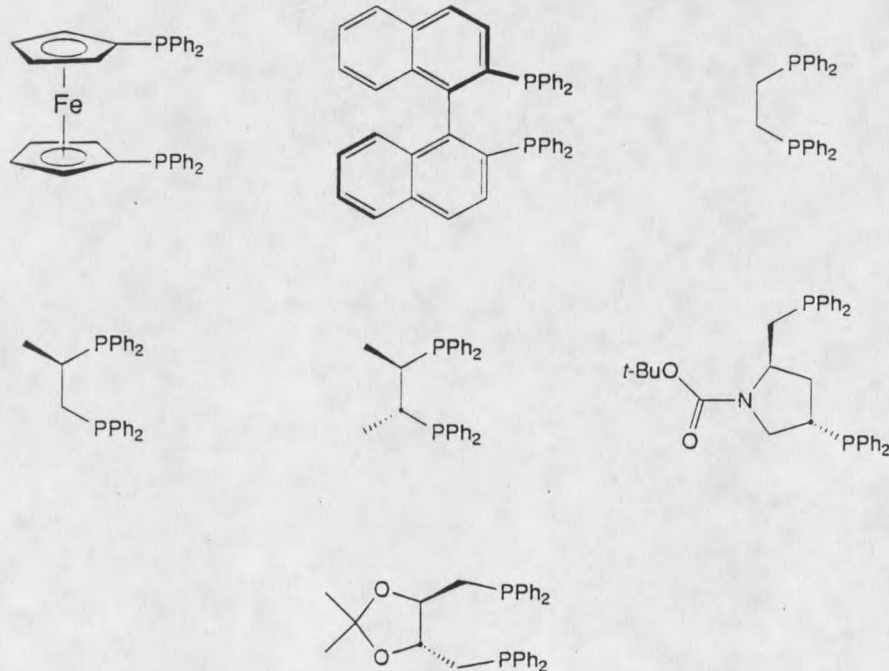


Figure 12. Commercial Homochiral Bisphosphines

that enantioselective [4+2] cycloisomerization could occur by utilizing *chiral* bisphosphine ligands. To this end, we initially surveyed a variety of commercially available bisphosphines as a prelude to ligand design (Figure 12).

It was demonstrated that there is indeed a structural and conformational dependence for the catalysis of this reaction. Furthermore, the bisphosphines which formed *flexible* 7-membered chelate rings proved most effective in terms of the overall rate of cyclization. These findings are in agreement with a study conducted by Sheehan in which the rate of cyclization increased with increasing tether length (Figure 13).⁹⁸ The rigid carbon skeletons of BINAP⁵²

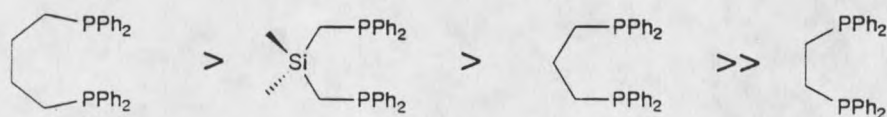
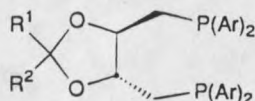


Figure 13. Annular Dependency of Cyclization

and BPPM¹⁰¹ ligands (Figure 12) result in decreased flexibility within the chelate ring. This suggests that the bisphosphine-rhodium complexes which possess a high degree of angular freedom may be more effective as catalysts for the asymmetric [4+2] cycloisomerization. An investigation of the effects of dihedral angle variations on cyclization efficiency is currently being pursued in our laboratories.

Electronic and Torsional Derivatives of (+)-DIOP

Based on the aforementioned preliminary studies, we initially chose a family of ligands (3a-3g, Figure 14) derived from commercially available (2*R*,3*R*)-tartaric acid. This feature guaranteed both control of the *absolute* stereochemistry of the ligand and the formation of a flexible 7-membered chelate ensemble. In this family of ligands the conformational bias of the dioxolane ring was subject to facile modification through alteration of the 1,3 dioxolane substituents at the 2-position. In addition, the electronic and steric characteristics of the ligating



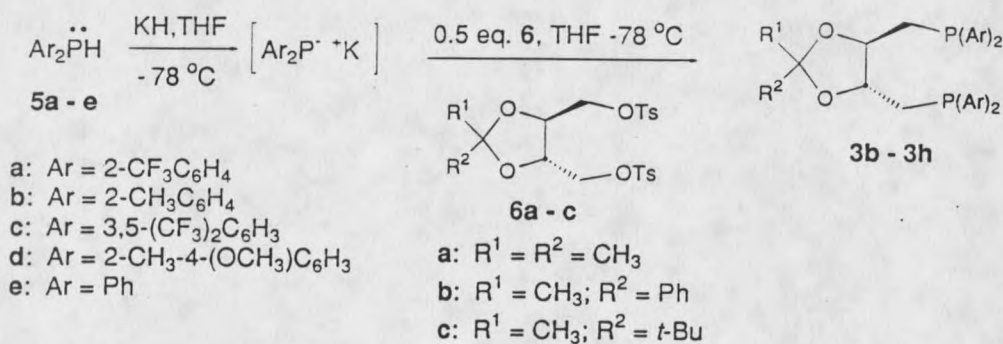
- 3a: Ar = Ph; R¹ = R² = CH₃
 3b: Ar = Ph; R¹ = Ph; R² = CH₃
 3c: Ar = Ph; R¹ = *t*-C₄H₉; R² = CH₃
 3d: Ar = 3,5-(CF₃)₂C₆H₃; R¹ = R² = CH₃
 3e: Ar = 2-CH₃C₆H₄; R¹ = R² = CH₃
 3f: Ar = 2-CF₃C₆H₄; R¹ = R² = CH₃
 3g: Ar = 2-CF₃C₆H₄; R¹ = Ph; R² = CH₃
 3h: Ar = 2-CH₃-4-(OCH₃)C₆H₃; R¹ = R² = CH₃

Figure 14. Homochiral Bisphosphines Derived from (L)-Tartaric Acid

phosphorus centers could be easily adjusted by the substitution of different aryl moieties bound to phosphorus. The resulting set of homogeneous ligands consisted of

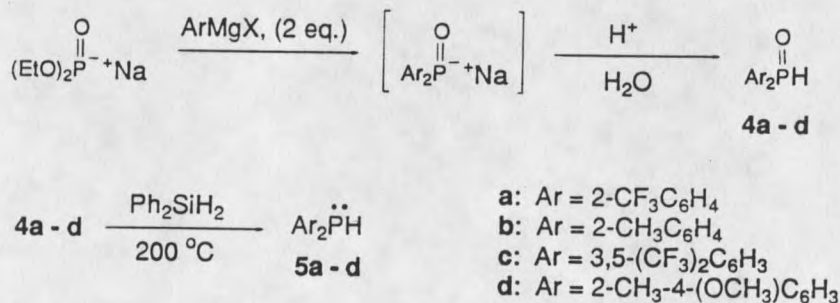
electronic and torsional derivatives of the commercially available (4*R*,5*R*)-(+)-DIOP ligand **3a**.

The synthesis of this family of Type A bisphosphine ligands involved double substitution of the corresponding (4*R*,5*R*)-4,5-bis(*p*-tosyloxymethyl)-1,3-dioxolanes^{3d} with various diaryl metallophosphides. The ligands **3b-3g** were prepared as follows (Scheme 17). The formation of the



Scheme 17

desired potassium diarylphosphide was effected by deprotonation (KH, THF) of the corresponding diarylphosphine (**5a-5e**) at $-78\text{ }^\circ\text{C}$. To the resulting deep red solutions were



Scheme 18

added 0.5 equivalent of a (4*R*,5*R*)-4,5-bis(*p*-tosyloxymethyl)-1,3-dioxolane (6a-6c) in THF (-78 °C). The resulting mixtures were subsequently stirred at 25 °C until disubstitution was complete, as determined by TLC and GC analysis. Following the method of Hobbs,⁶¹ the diaryl monophosphine precursors were prepared as shown in Scheme 18. Treatment of sodium diethylphosphinite with the desired aryl Grignard reagent (2 equiv.) in THF (or Et₂O), followed by acidic work-up gave rise to the corresponding diarylphosphine oxides (4a-4d). Subsequent reduction with diphenylsilane afforded the diaryl phosphines 5a-5d in nearly quantitative yields.

Enantioselective [4+2] Cycloisomerization

The use of these new bisphosphine ligands as chiral modifiers in the Rh(I) catalyzed [4+2] cycloisomerization reaction resulted in moderate to good levels of enantioselection in representative ene-diene and diene-yne substrates (7a-c and 10, Figure 15). The catalytic species were generated *in situ* by the addition of the bisphosphine ligand (1 equiv./equiv. Rh) to a solution of [RhCl(C₆H₁₄)₂]₂ in CH₂Cl₂ (or THF) in a manner analogous to that described previously. The enantioselectivity of the cyclization was quantified by conversion of the product bicycles 8a, b and 11 to a diastereomeric mixture of Mosher's esters¹⁰² 13a, b

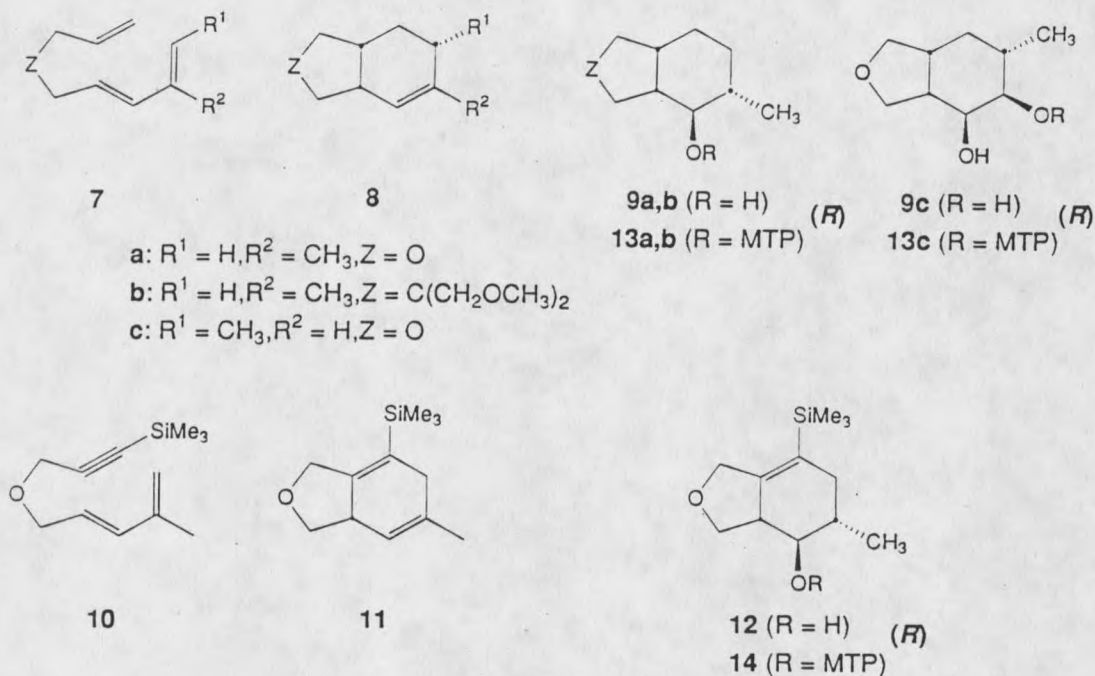


Figure 15. Ene-diene and Diene-yne Substrates

and 14 via hydroboration / oxidation [(a) BMS, (b) H_2O_2 , OH^-] followed by esterification. For the cycloadduct 8c, catalytic bis-hydroxylation (OsO_4/NMO) followed by *selective* esterification of the *equatorial* hydroxyl of the resulting diol 9c, was used to prepare the Mosher ester 13c. In all cases, the corresponding racemic Rh(I) catalyzed cyclizations were performed by using $(i\text{-C}_3\text{F}_6\text{HO})_3\text{P}$: as the achiral modifier so that accurate product analysis and ee determinations could be made. The results obtained for the asymmetric Rh(I) catalyzed intramolecular [4+2] cycloisomerization of ene-dienes and diene-ynes are summarized in Table 5.

The absolute stereochemistry of the cycloadducts was assigned by using the method first described by Mosher.¹⁰² As shown in the Newman projections (Figure 16), the methyl group syn to the phenyl ring is further upfield in 13a(*R*) due to through-space interaction with the phenyl moiety on the MTPA ester. The ratios of diastereomers for 13a, 13c and 14 were measured by integration of the ester methine proton resonances, which were well resolved at 300 MHz, at

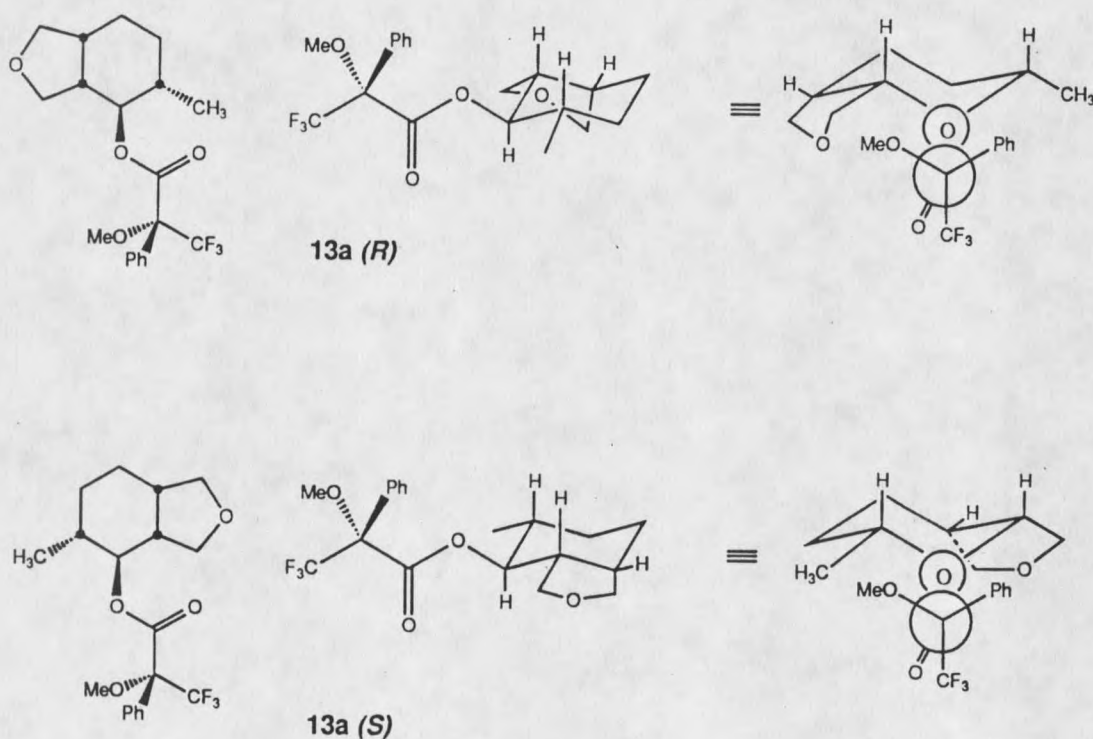


Figure 16. Absolute Configuration of Cycloadducts

4.81 and 4.91 ppm for 13a, at 4.85 and 4.95 ppm for 13c and at 4.82 and 4.92 ppm for 14. The ester methine proton resonances for the two diastereomeric esters of 13b were

Table 5. Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations Mediated by Homochiral Bisphosphines

Entry	Cycloadduct ^a	Ligand	Isolated Yield (%)	Ester	de ^{ab}
1	8a	3a	86	13a	7(R)
2	8a	3b	79	13a	20(S)
3	8a	3c	73	13a	11(S)
4	8a	3d	85	13a	2(R)
5	8a	3e	72	13a	42(S)
6	8a	3f	79	13a	62(R)
7	8a	3g	92	13a	10(R)
8	8b	3a	83	13b	10(R)
9	8b	3e	69	13b	67(S)
10	8b	3f	83	13b	28(R)
11	8c	3a	84	13c	73(R)
12	8c	3b	73	13c	47(S)
13	8c	3c	72	13c	54(S)
14	8c	3d	76	13c	2(R)
15	11	3a	89	14	52(R)
16	11	3b	76	14	87(S)
17	11	3e	81	14	37(S)
18	11	3f	99	14	42(S)
19	11	3g	91	14	13(R)

^aEster de = cycloadduct ee. ^bR or S refers to the stereochemistry of the carbon bearing the MTPO group in the esters 13a-c and 14.

resolved at 500 MHz at 4.82 and 4.86 ppm. Absolute stereochemical assignments for the Mosher's esters 13b, c and 14 were made in a similar fashion.

The data suggests that both the magnitude and the *absolute sense* of asymmetric induction are affected by this homogeneous set of bisphosphines.

Torsional alteration of the 1,3-dioxolane ring, via ketal substitution, has been suggested to result in a

perturbation of the conformational array of the aryl substituents on phosphorus.^{9,85,88,103,104}

The observed reversal in the absolute sense of asymmetric induction when ligands 3b and c were used relative to 3a (entries 2, 3, 12, 13 and 16) may have been due to an altered "edge-face"¹⁰³ arrangement of the aryl groups. Both the facial approach and subsequent binding of the substrate to the rhodium center may have been significantly adjusted.

Such conformational alteration may also arise from the substitution of bulky groups at the 2-position of the respective phenyl rings on phosphorus. Substantial variations in ee's, relative to 3a, were observed when ligands 3e and 3f [bearing 2-(methyl)phenyl and 2-(trifluoromethyl)phenyl phosphine substituents respectively] were used (entries 5-6, 9-10 and 17-18). The aryl substituents in these cases were expected to exert a large degree of steric "pseudochirality" at phosphorus.¹⁰⁵ However, a reversal of absolute stereoinduction was observed only for the ligand bearing a 2-(methyl)phenyl substituent (3e) compared to 3a (entries 5, 9 and 17). For the dien-yne substrate 10, however, the employment of ligands 3e or 3f as the chiral modifiers did induce reversed absolute stereoinduction suggesting that the asymmetric mode of cyclization may also be substrate dependent (entry 18). Furthermore, a comparison of entries 1, 4, 11 and 14 reveals

that the magnitude of asymmetric induction is not influenced by electronic effects alone, but rather a combination of electronic and steric factors. That torsional effects derived from 1,3-dioxolane substitution may interfere with electronic/steric perturbations at phosphorus can be ascertained by comparing entries 2, 7, 16 and 19. The first instances of reversed absolute stereoinduction derived from bisphosphine structure variations, within a homogeneous set, have been established for carbocyclizations with the preceding examples.

Homochiral Bisphosphino Hexane and Pentane Ligands

Our motivation for developing a second generation of homochiral bisphosphine ligands originated more from our interests in ligand design than from our desire to optimize the asymmetric [4+2] cycloisomerization reaction. The series II ligands described below are divided into two categories: (1) electron rich and (2) electron deficient bisphosphines. Within each of these subclasses, we prepared novel, Type A homochiral bisphosphines which would give rise to both 6- and 7-membered transition-metal chelates.

In a manner similar to that previously described the electron deficient bisphosphines 15a,b and 16a were prepared from (2*S*,5*S*)-2,5-dihydroxyhexane and (2*S*,4*S*)-2,4-dihydroxypentane respectively (Figure 17).

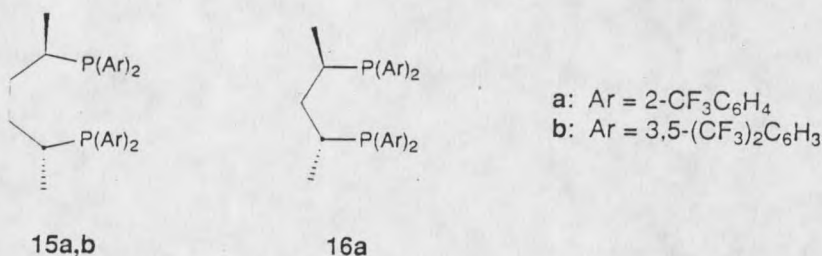


Figure 17. Electron Deficient Bisphosphines Derived from (2*S*,5*S*)-2,5-dihydroxyhexane and (2*S*,4*S*)-2,4-dihydroxypentane.

A solution of the respective ditosylates (0.5 equiv. in DMF) was added to a preformed solution (THF) of the desired potassium diarylphosphide at -50 °C. The resulting mixtures were then stirred at 25 °C until complete alkylation had occurred. Since these ligands constitute 1- and 2-carbon homologs of CHIRAPHOS, a degree of structural rigidity should be guaranteed by their chiral carbon frameworks through the conformational limitations within the potential chelate rings.

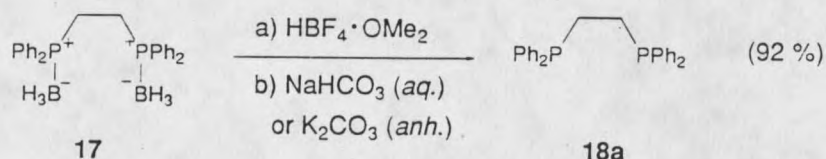
Phosphine-Borane Decomplexation with HBF₄·OMe₂

In a concurrent study aimed at the rational design of homochiral monophosphine precursors in which chirality resides at phosphorus, we discovered a facile method for the efficient decomplexation of phosphine-boranes. Typical procedures employed for converting such complexes into free-phosphines involve heating the borane-adducts with a large excess of a secondary amine (e.g., morpholine or

diethylamine)^{35b} or a stoichiometric quantity of DABCO.³⁷

This method finds its limitations in that hindered, *highly basic* phosphines typically require more vigorous reaction conditions for successful amine mediated exchange.

In a model system, treatment of DPPE·(BH₃)₂ (Eq. 18, (17)) with a variety of acids,^{59b} including CH₃SO₃H [(5 equiv/equiv BH₃), CH₂Cl₂, -5 °C → 25 °C, 12 h] followed by hydrolysis (NaHCO₃ aq., 0 °C) (Eq. 18).¹⁰⁶ Of the various acids examined, HBF₄·OMe₂ proved to be the most effective



Eq. 18

in terms of rate and isolated yield of free phosphine. Although reaction conditions can be modified to suit a particular phosphine-borane, we utilized a *standard* set of conditions (Eq. 18) for the decomplexation of representative bisphosphine-boranes (Figure 18).

¹H NMR analysis of methyldiphenylphosphine-borane (22) decomplexation with HBF₄·OMe₂ (1 equiv) in CDCl₃ revealed consumption of 22 with concomitant formation of a product possessing a down field shifted methyl doublet of doublets at 2.41 ppm (J^{H-P}=15.22 Hz and J^{H-F}=5.82 Hz) (Eq. 19). In addition, ³¹P NMR analysis revealed the formation of a product possessing an upfield shifted resonance at 1.98 ppm

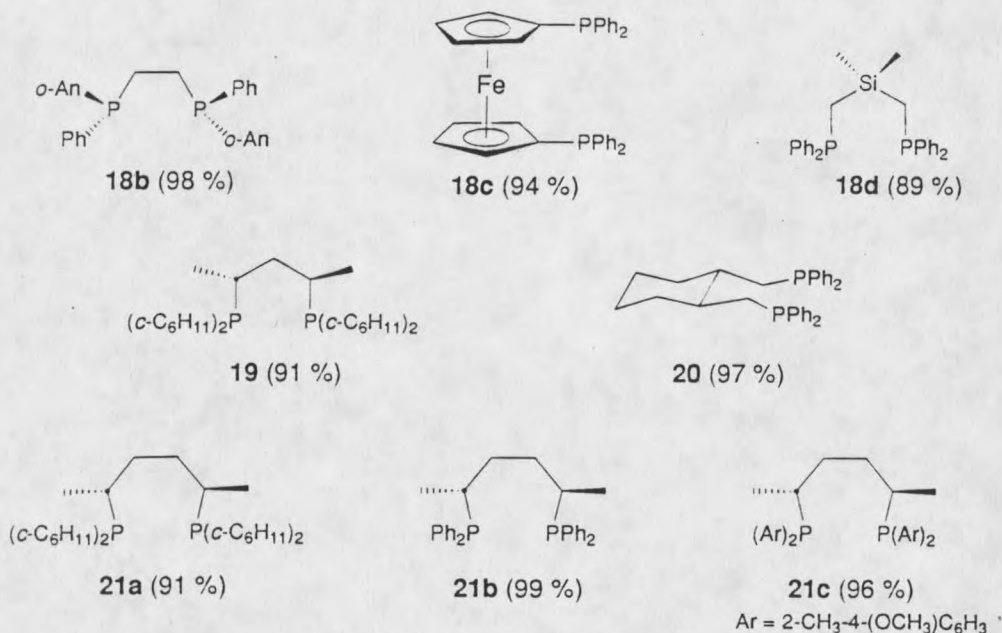
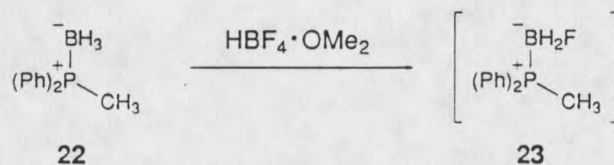


Figure 18. Decomplexation of Bisphosphine-Borane Adducts



Eq. 19

(doublet of multiplets, $J^{\text{P-F}} = 521 \text{ Hz}$). The appearance of these new resonances¹⁰⁷ is consistent with the intermediacy of the phosphine-fluoroborane complex 23.

An alternative work-up may also be employed in order to eliminate the aqueous hydrolysis step. A solution of the fluoro-borane intermediate (derived from the reaction of $\text{DPPE} \cdot (\text{BH}_3)_2$ (17) and $\text{HBF}_4 \cdot \text{OMe}_2$) can be treated with excess

anhydrous K_2CO_3 for several hours. The free phosphine 18a is subsequently obtained in essentially quantitative yield by filtration and concentration *in vacuo* (Eq. 18).

Electron Rich Homochiral Bisphosphines

Through the use of the above decomplexation procedure the novel electron rich bisphosphines 19, 20a and 21a-c (Figure 18) were prepared from the corresponding diborane

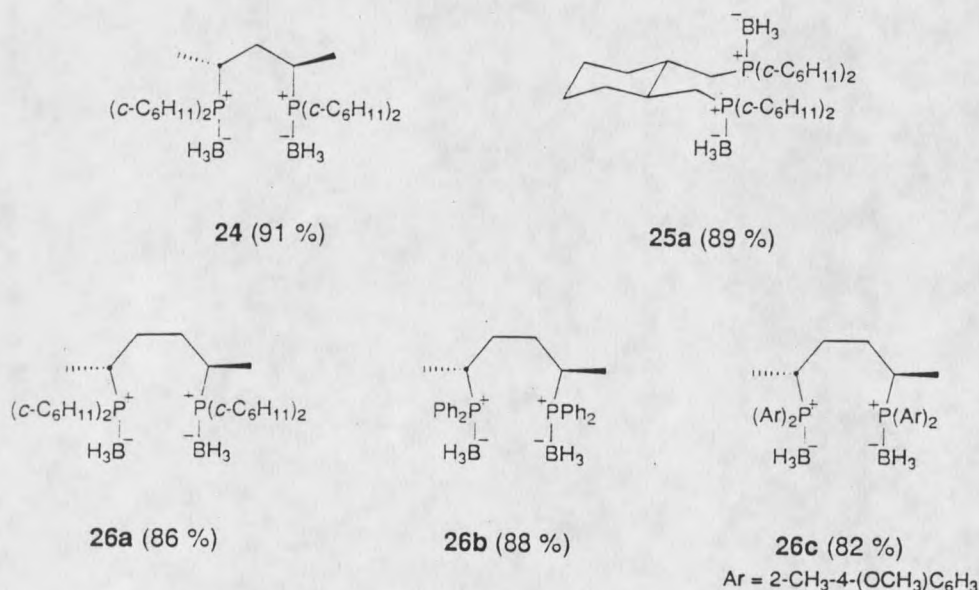
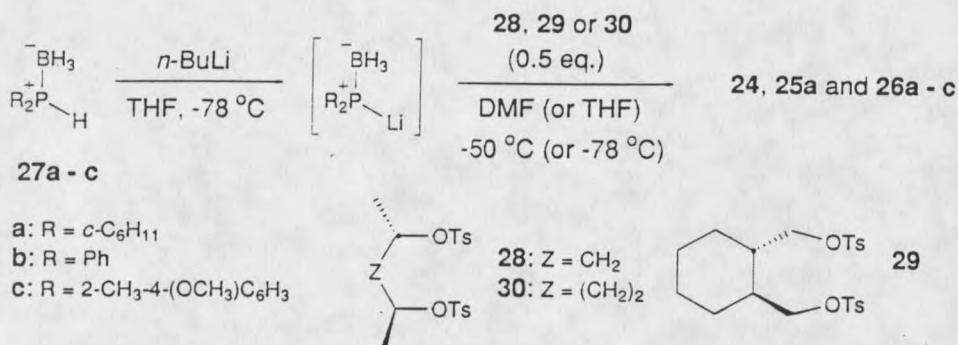


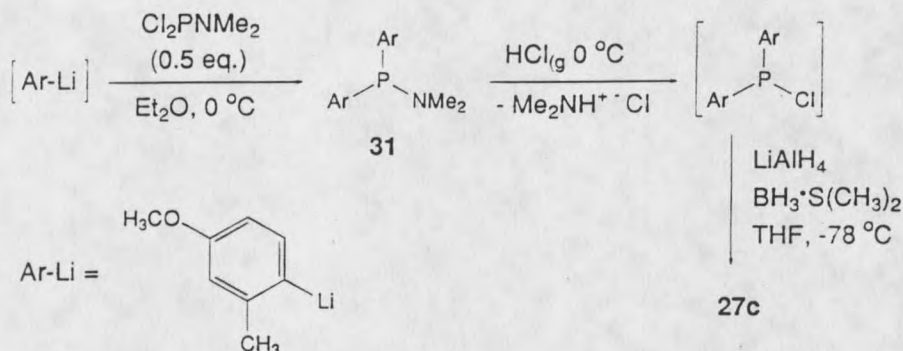
Figure 19. Electron Rich Homochiral Bisphosphine-Boranes adducts 24, 25a and 26a-c (Figure 19). Accordingly, alkylation of lithium boronatodialkylphosphide (or boronatodiarylphosphide) in DMF (or THF/HMPA) at $-50\text{ }^\circ\text{C}$ (or $-78\text{ }^\circ\text{C}$) with the desired ditosylate (28, 29 or 30) (Scheme 19) provided the bisphosphine-borane adducts in



Scheme 19

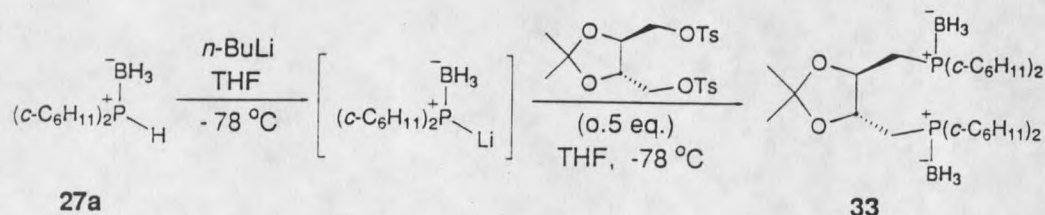
excellent yields (Figure 19). Decomplexation (HBF₄·OMe₂, CH₂Cl₂, -5 °C → 25 °C) provided the corresponding homochiral bisphosphines in excellent yields (Figure 18).

The secondary boronatophosphines 27a and b were prepared from commercially available dicyclohexylphosphine and diphenylphosphine respectively, by treatment with 1.1 equivalents of BH₃·S(CH₃)₂ (10.2 M solution containing free SMe₂). The preparation of the boronatodiarylphosphine 27c was as follows (Scheme 20). To a solution of Cl₂PNMe₂¹⁰⁹ in Et₂O 0 °C), was added 2 equivalents of 4-lithio-3-methylanisole.¹¹⁰ The mixture was warmed slowly to 25 °C. After distillation (*in vacuo*) the resulting N,N-dimethylaminodiarylphosphine (31) was treated with anhydrous HCl (Et₂O, 0 °C). Subsequent filtration and concentration of the chlorodiarylphosphine was then followed by reduction/complexation (LiAlH₄/BH₃·S(CH₃)₂) in a manner analogous to that described by Imamoto (Eq. 8).^{35b}



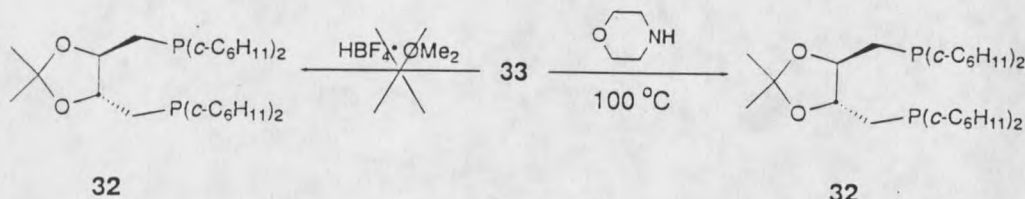
Scheme 20

The electron rich ligand Cy-DIOP (32), derived from (L)-tartrate, was also prepared by the reaction of lithium boronatodicyclohexylphosphide with (4*R*, 5*R*)-4,5-bis(*p*-tosyloxymethyl)-2,2-dimethyl-1,3-dioxolane (THF, -78°C) to give the bisphosphine-borane adduct (33) in 86% yield (Scheme 21). Decomplexation of 33 could not be effected by treatment with $\text{HBF}_4\cdot\text{OMe}_2$ without significant ketal cleavage (Eq. 20). The Cy-DIOP bisphosphine was, however, obtained in high yield from 33 by treatment with excess morpholine (100°C). This procedure constitutes the most efficient



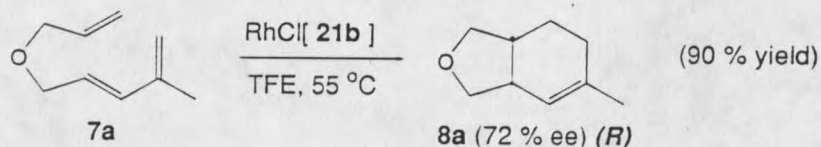
Scheme 21

synthesis to date of this highly electron rich bisphosphine.^{42c}



The conventional methods for preparing such electron rich phosphines, involving alkylation of *strongly basic* dialkyl (or diaryl) metallophosphides with a homochiral ditosylate (or dihalide),^{42c} often results in diminished yields. This occurs as a consequence of competing side reactions (e.g., base mediated elimination). The previously described procedure, when utilized with the $\text{HBF}_4 \cdot \text{OMe}_2$ decomplexation method, is a convenient and highly efficient method for synthesizing a wide range of stereochemically varied mono- and bisphosphines.

Concurrent with the above research we briefly examined the efficacy of the hexane derived ligands (21a-c) as chiral modifiers for the asymmetric [4+2] cycloisomerization reaction. Through the use of (2*R*,5*R*)-2,5-bis(diphenylphosphino)hexane (21b), we obtained an ee of 72% for the cycloisomerization of precycloadduct 7a (Eq. 21). This result was not surprising since ligand homochirality was now in a closer proximity to the actual site of catalysis.



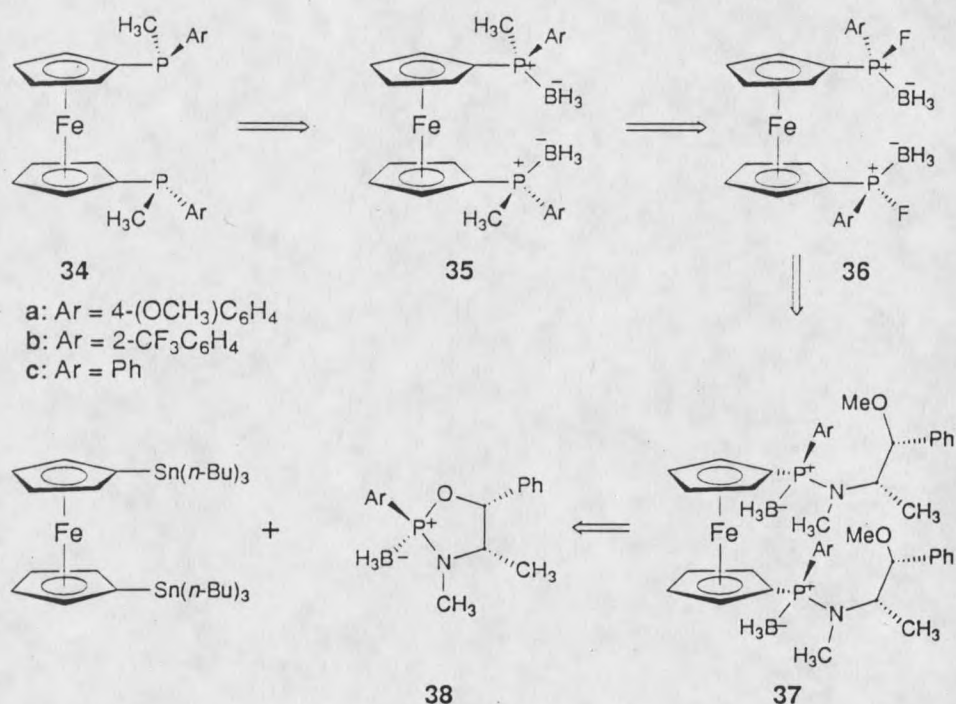
Eq. 21

Design of Phosphorus-Centered Homochiral
Bisphosphino Ferrocene Ligands

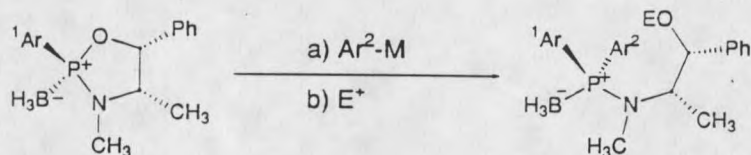
Our interests in designing ligands for asymmetric catalysis also encouraged the development of a third generation of homochiral bisphosphines in which the chirality resides at phosphorus. The introduction of an efficient method for preparing a set of sterically and electronically distinguished ferrocenyl bisphosphines (**34a-c**) was our specific goal (Scheme 22).

Retrosynthetic analysis suggested the diborane adducts **35a-c** to arise from hydrogen fluoride cleavage of both phosphorus-nitrogen bonds of the bis(boronatoaminophosphino)ferrocenes (**35a-c**) followed by alkylation of the resulting bis(fluorophosphino)ferrocenes (**36a-c**). The former step in which the ephedrine moiety would be removed was anticipated to proceed without a loss of the stereochemistry at phosphorus. We envisioned the utilization of a strategy established by Juge³² and Brown³⁴

for the formation of boronatodiarylamino phosphines from oxazaphospholidine-boranes (Eq. 22). Accordingly, tandem



Scheme 22



Eq. 22

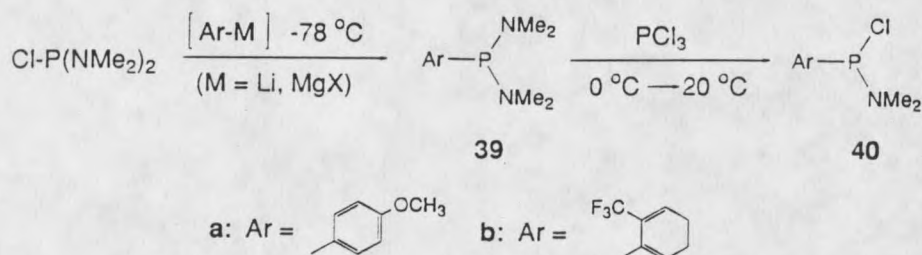
ring opening of the desired oxazaphospholidine boranes with 1,1'-dilithioferrocene could likely give rise to the bis(boronato-aminophosphino)ferrocenes 37a-c. In the course

of these investigations we devised an *improved* procedure for synthesizing 2-substituted 3,4-dimethyl-5-phenyl oxazaphospholidine-borane derivatives (38a-c). The pursuit of this initial strategy for preparing homochiral ferrocenyl bisphosphines is described below.

The synthesis of oxazaphospholidine-boranes was originally described by Juge and Brown (Scheme 5).^{32,34} These approaches utilize a thermal condensation of bis(diethylamino)phenyl phosphine with (-)-ephedrine followed by borane complexation. The thermal condensation reaction described for these procedures was found to be very unreliable for a diverse set of bis(diethyl)aryl phosphines.¹¹² The methodology developed in our laboratories involved initial phosphorus-oxygen bond formation, via ionic coupling with chloro(dimethyl)amino phosphines, followed by thermal cyclization. Borane complexation was then achieved *in situ* with $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$. This highly efficient method has been utilized in our laboratories to prepare a wide range of oxazaphospholidine derivatives.¹¹² Also, several of these chiral precursors are currently being incorporated into the synthesis of electronically and sterically differentiated homochiral bisphosphine ligands.

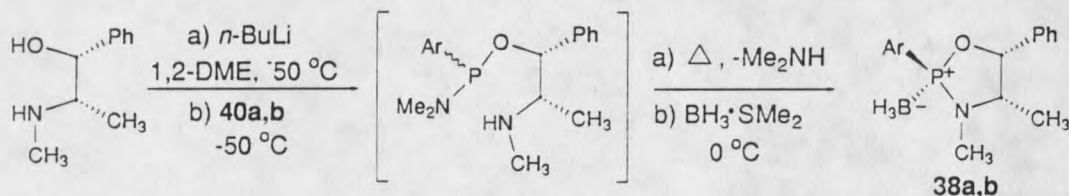
Bis(dimethylamino)arylphosphines 39a,b (Scheme 23) derived by the reaction of the requisite organolithium (or Grignard) reagents with chloro-bis(dimethylamino)phosphine¹⁰⁹ ($-78^\circ\text{C} \rightarrow 20^\circ\text{C}$) were treated with 1.0 equivalent of PCl_3 ,

(0 °C → 20 °C) to give the corresponding chloro(dimethylamino)arylphosphines (**40a,b**). Dropwise addition of the desired chloro(dimethylamino)arylphosphine



Scheme 23

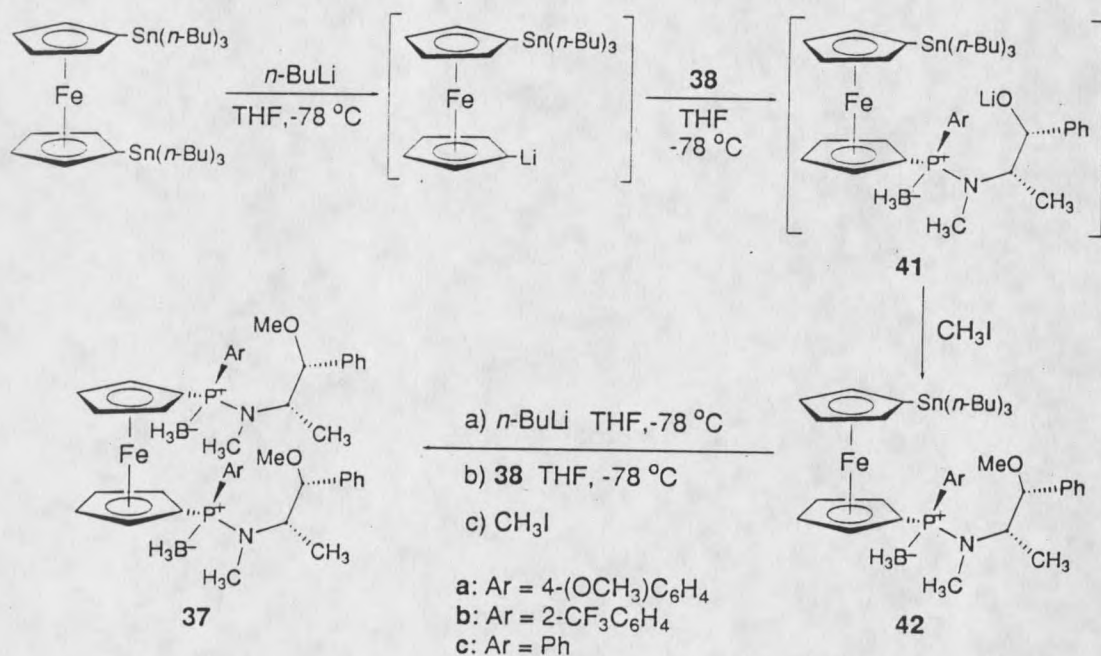
to a preformed solution of monolithiated (-)-ephedrine in 1,2-DME (-50 °C) was followed by vigorous stirring and warming to 20 °C (Scheme 24). Subsequent thermal



Scheme 24

cyclization was achieved by heating at reflux for 12-18 h¹¹³ with concomitant expulsion of Me₂NH. Borane complexation (1.1 equiv. of BH₃·S(CH₃)₂, 0 °C) was then accomplished *in situ* to form the corresponding oxazaphospholidine-borane complexes (**38a,b**) in excellent yield after recrystallization.

The bis(boronatoamino-phosphino)ferrocenes (37a-c) were prepared by the sequential alkylation the desired oxazaphospholidine-boranes with lithioferrocene. As shown in Scheme 25, monolithiation of bis(tri-*n*-butylstannyl)ferrocene with *n*-BuLi (THF, -78 °C, 1 h)¹²⁹



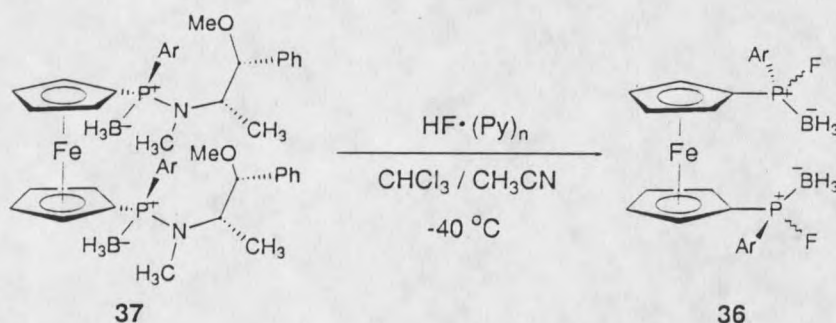
Scheme 25

followed by addition of 38a-c (1.05 equiv. in THF, -78 °C) with warming to -20 °C afforded reaction mixtures containing the lithium alkoxides 41a-c. Subsequent reaction with CH₃I (10 equiv., -20 °C) gave rise to the tri-*n*-butyl stannyl-ferrocenyl aminophosphine-boranes (42a-c). The second oxazaphospholidine moiety was added in an analogous manner to afford the bis(boronato-aminophosphino)ferrocenes 37a-c in good yields. A concurrent study conducted by Meigun

Jiang, formerly of these laboratories, revealed that the acid catalyzed methanolysis of aminophosphine borane derivatives proceeded in excellent yield with high stereoselectivity. In agreement with the findings of Juge,³⁴ Jiang obtained the highest selectivities with CH_3OH in the presence of 0.125 M H_2SO_4 or alternatively $\text{CH}_3\text{SO}_3\text{H}$.^{114a}

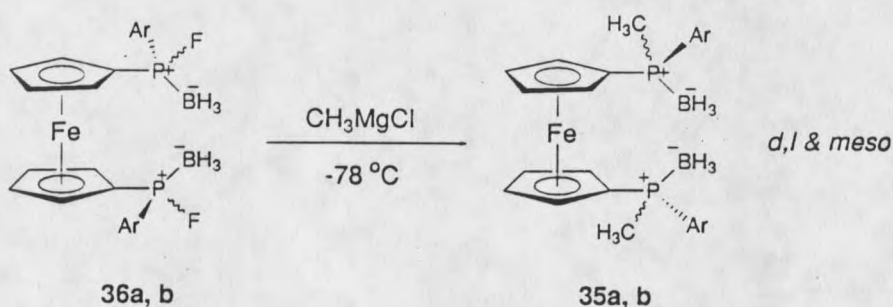
In a similar manner, we treated the ferrocenyl aminophosphine-boranes 37a-c with 0.125 M H_2SO_4 in CH_3OH at 0 °C with warming to 20 °C (Scheme 26). To our dismay, the ferrocene component proved to be quite unstable under these reaction conditions. This led to the pursuit of alternative methods for the conversion of ferrocenylaminophosphine-boranes to subsequent ligand precursors.

The hydrofluorination of 37a-c with $\text{HF} \cdot (\text{Py})_n$ (5 equiv./equiv. P-N) in $\text{CHCl}_3/\text{CH}_3\text{CN}$ was conducted at -40 °C for 5 days to give rise to the corresponding fluorophosphine borane complexes (36a-c) in excellent yield (Scheme 26). Both ^1H and ^{31}P NMR as well as HPLC (*non-chiral*) analysis indicated formation of a single product, which suggested the reaction proceeded with either *complete* inversion or *complete* retention of configuration at phosphorus. Displacement of the resulting fluorophosphine-borane derivatives with CH_3MgCl (Et_2O or THF, -78 °C) revealed that the hydrofluorination reaction may not have been stereoselective since phosphorus stereochemistry had indeed



Scheme 26

been scrambled in the two step reaction sequence (Scheme 27).



Scheme 27

This observation was verified in studies conducted by Jiang in which several related mono-aminophosphine-borane complexes were treated with $\text{HF}\cdot(\text{Py})_n$. According to Jiang, in every case the fluorophosphine boranes were formed in essentially racemic mixtures as determined by *chiral* HPLC. Jiang further demonstrated that neither solvent polarity, temperature nor phosphorus structure significantly improved the stereochemical outcome in this reaction.

We rationalized the observed racemization as having been due to a strong affinity of the phosphine for unsolvated fluoride ions. Umezawa reported that in $\text{HF}-(\text{amine})_n$ reagents, the concentration of free fluoride increases with less basic amines.¹³⁰ Even in the polar solvent CH_3CN , the fluoride concentration must have been exceedingly high. A thorough investigation of the hydrofluorination of mono-aminophosphine-boranes was conducted by Jiang.^{114a} Furthermore, the utilization of $\text{BF}_3 \cdot \text{OEt}_2$ as a fluoride ion scavenger is currently under investigation in our laboratories.

Within the scope of ferrocene ligand synthesis, the search for efficient methods to circumvent these stereochemical problems is ongoing in our laboratories as the rational design of homochiral bisphosphines continues.

CONCLUSION

Highly versatile methods for synthesizing homochiral 1,4 and 1,3 bisphosphines of two discreet structural families have been developed. A homogeneous set of electronic and torsional derivatives of the bisphosphine (4*R*,5*R*)-(+)-DIOP have been efficiently prepared from commercially available (L)-tartaric acid. The comprehensive synthesis of novel, *electron-rich*, carbon-centered, homochiral 1,4 and 1,3-bisphosphines was achieved via a newly developed, facile method for phosphine-borane decomplexation. The influence of 1,4-bisphosphine structure on the efficiency and stereochemical outcome of Rh(I) catalyzed intramolecular [4+2] cycloisomerizations of enedienes and dien-ynes was investigated. Both the magnitude and absolute sense of asymmetric induction were affected by ligand architecture. Furthermore, a practical approach to the synthesis of a family of sterically and electronically distinguished homochiral bisphosphinoferrocene ligands was introduced. The installation of homochirality at phosphorus was achieved, for ligand precursors, through the use of 2-substituted 3,4-dimethyl-5-phenyl oxazaphospholidine-borane complexes prepared by a substantially *improved* method.

EXPERIMENTAL

Physical Data: ^1H NMR and ^{13}C NMR were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. ^{31}P NMR was measured at 202 MHz with a Bruker AM-500 spectrometer. ^1H NMR chemical shifts are reported as δ values in ppm relative to the residual protons of CDCl_3 (7.24) or C_6D_6 (7.15). ^{13}C NMR chemical shifts are reported as δ values in ppm relative to CDCl_3 (77.0) or C_6D_6 (128.0). ^{31}P NMR chemical shifts are reported as δ values in ppm relative to H_3PO_4 (85%) (0.0) or triphenylphosphine (-6.0). ^1H NMR and ^{31}P NMR coupling constants are reported in Hz and refer to real or apparent multiplicities which are indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); sx (sextet); br (broad); m (multiplet); app d (apparent doublet); app t (apparent triplet); dd (doublet of doublets); etc.

High-resolution mass spectra were measured on a VG Analytical 7070E spectrometer by Dr. L. J. Sears. Infrared spectra were recorded with either a Bruker IFS 25 IR, a Perkin-Elmer 1800 FTIR or a Perkin-Elmer 237B grating IR.¹¹⁵ Melting points were determined with either a Fisher-Johns or a Mel-Temp II melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. Elemental Analysis was performed by Desert Analytics, Tucson, AZ.

Chromatography: Analytical gas chromatography was performed on a Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3390A reporting integrator and a 15m X 0.54mm ID column with DB5 (or SE-45 or equivalent) bonded phase. Preparative gas chromatography was performed on a Varian Model 3300 Gas Chromatograph equipped with a thermal conductivity detector, a Hewlett-Packard 3390A reporting integrator and a 1.8m X 4mm column with a 10% silicone OV-17 chromosorb adsorbent phase.

High Performance Liquid Chromatography was performed on an IBM LC/9533 Ternary Gradient Liquid Chromatograph equipped with an IBM LC/9523 Variable UV Detector. For general analytical separations an IBM 250mm X 4.5mm ID column packed with IBM 5 μ m spherical silica was used in conjunction with a Linear Model 156 chart recorder. For chiral separations a CHIRALPAK¹¹⁶ AD 250mm X 4.6mm ID column packed with Amylose tris(3,5-dimethylphenyl carbamate) coated on a 10 μ m silica-gel substrate was used in conjunction with a Hewlett-Packard 3390A reporting integrator.

Thin layer chromatography was performed on plates supplied by Alltech Associates (K42-G). Visualization of plates was accomplished by one or more of the following: a) UV illumination; b) exposure to I₂ vapor; c) KMnO₄ oxidation; or d) anisaldehyde derivatization. All column

chromatography was performed according to Still¹¹⁷ on E. Merck 230-400 ASTM mesh, 0.040-0.063 mm particle size, silica gel 60. Solvent systems used for elution are reported in % volume/volume.

Materials: Tetrahydrofuran (THF), 1,2-dimethoxyethane (1,2-DME), benzene, heptane and hexane were distilled from K. Diethyl ether (Et₂O) was distilled from Na-benzophenone. Dimethylformamide (DMF) was distilled from CaH₂ at 20 torr, while dichloromethane (CH₂Cl₂), acetonitrile (CH₃CN), toluene, 2-butanol and 2,2,2-trifluoroethanol (TFE) were distilled from CaH₂ at atmospheric pressure under an inert atmosphere of argon or nitrogen. Purification of methanol was accomplished by distillation from Mg(OCH₃)₂ under an atmosphere of argon.

The molarities indicated for organolithium reagents were established by titration with a standard solution of 2-butanol in xylene using 1,10-phenanthroline as indicator. Grignard reagents were titrated in the same manner. Periodically these reagents were titrated for total base content with a standard solution of potassium biphthalate using phenolphthalein as indicator.

All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried vessels. Concentrations were performed under reduced pressure with a Buchi rotary evaporator and "drying" of an organic solution was accomplished with anhydrous Na₂SO₄ or MgSO₄.

Ligand Synthesis -- Phosphine Substituents

Bis(2-trifluoromethylphenyl)phosphine Oxide (4a).¹¹⁸ An oven-dried three-necked round-bottomed flask was fitted with a pressure equalizing addition funnel, condenser and magnetic stirring bar. The vessel was charged with Mg powder (-50 mesh, 99+%) (4.86 g, 0.200 mol) and purged with nitrogen. THF (20 mL) was then added followed by 2-bromobenzotrifluoride (4.13 g, 0.0180 mol) by syringe. The reaction mixture was gently heated in order to initiate the Grignard reaction. The remainder of the 2-bromobenzotri-fluoride (41.4 g, 0.184 mol) was dissolved in THF (60 mL) and added to the activated Mg mixture over a period of 1 h. Subsequently, the reaction mixture was refluxed for an additional 2 h. Meanwhile, an oven-dried, round-bottomed flask was charged with NaH (60% oil dispersion, 4.00 g, 0.100 mol) and the oil was removed by trituration with pentane (3 x 15 mL). THF (75 mL) was then added and the flask was purged with nitrogen. The mixture was cooled to 0 °C and freshly distilled diethyl phosphite (13.8 g, 0.100 mol) was added dropwise over a period of 15 min. The grey slurry was then warmed to 25 °C and stirred for an additional 1 h. The resulting solution of sodium diethyl phosphite was added via cannula to the 2-trifluoromethylphenylmagnesium bromide mixture at 0 °C over a period of 1 h. Subsequently, the reaction mixture

was refluxed for 8 h. After cooling to 0 °C, conc. HCl (40 mL) in cold water (80 mL) was added slowly whereupon a small quantity of tan ppt. formed in the red solution. This mixture was poured into a separatory funnel containing Et₂O (200 mL) and water (100 mL). The organic layer was separated and the aqueous layer was extracted with Et₂O (2 x 20 mL). The organic layers were combined, washed with water (2 x 10 mL), dried (MgSO₄) and the solvents were evaporated under reduced pressure. The resulting tan solid was purified by bulb-to-bulb sublimation (160 °C, 25 μ torr) to yield 24.4 g (72%) of 4a as a yellow crystalline material: mp 124.2-126.8 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.54 (d sept., J = 2.8, J^{P-H} = 537 Hz, 1H, P-H), 7.96 (m, 1H, Ar-H), 7.92 (m, 1H, Ar-H), 7.77 (m, 2H, Ar-H), 7.70 (m, 4H, Ar-H); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 134.5 (CH), 134.4 (CH), 132.7 (CH), 132.0 (CH), 131.9 (CH), 130.0 (C), 127.0 (CH), 125.5 (C), 121.7 (C); ³¹P NMR (202 MHz, CDCl₃) δ 9.0 (d, J^{H-P} = 538 Hz); IR (KBr) 1314, 1170, 1118, 1036, 940, 770, 700, 516 cm⁻¹. Anal. Calcd for C₁₄H₉F₆OP: C, 49.69; H, 2.68; F, 33.72. Found: C, 49.40; H, 2.67; F, 33.83.

Bis(2-trifluoromethylphenyl)phosphine (5a).¹¹⁸ An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with 4a (1.50 g, 4.66 mmol) and purged with nitrogen. Diphenylsilane (903 mg, 4.89 mmol) was then added by syringe

at 25 °C. The reaction mixture was heated and stirred at 140 °C for 30 min whereupon it became homogeneous. The solution was then stirred at 210 °C, for 2.5 h.

Subsequently, the phosphine was distilled directly from the reaction mixture (40 °C, 10 μ torr) to provide 1.40 g (93%) of 5a as a clear viscous oil.

Bis(2-methylphenyl)phosphine Oxide (4b).⁴³ The reaction of 2.0 equivalents of 2-methylphenylmagnesium bromide (9.8 g, 0.050 mol) with sodium diethyl phosphite (4.0 g, 0.025 mol) in Et₂O (50 mL) was carried out as described for the 2-trifluoromethylphenyl analogue 4a.

Bis(2-methylphenyl)phosphine (5b).⁴³ The reduction of 4b (1.50 g, 6.51 mmol) with diphenylsilane was carried out as described above for 4a.

Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c). The reaction of 2.0 equivalents of 3,5-bis(trifluoromethyl)phenylmagnesium bromide (15.9 g, 0.050 mol) with sodium diethyl phosphite (4.0 g, 0.025 mol) in Et₂O (50 mL) was carried out as described for the 2-trifluoromethylphenyl analogue 4a. When the reaction was complete, the mixture was cooled to 0 °C and conc. HCl (8.5 mL) in cold water (16.5 mL) was added slowly. This mixture was poured into a separatory funnel containing Et₂O (50 mL) and water (25 mL). The organic layer was separated and the aqueous layer was extracted with Et₂O (2 x 5 mL). The organic layers were

combined, washed with water (2 x 2.5 mL), brine (5 mL), dried (MgSO_4) and the solvents were evaporated under reduced pressure. The resulting tan solid was washed with a 30% Et_2O / pentane solution (4 x 10 mL) to yield 8.18 g (69%) of **4c** as a light yellow solid. This material was further purified by sublimation: mp 122.7-124.5 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.29 (d, $J^{\text{H-P}} = 506$ Hz, 1H, P-H), 8.20 (s, 2H, Ar-H), 8.16 (s, 2H, Ar-H), 8.13 (s, 2H, Ar-H); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 132.5 (C), 130.7 (CH), 127.2 (CH), 124.3 (C), 120.7 (C); ^{31}P NMR (202 MHz, CDCl_3) δ 14.3 (dt, $J = 11.8$ Hz, $J^{\text{P-H}} = 505$ Hz); IR (film) 1370, 1285, 1190, 1150, 910 cm^{-1} . Anal. Calcd. for $\text{C}_{16}\text{H}_7\text{F}_{12}\text{OP}$: C, 40.51; H, 1.49; F, 48.09. Found: C, 40.27; H, 1.41; F, 47.71.

Bis[3,5-bis(trifluoromethyl)phenyl]phosphine (5c). The reduction of **4c** (1.50 g, 3.15 mmol) with diphenylsilane was carried out as described above for **4a**. The phosphine was distilled directly from the reaction mixture (65 °C, 10 μtorr) to provide 1.29 g (89%) of **5c** as a white solid.

Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d). The reaction of 2.0 equivalents of 4-methoxy-2-methylphenyl-magnesium bromide¹¹⁹ (10.5 g, 0.050 mmol) with sodium diethyl phosphite (4.0 g, 0.025 mol) in Et_2O (50 mL) was carried out as described for the 2-trifluoromethylphenyl analogue **4a**.

^1H NMR (500 MHz, C_6D_6) δ 8.06 (d, $J^{\text{H-P}} = 471$ Hz, 1H, P-H), 7.67 (dd, $J = 15.1, 9.1$ Hz, 2H, Ar-H), 6.66-6.57 (m, 4H, Ar-

H), 3.38 (s, 6H, OCH₃), 2.23 (s, 6H, CH₃); ³¹P NMR (202 MHz, C₆D₆) δ 13.9 (d with fine structure, J^{P-H} = 471 Hz); IR (film) 3003, 2940, 2838, 2280, 1600, 1567, 1489, 1464, 1305, 1240 cm⁻¹.

Bis(4-methoxy-2-methylphenyl)phosphine (5d). The reduction of 4d (1.22 g, 5.00 mmol) with diphenylsilane was carried out as described above for 4a to yield the phosphine 5d as a viscous clear oil: ³¹P NMR (202 MHz, CDCl₃) δ -62.4 (d, J = 218 Hz).

Boronato-dicyclohexyl phosphine (27a). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with dicyclohexylphosphine (431 mg, 2.22 mmol) and purged with argon. Et₂O (3.0 mL) was then added and the solution was cooled to 0 °C. BH₃·S(CH₃)₂ (0.33 mL of a 10.1 M solution in S(CH₃)₂, 3.33 mmol) was then added slowly by syringe. The reaction mixture was warmed slowly to 25 °C and stirred for an additional 2 h. The solvents were evaporated under reduced pressure and the resulting residue was triturated with Et₂O (3 x 2.0 mL) to give 456 mg (99%) of 27a as a white solid: mp 78.6 - 80.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.11 (app d sx, J = 4.9 Hz, J^{H-P} = 351 Hz, P-H), 1.80 (m, 10H, CH₂), 1.71 (br, 2H, P-CH), 1.25 (m, 10H, CH₂), 0.40 (br q, J^{H-B} = 94.7 Hz, 3H, BH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 29.4, 29.2, 28.8, 28.6, 27.7, 26.7, 26.5, 26.3,

25.7; ^{31}P NMR (202 MHz, CDCl_3) δ 17.3 (br d, $J^{\text{P-H}} = 351$ Hz); IR (film) 2929, 2853, 2382, 2350, 1449, 1062 cm^{-1} . Anal. Calcd. for $\text{C}_{12}\text{H}_{26}\text{BP}$: C, 67.93; H, 12.36; P, 14.61. Found: C, 68.14; H, 12.02; P, 14.50.

Boronato-diphenyl phosphine (27b). The reaction of diphenylphosphine (1.86 g, 10.0 mmol) with $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (1.08 mL of a 10.2 M solution containing free $\text{S}(\text{CH}_3)_2$, 11.0 mmol) was carried out as described for 27a. The phosphine-borane adduct was isolated (1.96 g, 98%) as a viscous clear oil: ^1H NMR (300 MHz, CDCl_3) δ 7.68-7.61 (m, 2H, Ph-H), 7.50-7.41 (m, 8H, Ph-H), 6.29 (dq, $J = 6.9$ Hz, $J^{\text{H-P}} = 378$ Hz, 1H, P-H), 1.65-0.5 (br q, $J^{\text{H-B}} = 97.3$ Hz, 3H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 133.1 (CH), 132.9 (CH), 131.6 (CH), 129.2 (CH), 129.0 (CH), 128.5 (C); ^{31}P NMR (202 MHz, CDCl_3) δ 0.8 (d, $J^{\text{P-H}} = 337$ Hz); IR (film) 2388, 1483, 1438, 1109, 1059 cm^{-1} .

4-Lithio-3-methylanisole. An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a pressure equalizing addition funnel, glass stopper, condenser, magnetic stirring bar and glass beads. The vessel was purged with argon and charged with Et_2O (20 mL). The stopper was removed and replaced with a conical funnel while a constant flow of argon was passed through the flask. Lithium wire, doped with 1% Na (0.385 g, 55.0 mmol, prewashed with toluene), was held with forceps over the

funnel and cut with clean scissors into 2 mm pieces such that they dropped directly into the ether. 4-Bromo-3-methylanisole¹¹⁹ (5.02 g, 25.0 mmol) in Et₂O (50 mL) was added slowly to the lithium / Et₂O suspension, via addition funnel, so that the suspension was maintained at a reflux. Upon completion of the addition, the yellow solution was stirred vigorously for an additional 3 h at room temperature.

Bis(4-methoxy-2-methylphenyl)-N,N-dimethylaminophosphine (31). An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a pressure equalizing addition funnel, 2 glass stoppers and a magnetic stirring bar. The vessel was purged with argon, charged with Me₂NPCl₂¹⁰⁹ (1.83 g, 12.5 mmol) in Et₂O (50 mL) and cooled to -78 °C. 4-Lithio-3-methyl anisole (3.20 g, 25.0 mmol) in Et₂O (approx. 70 mL) was added slowly via addition funnel. Upon completion of the addition, the mixture was then warmed slowly to 25 °C. After dilution with anhydrous Et₂O (20 mL), the solution was filtered under argon through Activity II neutral alumina. Concentration of the solution followed by purification by distillation (160-165 °C, 5 μ torr) gave 3.33 g (84%) of 31 as a highly viscous clear oil: ¹H NMR (300 MHz, CDCl₃) δ 6.99 (dd, J = 3.9, 8.4 Hz, 2H, Ar-H), 6.70 (m, 4H, Ar-H), 3.78 (s, 6H, OCH₃), 2.65 (d, J = 8.2 Hz, 6H, N(CH₃)₂), 2.27 (s, 6H, CH₃); ³¹P NMR (202 MHz, CDCl₃) δ 49.7 (s).

Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c).

Method A: An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a glass stopper, gas outlet and magnetic stirring bar. The vessel was purged with argon, charged with **31** (0.850 g, 2.68 mmol) in Et₂O (107 mL) and cooled to 0 °C. Dry HCl (0.219 g, 6.00 mmol) was slowly bubbled into the solution. A white precipitate formed and the reaction was warmed to 25 °C. After stirring at 25 °C for 5 h the Me₂NH₂⁺Cl⁻ salts were filtered off (under argon) and the filtrate was concentrated *in vacuo*. The resulting bis(4-methoxy-2-methylphenyl)chloro phosphine was dissolved in THF (1.5 mL) and added *slowly via* addition funnel to an oven-dried, round-bottomed flask containing LiAlH₄ (0.122 g, 3.20 mmol), BH₃·S(CH₃)₂ (0.32 mL of a 10.2 M solution containing free S(CH₃)₂, 3.25 mmol) and THF (2.0 mL), at 0 °C. Upon completion of the addition, the mixture was warmed to 25 °C and stirred for an additional 2 h. After the reaction was quenched with 5 M HCl (1.5 mL) and ice (3.0 g), the mixture was diluted with Et₂O (4.0 mL). The organic phase was separated and the aqueous phase was extracted with Et₂O (2 x 2.0 mL). The organic layers were combined, washed with brine (5.0 mL), dried (MgSO₄) and solvents were evaporated under reduced pressure. The viscous beige residue was purified by flash chromatography on silica gel (20% EtOAc / hexane for elution) to give 317 mg (42%) of **27c** as a white crystalline solid: mp 97.3-99.9 °C; ¹H NMR

(300 MHz, CDCl_3) δ 7.50 (dd, $J = 8.9, 13.6$ Hz, 2H, Ar-H), 6.76 (br s, 4H, Ar-H), 6.39 (dq, $J = 6.5$ Hz, $J^{\text{H-P}} = 376$ Hz, 1H, P-H), 3.79 (s, 6H, OCH_3), 2.28 (s, 6H, CH_3), 1.54-0.4 (br envelope, 3H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 162.3 (C), 143.9 (C), 143.7 (C), 135.8 (CH), 135.6 (CH), 117.1 (CH), 117.0 (CH), 111.8 (CH), 111.6 (CH), 75.2 (C), 70.3 (C), 55.2 (CH_3), 21.1 (CH_3); ^{31}P NMR (202 MHz, CDCl_3) δ -17.0 (d, $J = 415$ Hz); IR (film) 2358, 1599, 1564, 1489, 1455, 1303, 1242, 1079 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{P}$ ($\text{M}^+ - \text{BH}_3$) 274.1124, found 274.1122.

Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c).

Method B: The reaction of Bis(4-methoxy-2-methylphenyl)phosphine (5d) (0.750 g, 2.74 mmol) with $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (0.30 mL of a 10.2 M solution containing free $\text{S}(\text{CH}_3)_2$, 3.01 mmol) was carried out as described for 27a. The phosphine borane adduct was isolated (758 mg, 2.63 mmol, 96%) as a white crystalline solid.

Ligand Synthesis-Tartaric Acid Series
(1,4-diphosphines)

(4R,5R)-4,5-Bis(carbomethoxy)-2,2-dimethyl-1,3-dioxolane (100a). An oven-dried, round-bottomed flask was fitted with a short path distillation apparatus and magnetic stirring bar. The vessel was charged with dimethyl-L-tartrate (17.8 g, 100 mmol), 2,2-dimethoxypropane (12.5 g, 120 mmol), benzene (40 mL) and (1S)-(+)-10-camphorsulfonic

acid (38.0 mg, 0.160 mmol). The reaction mixture was heated slowly and methanol was collected as the distillate over a period of 3 h. Subsequently, the reaction mixture was cooled to 25 °C, anhydrous Na₂CO₃ (21.2 g, 200 mmol) was added and the mixture was stirred for 30 min. The excess Na₂CO₃ was removed by filtration and the solvents were evaporated under reduced pressure. The resulting oily residue was distilled (70 °C, 125 μ torr) to yield 17.3 g (89%) of the title compound as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 4.68 (s, 2H, CH), 3.70 (s, 6H, OCH₃), 1.39 (s, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 170.0 (C), 113.7 (C), 76.8 (CH), 52.6 (CH₃), 26.2 (CH₃); IR (film) 2994, 2958, 1758, 1440, 1376, 1214, 1112, 1014, 860 cm⁻¹.

(4S,5S)-4,5-Bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (101a). An oven-dried, round-bottomed flask was fitted with a pressure equalizing addition funnel, rubber septum and magnetic stirring bar. The vessel was charged with LiAlH₄ (1.21 g, 32.0 mmol), Et₂O (75 mL) and purged with nitrogen. The grey suspension was cooled to -5 °C and a solution of 100a (3.32 g, 15.0 mmol) in Et₂O (25 mL) was added dropwise over a period of 1 h. The reaction mixture was warmed to 25 °C for 10 min and subsequently refluxed for an additional 1 h. After cooling to 0 °C, excess LiAlH₄ was quenched slowly with water (10 mL). The resulting white slurry was filtered through a pad of celite. After rinsing

the solids with a 50% THF / EtOAc solution (4 x 10 mL), the filtrate was collected, washed with brine and dried (Na_2SO_4). The solvents were evaporated under reduced pressure to yield 2.29 g (94%) of the crude alcohol as an oil. This material was purified by bulb-to-bulb distillation to yield 2.11 g (87%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 3.96 (m, 2H, CH), 3.76 (dd, $J = 2.2, 10.9$ Hz, 2H, CH_2), 3.66 (dd, $J = 2.2, 10.9$ Hz, 2H, CH_2), 2.44 (br s, 2H, OH), 1.40 (s, 6H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 115.7 (C), 80.3 (CH), 62.1 (CH_2), 27.0 (CH_3); IR (film) 3368, 2962, 1260, 1022, 800, 686 cm^{-1} .

(4*S*,5*S*)-4,5-Bis[(*p*-tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (6a). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with 101a (2.00 g, 12.3 mmol), CH_2Cl_2 (30 mL) and pyridine (2.04 g, 25.8 mmol). The mixture was cooled to 0 °C and then *p*-toluenesulfonyl chloride (4.92 g, 25.8 mmol) was added in small portions over a period of 1 h. The mixture was stirred at 0 °C for an additional 19 h. Subsequently, the resulting white slurry was diluted with CH_2Cl_2 (15 mL) and poured into a separatory funnel containing 10% aqueous HCl (10 mL). The organic layer was separated and washed twice more with 10% aqueous HCl (10 mL) saturated aqueous NaHCO_3 (10 mL) and dried (Na_2SO_4). Solvent was evaporated under reduced pressure to yield 5.27 g (91%)

of 6a as a beige solid. This material was recrystallized from abs. ethanol to yield 4.81 g (83%) of the title compound as a white crystalline solid: mp 75.7-78.3 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, J = 8.2 Hz, 4H, Ar-H), 7.34 (d, J = 8.2 Hz, 4H, Ar-H), 4.05 (m, 4H, CH₂), 3.98 (m, 2H, CH), 2.45 (s, 6H, CH₃), 1.28 (s, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 145.2 (C), 132.5 (C), 130.0 (CH), 127.9 (CH), 110.8 (C), 75.0 (CH), 68.4 (CH₂), 26.7 (CH₃), 21.6 (CH₃); IR (KBr) 2985, 2935, 1597, 1359, 1236, 1191, 1174, 1097, 989, 973, 854, 835, 813, 785, 664, 554, 513 cm⁻¹.

(4R,5R)-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f). The following procedure is a modification of one described by Hobbs and Knowles.⁶¹ An oven-dried, round-bottomed flask was charged with KH (35% oil dispersion, 253 mg, 2.21 mmol) and the oil was removed by trituration with pentane (3 x 2 mL). The flask was then purged with argon and cooled to -78 °C. A solution of 5a (677 mg, 2.10 mmol) in THF (1.75 mL) was added in a dropwise manner over 10 min. The reaction was stirred at -78 °C for an additional 15 min, then warmed to 25 °C. After stirring at 25 °C for 5 min, the reaction was re-cooled to -78 °C, and a solution of 6a (470 mg, 1.00 mmol) in THF (3.0 mL) was added slowly via syringe. The mixture was warmed to 25 °C and stirred for an additional 12 h. The solvents were

evaporated under reduced pressure and the resulting residue was dissolved in degassed Et₂O (10 mL). This solution was washed with degassed water (3 x 5 mL). The organic layer was separated, dried (MgSO₄) and the solvents evaporated *in vacuo* to yield a light yellow solid material. Purification was achieved by recrystallization (under argon) from abs. ethanol to yield 670 mg (87%) of the title compound as a white crystalline solid: mp 140.6-142.9 °C; $[\alpha]_D^{25}$ -27.0 (*c* = 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.67 (m, 4H, Ar-H), 7.51 (m, 8H, Ar-H), 7.43 (m, 4H, Ar-H), 4.00 (m, 2H, CH), 2.40 (dd, *J* = 5.1, 15.9 Hz, 2H, CH₂), 2.25 (dd, *J* = 5.1, 15.9 Hz, 2H, CH₂), 1.26 (s, 6H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 134.0 (CH), 133.6 (CH), 131.6 (CH), 131.5 (CH), 128.9 (CH), 126.7 (C), 121.2 (C), 109.3 (C), 79.1 (CH), 79.0 (CH), 32.8 (CH₂), 32.5 (CH₂), 26.9 (CH₃); ³¹P NMR (202 MHz, CDCl₃) δ -33.6 (septet, *J* = 50 Hz); IR (KBr) 3075, 2984, 2929, 2893, 1594, 1573, 1308, 1262, 1169, 1112, 1033, 764 cm⁻¹. Anal. Calcd. for C₃₅H₂₈F₁₂O₂P₂: C, 54.56; H, 3.66; F, 29.59; P, 8.04. Found: C, 54.55; H, 3.58; F, 29.38; P, 8.0 (min).

(4*R*,5*R*)-4,5-Bis[[bis(2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e). Prepared according to the method of Kagan:⁴³ $[\alpha]_D^{25}$ -36.6 (*c* = 0.3, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.20-7.04 (m, 16H, Ar-H), 3.78 (app sx, *J* = 5.1 Hz, 2H, CH), 2.48 (s, 6H, Ar-CH₃), 2.31 (s, 6H, CH₃), 2.25 (m, 4H, CH₂), 1.32 (s, 6H, CH₃); ¹³C NMR (75 MHz,

CDCl_3 , ^1H decoupled) δ 131.8 (CH), 130.9 (CH), 130.1 (CH), 128.7 (CH), 128.5 (C), 126.2 (C), 125.9 (CH_3), 108.8 (C), 104.4 (CH), 31.0 (CH_2), 27.2 (CH_3); ^{31}P NMR (202 MHz, CDCl_3) δ -43.9 (s); IR (film) 3054, 2932, 2872, 1450, 1228, 746, 716 cm^{-1} .

(4R,5R)-4,5-Bis[[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d). The reaction of 2.05 equivalents of potassium bis[3,5-bis(trifluoromethyl)phenyl phosphide (577 mg, 1.16 mmol) with 6a (267 mg, 0.568 mmol) in THF (3.0 mL) was carried out as described above for the preparation of 3f. After the usual workup, the organic layer was separated, dried (MgSO_4) and the solvents evaporated in vacuo to yield a beige solid. This material was purified by recrystallization (under argon) from abs. ethanol to yield 486 mg (82%) of the title compound as a white crystalline solid: mp 123-127 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{25}$ -9.0 ($c = 1.0$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.85 (m, 12H, Ar-H), 4.04 (app sx, $J = 4.3$ Hz, 2H, CH), 2.37 (m, 4H, CH_2), 1.28 (s, 6H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 132.9 (CH), 132.6 (CH), 124.8 (C), 123.6 (C), 123.3 (C), 121.2 (C), 109.9 (C), 79.4 (CH), 79.2 (CH), 31.1 (CH_2), 30.9 (CH_2), 26.6 (CH_3); ^{31}P NMR (CDCl_3) δ -17.2 (s); IR (film) 3040, 1385, 1270, 1212, 1130, 764 cm^{-1} . Anal. Calcd. for $\text{C}_{39}\text{H}_{24}\text{F}_{24}\text{O}_2\text{P}_2$: C, 44.93; H, 2.32; F, 43.74. Found: C, 45.16; H, 2.20; F, 43.70.

(4R,5R)-4,5-Bis[[bis(4-methoxy-2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3h). The reaction of 2.10 equivalents of potassium bis-4-methoxy-2-methylphenylphosphide (656 mg, 2.10 mmol) with 6a (470 mg, 1.00 mmol) in THF (4.75 mL) was carried out as described above for the preparation of 3f: mp 43.5-53.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.14 (dd, J = 8.2, 3.6 Hz, 2H, Ar-H), 7.03 (dd, J = 8.3, 3.9 Hz, 2H, Ar-H), 6.72-6.62 (m, 8H, Ar-H), 3.77 (s, 6H, OCH₃), 3.75 (s, 6H, OCH₃), 3.73 (m, 2H, Ar-H), 2.44 (s, 6H, CH₃), 2.28 (s, 6H, CH₃), 2.16 (m, 4H, CH₂), 1.33 (s, 6, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 159.9, 134.2, 133.1, 132.1, 127.7, 115.9, 115.6, 111.8, 111.4, 79.8, 78.5, 55.0, 53.3, 31.7, 31.6, 27.2, 21.6, 21.3, 21.1; ³¹P NMR (202 MHz, CDCl₃) δ -48.5 (s).

(4R,5R)-4,5-Bis[(boronatodicyclohexyl phosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was charged with 27a (312 mg, 1.50 mmol) and THF (4.0 mL), purged with argon and cooled to -78 °C. n-BuLi (0.52 mL of a 2.86 M solution in heptane, 1.50 mmol) was added dropwise to the reaction mixture over a period of 10 min. The reaction was stirred at -78 °C for an additional 10 min, then warmed to 25 °C for 5 min. Upon cooling to -78 °C, a solution of 6a (346 mg, 0.735 mmol) in THF (4.0 mL) was added slowly via syringe. The mixture was then allowed to warm slowly to 25 °C. After

stirring at 25 °C for 9 h, 10% aqueous HCl (2 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et₂O (4 x 5 mL). The organic layers were combined, washed with water (2 x 5 mL), dried (MgSO₄) and the solvents were evaporated under reduced pressure. The resulting white solid was recrystallized from cold heptane to yield 302 mg (86%) of the title compound as a white crystalline solid: mp 181.9-185.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.92 (m, 2H, CH), 2.05-1.50 (m, 30H, CH₂ and Cy-H envelope), 1.35 (s, 6H, CH₃), 1.45-1.10 (m, 19H, Cy-H envelope), 0.90-0.30 (br envelope, 6H, BH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 32.8, 32.4, 32.2, 31.8, 27.4, 27.2, 27.1, 26.8, 26.1, 25.9, 22.6, 22.2; ³¹P NMR (202 MHz, CDCl₃) δ 25.4 (s).

(4R,5R)-4,5-Bis[(dicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (32). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was charged with 33 (138 mg, 0.25 mmol), morpholine (2.0 mL) and purged with argon. The reaction was stirred at 100 °C for 2 h. The solvent was removed *in vacuo* and the resulting residue was recrystallized from abs. ethanol (degassed) to yield 128 mg (98%) of the title compound as a white crystalline solid: mp 176.8-180.0 °C; ¹H NMR (300 MHz, C₆D₆) δ 4.17 (app q, J = 3.9 Hz, 2H, CH), 2.14-1.48 (overlapping multiplets, 28H, Cy-H), 1.50 (s, 6H,

CH_3), 1.48-0.95 (overlapping multiplets, 20H, Cy-H); ^{31}P NMR (202 MHz, C_6D_6) δ -13.9 (S).

(4R,5R)-4,5-Bis(carbomethoxy)-2-methyl-2-phenyl-1,3-dioxolane (100b). The reaction of 1,1-dimethoxy-1-phenylethane (16.1 g, 0.120 mol) with dimethyl-L-tartrate (17.8 g, 0.100 mol) was carried out as described above for 100a. Upon evaporation of the solvent *in vacuo*, the resulting oily material was distilled (105 °C, 0.25 μ torr) to yield 25.8 g (92%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.49 (m, 2H, Ph-H), 7.30 (m, 3H, Ph-H), 4.87 (d, J = 5.5 Hz, 1H, CH), 4.80 (d, J = 5.5 Hz, 1H, CH), 3.85 (s, 3H, CH_3), 3.54 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 169.5 (C), 169.3 (C), 141.6 (C), 128.4 (CH), 128.0 (CH), 125.5 (CH), 113.3 (C), 77.3 (CH), 76.5 (CH), 52.8 (CH_3), 52.3 (CH_3), 28.1 (CH_3); IR (film) 2998, 2956, 1751, 1688, 1440, 1376, 1342, 1250, 1199, 1138, 1096, 1070, 1026, 880, 768, 704 cm^{-1} .

(4S,5S)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b). The reduction of 100b (4.21 g, 15.0 mmol) with LiAlH_4 (1.21 g, 32.0 mmol) was carried out as described above for the preparation of diol 101a from 100a. Upon evaporation of the solvent under reduced pressure, 2.46 g (73%) of 101b was obtained as a white crystalline solid: mp 68.3-71.0 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.46 (m, 2H,

Ph-H), 7.37-7.30 (m, 3H, Ph-H), 4.14 (m, 1H, CH), 3.90 (m, 1H, CH), 3.72 (m, 2H, CH₂), 3.55 (dd, J = 5.1, 8.2 Hz, 2H, CH₂), 1.91 (brs, 2H, OH), 1.67 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 128.4 (CH), 128.3 (CH), 128.0 (CH), 126.6 (C), 125.2 (CH), 124.8 (CH), 109.6 (C), 79.0 (CH), 78.5 (CH), 62.5 (CH₂), 62.2 (CH₂), 28.9 (CH₃); IR (KBr) 3292, 3004, 2946, 2904, 2876, 1374, 1244, 1198, 1052, 1024, 912, 704 cm⁻¹.

(4*S*,5*S*)-4,5-Bis[(*p*-tosyloxy)methyl]-2-methyl-2-phenyl-1,3-dioxolane (6b). The title compound was prepared from 101b (2.00 g, 8.90 mmol), toluenesulfonyl chloride (3.38 g, 17.8 mmol), pyridine (1.41 g, 17.8 mmol) and CH₂Cl₂ (25 mL) in a manner described above for 6a. Upon evaporation of solvent under reduced pressure, a light yellow solid was obtained. This material was recrystallized from abs. ethanol to yield 3.98 g (84%) of 6b as a white crystalline solid: mp 168.2-169.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.79 (d, J = 7.5 Hz, 2H, Ar-H), 7.65 (d, J = 7.5 Hz, 2H, Ar-H), 7.35 (d, J = 8.0 Hz, 2H, Ar-H), 7.30 (d, J = 8.0 Hz, 2H, Ar-H), 7.26-7.22 (m, 5H, Ph-H), 4.13 (d, J = 4.6 Hz, 2H, CH₂), 4.06 (app q, J = 6.1 Hz, 1H, CH), 3.80 (m, 2H, CH₂), 3.64 (dd, J = 5.4, 10.3 Hz, 1H, CH), 2.44 (s, 6H, CH₃), 1.51 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 132.4, 129.9, 128.2, 128.0, 127.9, 127.8, 124.7, 110.9, 76.0, 75.6, 68.6, 68.5, 28.6, 21.5; IR (KBr) 3068, 2996, 2956, 1598, 1356, 1190, 1176, 1058, 964, 874, 814, 570, 556 cm⁻¹.

(4*R*,5*R*)-4,5-Bis[(diphenylphosphino)methyl]-2-methyl-2-phenyl-1,3-dioxolane (3b). An oven-dried, round-bottomed flask fitted with a rubber septum and magnetic stirring bar was charged with KH (35% oil dispersion, 253 mg, 2.21 mmol) and the oil was removed by trituration with pentane (3 x 2 mL). The flask was then purged with argon, cooled to -40 °C and charged with a solution of diphenylphosphine (391 mg, 2.10 mmol) in DMF (1.75 mL) in a dropwise manner over a period of 10 min. During this time H₂ evolved and the solution became dark red. The reaction was stirred at -40 °C for an additional 10 min, then warmed to 25 °C for 5 min. Upon cooling to -40 °C, a solution of 6b (533 mg, 1.00 mmol) in DMF (3.0 mL) was added slowly via syringe. The mixture was warmed to 25 °C and stirred for an additional 12 h. Subsequently, solvents were evaporated under reduced pressure and the resulting residue was dissolved in degassed anhydrous Et₂O (10 mL). This solution was washed with degassed water (3 x 5 mL), brine (5 mL), dried (MgSO₄) (all under argon) and the solvent evaporated *in vacuo* to yield 499 mg (89%) of 3b as a beige, highly viscous oil. Attempts to crystallize this material were unsuccessful: $[\alpha]_D^{25}$ -7.0 (*c* = 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.5-7.1 (m, 25H, Ar-H), 4.05 (app p, *J* = 6.6 Hz, 1H, CH), 3.75 (app p, *J* = 6.2 Hz, 1H, CH), 2.46 (dd, *J* = 5.4, 14.3 Hz, 1H, CHH), 2.41 dd, *J* = 7.2, 14.3 Hz, 1H, CHH), 2.20 (dd, *J* = 7.7, 13.8 Hz, 1H, CHH), 2.12 (dd,

$J = 5.7, 13.8$ Hz, 1H, CHH), 1.54 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 133.2, 133.0, 132.8, 132.6, 128.4, 127.9, 127.5, 125.2, 109.0, 81.2, 80.1, 29.1; ^{31}P NMR (202 MHz, CDCl_3) δ -23.1 (d, $J = 57$ Hz); IR (film) 3054, 2924, 2854, 2436, 1178, 1160, 1120, 1098, 1070, 694 cm^{-1} .
 Anal. Calcd. for $\text{C}_{36}\text{H}_{34}\text{O}_2\text{P}_2$: C, 77.11; H, 6.12; P, 11.06.
 Found: C, 75.60; H, 6.26; P, 9.25.

(4R,5R)-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g). The reaction of 2.1 equivalents of potassium bis(2-trifluoromethylphenyl)phosphide (757 mg, 2.10 mmol) with 6b (533 mg, 1.00 mmol), in DMF (4.75 mL), was carried out as described above for the preparation of 3b. Upon workup, evaporation of the solvents *in vacuo* yielded an orange foamy material. Chromatographic purification (under argon) on degassed silica gel (15% EtOAc / hexane (degassed) for elution) provided 633 mg (76%) of 3g as a white foam. Attempts to crystallize this material were unsuccessful:
 $[\alpha]_{\text{D}}^{25} -13.0$ ($c = 1.0$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.70-7.65 (m, 5H, Ph-H), 7.53-7.41 (m, 12H, Ar-H), 7.25 (m, 2H, Ar-H), 7.17 (m, 2H, ArH), 4.14 (app p, $J = 6.2$ Hz, 1H, CH), 3.83 (app p, $J = 6.5$ Hz, 1H, CH), 2.41 (app p, $J = 3.1$ Hz, 2H, CH_2), 2.14 (m, 2H, CH_2), 1.46 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 140.9, 138.8, 138.6, 138.5, 136.3, 136.2, 133.7, 133.6, 132.6, 132.3, 131.5, 129.7, 127.4, 127.1, 121.3, 114.1, 85.1, 84.1, 33.6; ^{31}P NMR

(202 MHz, CDCl_3) δ -33.2 (app dp, $J = 25, 52$ Hz); IR (KBr) 3854, 3066, 2960, 2934, 1442, 1312, 1262, 1172, 1114, 1036, 768, 692 cm^{-1} . Anal. Calcd. for $\text{C}_{40}\text{H}_{30}\text{F}_{12}\text{O}_2\text{P}_2$: C, 57.70; H, 3.63; F, 27.40. Found: C, 59.19; H, 3.76; F, 27.80.

(4*R*,5*R*)-4,5-Bis(carbomethoxy)-2-*t*-butyl-1,3-dioxolane (100c). The following procedure is a modification of one described by Seebach.^{88b} An oven-dried, round-bottomed flask was charged with dimethyl-L-tartrate (3.56 g, 20 mmol), trimethylacetaldehyde (5.5 mL, 50 mmol), benzene (30 mL) and (1*S*)-(+)-10-camphorsulfonic acid (10 mg, 0.04 mmol). The mixture was refluxed for 20 h with azeotropic removal of water. The solvent was removed *in vacuo* and the residue was dissolved in Et_2O (30 mL), washed with saturated aqueous Na_2CO_3 (2 x 10 mL), water (10 mL) and brine (10 mL). The organic layer was then dried (MgSO_4) and the solvent was removed by evaporation under reduced pressure. Bulb-to-bulb distillation of the resulting residue (82 °C, 0.25 μtorr) afforded 3.67 g (74%) of the title compound as a clear oil. ^1H NMR (300 MHz, CDCl_3) δ 4.85 (s, 1H, *t*-BuCH), 4.74 (d, $J = 4.3$ Hz, 1H, CH), 4.64 (d, $J = 4.3$ Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 170.3 (C), 169.2 (C), 112.8 (CH), 77.0 (CH), 52.5 (CH_3), 33.9 (C), 24.0 (CH_3); IR (film) 2960, 2876, 1804, 1752, 1486, 1438, 1410, 1366, 1216, 1120, 1044, 972 cm^{-1} .

(4*S*,5*S*)-4,5-Bis(hydroxymethyl)-2-*t*-butyl-1,3-dioxolane (101c). The reduction of 100c (2.46 g, 10.0 mmol) with LiAlH₄ (794 mg, 21.0 mmol) was carried out as described above for the preparation of diol 101a from 100a. Upon evaporation of the solvent under reduced pressure, 1.53 g (81%) of 101c was obtained as a white crystalline solid: mp 47.7-49.6 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.70 (s, 1H, *t*-BuCH), 3.93 (ddd, *J* = 4.0, 4.6, 7.1 Hz, 2H, CH), 3.82 (dd, *J* = 4.0, 11.6 Hz, 2H, CH₂), 3.71 (dd, *J* = 7.1, 11.6 Hz, 2H, CH₂), 2.06 (br s, 2H, OH), 0.90 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 110.1 (CH), 78.6 (CH), 78.0 (CH), 62.3 (CH₂), 34.3 (C), 24.1 (CH₃); IR (KBr) 3264, 2974, 2940, 2884, 1482, 1406, 1392, 1358, 1136, 1122, 1052, 1040, 1020, 982 cm⁻¹.

(4*S*,5*S*)-4,5-Bis[(*p*-tosyloxy)methyl]-2-*t*-butyl-1,3-dioxolane (6c). The title compound was prepared from 101c (1.50 g, 7.9 mmol), toluenesulfonyl chloride (3.00 g, 15.8 mmol), pyridine (1.25 g, 15.8 mmol) and CH₂Cl₂ (20 mL) in a manner described above for 6a. Evaporation of solvent under reduced pressure yielded a white solid. Purification of this material was accomplished by recrystallization from abs. ethanol to give 3.35 g (85%) of 6c as a white crystalline solid: mp 111-113 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.33 (d, *J* = 8.1 Hz, 4H, Ar-H), 4.53 (s, 1H, *t*-BuCH), 4.00 (m, 6H, CH₂, CH), 2.44 (s, 6H, Ar-CH₃), 0.76 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, ¹H

decoupled) δ 145.1 (C), 132.5 (C), 129.9 (CH), 127.9 (CH), 110.8 (CH), 75.1 (CH), 68.3 (CH₂), 33.9 (C), 23.8 (CH₃), 21.5 (CH₃); IR (KBr) 2960, 2906, 2870, 1598, 1366, 1352, 1190, 1178, 1122, 1094, 1012, 982, 918, 808, 784, 682, 570, 552 cm⁻¹.

(4*R*,5*R*)-4,5-Bis[(diphenylphosphino)methyl]-2-*t*-butyl-1,3-dioxolane (3c). The reaction of 2.1 equivalents of potassium diphenylphosphide (471 mg, 2.10 mmol) with 6c (499 mg, 1.00 mmol), in THF (4.75 mL), was carried out as described for the preparation of 3b. Upon evaporation of solvent under reduced pressure, 463 mg (88%) of a clear oil was obtained. This material solidified upon standing in abs. ethanol. Recrystallization from abs. ethanol afforded 447 mg (85%) of 3c as a white crystalline material: mp 79.7-81 °C; $[\alpha]_D^{25}$ -10.0 (c = 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.40 (m, 8H, Ar-H), 7.28-7.23 (m, 12H, Ar-H), 4.56 (s, 1H, *t*-BuCH), 4.00 (app p, J = 6.6 Hz, 1H, CH), 3.90 (app p, J = 6.6 Hz, 1H, CH), 2.32 (m, 4H, CH₂), 0.70 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 138.4 (C), 138.0 (C), 133.1 (CH), 132.8 (CH), 132.7 (CH), 132.6 (CH), 128.6 (CH), 128.4 (CH), 109.5 (CH), 80.9 (CH), 79.8 (CH), 34.2 (C), 32.5 (CH₂), 32.3 (CH₂), 24.2 (CH₃); ³¹P NMR (202 MHz, CDCl₃) δ -22.5 (d, J = 152 Hz); IR (KBr) 3070, 3052, 2958, 2932, 2900, 2870, 1480, 1434, 1408, 1366, 1096, 1046, 998, 980, 740, 722, 696, 502 cm⁻¹; high resolution

mass spectrum calcd. for $C_{33}H_{36}O_2P_2(M^+)$ 526.2193, found 526.2190.

Ligand Synthesis--Hexane Series (1,4-diphosphines)

(2*S*,5*S*)-2,5-Hexandiol (102). The title compound was prepared from acetonylacetone (5.71 g, 0.050 mol) according to the method of Lieser.¹²⁰ The mixture was filtered through celite and the solids were rinsed with EtOAc (4 x 50 mL). The filtrate was collected and the organic layer separated. The aqueous layer was continuously extracted with EtOAc for 3 days. The combined organics were dried ($MgSO_4$) and concentrated under reduced pressure to yield a beige viscous oil. Purification of this material was accomplished by column chromatography on silica gel (EtOAc for elution) to yield 4.49 g (75%) of 102 as a white solid.

Recrystallization from *t*-butyl-methyl ether afforded 3.96 g (67%) of 102 as a white crystalline solid: mp 50.4–53.2 °C;

1H NMR (300 MHz, $CDCl_3$) δ 3.78 (m, 2H, CH), 3.15 (br s, 2H, OH), 1.53 (m, 4H, CH_2), 1.17 (d, $J = 6.2$ Hz, 6H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 1H decoupled) δ 68.1 (CH), 35.9 (CH_2), 23.6 (CH_3).

(2*S*,5*S*)-2,5-Bis-(*p*-tosyloxy)hexane (30). The title compound was prepared from 102 (1.18 g, 10.0 mmol), toluenesulfonyl chloride (3.80 g, 20.0 mmol), pyridine (1.58 g, 20.0 mmol) and CH_2Cl_2 (30 mL) in a manner described above for 6a. Upon evaporation of solvent under reduced

pressure, a white solid material was obtained.

Recrystallization from heptane:methylcyclohexane (1:9)

afforded 3.54 g (83%) of 30 as a white crystalline solid:

mp 94.5-97 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 4H, Ar-H), 7.32 (d, $J = 8.2$ Hz, 4H, Ar-H), 4.50 (m, 2H, CH), 2.43 (s, 6H, Ar- CH_3), 1.54 (m, 4H, CH_2), 1.11 (d, $J = 6.3$ Hz, 6H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 144.6 (C), 134.8 (C), 129.8 (CH), 127.7 (CH), 79.0 (CH), 31.7 (CH_3), 21.6 (CH_2), 20.8 (CH_3); IR (KBr) 3004, 2980, 2954, 2930, 1598, 1450, 1438, 1378, 1323, 1308, 1294, 1189, 1171, 1096, 892, 852, 820, 758, 688, 578, 544, 522 cm^{-1} .

(2R,5R)-2,5-Bis(diphenylphosphino)hexane (21b). Method

A: An oven-dried, round-bottomed flask was charged with KH (35% oil dispersion, 253 mg, 2.21 mmol) and the oil was removed by trituration with pentane (3 x 2 mL). The vessel was then purged with argon and cooled to -40 °C. A solution of diphenylphosphine (391 mg, 2.10 mmol) in DMF (2.0 mL) was added in a dropwise manner over a period of 10 min. The reaction mixture was warmed to 0 °C and stirred for 1 h after which it was warmed to 25 °C and stirred for an additional 15 min. Upon cooling to -40 °C, a solution of 30 (427 mg, 1.00 mmol) in DMF (3.0 mL) was added via syringe and the mixture was stirred at 25 °C for 18 h. After the usual workup (see preparation of 3b), evaporation of the solvent under reduced pressure yielded 405 mg (89%) of a

white solid. This material was recrystallized from degassed methylcyclohexane at 0 °C to give 382 mg (84%) of 21b as a white crystalline solid: mp 179.3-183.6 °C; $[\alpha]_D^{25} +7.0$ (c = 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.67 (m, 8H, Ar-H), 7.5-7.3 (m, 12H, Ar-H), 2.25 (m, 2H, CH), 1.61 (m, 4H, CH₂), 1.07 (d, J = 7.1 Hz, 3H, CH₃), 0.09 (d, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) 131.4, 130.9, 128.4, 32.8, 32.1, 27.6, 11.9; ³¹P NMR (202 MHz, CDCl₃) δ -1.8 (s); IR (KBr) 3068, 3052, 2956, 2930, 2880, 2852, 1480, 1458, 1432, 1376, 1196, 1092, 1068, 1026, 738, 696, 658, 510 cm⁻¹; high resolution mass spectrum calcd. for C₃₀H₃₂P₂(M⁺) 454.1982, found 454.1979.

(2R,5R)-2,5-Bis[bis(2-trifluoromethylphenyl)phosphino]hexane (15a). The reaction of 2.1 equivalents of potassium bis(2-trifluoro-methylphenyl)phosphide (757 mg, 2.10 mmol) with 30 (427 mg, 1.00 mmol), in DMF (50 mL), was carried out as described above for the preparation of 21b (method A).

Upon evaporation of the solvent under reduced pressure, 684 mg (94%) of a light yellow solid was obtained. This material was recrystallized from methylcyclohexane to give 596 mg (82%) of 15a as a white crystalline solid: mp 182-186 °C; $[\alpha]_D^{25} +39.0$ (c = 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.70-7.35 (m, 16H, Ar-H), 2.03 (m, 2H, CH), 1.57 (m, 2H, CH₂), 1.29 (m, 2H, CH₂), 0.91 (d, J = 6.6 Hz, 3H, CH₃), 0.87 (d, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H

decoupled) δ 135.9 (C), 133.8 (CH), 133.1 (CH), 131.2 (CH), 128.9 (CH), 126.9 (C), 126.7 (C), 32.0 (CH₂), 31.8 (CH₂) 31.1 (CH), 15.9 (CH₃), 15.7 (CH₃); ³¹P NMR (202 MHz, CDCl₃) δ -20.3 (unresolved septet, J = 44 Hz); IR (KBr) 3072, 2974, 2964, 2936, 2882, 1594, 1572, 1470, 1442, 1384, 1311, 1260, 1172, 1110, 1036, 958, 876, 770, 746, 738, 690, 646, 596, 524, 512 cm⁻¹. Anal. Calcd. for C₃₄H₂₈F₁₂P₂: C, 56.71; H, 3.88; F, 31.38; P, 8.53. Found: C, 56.72; H, 3.88; F, 31.13; P, 8.05.

(2R,5R)-2,5-Bis(boronato-diphenylphosphino)hexane

(26b). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was purged with argon, cooled to -78 °C and charged with 27b (100 mg, 0.50 mmol) and THF (1.5 mL). n-BuLi (88.0 μ L of a 5.80 M solution in heptane, 0.51 mmol) was added dropwise via syringe over a period of 10 min. The reaction was stirred at -78 °C for an additional 10 min then warmed to 25 °C for 10 min. After cooling to -40 °C, a solution of 30 (102 mg, 0.24 mmol) in DMF (1.0 mL) was added slowly via syringe. Upon completion of the addition, the mixture was then warmed slowly to 25 °C. After stirring at 25 °C for 9 h, the mixture was diluted with Et₂O (2.0 mL) and added to 10% aqueous HCl (3.0 mL) contained in a separatory funnel. The organic layer was separated and the aqueous layer was extracted with Et₂O (4 x 2.0 mL). The organic layers were combined, washed with water (2 x 2.0 mL), brine (2.0 mL),

dried (MgSO_4) and the solvents were removed *in vacuo*. The resulting beige residue was purified by flash chromatography on silica gel (20% EtOAc / hexane for elution) to yield 83.3 mg (72%) of **26b** as a white solid: mp 153.4-154.8 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.68-7.62 (m, 8H, Ph-H), 7.47-7.36 (m, 12H, Ph-H), 2.37 (app sept., $J = 7.4$ Hz, 2H, CH), 1.52 (m, 4H, CH_2), 1.04 (d, $J = 6.9$ Hz, 3H, CH_3), 0.98 (d, $J = 6.9$ Hz, 3H, CH_3), 1.45-0.20 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 132.7 (CH), 132.6 (CH), 132.5 (CH), 132.4 (CH), 131.1 (CH), 128.9 (C), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.3 (C), 29.5 (CH), 29.4 (CH), 28.7 (CH_2), 28.2 (CH_2), 13.7 (CH_3); ^{31}P NMR (202 MHz, CDCl_3) δ 23.9 (s); IR (film) 2928, 2385, 1436, 1107, 1064 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{30}\text{H}_{32}\text{P}_2(\text{M}^+-\text{B}_2\text{H}_6)$ 454.1982, found 454.1980.

(2*R*,5*R*)-2,5-Bis(boronato dicyclohexylphosphino)hexane (**26a**). The reaction of lithium boronatodicyclohexylphosphide (112 mg, 0.525 mmol) with **30** (107 mg, 0.25 mmol) was carried out as described for the boronato diphenylphosphine analogue (**26b**). After the described workup, evaporation of the solvents under reduced pressure yielded a white residue. This material was purified by crystallization from 10% EtOAc / hexane to yield 112 mg (90%) of **26a** as a white crystalline solid: mp 203.2-205.4 °C; ^1H NMR (300 MHz, CDCl_3) δ 1.95-1.60 (m, 35H, Cy-H envelope), 1.55-1.20 (m, 15H, CH, CH_2 and Cy-H envelope),

1.18 (d, $J = 7.0$ Hz, 3 H, CH_3), 1.16 (d, $J = 7.0$ Hz, 3H, CH_3), 0.8-0.5 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 31.6, 31.5, 31.2, 31.1, 30.5, 30.4, 28.2, 27.9, 27.8, 27.7, 27.3, 27.2, 26.1, 25.4, 25.0, 14.6; ^{31}P NMR (202 MHz, CDCl_3) δ 31.1 (br s); IR (film) 2927, 2853, 2362, 2342, 1067 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{30}\text{H}_{59}\text{BP}_2(\text{M}^+-\text{BH}_3)$ 492.2196, found 492.4185.

(2*R*,2*R*)-2,5-Bis[boronato-bis(4-methoxy-2-methylphenyl)phosphino]hexane (26c). The reaction of lithium [bis(4-methoxy-2-methylphenyl)boronato]phosphide (154 mg, 0.525 mmol) with 30 (107 mg, 0.250 mmol) was carried out as described for the boronato diphenylphosphine analogue (26b). After the described workup, evaporation of the solvents under reduced pressure yielded a white solid. This material was purified by crystallization from methylcyclohexane to yield 143 mg (87%) of 26c as a white crystalline solid: mp 149.3-153.1 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.77 (dd, $J = 11.5, 10.5$ Hz, 2H, Ar-*H*), 7.49 (app t, $J = 10.5$ Hz, 2H, Ar-*H*), 6.77 (app d, $J = 8.5$ Hz, 4H, Ar-*H*), 6.66 (app d, $J = 17.2$ Hz, 4H, Ar-*H*), 3.81 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 2.54 (m, 2H, CH), 2.08 (s, 6H, CH_3), 1.99 (s, 6H, CH_3), 1.76 (m, 4H, CH_2), 1.09 (d, $J = 6.7$ Hz, 3H, CH_3), 1.04 (d, $J = 6.8$ Hz, 3H, CH_3), 1.9-0.2 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 161.7, 161.0, 144.7, 144.2, 135.8, 135.3, 134.1, 133.6, 129.7, 127.6, 117.6, 111.1, 79.5, 55.0, 28.1, 27.7, 21.7,

20.3, 14.4; ^{31}P NMR (202 MHz, CDCl_3) δ 21.4 (s); IR (film) 2933, 2383, 1598, 1565, 1489, 1464, 1302, 1237, 1075 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{38}\text{H}_{48}\text{O}_2\text{P}_2(\text{M}^+-\text{B}_2\text{H}_6)$ 630.3030, found 630.3028.

(2R,5R)-2,5-Bis(diphenylphosphino)hexane (21b).

Method B: A flame-dried test tube (16 mm x 100 mm) equipped with a stirring flea was charged with 26b (48.2 mg, 0.10 mmol), CH_2Cl_2 (1.0 mL) and purged with argon. After cooling the mixture to -5°C , $\text{HBF}_4\cdot\text{OMe}_2$ (134 mg, 1.0 mmol) was added by syringe. An exothermic reaction ensued and gas evolved. The reaction mixture was then warmed to 25°C and stirred for an additional 12 h. Subsequently, the mixture was diluted with degassed anhydrous Et_2O (2.0 mL) and added to degassed, saturated aqueous NaHCO_3 (5.0 mL) contained in a small Erlenmeyer flask. The mixture was stirred vigorously under argon for 10 min. then poured into a separatory funnel. The organic layer was separated and the aqueous layer was extracted (under argon) with degassed, anhydrous Et_2O (2 x 2.0 mL). The organic layers were combined, washed with degassed water (2 x 3.0 mL), brine (3.0 mL), dried (MgSO_4) (all under argon) and the solvents were removed *in vacuo*. The resulting white solid was recrystallized from degassed methylcyclohexane at 0°C to give 45.3 mg (99%) of 21b as a white crystalline solid.

(2R,5R)-2,5-Bis(dicyclohexylphosphino)hexane (21a).

The reaction of (26a) (49.8 mg, 0.10 mmol) with $\text{HBF}_4 \cdot \text{OMe}_2$ (134 mg, 1.0 mmol), in CH_2Cl_2 (1.0 mL), was carried out as described above for the decomplexation of 26b. Upon evaporation of solvents under reduced pressure 43.5 mg (91%) of 21a was obtained as a white solid: mp 184.6–187.3 °C; ^1H NMR (300 MHz, CDCl_3) δ 1.96–1.60 (m, 35H, Cy-H envelope), 1.60–1.05 (m, 15H, CH, CH_2 and Cy-H envelope), 1.18 (d, $J = 7.2$ Hz, 3H, CH_3), 1.13 (d, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 35.9, 35.1, 30.2, 29.4, 28.7, 28.5, 27.0, 26.9, 26.8, 26.6, 26.5, 26.3, 26.1, 13.3; ^{31}P NMR (202 MHz, CDCl_3) δ 11.1 (s); IR (film) 2929, 2852, 1449, 1157 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{30}\text{H}_{55}\text{P}_2(\text{M}^+-\text{H})$ 477.3783, found 477.3780.

(2R,5R)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino]hexane (21c). The reaction of 26c (65.8 mg, 0.10 mmol) with $\text{HBF}_4 \cdot \text{OMe}_2$ (134 mg, 1.0 mmol), in CH_2Cl_2 (1.0 mL), was carried out as described above for the decomplexation of 26b. Upon evaporation of solvents under reduced pressure, 60.5 mg (96%) of 21c was obtained as a white crystalline solid: mp 178.4–181.9 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.17–7.08 (m, 4H, Ar-H), 6.71–6.63 (m, 8H, Ar-H), 3.78 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 2.44 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.10 (m, 2H, CH), 1.47 (m, 4H, CH_2), 0.92 (d, $J = 7.7$ Hz, 3H, CH_3), 0.87 (d, $J = 7.7$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 159.7, 144.8, 144.6, 133.2, 132.5, 115.7,

115.6, 111.7, 54.9, 52.0, 31.5, 30.5, 29.6, 21.4, 16.1, 15.8; ^{31}P NMR (202 MHz, CDCl_3) δ -32.4 (s); IR (film) 2925, 2852, 1595, 1564, 1483, 1464, 1296, 1238, 1071 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{38}\text{H}_{48}\text{O}_4\text{P}_2(\text{M}^+)$ 630.3030, found 630.3028.

Ligand Synthesis--Cyclohexane (1,4-diphosphine)

(1*S*,2*S*)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl]cyclohexane (25a). The reaction of lithium boronatodicyclohexylphosphide (56.1 mg, 0.263 mmol) with (1*S*,2*S*)-1,2-di(*p*-tosyloxymethyl)cyclohexane¹²¹ (56.5 mg, 0.125 mmol) was carried out as described for 26b in THF (2.0 mL). After the described workup, evaporation of the solvents under reduced pressure yielded 59.2 mg (89%) of 25a as a white residue. This material was purified by recrystallization from heptane (distilled from K) to give a white crystalline solid: mp 93.6-96.2 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.00-1.46 (br envelope, 32H, Cy-*H*), 1.45-1.00 (br envelope, 26H, Cy-*H*), 0.90-0.40 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 38.7, 38.6, 33.9, 33.2, 33.1, 32.7, 32.6, 27.8, 27.1, 27.0, 26.9, 26.6, 26.1, 25.8, 24.9, 23.8, 23.4; ^{31}P NMR (202 MHz, CDCl_3) δ 25.8 (s); IR (film) 2927, 2853, 2372, 1447, 1063 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{32}\text{H}_{60}\text{BP}_2(\text{M}^+-\text{BH}_4)$ 517.2274, found 517.4264.

Ligand Synthesis--Pentane Series (1,3-diphosphines)

(2*R*,4*R*)-2,4-Bis([bis(2-trifluoromethylphenyl)phosphino]pentane (16a). An oven-dried, round-bottomed flask was charged with KH (35% oil dispersion, 425 mg, 3.71 mmol) and the oil was removed by trituration with pentane (3 x 4 mL). The vessel was then purged with nitrogen and cooled to -78 °C. A solution of Bis(2-trifluoromethyl-phenyl)phosphine (1.20 g, 3.71 mmol) in THF (4.0 mL) was added in a dropwise manner over a period of 10 min. A bright red solution formed and the mixture was stirred at -78 °C for 30 min, then warmed to 0 °C for 1 h. Upon cooling to -78 °C, a solution of (2*S*,4*S*)-2,4-di(*p*-tosyloxy) pentane¹²² (0.75 g, 1.82 mmol) in THF (5.0 mL) was added slowly via syringe. The mixture was warmed slowly to 25 °C and stirred at this temperature for 10 h. Degassed H₂O was added (10 mL) and the solvents were removed *in vacuo*. The resulting aqueous mixture was extracted with degassed Et₂O (3 x 10 mL) under argon. The combined organic layers were washed with brine (degassed) 2 x 5 mL), dried (MgSO₄) and the solvents were evaporated under reduced pressure to yield an orange-brown residue. This material was purified by crystallization from abs. ethanol (degassed) to give 0.92 g (71%) of the title compound as a white crystalline solid: ³¹P NMR (202 MHz, CDCl₃) δ -31.5 (d. of m).

(2*R*,4*R*)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was purged with argon, cooled to -78 °C and charged with 27a (54.7 mg, 0.263 mmol) and THF (0.5 mL). *n*-BuLi (40.3 μ L of a 7.17 M solution in heptane, 0.289 mmol) was added dropwise via syringe over a period of 10 min, followed by the addition of HMPA (0.5 mL). The reaction was stirred at -78 °C for 30 min then warmed to 0 °C for 20 min. After cooling to -40 °C, a solution of (2*S*,4*S*)-2,4-di(*p*-tosyloxy)pentane¹²² (51.5 mg, 0.125 mmol) in DMF (0.5 mL) was added slowly via syringe. Upon completion of the addition, the mixture was then warmed slowly to 25 °C. After stirring at 25 °C for 3 h, the mixture was diluted with Et₂O (1.0 mL) and added to 10% aqueous HCl (1.5 mL) contained in a separatory funnel. The organic layer was separated and the aqueous layer was extracted with Et₂O (4 x 1.0 mL). The organic layers were combined, washed with water (2 x 2.0 mL), brine (2.0 mL), dried (MgSO₄) and the solvents were removed *in vacuo*. The resulting beige residue was purified by flash chromatography on silica gel (10% EtOAc / hexane for elution) to yield 58 mg (91%) of 24 as a white solid. This material was recrystallized from hexane at 0 °C: mp 91.1-104.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.04-1.57 (br envelope, 24H, CH and Cy-H), 1.50-1.12 (br envelope, 24H, CH₂ and Cy-H), 0.86 (app t, *J* = 6.1 Hz, 6H, CH₃), 1.01-0.20 (br envelope, 6H, BH₃);

^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 34.9, 34.5, 26.5, 26.4, 25.9, 25.7, 24.8, 22.3, 13.9; ^{31}P NMR (202 MHz, CDCl_3) δ 24.1 (s); IR (film) 2929, 2852, 2365, 1449, 889 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{29}\text{H}_{56}\text{BP}_2(\text{M}^+-\text{BH}_4)$ 477.1961, found 477.3950.

(2R,4R)-2,4-Bis(dicyclohexylphosphino)pentane (19).

The reaction of 24 (19.8 mg, 0.041 mmol) with $\text{HBF}_4 \cdot \text{OMe}_2$ (54.9 mg, 0.41 mmol), in CH_2Cl_2 (0.5 mL) was carried out as described for the decomplexation of 26b. Upon evaporation of the solvents, under reduced pressure 17.0 mg (91%) of 19 was obtained as a white solid: mp 182.3-184.9 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 2.03 (m, 2H, CH), 1.95-1.64 (m, 22H, Cy-H envelope), 1.53 (s, 2H, CH_2), 1.47-1.15 (m, 22H, Cy-H envelope), 1.17 (d, $J = 7.1$ Hz, CH_3), 1.12 (d, $J = 7.0$ Hz, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 31.8, 31.1, 30.0, 28.1, 27.8, 27.5, 27.3, 27.2, 26.0, 25.4, 25.0, 15.8; ^{31}P NMR (202 MHz, C_6D_6) δ 6.5 (s); high resolution mass spectrum calcd. for $\text{C}_{29}\text{H}_{54}\text{P}_2(\text{M}^+)$ 464.3704, found 464.3700.

Substrate Synthesis-Ene-dienes and Dien-yne

Ethyl-4-methyl-2(E),4-pentadienoate (103). An oven-dried, round-bottomed flask was fitted with a pressure equalizing addition funnel, rubber septum and magnetic stirring bar. The vessel was charged with NaH (60% oil dispersion, 2.00 g, 50.0 mmol) and the oil was removed by trituration with pentane (3 x 10 mL). The flask was then

purged with nitrogen, charged with THF (100 mL) and cooled to -5°C . A solution of triethylphosphonoacetate (10.7 g, 47.6 mmol) in THF (20 mL) was added dropwise over 30 min. and the mixture was allowed to warm slowly to 25°C . After stirring at 25°C for 1 h, the solution was recooled to -5°C . Methacrolein (4.00 g, 57.2 mmol) was added dropwise over a period of 5 min. and the mixture was stirred at 25°C for an additional 30 min. Subsequently, ice water (50 mL) was added, the organic layer was separated and the aqueous layer was extracted with hexane (4 x 20 mL). The combined organic layers were washed with brine (2 x 10 mL), dried (MgSO_4) and solvent was evaporated under reduced pressure. The resulting oily residue was distilled (89°C , 10 torr) to yield 6.04 g (91%) of the title compound as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 7.35 (d, $J = 15.7$ Hz, 1H, $-\text{CH}=\text{CH}-$), 5.83 (d, $J = 15.7$ Hz, 1H, $-\text{CH}=\text{CH}-$), 5.31 (d, $J = 4.8$ Hz, 2H, $\text{CH}_2=\text{CCH}_3$), 4.20 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 1.87 (s, 3H, $\text{CH}_2=\text{CCH}_3$), 1.28 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 167.1 (C), 146.9 (CH), 140.5 (C), 124.1 (CH_2), 118.8 (CH), 60.3 (CH_2), 18.0 (CH_3), 14.3 (CH_3); IR (film) 2980, 1716, 1632, 1608, 1454, 1366, 1308, 1270, 1240, 1174, 1096, 1038, 982, 910, 866 cm^{-1} .

4-Methyl-2(E),4-pentadien-1-ol (104). An oven-dried, round-bottomed flask was fitted with a pressure equalizing addition funnel, rubber septum and magnetic stirring bar.

The vessel was charged with LiAlH_4 (1.72 g, 45.3 mmol), Et_2O (65 mL) and purged with nitrogen. The grey suspension was cooled to -5°C and then a solution of 103 (6.04 g, 43.1 mmol) in Et_2O (35 mL) was added dropwise over a period of 1 h, during which time evolution of H_2 occurred. The reaction mixture was warmed to 25°C and stirred for an additional 30 min. After the reaction was quenched at 0°C with water (10 mL), the resulting white slurry was filtered through a pad of celite. After rinsing the solids with a 50% THF / EtOAc solution (4 x 10 mL), the filtrate was collected, washed with brine (10 mL) and dried (MgSO_4). The solvent was evaporated under reduced pressure to yield 3.89 g (92%) of the crude alcohol as an oil. This material was purified by bulb-to-bulb distillation to yield 3.77 g (89%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 6.32 (d, $J = 15.7$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 5.77 (dt, $J = 5.7, 15.7$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 4.96 (s, 2H, $\text{CH}_2=\text{C}$), 4.18 (d, $J = 5.7$ Hz, 2H, CH_2), 1.87 (s, 1H, OH), 1.83 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 141.3 (C), 134.1 (CH), 128.4 (CH), 116.7 (CH_2), 63.5 (CH_2), 18.4 (CH_3); IR (film) 3370, 2972, 2918, 2866, 1610, 1452, 1376, 1098, 1032, 1002, 968, 886 cm^{-1} .

8-Methyl-4-oxo-1,6(E),8-nonatriene (7a). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with NaH (60% oil dispersion, 897 mg, 22.4 mmol) and the oil was

removed by trituration with pentane (3 x 5 mL). The flask was then purged with nitrogen, charged with THF (50 mL) and cooled to 0 °C. To the resulting suspension **104** (2.00 g, 20.4 mmol) was slowly added via syringe, during which time evolution of H₂ occurred. The reaction mixture was warmed to 25 °C and stirred for an additional 30 min. Upon cooling to 0 °C, allyl bromide (2.59 g, 21.4 mmol) was added dropwise via syringe and the mixture was allowed to warm slowly to 25 °C. After stirring at 25 °C for 12 h, ice water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄) and solvent was evaporated under reduced pressure. The resulting yellow oil was purified by bulb-to-bulb distillation to yield 2.76 g (98%) of the title compound as colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 6.32 (d, J = 15 Hz, 1H, CH₂CH=CH), 5.90 (ddt, J = 5.6, 10.6, 17.1 Hz, 1H, CH₂CH=CH₂), 5.72 (dt, J = 6.2, 15.7 Hz, 1H, CH₂CH=CH), 5.27 (d, J = 17.1 Hz, 1H, HCH=CH), 5.17 (d, J = 10.6 Hz, 1H, HCH=CH), 4.96 (s, 2H, CH₂=CCH₃), 4.04 (d, J = 6.2 Hz, 2H, CH₂), 3.97 (d, J = 5.6 Hz, 2H, CH₂), 1.83; s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 141.4 (C), 135.4 (CH), 134.7 (CH), 125.9 (CH), 117.0 (CH₂), 116.7 (CH₂), 71.1 (CH₂), 70.6 (CH₂), 18.4 (CH₃); IR (film) 2970, 2914, 2854, 1728, 1662, 1448, 1378, 1360, 1250, 1110, 1074,

988, 960, 924, 868 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_9\text{H}_{14}\text{O}$ (M^+) 138.1045, found 138.1045.

8-Methyl-4-oxo-6(E),8-nonadien-1-yne (105). The reaction of 1.05 equivalents of propargyl bromide (2.55 g, 21.4 mmol) with sodium 4-methyl-2(E),4-pentadien-1-oxide (2.45 g, 20.4 mmol), in THF (50 mL), was carried out as described above for 7a. Bulb-to-bulb distillation of the resulting yellow oil yielded 2.51 g (90%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 6.35 (d, $J = 15.7$ Hz, 1H, $\text{CH}_2\text{CHC}=\text{CH}$), 5.71 (dt, $J = 6.3, 15.7$ Hz, 1H, $\text{CH}_2\text{CHC}=\text{CH}$), 5.00 (s, 2H, $\text{H}_2\text{C}=\text{C}-$), 4.14 (t, $J^a = 2.4$ Hz, 2H, CH_2), 4.13 (d, $J = 6.3$ Hz, 2H, CH_2), 2.43 (t, $J^a = 2.4$ Hz, 1H, $\text{C}\equiv\text{CH}$), 1.84 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 141.2 (C), 136.2 (CH), 124.9 (CH), 117.1 (CH_2), 79.7 (CH), 74.3 (C), 70.1 (CH_2), 56.9 (CH_2), 18.4 (CH_3); IR (film) 2974, 2946, 2854, 2116, 1610, 1440, 1354, 1120, 1084, 1044, 1018, 970, 892, 668 cm^{-1} .

8-Methyl-4-oxo-1-(trimethylsilyl)-6(E),8-nonadien-1-yne (10). An oven-dried, round-bottomed flask was fitted with a pressure equalizing addition funnel, rubber septum and magnetic stirring bar. The vessel was charged with 105 (2.00 g, 14.7 mmol), THF (50 mL), purged with nitrogen and cooled to -78°C . To this solution was added $n\text{-BuLi}$ (3.2 mL of a 4.65 M solution in heptane, 14.8 mmol) over a period of 15 min. The resulting light yellow solution was warmed to

-15 °C and stirred for an additional 15 min. The reaction was then recooled to -78 °C, and chlorotrimethylsilane (1.92 g, 17.6 mmol) was added slowly via syringe. A light brown precipitate formed immediately and the mixture was warmed slowly to 25 °C. After stirring at 25 °C for 2 h, saturated aqueous NH_4Cl (5 mL) was added, the organic layer was separated and the aqueous layer was extracted with hexane (4 x 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO_4) and solvent was evaporated under reduced pressure. The resulting yellow oil was purified by flash chromatography on silica gel (25% EtOAc / hexane for elution) to give 2.18 g (70%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 6.34 (d, J = 15.7 Hz, 1H, $\text{CH}_2\text{HC}=\text{CH}$), 5.70 (dt, J = 6.5, 15.7 Hz, 1H, $\text{CH}_2\text{HC}=\text{CH}$), 4.97 (s, 2H, $\text{H}_2\text{C}=\text{C}$), 4.14 (s, 2H), 4.11 (d, J = 6.5 Hz, 2H, CH_2), 1.85 (s, 3H, CH_3), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 141.3 (C), 136.2 (CH), 125.1 (CH), 117.0 (CH_2), 101.5 (C), 91.4 (C), 70.2 (CH_2), 57.9 (CH_2), 18.4 (CH_3), -0.21 (CH_3); IR (film) 2960, 2850, 2174, 1612, 1454, 1352, 1250, 1120, 1086, 1018, 996, 968, 890, 844, 760, 700 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{12}\text{H}_{20}\text{SiO}$ (M^+) 208.1284, found 208.1284.

4-Oxo-1,6(E),8(E)-decatriene (7c). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with NaH (60%

oil dispersion, 897 mg, 22.4 mmol) and the oil was removed by trituration with pentane (3 x 5 mL). The flask was then purged with nitrogen, charged with THF (50 mL) and cooled to 0 °C. *Trans,trans*-2,4-hexadien-1-ol (2.00 g, 20.4 mmol) was slowly added via syringe, during which time evolution of H₂ occurred. The reaction mixture was warmed to 25 °C and stirred for an additional 30 min. Upon cooling to 0 °C, allyl bromide (2.59 g, 21.4 mmol) was added dropwise via syringe and the mixture was allowed to warm slowly to 25 °C. After stirring at 25 °C for 12 h, ice water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄) and the solvent was evaporated under reduced pressure. The resulting yellow oil was purified by bulb-to-bulb distillation to yield 2.79 g (99%) of the title compound as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 6.19 (dd, J = 10.5, 15.1 Hz, 1H, CH₂CH=CH), 6.05 (dd, J = 10.5, 14.7 Hz, 1H, CH₃CH=CH), 5.88 (ddt, J = 6.0, 10.5, 17.1 Hz, 1H, HCH=CHCH₂), 5.68 (dq, J = 6.8, 14.7 Hz, 1H, CH₃CH=CH), 5.62 (dt, J = 6.5, 15.1 Hz, 1H, CH₂CH=CH), 5.26 (d, J = 17.1 Hz, 1H, HCH=CHCH₂), 5.15 (d, J = 10.5 Hz, 1H, HCH=CHCH₂), 3.98 (d, J = 6.5 Hz, 2H, CH₂), 3.95 (d, J = 6.0 Hz, 2H, CH₂), 1.73 (d, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 134.9 (CH), 133.2 (CH), 130.8 (CH), 129.9 (CH), 126.7 (CH), 116.8 (CH₂), 70.9 (CH₂),

70.5 (CH₂), 18.0 (CH₃); IR (film) 3020, 2984, 2962, 2934, 2916, 2852, 1742, 1448, 1374, 1358, 1240, 1114, 1082, 1050, 990, 924 cm⁻¹; high resolution mass spectrum calcd. for C₉H₁₄O(M⁺) 138.1045, found 138.1044.

4-Oxo-6(E),8(E)-decadien-1-yne (1). The reaction of 1.05 equivalents of propargyl bromide (2.55 g, 21.4 mmol) with sodium *trans,trans*-2,4-hexadien-1-oxide (2.45 g, 20.4 mmol), in THF (50 mL), was carried out as described above for 7c. Bulb-to-bulb distillation of the resulting yellow oil yielded 2.59 g (97%) of the title compound as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 6.20 (dd, J = 10.4, 15.2 Hz, 1H, CH₂CH=CH), 6.04 (dd, J = 10.4, 13.6 Hz, 1H, CH₂CH=CH), 5.69 (dq, J = 6.7, 13.6 Hz, 1H, CH₃CH=CH), 5.57 (dt, J = 6.5, 15.2 Hz, 1H, CH₂CH=CH), 4.10 (d, J⁴ = 2.3 Hz, 2H, CH₂C≡CH), 4.05 (d, J = 6.5 Hz, 2H, CH₂), 2.40 (t, J = 2.3 Hz, 1H, C≡C-H), 1.74 (d, J = 6.7 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 135.2 (CH), 130.7 (CH), 130.4 (CH), 125.6 (CH), 79.8 (C), 74.2 (C), 69.9 (CH₂), 56.7 (CH₂), 18.0 (CH₃); IR (film) 3298, 3022, 2914, 2854, 2116, 1662, 1442, 1356, 1266, 1114, 1082, 1060, 990, 926, 668 cm⁻¹.

4-Oxo-1-(trimethylsilyl)-6(E),8(E)-decadien-1-yne (106).¹²³ The reaction of 1 (2.00 g, 14.7 mmol) with chlorotrimethylsilane (1.92 g, 17.6 mmol) was carried out as described previously for 10. Bulb-to-bulb distillation of

the resulting yellow oil yielded 2.78 g (89%) of the title compound as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 6.20 (dd, $J = 12.1, 15.1$ Hz, 1H, $\text{CH}_2\text{-CH=CH}$), 6.04 (dd, $J = 8.0, 12.1$ Hz, 1H, $\text{CH}_3\text{CH=CH}$), 5.71 (dq, $J = 6.8, 8.0$ Hz, 1H, $\text{CH}_3\text{CH=CH}$), 5.59 (dt, $J = 6.4, 15.1$ Hz, 1H, $\text{CH}_2\text{CH=CH}$), 4.11 (s, 2H, CH_2), 4.05 (d, $J = 6.4$ Hz, 2H, CH_2), 1.75 (d, $J = 6.8$ Hz, 3H, CH_3), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 134.0 (CH), 130.6 (CH), 130.2 (CH), 125.7 (CH), 101.5 (C), 91.3 (C), 69.9 (CH_2), 57.5 (CH_2), 17.9 (CH_3), -0.3 (CH_3); IR (film) 3020, 2960, 2914, 2852, 2174, 1662, 1440, 1350, 1250, 1114, 1100, 1082, 1026, 990, 926, 844, 760, 700, 654, 622 cm^{-1} .

1-Chloro-4-methyl-2(E),4-pentadiene (107). The following procedure is a modification of one described by Meyers and Collington.¹²⁴ A stirred mixture of 104 (4.91 g, 50.0 mmol) and 2,6-lutidine (5.89 g, 55.0 mmol), under nitrogen, was treated with LiCl (2.12 g, 50.0 mmol) dissolved in dry DMF (30 mL). On cooling to 0 °C, a suspension was formed which was treated dropwise with methanesulfonylchloride (6.30 g, 55.0 mmol). Stirring was continued at 0 °C for 4 h. The pale yellow reaction mixture was then poured into a separatory funnel containing ice water (15 mL) and pentane (20 mL). The organic layer was separated, and the aqueous layer was extracted with cold pentane (3 x 10 mL). The combined organic layers were washed with saturated aqueous CuNO_3 (3 x 10 mL), water

(2 x 10 mL), dried (Na_2SO_4) and the solvents were evaporated under reduced pressure. The resulting yellow residue was filtered through neutral activity II alumina (hexane for eluent) to yield 3.61 g (62%) of the title compound as a clear oil. ^1H NMR (300 MHz, CDCl_3) δ 6.36 (d, $J = 15.5$ Hz, 1H, $\text{CH}=\text{CHCH}_2$), 5.75 (dt, $J = 7.2, 15.5$ Hz, 1H, $\text{CH}=\text{CHCH}_2$), 5.02 (s, 2H, $\text{H}_2\text{C}=\text{C}$), 4.13 (d, $J = 7.2$ Hz, 2H, $\text{CH}_2\text{-Cl}$), 1.84 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 142.3 (C), 137.0 (CH), 124.9 (CH), 118.3 (CH_2), 45.3 (CH_2), 18.4 (CH_3); IR (film) 2926, 1672, 1442, 1248, 1176, 966, 894 cm^{-1} .

4,4-Bis(carboethoxy)-8-methyl-1,6(E),8-nonatriene

(108). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with NaH (60% oil dispersion, 808 mg, 20.2 mmol) and the oil was removed by trituration with pentane (3 x 5 mL). The flask was then purged with nitrogen, charged with THF (100 mL) and cooled to 0 °C. Diethyl-allyl malonate (3.64 g, 18.2 mmol) was slowly added via syringe and stirring was continued at 0 °C for 1 h. To the resulting suspension 107 (2.33 g, 20.0 mmol) was added dropwise via syringe over a period of 1 h. The reaction mixture was warmed slowly to 25 °C. After stirring at 25 °C for 4 h, 5% aqueous HCl (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with hexane (4 x 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO_4) and the solvent was evaporated

under reduced pressure. The resulting pale yellow oil was purified by flash chromatography on silica gel (15% EtOAc / hexane for elution) to give 4.68 g (92%) of the title compound as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 6.07 (d, $J = 15.6$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 5.68 (ddt, $J = 6.3$, 7.0 Hz, 1H, $\text{CH}_2\text{CH}=\text{CHH}$), 5.38 (dt, $J = 7.8$, 15.6 Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}$), 5.03 (d, $J = 7.0$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CHH}$), 4.95 (d, $J = 10.1$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CHH}$), 4.79 (d, $J = 5.5$ Hz, 2H, CH_2), 4.13 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 4.10 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 2.59 (d, $J = 7.8$ Hz, 2H, $\text{CH}_2\text{CH}=\text{CH}$), 2.55 (d, $J = 6.3$ Hz, 2H, $\text{CH}_2\text{CH}=\text{CHH}$), 1.72 (s, 3H, CH_3), 1.18 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.16 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 170.5 (C), 168.6 (C), 141.4 (C), 136.8 (CH), 132.3 (CH), 123.5 (CH), 118.8 (CH_2), 115.4 (CH_2), 61.1 (CH_2), 60.9 (CH_2), 57.5 (C), 36.9 (CH_2), 35.7 (CH_2), 18.3 (CH_3), 13.9 (CH_3); IR (film) 2982, 2938, 1734, 1642, 1610, 1368, 1276, 1240, 1208, 1188, 1152, 1096, 1036 cm^{-1} .

4,4-Bis(hydroxymethyl)-8-methyl-1,6(E),8-nonatriene (109). An oven-dried, round-bottomed flask was fitted with a pressure equalizing addition funnel, rubber septum and magnetic stirring bar. The vessel was charged with LiAlH_4 (1.22 g, 32.2 mmol), Et_2O (50 mL), purged with nitrogen and cooled to -5°C . A solution of 108 (4.5 g, 16.1 mmol) in Et_2O (150 mL) was added dropwise over a period of 1 h, during which time evolution of H_2 occurred. The reaction

mixture was warmed to 25 °C and stirred for an additional 2 h. Upon quenching the reaction at 0 °C with water (10 mL), the resulting white slurry was filtered through a pad of celite. After rinsing the solids with Et₂O (3 x 10 mL), the filtrate was collected, washed with brine (10 mL) and dried (MgSO₄). The solvent was evaporated under reduced pressure and the resulting oil was purified by bulb-to-bulb distillation to yield 3.06 g (97%) of the alcohol as a clear oil: ¹H NMR (300 MHz, CDCl₃) δ 6.18 (d, J = 15.6 Hz, 1H, CH=CH), 5.82 (ddt, J = 7.0, 9.4, 15.3 Hz, 1H, CH=CHH), 5.63 (dt, J = 7.0, 15.6 Hz, 1H, CH=CH), 5.09 (dd, J = 2.6, 26.4 Hz, 1H, CH=CHH), 5.08 (dd, J = 1.5, 9.4 Hz, 1H, CH=CHH), 4.87 (s, 2H, CH₂=C), 3.56 (s, 4H, CH₂O), 2.48 (br, 2H, OH), 2.13 (d, J = 7.0 Hz, 2H, CH₂CH=C), 2.06 (d, J = 7.0 Hz, 2H, CH₂CH=C), 1.82 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 141.7 (C), 136.0 (CH), 133.8 (CH), 125.2 (CH), 117.9 (CH₂), 114.9 (CH₂), 67.8 (CH₂), 65.2 (CH₂) 42.4 (C), 36.1 (CH₂), 34.7 (CH₂), 18.5 (CH₃); IR (film) 3362, 2924, 1440, 1120, 1030, 970, 916, 886, 738 cm⁻¹.

4,4-Bis(methoxymethyl)-8-methyl-1,6(E),8-nonatriene

(7b). An oven-dried, round-bottomed flask was fitted with a rubber septum and magnetic stirring bar. The vessel was charged with NaH (60% oil dispersion, 1.37 g, 34.3 mmol) and the oil was removed by trituration with pentane (3 x 5 mL). The flask was then purged with nitrogen, charged with DMF (50 mL) and cooled to 0 °C. A solution of 109 (3.05 g,

15.6 mmol) in DMF (25 mL) was added slowly via cannula, during which time evolution of H_2 occurred. The reaction mixture was stirred at 0 °C for an additional 2 h, then warmed to 25 °C for 30 min. The resulting grey-green suspension was recooled to 0 °C and methyl iodide (4.90 g, 34.5 mmol) was added dropwise via syringe. The mixture was allowed to warm slowly to 25 °C. After stirring at 25 °C for 12 h, ice water (15 mL) was added, the organic layer was separated and the aqueous layer was extracted with hexane (4 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The resulting pale yellow oil was purified by flash chromatography on silica gel (5% EtOAc / hexane for elution) to give 3.01 g (86%) of the title compound as a colorless oil: 1H NMR (300 MHz, $CDCl_3$) δ 6.13 (d, J = 15.6 Hz, 1H, $CH_2CH=CH$), 5.78 (ddt, J = 4.5, 7.6, 11.7 Hz, 1H, $CH_2CH=CHH$), 5.62 (dt, J = 7.7, 15.6 Hz, 1H, $CH_2CH=CH$), 5.05 (s, 1H, $CH_2CH=CHH$), 5.01 (d, J = 4.5 Hz, 1H, $CH_2CH=CHH$), 4.85 (s, 2H, $C=CH_2$), 3.31 (s, 6H, CH_3), 3.16 (s, 4H, CH_2), 2.09 (d, J = 7.7 Hz, 2H, $CH_2CH=CH$), 2.05 (d, J = 7.6 Hz, 2H, $CH_2CH=CHH$), 1.83 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 1H decoupled) δ 142.1 (C), 135.7 (CH), 134.4 (CH), 126.0 (CH), 117.4 (CH_2), 114.4 (CH_2), 75.2 (2 CH_2), 59.1 (2 CH_3), 42.3 (C), 36.8 (CH_2), 35.5 (CH_2), 18.7 (CH_3); IR (film) 3078, 2978, 2922, 2876, 2810, 1640, 1608, 1478,

1450, 1378, 1198, 1110, 970, 914, 882 cm^{-1} . Anal. Calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_2$: C, 74.95; H, 10.78. Found: C, 74.84; H, 10.59.

Rh(I) Mediated Alkene Cycloisomerizations

General Information: All new Rh(I) complexes were generated *in situ* by the reaction of $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ with 4 equivalents of mono-phosphine or phosphite ligands or 2 equivalents of the bisphosphine ligands. Tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite and $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ were prepared by Derek J. Sheehan according to the procedures of Denney¹²⁶ and Van Der Ent¹²⁵ respectively. Discounted $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ was provided by the Johnson Matthey Corporation on the "Precious metals on loan" program. (*R,R*)-*trans*-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (DIOP) was purchased from the Strem Chemical Company. $(\text{Ph}_3\text{P})_3\text{RhCl}$ was purchased from the Aldrich Chemical Company.

1,3,5 α ,7 α B-Tetrahydro-5-methyl-4-(trimethylsilyl)-isobenzofuran (110).¹²³ A flame-dried test tube (25 x 150mm) equipped with a stirring flea and rubber septum was charged with $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ (35.88 mg, 0.0500 mmol) and flushed with argon. The Rh dimer was then dissolved by the addition of THF (2.0 mL). Tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite (106.4 mg, 0.200 mmol) was added via syringe. To the resulting bright yellow solution was added 2,2,2-trifluoroethanol (TFE) (6.0 mL), followed by 106 (417 mg, 2.00 mmol). The reaction mixture was then heated

at 55 °C for 3.0 h. Upon completion of cyclization, the solution was transferred to a 25 mL round-bottomed flask and solvent was evaporated under reduced pressure. The residue was then dissolved in CH₂Cl₂ (15 mL) and the solution was concentrated again. This process was repeated 3 more times. Bulb-to-bulb distillation of the resulting residue gave 372 mg (89%) of the title compound as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 5.60 (s, 2H, HC=CH), 4.36 (d, J = 12.3 Hz, 1H, OCHH), 4.17 (d, J = 12.3 Hz, 1H, OCHH), 4.09 (dd, J = 7.3, 7.4 Hz, 1H, OCHH_a), 3.22 (dd, J = 7.3, 11.4 Hz, 1H, OCH_bH), 3.02 (q, J = 7.1 Hz, 1H, CHCH₃), 2.89 (m, 1H, CH), 1.13 (d, J = 7.1 Hz, 3H, CH₃), 0.11 (s, 9H, Si(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 146.6 (C), 134.2 (CH), 130.3 (C), 119.8 (CH), 71.5 (CH₂), 69.7 (CH₂), 40.1 (CH), 34.5 (CH), 23.1 (CH₃), 0.26 (CH₃); IR (film) 2960, 2854, 1628, 1250, 1044, 1016, 894, 838, 788, 766 cm⁻¹.

1,3,3aβ,6,7,7aβ-hexahydro-5-methylisobenzofuran (8a).

A flame-dried test tube (25 x 150mm) equipped with a stirring flea and rubber septum was charged with [(C₈H₁₄)₂RhCl]₂ (35.88 mg, 0.0500 mmol) and flushed with argon. The Rh dimer was then dissolved by the addition of THF (8.0 mL). To this solution was added tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite (106.4 mg, 0.200 mmol). To the resulting bright yellow solution was added 7a (276.5 mg, 2.00 mmol). The reaction mixture was then heated at 55 °C for 1.5 h. Upon completion of cyclization, the solution was

transferred to a 25 mL round-bottomed flask and solvent was evaporated under reduced pressure. Bulb-to-bulb distillation of the resulting gold-orange residue yielded 246 mg (89%) of the title compound as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 5.33 (s, fine structure, 1H, $\text{CH}=\text{C}$), 3.94 (dd, $J = 1.8, 7.2$ Hz, 1H, OCHH), 3.90 (dd, $J = 1.8, 7.7$ Hz, 1H, OCHH), 3.58 (dd, $J = 4.7, 7.6$ Hz, 1H, OCHH-CH-), 3.43 (dd, $J = 7.3, 7.6$ Hz, 1H, OCHH-CH-), 2.65 (m, 1H, CH), 2.30 (m, 1H, CH), 1.92 (t, $J = 5.8$ Hz, 2H, CH_2), 1.68 (s, 3H, CH_3), 1.65 (m, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 135.5 (C), 120.3 (CH), 73.0 (CH_2), 72.5 (CH_2), 53.2 (CH_2), 39.3 (CH), 36.1 (CH), 27.6 (CH_2), 23.7 (CH_3); IR (film) 2972, 2944, 2920, 2856, 1442, 1356, 1108, 1084, 1046, 1030, 970, 894, 734, 670, 638 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_9\text{H}_{14}\text{O}(\text{M}^+)$ 138.1045; found 138.1045.

[4+2] cycloisomerization of 7a with homochiral

bisphosphine ligands: A flame-dried test tube (25 x 150mm) equipped with a stirring flea was charged with $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ (35.88 mg, 0.0500 mmol) and flushed with argon. The Rh dimer was then dissolved by the addition of CH_2Cl_2 (0.5 mL). A smaller flame-dried test tube (12 x 75mm) was charged with the desired bisphosphine ligand (0.120 mmol) (see Table I), and flushed with argon. The ligand was then dissolved by the addition of CH_2Cl_2 (1.5 mL) and the resulting solution was transferred to the $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ solution via syringe. To the resulting red-orange solution was added 2,2,2-

trifluoroethanol (TFE) (6.0 mL), followed by 7a (276.5 mg, 2.00 mmol). The reaction mixture was then heated at 55 °C for the time indicated in Table I. Upon completion of cyclization, the solution was transferred to a 25 mL round-bottomed flask and solvent was evaporated under reduced pressure. The residue was then dissolved in CH₂Cl₂ (15.0 mL) and the solution was concentrated again. This process was repeated 3 more times. Bulb-to-bulb distillation of the resulting residue gave 8a as a colorless oil (isolated yields given in Table 6).

Table 6. Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 7a

Entry	Ligand	M.W.	Time	Yield (isolated)
1	3a	498.57	2.5 hr	86% (237 mg)
2	3f	770.57	2.5 hr	79% (219 mg)
3	3g	832.64	20.0 hr	92% (254 mg)
4	3b	560.64	3.0 hr	79% (218 mg)
5	3e	554.69	60.0 hr	72% (199 mg)
6	3c	526.63	4.0 hr	73% (202 mg)
7	3d	1042.57	12.0 hr	85% (234 mg)
8	21b	454.56	4.0 hr	90% (249 mg)

3a β , 6, 7, 7a β -Tetrahydro-2,2-bis(methoxymethyl)-5-methylindan (8b). The cycloaddition of 7b (448 mg, 2.00 mmol) with tris-(1,1,1,3,3,3-hexafluoro-2-propyl) phosphite (106.4 mg, 0.200 mmol) and [(C₈H₁₄)₂RhCl]₂ (35.88 mg, 0.0500 mmol), in THF (2.0 mL) and TFE (6.0 mL), was carried out according to the procedure given for 110. The reaction was heated at 55 °C for 5 h and worked up in

the manner given for 110. Bulb-to-bulb distillation of the resulting residue yielded 320 mg (71%) of the title compound as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 5.27 (s, 1H, $\text{CH}=\text{C}$), 3.32 (s, 6H, CH_3O), 3.29 (s, 2H, CH_2O), 3.18 (s, 2H, CH_2O), 2.41 (m, 1H, CH), 2.06 (m, 1H, CH), 1.84 (dt, $J = 2.1, 5.9$ Hz, 2H, CH_2), 1.71 (dd, $J = 7.6, 13.1$ Hz, 1H, $\text{CH}_\beta\text{H}_\alpha$), 1.62 (s, 3H, CH_3), 1.59 (dd, $J = 7.8, 13.7$ Hz, 1H, $\text{CH}_\beta\text{H}_\alpha$), 1.46 (m, 2H, CH_2), 1.25 (dd, $J = 7.2, 13.7$ Hz, 1H, $\text{CH}_\beta\text{H}_\alpha$), 1.21 (dd, $J = 8.3, 13.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 132.9 (C), 124.6 (CH), 78.6 (CH_2), 76.9 (CH_2), 59.1 (CH_3), 46.9 (C), 38.9 (CH), 38.7 (CH_2), 36.7 (CH_2), 36.0 (CH), 28.1 (CH_2), 25.9 (CH_2), 23.7 (CH_2); IR (film) 2890, 2855, 2850, 2840, 2810, 1450, 1185, 1110, 970 cm^{-1} .

[4+2] cycloisomerization of 7b with homochiral bisphosphine ligands: Cycloisomerization was carried out as described above for 7a using 7b (448 mg, 2.00 mmol). Refer to Table 7 for ligands, reaction times and yields.

Table 7. Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerizations of 7b

Entry	Ligand	M.W.	Time	Yield (isolated)
1	3f	770.57	8 hr	83% (374 mg)
2	3e	554.69	60 hr	69% (309 mg)
3	3a	498.55	24 hr	83% (375 mg)

1,3,5,7a β -Tetrahydro-6-methyl-4-(trimethylsilyl)isobenzofuran (11). A flame-dried test tube (25 x 150mm) equipped with a stirring flea was charged with Wilkinson's catalyst¹²⁷ (92.5 mg, 0.100 mmol) and flushed with argon. The catalyst was then dissolved by the addition of CH₂Cl₂ (2.0 mL). To the resulting deep red solution was added 2,2,2-trifluoroethanol (TFE) (6.0 mL), followed by 10 (417 mg, 2.00 mmol). The reaction mixture was then heated at 55 °C for 5.5 h. Upon completion of cyclization, the solution was transferred to a 25 mL round-bottomed flask and solvent was evaporated under reduced pressure. The residue was then dissolved in CH₂Cl₂ (15 mL) and the solution was concentrated again. This process was repeated 3 more times. Bulb-to-bulb distillation of the resulting residue yielded 367 mg (88%) of the title compound as a clear oil. ¹H NMR (300 MHz, CDCl₃) δ 5.42 (s, 1H, CH=C), 4.43 (br d, J = 12.9 Hz, 1H, OCHH), 4.28 (br d, J = 12.9 Hz, 1H, OCHH), 4.15 (dd, J = 7.5, 7.6 Hz, 1H, OCH_BH _{α}), 3.22 (dd, J = 7.5, 11.4 Hz, 1H, OCH_BH _{α}), 3.10 (m, 1H, CH), 2.61 (m, 2H, CH₂), 1.73 (s, 3H, CH₃), 0.09 (s, 9H, Si(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 147.9 (C), 135.0 (C), 124.2 (C), 117.5 (CH), 71.8 (CH₂), 69.4 (CH₂), 41.9 (CH), 35.0 (CH₂), 22.6 (CH₃), -1.47 (CH₃); IR (film) 2956, 2850, 1642, 1450, 1248, 1182, 1064, 1030, 918, 892, 860, 836, 800, 752, 692, 628 cm⁻¹. Anal. Calcd. for C₁₂H₂₀OSi: C, 69.17; H, 9.67. Found: C, 69.18; H, 9.47.

[4+2] cycloisomerization reaction of 10 with homochiral bisphosphine ligands: Cycloisomerization was carried out as described above for 7a using 10 (417 mg, 2.00 mmol). Refer to Table 8 for ligands, reaction times and yields.

Table 8. Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerization of 10

Entry	Ligand	M.W.	Time	Yield (isolated)
1	3a	498.57	2.0 hr	89% (371 mg)
2	3f	770.57	2.0 hr	99% (412 mg)
3	3g	832.64	1.5 hr	91% (379 mg)
4	3b	560.64	1.5 hr	76% (318 mg)
5	3e	554.69	2.0 hr	81% (329 mg)
6	15a	726.56	1.5 hr	76% (317 mg)

1,3,3a β ,4,5 α ,7a β -hexahydro-5-methylisobenzofuran (8c).

The cycloaddition of 7c (276.5 mg, 2.00 mmol) with tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite (106.4 mg, 0.200 mmol) and $[(C_8H_{14})_2RhCl]_2$ (35.88 mg., 0.0500 mmol), in THF (8.0 mL), was carried out according to the procedure given for 8a. The reaction was heated at 55 °C for 2.0 h, and worked up in the manner given for 8a. Bulb-to-bulb distillation of the gold-orange residue yielded 232 mg (84%) of the title compound as a colorless oil: 1H NMR (300 MHz, $CDCl_3$) δ 5.55 (s, 2H, HC=CH), 3.91 (dd, J = 7.2, 7.9 Hz, 2H, OCH_2), 3.53 (dd, J = 1.9, 8.5 Hz, 1H, $OCHH-CH-$), 3.30 (dd, J = 7.9, 9.6 Hz, 1H, $OCHH-CH-$), 2.58 (m, 1H, CH), 2.25 (m, 1H, CH), 2.10 (m, 1H, $CHCH_3$), 1.61 (dt, J = 4.5, 12.9 Hz, 1H, CH_2H_α), 1.03 (dt, J = 11.3, 12.9 Hz, 1H, CH_2H_α), 0.96 (d,

$J = 7.1 \text{ Hz}$, 3H , CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 135.4 (CH), 124.7 (CH), 74.7 (CH_2), 72.7 (CH_2), 39.0 (CH), 37.4 (CH), 34.5 (CH_2), 30.1 (CH), 21.5 (CH_3); IR (film) 3016, 2956, 2926, 2854, 1456, 1372, 1098, 1066, 1018, 990, 912, 738, 708 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_9\text{H}_{14}\text{O}(\text{M}^+)$ 138.1041, found 138.1045.

[4+2] cycloisomerization of 7c with homochiral bisphosphine ligands: Cycloisomerization was carried out as described above for 7a using 7c (276.5 mg, 2.00 mmol). Refer to Table 9 for ligands, reaction times and yields.

Table 9. Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerization of 7c

Entry	Ligand	M.W.	Time	Yield (isolated)
1	3a	498.57	5 hr	84% (232 mg)
2	3b	560.64	2 hr	73% (202 mg)
3	3c	526.63	2 hr	72% (205 mg)
4	3d	1042.57	24 hr	76% (211 mg)

1,3,3a β ,4 α ,5 β ,6,7,7a β -Octahydro-4-hydroxy-5-methylisobenzofuran (9a). A flame-dried test tube (12 x 125mm) equipped with a stirring flea and rubber septum was charged with 8a (138 mg, 1.00 mmol) and THF (1.0 mL). The vessel was then flushed with nitrogen and cooled to -5°C . $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (121 μL of a 10.1 M solution containing free $\text{S}(\text{CH}_3)_2$, 1.21 mmol) was added dropwise over 5 min. The reaction was then warmed to 25°C and stirred for 4 h. After cooling to -5°C , abs. ethanol (0.5 mL) was added,

followed by NaOH (0.41 mL of a 3N solution, 1.22 mmol) and H_2O_2 (0.45 mL of a 30% aqueous solution, 3.99 mmol). The mixture was stirred vigorously for 4 h. Ice water (5.0 mL) was added, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic phases were dried (MgSO_4) and solvent was removed by vacuum evaporation. The resulting residue was purified by flash chromatography on silica gel (90% EtOAc / hexane for elution) to give 123 mg (79%) of the alcohol as a viscous beige oil: ^1H NMR (300 MHz, CDCl_3) δ 4.04 (app d, $J = 8.5$ Hz, 1H, CH-OH), 3.81 (dd, $J = 8.4, 8.8$ Hz, 1H, OCHH), 3.74 (dd, $J = 4.5, 8.4$ Hz, 1H, OCHH), 3.49 (dd, $J = 7.9, 10.9$ Hz, 1H, OCHH), 3.09 (dd, $J = 10.0, 10.9$ Hz, 1H, OCHH), 2.56 (m, 1H, CH), 1.90 (m, 1H, CH), 1.85 (br s, 1H, OH), 1.60 (m, 2H, CH_2), 1.36 (m, 1H, CH), 1.15 (m, 2H, CH_2), 1.00 (d, $J = 6.4$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 74.5 (CH), 71.9 (CH_2), 69.1 (CH_2), 47.3 (CH), 38.7 (CH), 38.2 (CH), 28.4 (CH_2), 22.6 (CH_2), 18.2 (CH_3); IR (film) 3406, 2926, 2870, 1716, 1456, 1062, 1042, 984, 884 cm^{-1} . Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_2$: C, 69.19; H, 10.32. Found: C, 69.12; H, 10.22.

3a β ,4 α ,5 β ,6,7,7a β -Hexahydro-4-hydroxy-2,2-bis(methoxymethyl)-5-methylindan (9b).

Hydroboration/oxidation of **8b** (224 mg, 1.00 mmol) was carried out as described above for **9a**. The resulting residue was purified by flash chromatography on silica gel

(25% EtOAc / hexane for elution) to give 209 mg (86%) of the alcohol as a white crystalline solid. mp 60.4-66.2 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.32 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.27 (d, $J = 4.1$ Hz, 1H, CH_2O), 3.18 (app dd, $J = 9.8, 8.5$ Hz, 2H, CH_2O), 2.96 (dd, $J = 9.8, 9.5$ Hz, 1H, CH_2O), 2.26 (m, 1H, CH-O), 1.75 (d, $J = 14.2$ Hz, 1H, CH_2), 1.65 (m, 1H, CH_2), 1.60-1.40 (m, 4H, CH and CH_2), 1.38 (d, $J = 10.3$ Hz, 2H, CH_2), 1.22 (m, 3H, CH and CH_2), 0.90 (d, $J = 5.8$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 78.8 (CH_2), 77.8 (CH_2), 77.5 (CH), 59.2 (CH_3), 48.1 (CH), 46.6 (C), 39.5 (CH), 39.4 (CH), 35.5 (CH_2), 35.3 (CH_2), 28.9 (CH_2), 25.7 (CH_2), 18.5 (CH_3); IR (KBr) 3040, 2950, 2900, 2875, 2850, 1450, 1260, 1090 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{14}\text{H}_{26}\text{O}_3$ (M^+) 242.1883, found 242.1882.

1,3,3a β ,4 α ,5 β ,6-Hexahydro-4-hydroxy-5-methyl-7-(trimethylsilyl)isobenzofuran (12). The hydroboration/oxidation of 11 (208 mg, 1.00 mmol) was carried out as described above for 9a. The resulting residue was purified by flash chromatography on silica gel (90% EtOAc / hexane for elution) to give 156 mg (69%) of the alcohol as a viscous beige oil: ^1H NMR (300 MHz, CDCl_3) δ 4.08 (d, $J = 8.5$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.85 (d, $J = 8.5$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.67 (dd, $J = 4.3, 8.4$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.33 (dd, $J = 7.9, 11.6$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.07 (dd, $J = 10.3, 10.4$ Hz, 1H, CH-OH), 2.53 (m, 1H, CHCH_3), 2.24 (app p, $J = 5.0$ Hz, 1H, CH), 1.94 (br s, 1H, OH), 1.64 (dd, $J = 4.4, 14.5$ Hz,

1H, $\text{CH}_2\text{H}_\alpha$), 1.34 (dd, $J = 12.4, 14.5$ Hz, 1H, $\text{CH}_2\text{H}_\alpha$), 1.01 (d, $J = 6.4$ Hz, 3H, CH_3), 0.02 (s, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 74.7 (CH_2), 71.1 (CH_2), 67.7 (CH_2), 49.8 (C), 44.8 (CH), 37.0 (CH), 31.4 (C), 18.0 (CH_2), -2.3 (CH_3), -4.1 (CH_3); IR (KBr) 3214, 2958, 2910, 2892, 1250, 1036, 866, 842 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{12}\text{H}_{24}\text{SO}_2$ ($\text{M}^+ + \text{H}_2$) 228.1546, found 228.1546.

1,3,3a β ,4 α ,5 α ,6 β ,7,7a β -Octahydro-4,5-bis(hydroxy)-6-methylisobenzofuran (9c). An oven-dried flask fitted with a stirring bar and rubber septum was charged with N-methylmorpholine-N-oxide (177 mg, 1.51 mmol), H_2O (0.60 mL) and acetone (0.30 mL). The OsO_4 catalyst (2.5% mol) was then added and the vessel was flushed with nitrogen. To the mixture was added 8c (196 mg, 1.42 mmol) via syringe and a two-phase solution was observed. The reaction mixture was stirred at 25 °C for 20 h. Saturated aqueous NaHSO_3 (25 mL) was subsequently added and the mixture was poured into a separatory funnel containing Et_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organics were washed with brine, dried (MgSO_4) and the solvent was evaporated under reduced pressure. The resulting residue was filtered through silica gel (EtOAc for elution) to give 186 mg (76%) of the alcohol as a tan solid. Recrystallization from CCl_4 yielded a white crystalline material: mp 41-42 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.90 (app

q, $J = 5.4, 9.0$ Hz, 2H, $\text{OCH}_2\text{H}_\alpha + \text{CH-OH}_{\text{eq}}$), 3.75 (dd, $J = 4.7, 8.3$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.61 (app d, $J = 8.2$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.54 (dd, $J = 8.3, 10.7$ Hz, 1H, $\text{OCH}_2\text{H}_\alpha$), 3.34 (br d, $J = 9.1$ Hz, 1H, CH-OH_{ax}), 2.65 (br d, $J = 9.1$ Hz, 1H, CH), 2.38 (m, 2H, $\text{CHCH}_3 + \text{OH}_{\text{ax}}$), 1.95 (br s, 1H, OH_{eq}), 1.85 (m, 1H, CH), 1.63 (app p, $J = 5.1, 8.6, 11.4$ Hz, 1H, $\text{CH}_2\text{H}_\alpha$), 1.15 (app sx, $J = 1.3$ Hz, 1H, $\text{CH}_2\text{H}_\alpha$), 1.00 (d, $J = 6.5$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 74.4 (CH_2), 74.3 (CH), 68.6 (CH), 67.6 (CH_2), 45.6 (CH), 35.5 (CH), 34.1 (CH_2), 31.3 (CH), 18.3 (CH_3); IR (KBr) 3404, 2950, 2926, 2868, 1108, 1092, 1052, 1032 cm^{-1} ; high resolution mass spectrum (CI) calcd. for $\text{C}_9\text{H}_{20}\text{O}_3\text{N}$ ($\text{M} + \text{NH}_4^+$) 190.1438, found ($\text{M} + \text{NH}_4^+$) 190.1443.

Preparation of Esters of (*R*)- α -Methoxy- α -trifluoromethylphenylacetic Acid. The following procedure was used to prepare all MTPA derivatives for NMR studies. (*S*)-(+)-MTPA-Cl was prepared from (*R*)-(+)-MTPA and distilled.¹⁰² A flame-dried test tube (12 x 125mm) equipped with a stirring flea and rubber septum was charged with 4-dimethylaminopyridine (DMAP) (51 mg, 0.42 mmol) and CH_2Cl_2 (0.50 mL). The solution was cooled to 0 °C and flushed with nitrogen. (*S*)(+)-MTPA-Cl (99 mg, 0.39 mmol) was added, followed by a solution of 9a (40 mg, 0.26 mmol) in CH_2Cl_2 (0.50 mL). The reaction mixture was then shaken and allowed to stand at 25 °C for an additional 15 h. The mixture was diluted with Et_2O (3 mL) and added to cold 5% aqueous HCl

(2.0 mL). The organic layer was separated and washed with cold saturated aqueous Na_2CO_3 (3.0 mL), followed by cold 5% aqueous CuSO_4 (3.0 mL). The organic layer was then washed with cold water until excess CuSO_4 was removed. The organic phase was dried (MgSO_4) and concentrated *in vacuo*. The resulting residue was dissolved in CH_2Cl_2 (2.0 mL) and the solution was concentrated again. This process was repeated 3 more times to give 94 mg (97%) of the two diastereomeric MTPA-esters (corresponding to 13a) as a beige solid. Purification of the final product can be accomplished by preparative GLC, however, care must be taken that both isomers are completely collected. All compounds gave ^1H NMR spectra consistent with their assigned structures, with full consideration of the nonequivalence of diastereotopic substituents.

Ferrocene Ligand Synthesis

General Information: Bis(tri-*n*-butylstannyl)ferrocene was prepared as described by Wright¹²⁹ and purified by column chromatography on activity II neutral alumina (100% hexane for eluent). Bis(dimethylamino)chlorophosphine ($\text{ClP}(\text{NMe}_2)$) was prepared according to the procedure of Noth.¹⁰⁹ Organolithium and Grignard reagents were prepared from the corresponding bromides in Et_2O or THF.

Bis(dimethylamino)-4-methoxyphenyl phosphine (39a). 4-Bromoanisole (18.7 g, 0.100 mol) was added to a solution of *n*-BuLi (36.9 mL of a 2.98 M solution in heptane 0.110 mol) in Et₂O (100 mL) at 0 °C. The reaction mixture was stirred for an additional 15 min at 0 °C. The resulting solution of 4-lithioanisole was then added dropwise to (Me₂N)₂P-Cl¹⁰⁹ (14.7 g, 0.085 mol) in Et₂O (50 mL) at -78 °C. The mixture was then warmed slowly to 25 °C. After dilution with anhydrous Et₂O (50 mL), the solution was filtered under argon through celite. Concentration of the solution followed by purification of the yellow liquid by fractional distillation (100-110 °C, 1.1 torr) gave 20.7 g (92%) of 39a as a viscous clear oil: ¹H NMR (300 MHz, CDCl₃) δ 7.29 dd, *J* = 5.3, 8.6 Hz, 2H, Ar-H), 6.89 (dd, *J* = 1.9, 8.6 Hz, 2H, Ar-H), 3.80 (s, 3H, CH₃), 2.72 (d, *J* = 9.2 Hz, 12H, NCH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 141.2, 140.6, 132.6, 132.4, 113.9 (2C), 55.2, 41.6 (2C), 41.4 (2C).

Bis(dimethylamino)-2-trifluoromethylphenyl phosphine (39b). Dichloro-2-trifluoromethylphenyl phosphine¹¹⁴ (24.7 g, 0.100 mol) in Et₂O (50 mL) was slowly added to a solution of dimethylamine (22.5 g, 0.500 mol) in Et₂O (100 mL) at -78 °C. The reaction mixture was then warmed slowly to 25 °C. The solution was filtered under argon through celite. Concentration of the solution followed by fractional distillation (80-95 °C, 0.150 torr) gave 18.9 g (72%) of 39b as a viscous clear oil.

Bis(dimethylamino)-phenyl phosphine (39c).¹¹⁴**Chloro-(dimethylamino)-4-methoxyphenyl phosphine (40a).**

PCl_3 (12.6 g, 0.092 mol) was slowly added to 39a (20.7 g, 0.092 mol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, then warmed to 25 °C for 1 h. Purification of the resulting product by fractional distillation (135-145 °C, 0.60 torr) gave 18.7 g (99%) of 40a as a viscous clear oil: ^1H NMR (300 MHz, CDCl_3) δ 7.60 (dd, J = 6.1, 8.7 Hz, 2H, Ar-H), 6.96 (dd, J = 1.6, 8.7 Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3), 2.65 (d, J = 13.0 Hz, 6H, NCH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 141.3, 140.6, 132.5, 132.2, 113.9 (2C), 55.3, 40.0, 39.9.

Chloro-(dimethylamino)-2-trifluoromethylphenyl phosphine (40b). Fractional distillation (55-65 °C (0.050 torr) gave 17.7 g (96%) of 40b: ^1H NMR (300 MHz, CDCl_3) δ 8.34 (dd, J = 3.1, 8.0 Hz, 1H, ArH), 7.72 (m, 1H, ArH), 7.64 (t, J = 7.1 Hz, 1H, ArH), 7.52 (t, J = 7.5 Hz, 1H, ArH), 2.60 (d, J = 12.9 Hz, 6H, NCH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 133.3, 133.2, 131.5, 130.1, 126.7, 126.1, 122.5, 40.0, 39.8.

Chloro-(dimethylamino)-phenyl phosphine (40c).

Fractional distillation (90-100 °C, 0.200 torr) gave 16.8 g (81%) of 40c.¹¹⁴

(2*R*,4*S*,5*R*)-2-(4-methoxyphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38a). To a solution of (-)-ephedrine (0.086 mol, 14.1 g) in 1,2-DME (125 mL) containing 1,10-phenanthroline (~5 mg) at -50 °C was added exactly 1 eq. of *n*-BuLi (21.5 mL of a 4.00 M solution in heptane, 0.086 mol). To this solution was added 40a (18.7 g, 0.0907 mol) in 1,2-DME (25 mL) at -50 °C. The resulting reaction mixture was then stirred vigorously and warmed slowly to 25 °C (~2 h), during which time a precipitate formed. A catalytic amount of chlorotrimethylsilane (500 μ L, 5 mol %) was then added²⁰ and the reaction mixture was refluxed for 10 h. After cooling to 0 °C, $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (8.5 mL of a 10.1 M solution, 0.086 mol) was added. The reaction mixture was then stirred for an additional 2 h at 25 °C. The resulting mixture was concentrated *in vacuo* to yield a beige viscous residue which was diluted with anhydrous benzene (100 mL) and filtered through florisil. Concentration of the solution followed by trituration with anhydrous methanol gave the title compound as a white solid. Recrystallization from anhydrous methanol afforded 22.2 g (82%) of the pure complex: mp 82 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.78 (dd, $J = 9.2, 9.4$ Hz, 2H, Ar-*H*), 7.40-7.20 (m, 5H, Ph-*H*), 6.95 (dd, $J = 1.7, 8.8$ Hz, 2H, Ar-*H*), 5.55 (dd, $J = 2.5, 5.9$ Hz, 1H, OCH), 3.82 (s, 3, OCH_3), 3.65 (m, 1H, NCH), 2.61 (d, $J = 10.9$ Hz, 3H, CHCH_3), 0.85 (d, $J = 6.6$ Hz, 3H, CH_3), 1.45-0.40 (br envelope, BH_3);

^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 136.6, 136.0, 133.4, 133.2, 128.3, 128.2 (2C), 126.7, 126.6 (2C), 114.2, 114.1, 83.7, 59.4, 55.4, 29.4, 13.4; ^{31}P NMR (202 MHz, CDCl_3) δ 131.9 (d, $J = 93.1$ Hz); IR (film) 2974, 2934, 2902, 2839, 2380, 2340, 1596, 1501, 1259, 1114, 966 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{17}\text{H}_{23}\text{BNO}_2\text{P}(\text{M}^+)$ 315.1559, found 315.1530.

(2R,4S,5R)-2-(2-Trifluoromethylphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38b).

Recrystallization from methylcyclohexane or methanol afforded 24.3 g (77%) 9f 38b: mp 106.6-108.0 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.83 (dd, $J = 7.5, 11.1$ Hz, 1H, ArH), 7.74 (m, 1H, ArH), 7.60 (m, 2H, ArH), 7.33 (m, 5H, PhH), 5.21 (dd, $J = 3.4, 6.0$ Hz, 1H, OCH), 3.66 (m, 1H, NCH), 2.97 (d, $J = 9.8$ Hz, 3H, NCH_3), 0.81 (d, $J = 6.6$ Hz, 3H, CH_3), 1.75-0.40 (br envelope, 3H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 136.0, 132.2, 132.1, 131.5, 131.2, 128.3 (2C), 128.2, 127.2, 126.2, 125.4, 121.8, 83.3, 58.3, 30.8, 13.1; ^{31}P NMR (202 MHz, CDCl_3) δ 131.3 (d, $J = 89.5$ Hz); IR (film) 2995, 2937, 2869, 2425, 2383, 1456, 1318, 1135, 973 cm^{-1} ; high resolution mass spectrum calcd. for $\text{C}_{17}\text{H}_{20}\text{BF}_3\text{NOP}(\text{M}^+)$ 353.1328, found 353.1315.

(2R,4S,5R)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (38c). Recrystallization from methanol afforded 27.5 g (80%) of 38c: mp 103.3-104.6 $^\circ\text{C}$;

^1H NMR (300 MHz, CDCl_3) δ 7.84 (m, 2H, PhH), 7.54 (m, 3H, PhH), 7.40 (m, 5H, PhH), 5.59 (dd, $J = 6.0, 3.0$ Hz, 1H, OCH), 3.67 (ddq, $J = 8.7, 6.5, 6.0$ Hz, 1H, NCH), 2.67 (d, $J = 11.0$ Hz, 3H, NCH_3) 0.81 (d, $J = 6.5$ Hz, 3H, CH_3), 1.70-0.20 (br envelope, 3H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 133.0, 131.7, 131.5, 129.3, 129.2 (2C), 129.0, 127.3 (2C), 84.8, 59.8, 30.1, 14.2; ^{31}P NMR (202 MHz, CDCl_3) δ 132.8 (d, $J = 96.0$ Hz); IR (film) 3060, 2976, 2386, 1436, 1207, 1177, 1113, 965, 748, 699 cm^{-1} .

1-(Tri-*n*-butylstannyl)-1'-[(*Rp*)-*N*-methyl,*N*-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxyphenyl)phosphino]ferrocene (42a). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was charged with 1,1'-bis(tri-*n*-butylstannyl)ferrocene (2.18 g, 2.86 mmol) and THF (20 mL), purged with argon and cooled to -78°C . *n*-BuLi (0.90 mL of a 3.33 M solution in heptane, 3.00 mmol) was added dropwise to the reaction mixture over a period of 10 min. The reaction mixture was then stirred at -78°C for an additional 1 h. A solution of 38a (0.992 g, 3.15 mmol) in THF (10 mL) was added slowly via syringe at -78°C . The mixture was stirred at -78°C for 1 h, then at -25°C for 1 h and finally at 0°C for 15 min. Upon cooling to -20°C , 10 equiv. of methyl iodide (4.06 g, 28.6 mmol) was added via syringe. The mixture was warmed slowly to 25°C and H_2O (10 mL) was added. The organic layer was separated and the

aqueous layer was extracted with Et₂O (4x15 mL). The organic layers were combined, washed with brine (2x10 mL), dried (MgSO₄) and the solvents were evaporated under reduced pressure. The resulting orange oil was purified by flash chromatography on silica gel (5% EtOAc / hexane for elution) to give 2.04 g (89%) of the title compound as a viscous orange oil: ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.28 (m, 7H, Ph-H and Ar-H), 6.82 (dd, J = 8.7, 1.8 Hz, 2H, Ar-H), 4.49 (s, 1H, Cp-H), 4.46 (s, 1H, Cp-H), 4.40 (s, 1H, Cp-H), 4.36 (s, 1H, Cp-H), 4.32 (s, 1H, Cp-H), 4.27 (d, J = 5.3 Hz, 1H, CHPh), 4.15 (s, 1H, Cp-H), 4.10 (s, 1H, Cp-H), 4.02 (m, 1H, CHCH₃), 3.98 (s, 1H, Cp-H), 3.81 (s, 3H, Ar-OCH₃), 3.19 (s, 3H, OCH₃), 2.36 (d, J = 8.4 Hz, 3H, NCH₃), 1.56-1.48 (m, 6H, SnCH₂), 1.32 (app sx, J = 7.6 Hz, 6H, SnCH₂CH₂), 1.15 (d, J = 6.8 Hz, 3H, CH₃), 0.99 (app dd, J = 10.6, 8.0 Hz, 6H, Sn(CH₂)₂CH₂), 0.89 (t, J = 7.2 Hz, 9H, Sn(CH₂)₃CH₃); ¹³C NMR (75 MHz, CDCl₃, ¹H decoupled) δ 140.1, 133.3, 133.2, 128.2, 127.3, 113.8, 113.6, 88.6, 75.8, 73.5, 71.9, 71.1, 57.3, 57.0, 55.2, 30.3, 29.1, 27.8, 13.7, 12.9, 10.3; ³¹P NMR (202 MHz, CDCl₃) δ 67.6 (s).

1-(Tri-*n*-butylstannyl)-1'-[(*Rp*)-*N*-Methyl,*N*-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-trifluoromethylphenyl)phosphino]ferrocene (42b). Purification by flash chromatography on silica gel (2% EtOAc / hexane for elution) afforded 0.967 g (70%) of 42b: ¹H NMR (300 MHz, CDCl₃) δ 8.18 (dd, J = 11.8, 9.0 Hz, 1H, ArH), 7.82 (m, 1H,

ArH), 7.55 (app p, $J = 9.0$ Hz, 2H, ArH), 7.40-7.10 (m, 5H, PhH), 4.78 (s, 1H, CpH), 4.56 (s, 1H, CpH), 4.43 (s, 3H, CpH), 4.31 (s, 1H, CpH), 4.08 (s, 1H, CpH), 4.00 (s, 1H, CpH), 3.95 (m, 1H, CHCH₃), 3.30 (s, 3H, OCH₃), 2.49 (d, $J = 9.0$ Hz, 3H, NCH₃), 1.64-1.40 (m, 6H, SnCH₂), 1.32 (app sx, $J = 7.4$ Hz, 6H, Sn(CH₂CH₂), 0.98 (m, 9H, Sn(CH₂)₂CH₂ and CH₃), 0.89 (t, $J = 7.2$ Hz, 9H, Sn(CH₂)₃CH₃); ³¹P NMR (202 MHz, CDCl₃) δ 32.9 (s).

1-(Tri-*n*-butylstannyl)-1'-[(*Rp*)-*N*-Methyl,*N*-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphino]ferrocene (42c). Purification by flash chromatography on silica gel (5% EtOAc / hexane for elution) afforded 0.715 g (71% of 42c: ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.20 (m, 10H, PhH), 4.48 (app d, $J = 6.5$ Hz, 2H, CpH), 4.42 (s, 1, CpH), 4.37 (s, 1H, CpH), 4.30 (m, 2H, CpH and CH), 4.15 (s, 1H, CpH), 4.10 (s, 1H, CpH), 4.00 m, 1H, CHCH₃), 3.98 (s, 1H, CpH), 3.20 (s, 3H, OCH₃), 2.38 (d, $J = 8.3$ Hz, 3H, NCH₃), 1.63-1.44 (m, 6H, SnCH₂), 1.32 (app sx, $J = 7.3$ Hz, 6H, SnCH₂CH₂), 1.15 (d, $J = 6.7$ Hz, 3H, CH₃), 0.98 (app dd, $J = 9.4, 6.9$ Hz, 6H, Sn(CH₂)₂CH₂), 0.89 (t, $J = 7.3$ Hz, 9H, Sn(CH₂)₃); ³¹P NMR (202 MHz, CDCl₃) δ 67.8 (br s).

1,1'-Bis[(*Rp*)-*N*-Methyl,*N*-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxyphenyl)phosphino]ferrocene (37a). An oven-dried, round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel

was charged with 42a (2.04 g, 2.54 mmol) and THF (10 mL), purged with argon and cooled to -78°C . $n\text{-BuLi}$ (1.00 mL of a 2.79 M solution in heptane, 2.79 mmol) was added dropwise to the reaction mixture over a period of 10 min. The reaction was then stirred at -78°C for an additional 1 h. A solution of 38a (0.84 g, 2.67 mmol) in THF (10 mL) was added slowly via syringe at -78°C . The mixture was warmed slowly to 0°C and then stirred at 0°C for an additional 2 h. Upon cooling to -20°C , 10 equiv. of methyl iodide (3.61 g, 25.4 mmol) was added via syringe. The mixture was warmed slowly to 25°C and H_2O (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (4x10 mL). The organic layers were combined, washed with brine (2x10 mL), dried (MgSO_4) and the solvents were evaporated under reduced pressure. The resulting orange residue was purified by flash chromatography on silica gel (20% EtOAc / hexane for elution) to give 1.26 g (60%) of the title compound as an orange foamy material: ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.18 (m, 14H, PhH and ArH), 6.80 (dd, $J = 8.5, 1.7$ Hz, 4H, ArH), 4.68 (s, 2H, CpH), 4.62 (s, 2H, CpH), 4.56 (s, 2H, CpH), 4.28 (d, $J = 5.4$ Hz, 2H, CH), 4.20 (s, 2H, CpH), 4.05 (m, 2H, CHCH_3), 3.79 (s, 6H, OCH_3), 3.20 (s, 6H, OCH_3), 2.37 (d, $J = 8.5$ Hz, 6H, NCH_3), 1.18 (d, $J = 6.8$ Hz, 6H, CH_3), 1.48-0.05 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, CDCl_3 , ^1H decoupled) δ 161.4, 139.9, 133.2, 133.0, 128.9, 128.2,

127.4, 127.3, 125.2, 124.2, 123.2, 113.8, 113.7, 88.4, 74.5, 73.7, 73.0, 72.9, 57.5, 57.3, 56.9, 55.2, 30.3, 13.0; ^{31}P NMR (202 MHz, CDCl_3) δ 67.4 (s).

1,1'-Bis[(Rp)-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-trifluoromethylphenyl)phosphino]ferrocene (37b). Purification by flash chromatography on silica gel (20% EtOAc /hexane for elution) afforded 0.451 g (43%) of 37b as a light orange solid: ^1H NMR (300 MHz, CDCl_3) δ 8.00 (dd, $J = 9.4, 8.2$ Hz, 2H, ArH), 7.83 (m, 2H, ArH), 7.55 (dt, $J = 9.4, 8.2$ Hz, 4H, ArH), 7.38-7.15 (m, 10H, PhH), 4.76 (s, 2H, CpH), 4.72 (d, $J = 8.2$ Hz, 4H, CpH and CH), 4.61 (s, 2H, CpH), 4.39 (s, 2H, CpH), 3.97 (m, 2H, CHCH_3), 3.28 (s, 6H, OCH_3), 2.46 (d, $J = 8.8$ Hz, 6H, NCH_3), 1.02 (d, $J = 7.0$ Hz, 6H, CH_3), 1.68-0.30 (br envelope, 6H, BH_3); ^{31}P NMR (202 MHz, CDCl_3) δ 76.2 (s).

1,1'-Bis[(Rp)-N-methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphino]ferrocene (37c). Purification by flash chromatography on silica gel (20% EtOAc / hexane for elution) afforded 0.449 g (62%) of 37c as an orange solid: ^{31}P NMR (202 MHz, CDCl_3) δ 68.2 (s).

1,1'-Bis[boronato-fluoro-(4-methoxyphenyl)phosphino]ferrocene (36a). An oven-dried teflon test-tube (12 x 125 mm) was fitted with a magnetic stirring bar and rubber septum. The vessel was charged with CHCl_3 (1.3 mL, distilled from and stored over P_2O_5). CH_3CN (0.13 mL) was

then added, the vessel was purged with argon and the mixture was cooled to 0 °C. The stopper was removed and while a constant flow of argon was passed through the flask, $\text{HF} \cdot (\text{Py})_x$ (66 mg, 1.5 equiv. w/w, ~3.3 mmol) was added to the vessel via a teflon pipet. The stopper was replaced and upon cooling to -78 °C, a solution of 37a (44 mg, 0.052 mmol) in CHCl_3 (1.3 mL) was slowly added. The mixture was warmed to -20 °C and stirred for an additional 48 h. The reaction mixture was quenched with 25% aqueous NH_4F (2.5 mL) and diluted with Et_2O (4.0 mL). The organic layer was separated, washed with 5% aqueous H_2SO_4 (2.0 mL), saturated aqueous NaHCO_3 (2.0 mL), brine (1.0 mL) and dried (MgSO_4). The solvents were evaporated under reduced pressure to afford 26 mg (95%) of the title compound as a dark orange oil: ^1H NMR (300 MHz, CDCl_3) δ 7.72 (dt, $J = 8.8, 3.0$ Hz, 4H, ArH), 6.99 (m, 4H, ArH), 4.81 (d, $J = 1.3$ Hz, 2H, CpH), 4.75 (s, 1H, CpH), 4.71 (s, 1H, CpH), 4.65 (s, 2H, CpH), 4.59 (s, 1H, CpH), 4.43 (s, 1H, CpH), 3.85 (s, 6H, OCH_3), 1.70-0.40 (br envelope, 6H, BH_3); ^{31}P NMR (202 MHz, CDCl_3) δ 145.5 (d, $J = 899$ Hz).

1,1'-Bis[boronato-fluoro-(2-trifluoromethylphenyl)phosphino]ferrocene (36b). Upon work-up, 150 mg (98%) of the title compound was obtained from 37b (235 mg, 0.255 mmol) and $\text{HF} \cdot (\text{Py})_x$ (353 mg, ~0.420 mmol): ^1H NMR (300 MHz, CDCl_3) δ 7.79 (m, 2H, ArH), 7.75-7.55 (m, 6H, ArH), 4.91 (s, 6H, CpH), 4.58 (s, 1H, CpH), 4.55 (s, 1H, CpH), 1.70-0.45 (br

envelope, 6H, BH₃); ³¹P NMR (202 MHz, CDCl₃) δ 152.9 (d, J = 961 Hz).

1,1'-Bis[boronato-methyl-(4-methoxyphenyl)phosphino]ferrocene (35a). An oven-dried round-bottomed flask was fitted with a magnetic stirring bar and rubber septum. The vessel was charged with 36a (66 mg, 0.126 mmol) and Et₂O (2.5 mL), purged with argon and cooled to -78 °C. Methyl magnesium chloride (1.26 mL of a 0.999 M solution in Et₂O, 1.26 mmol) was added dropwise to the reaction mixture. The solution was warmed slowly to 25 °C and stirred an additional 3 h. After quenching with saturated aqueous NH₄Cl (2.5 mL) the organic layer was separated and the aqueous layer was extracted with Et₂O (2x2.0 mL). The combined organic layers were washed with brine (2.0 mL), dried (MgSO₄) and the solvents were removed *in vacuo*. The resulting residue was filtered through a plug of silica gel (1% EtOAc / toluene) to give 61 mg (93%) of 35a as an orange solid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (app dq, J = 9.3, 1.5 Hz, 4H, ArH), 6.87 (app dt, J = 8.3, 1.6 Hz, 4H, ArH), 4.64-4.45 (m, 7H, CpH), 4.26 (s, 1H, CpH), 3.82 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 1.72 (d, J = 10.1 Hz, 3H, CH₃), 1.64 (d, J = 10.1 Hz, 3H, CH₃), 1.9-0.4 (br envelope, 6H, BH₃).

1,1'-Bis[boronato-methyl-(2-trifluoromethylphenyl)phosphino]ferrocene (35b). Purification by flash chromatography on silica gel (1% EtOAc / toluene for elution) afforded 109 mg (87%) of 35b as an orange solid: ^1H NMR (300 MHz, CDCl_3) δ 7.95-7.71 (m, 2H, ArH), 7.72 (m, 2H, ArH), 7.53 (m, 4H, ArH), 4.77 (s, 1H, CpH), 4.72 (s, 3H, CpH), 4.59 (s, 1H, CpH), 4.53 (s, 3H, CpH), 2.04 (d, $J = 10.1$ Hz, 6H, CH_3), 1.60-0.40 (br envelope, 6H, BH_3); ^{31}P NMR (202 MHz, CDCl_3) δ 14.2 (s).

APPENDIX

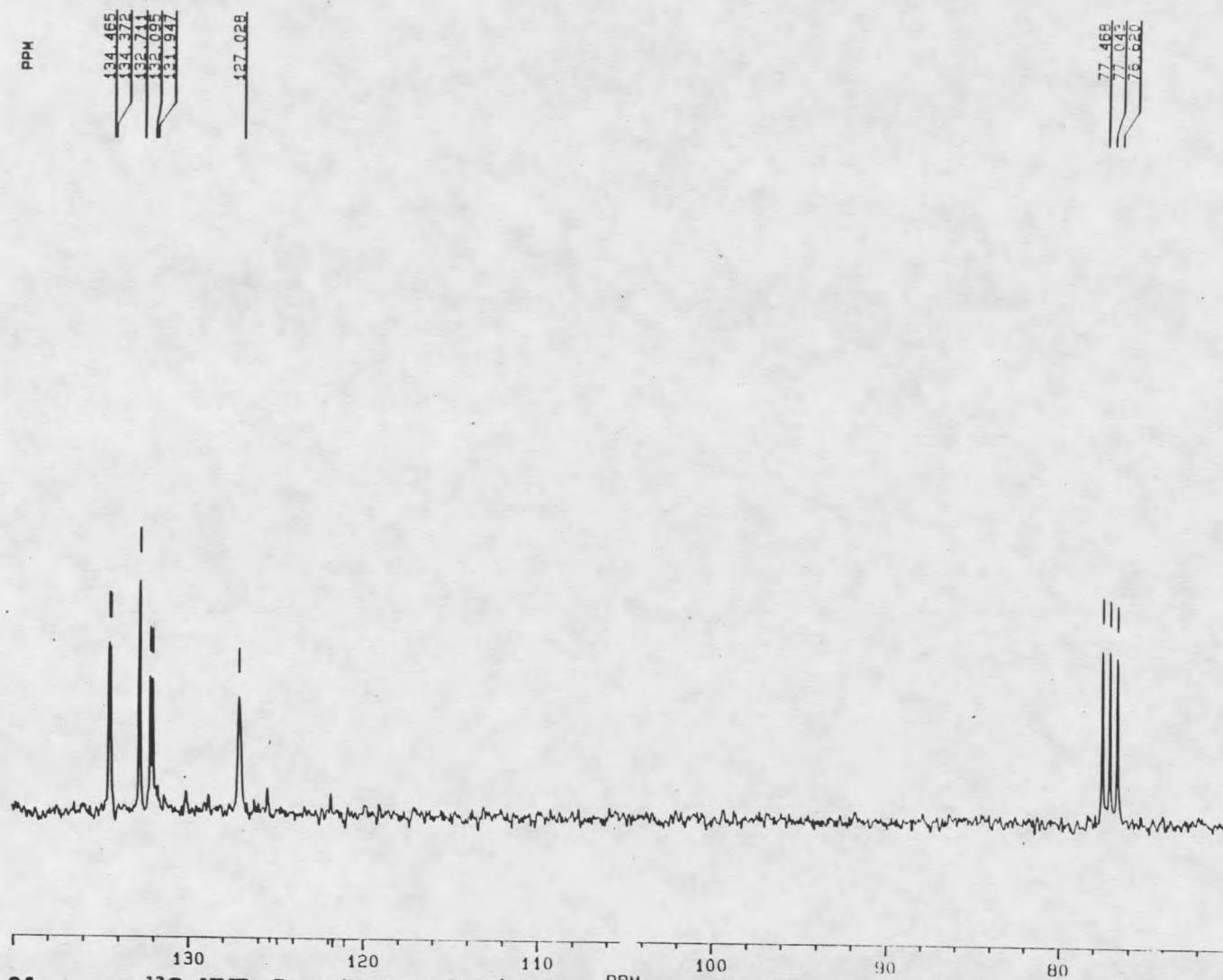


Figure 21. ^{13}C NMR Spectrum of Bis(2-trifluoromethylphenyl)phosphine Oxide (4a)



PPM

DATE 18-2-93

SF 202.459
SY 118.0
O1 -31378.686
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 16
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 4.000
GB 0.0
CX 25.00
CY 5.00
F1 30.001P
F2 -1.001P
HZ/CM 251.058
PPM/CM 1.240
SR -31379.55

0555.01

0555.01

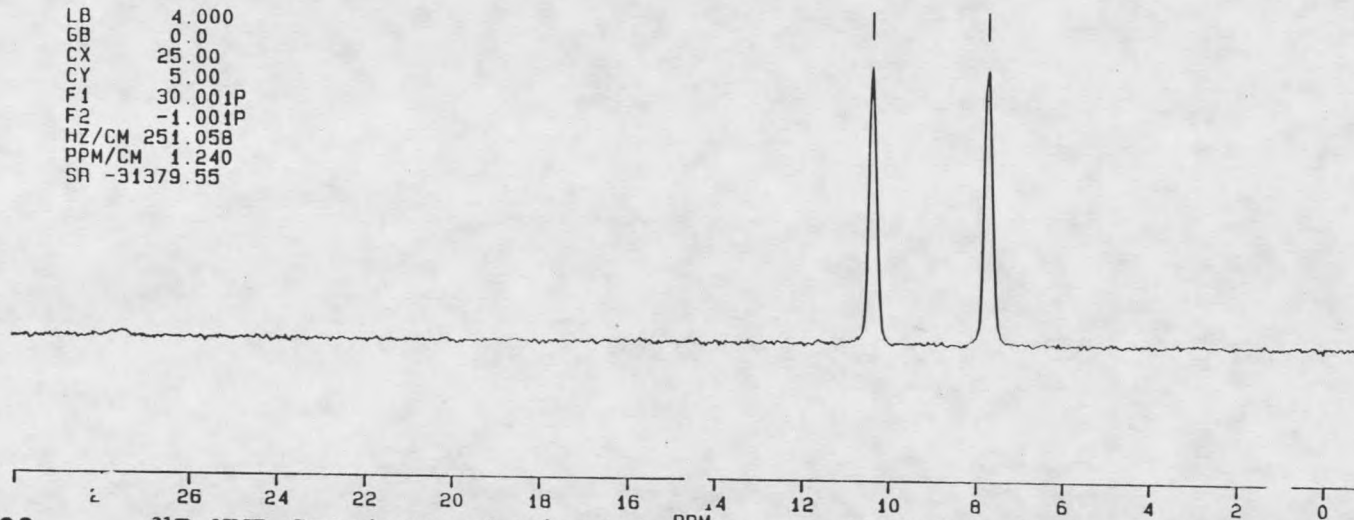


Figure 22. ^{31}P NMR Spectrum of Bis(2-trifluoromethylphenyl)phosphine Oxide (4a)

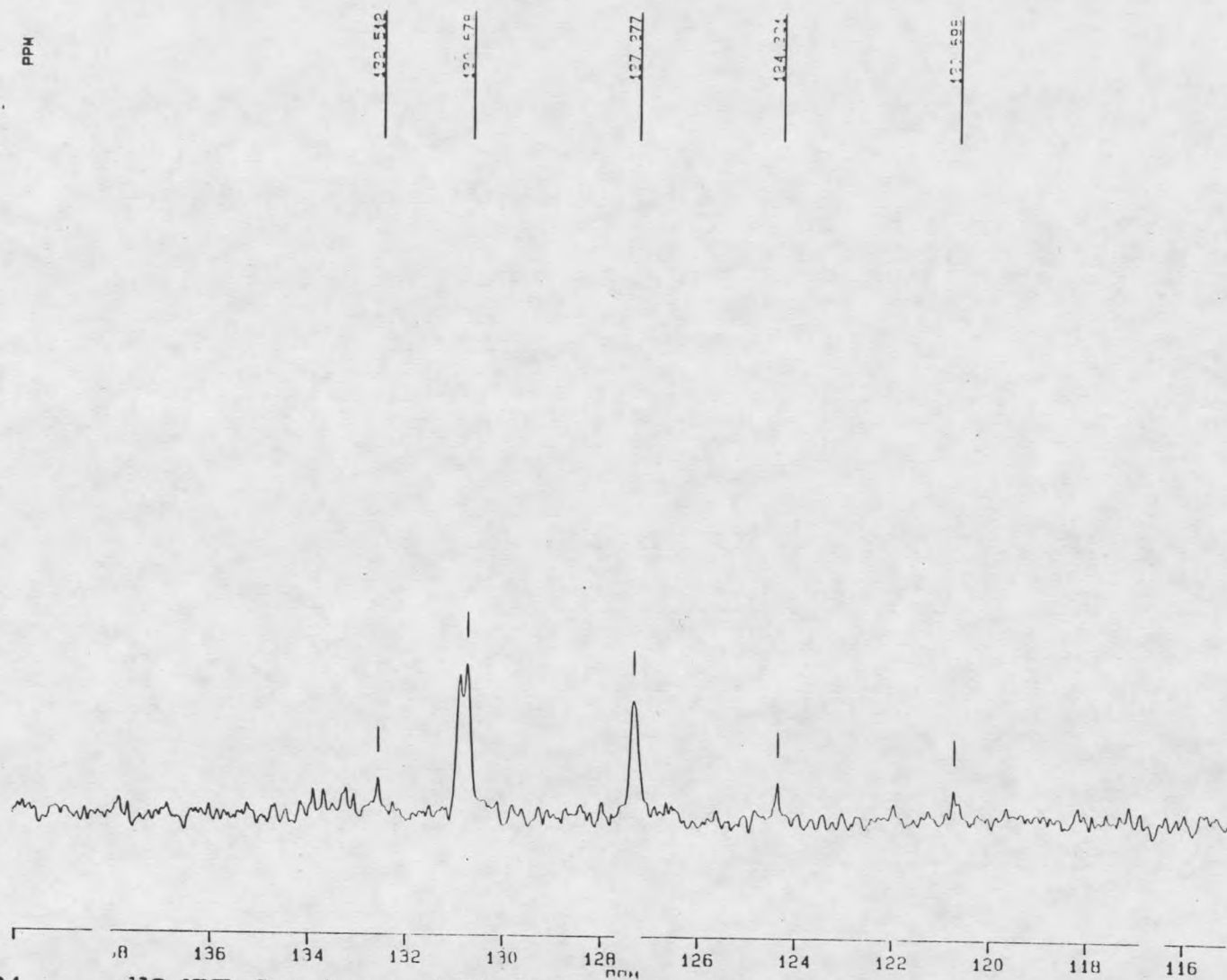


Figure 24. ^{13}C NMR Spectrum of Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c)



PPM

I124F.SER
ROW 0
DATE 24-11-92

SF 202.459
SY 118.0
O1 -31536.360
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 64
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 5.000
GB 0.0
CX 25.00
CY 5.00
F1 37.010P
F2 5.029P
HZ/CM 258.993
PPM/CM 1.279
SR -31415.16

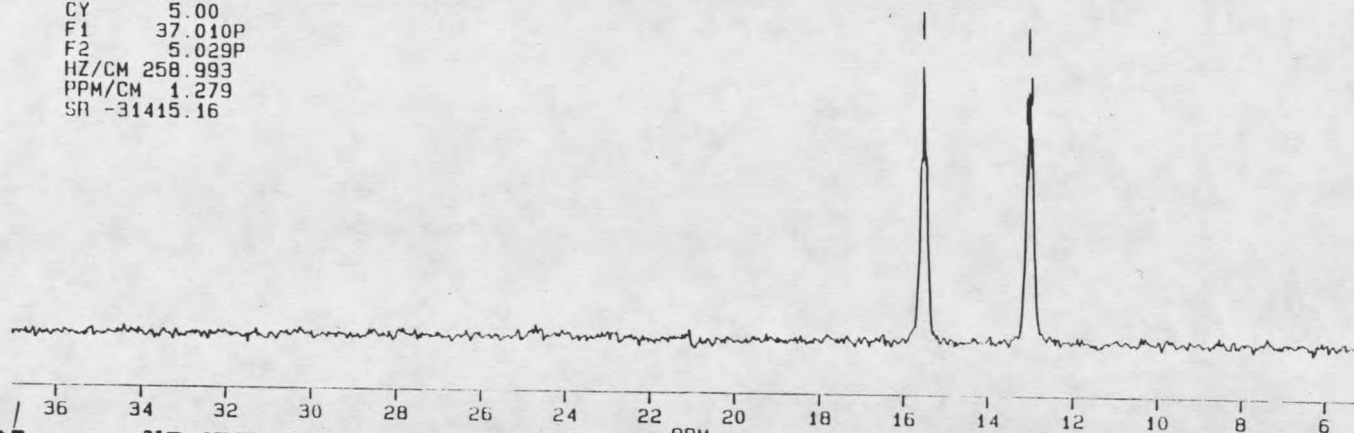
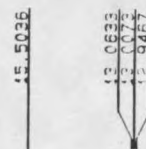


Figure 25. ³¹P NMR Spectrum of Bis[3,5-bis(trifluoromethyl)phenyl]phosphine Oxide (4c)

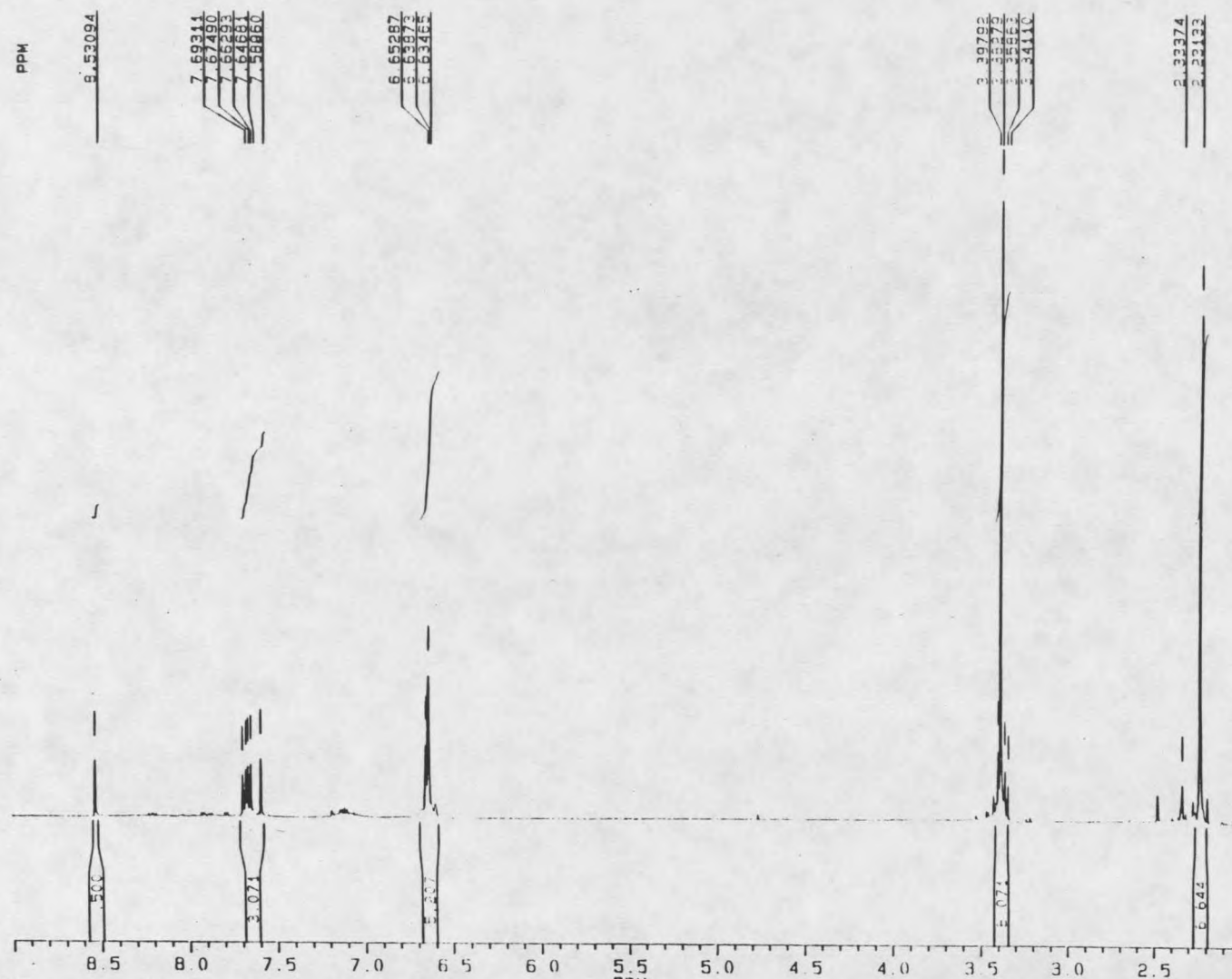


Figure 26. ¹H NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d)

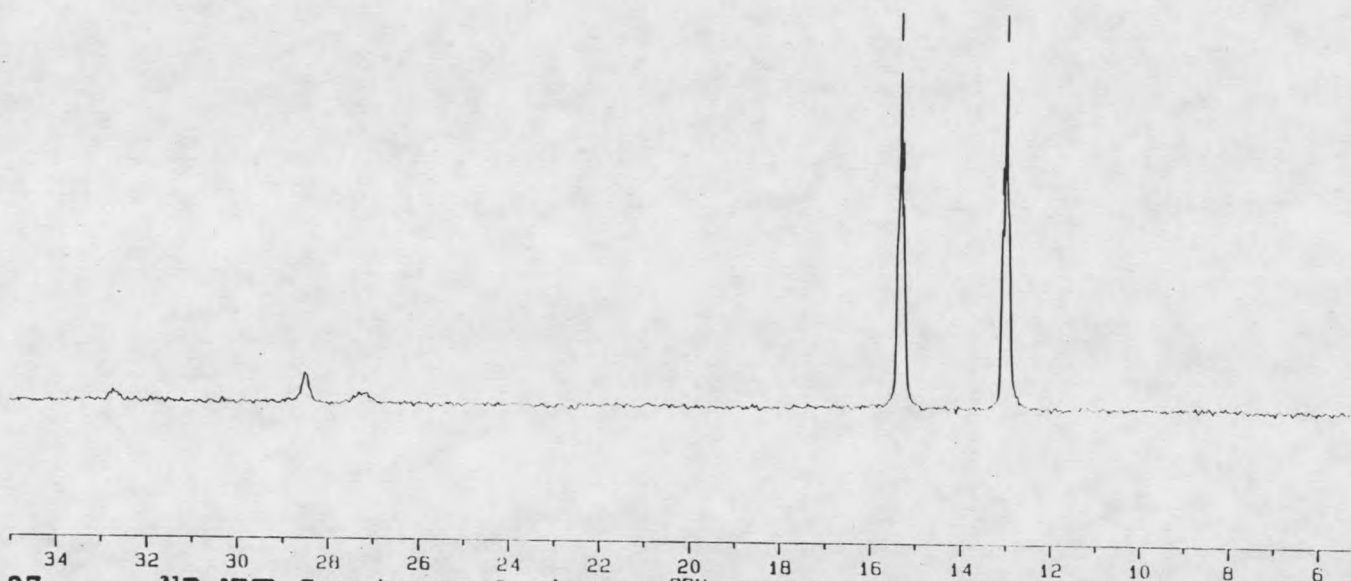
$$\begin{array}{r} 2097.47 \\ \hline 2064.67 \end{array}$$


Figure 27. ³¹P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine Oxide (4d)

HERTZ

-12645.8
-12734.1

155

Figure 28. ^{31}P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)phosphine (5d)

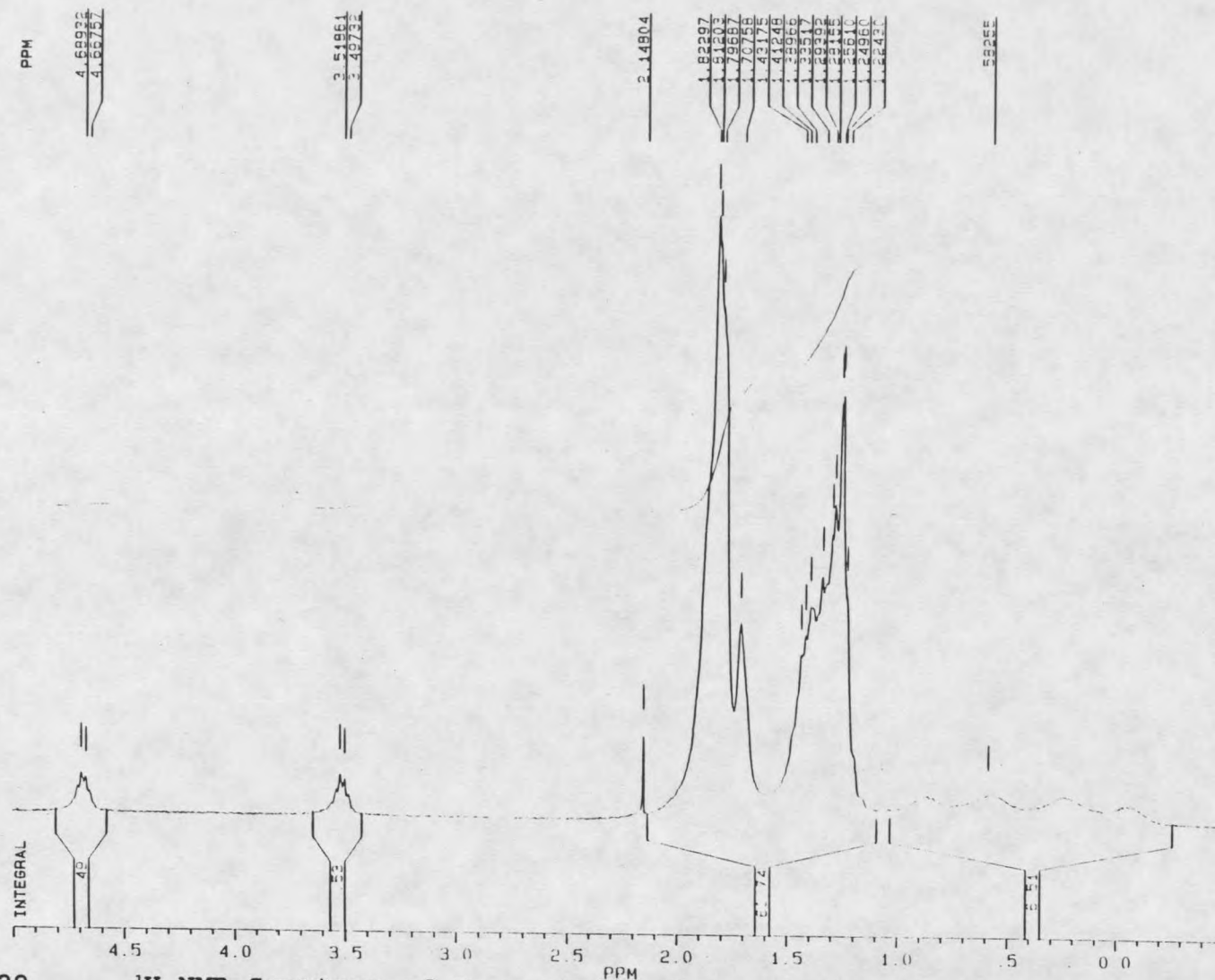


Figure 29. ^1H NMR Spectrum of Boronatodicyclohexyl phosphine (27a)



HERTZ

I130BDW.073
DATE 1-12-92SF 202.459
SY 118.0
Q1 -31536.360
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086PW 12.0
RD 5.000
AQ .197
RG 8192
NS 64
TE 297FW 150000
Q2 0.0
DP 63L P0LB 5.000
GB 0.0
CX 25.00
CY 4.00
F1 39.999P
F2 10.003P
HZ/CM 242.920
PPM/CM 1.200
SR -31440.59

3550.57

3248.24

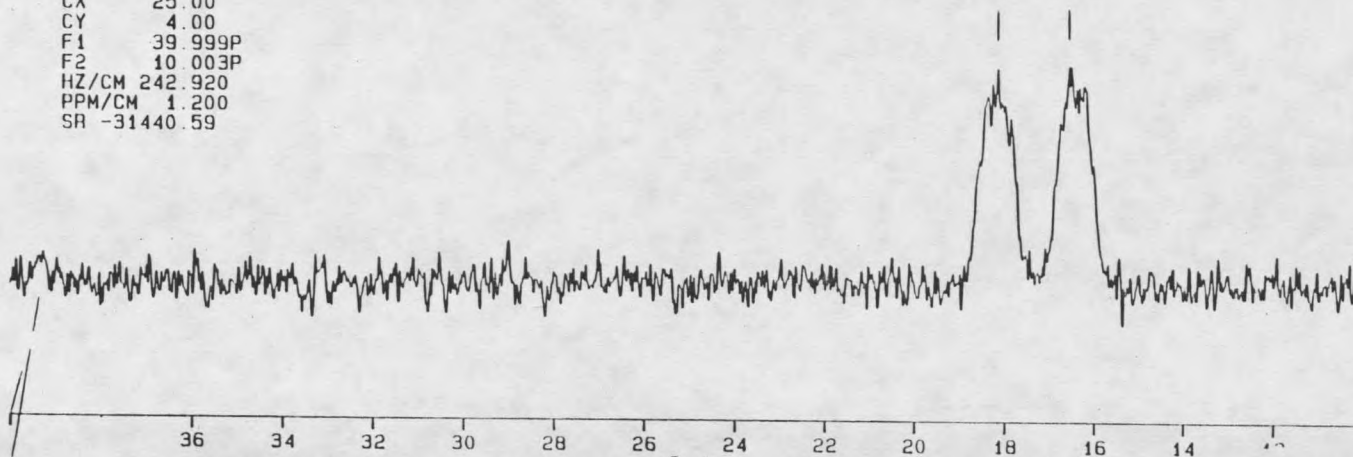


Figure 31.

³¹P NMR Spectrum of Boronatodicyclohexyl phosphine (27a)



Figure 32. ^1H NMR Spectrum of Boronatodiphenyl phosphine (27b)

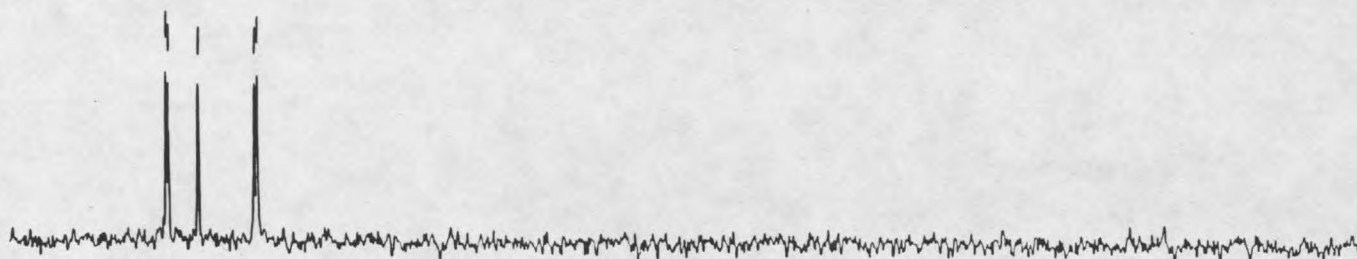


Figure 33. ^{13}C NMR Spectrum of Boronated phenyl phosphine (27b)

HEP72

100
80
60
40
20
0



161

Figure 34.

^{31}P NMR Spectrum of Boronatediphenyl phosphine (27b)

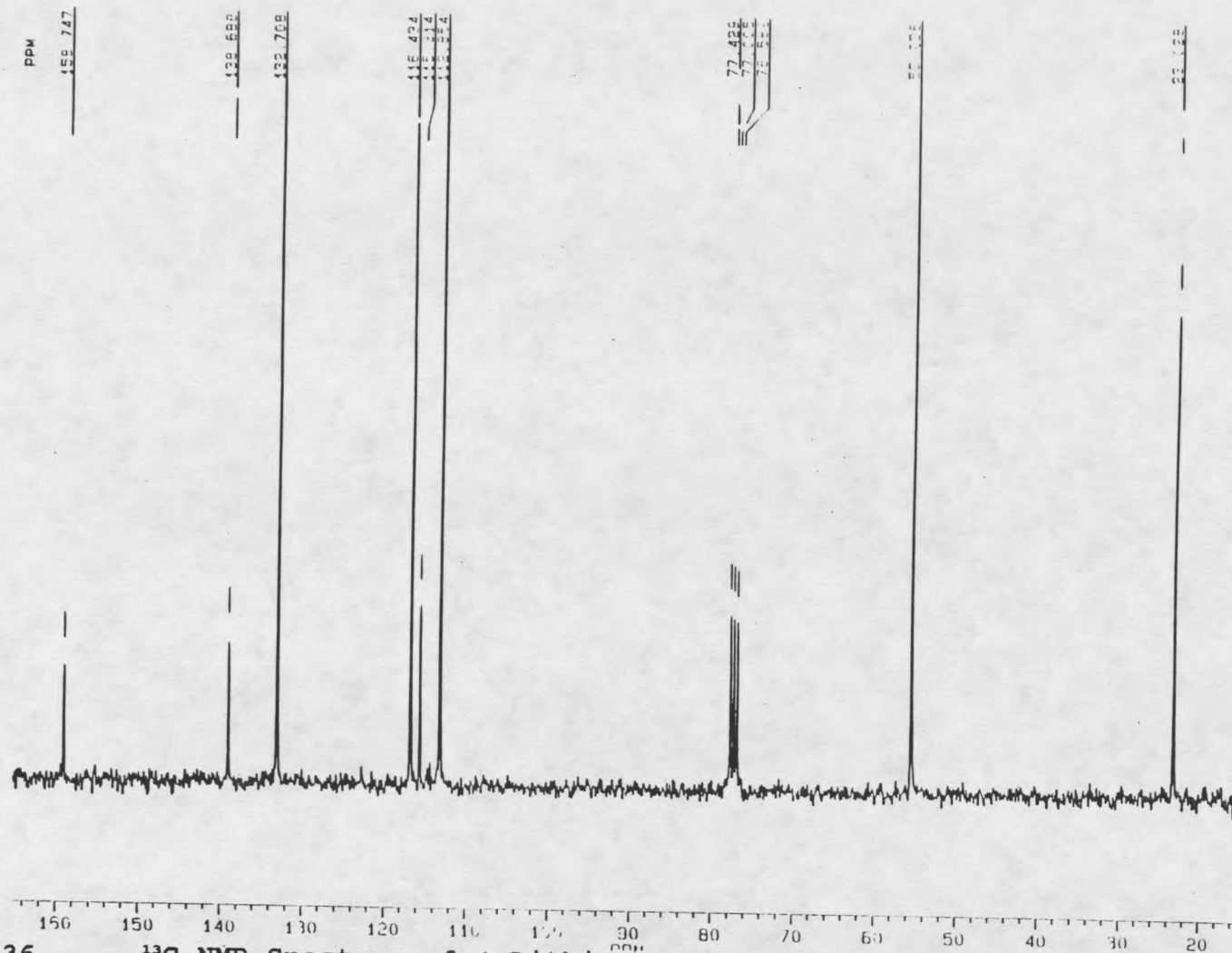
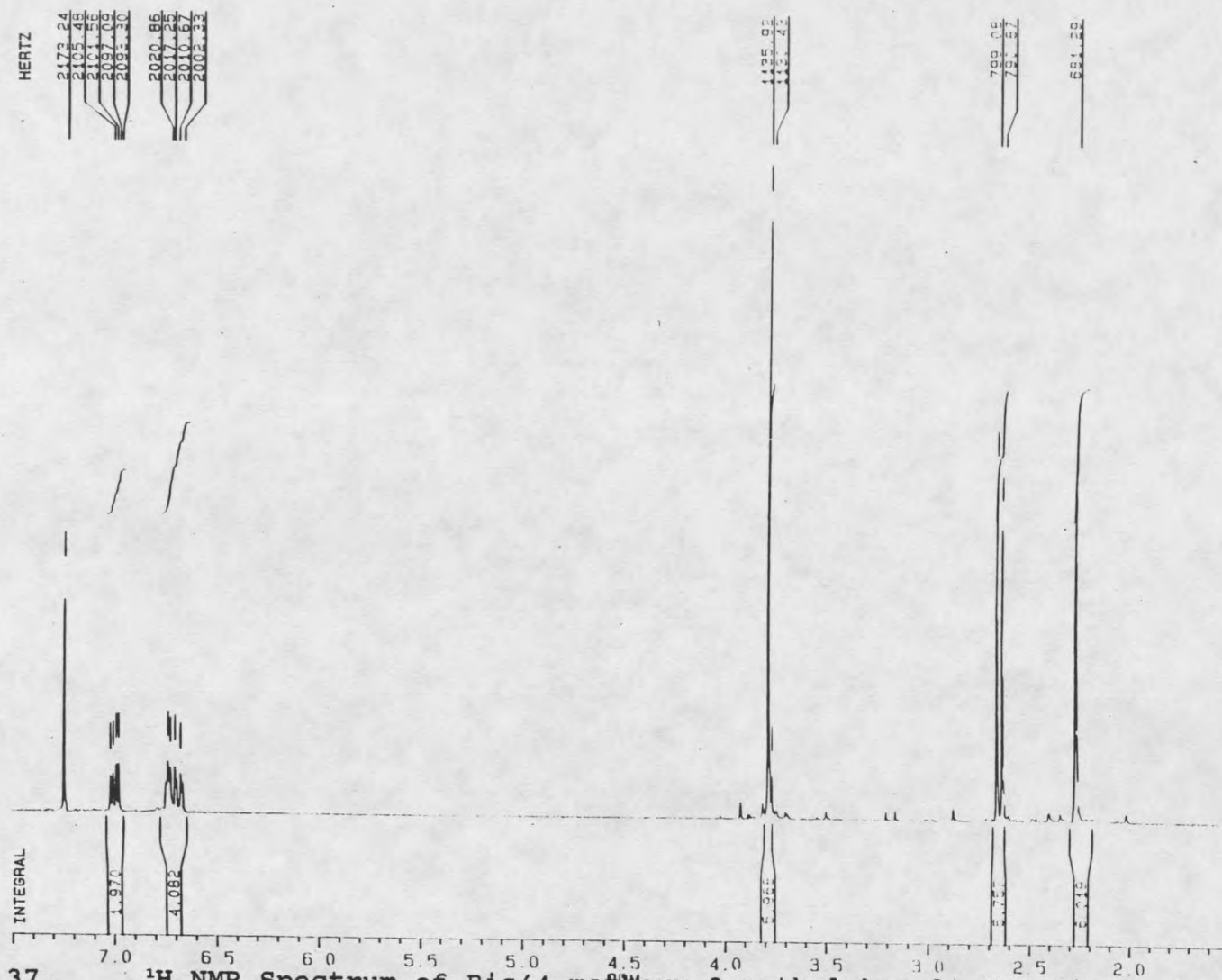


Figure 36. ^{13}C NMR Spectrum of 4-Lithio-3-methylanisole



ppm

49.7007

165

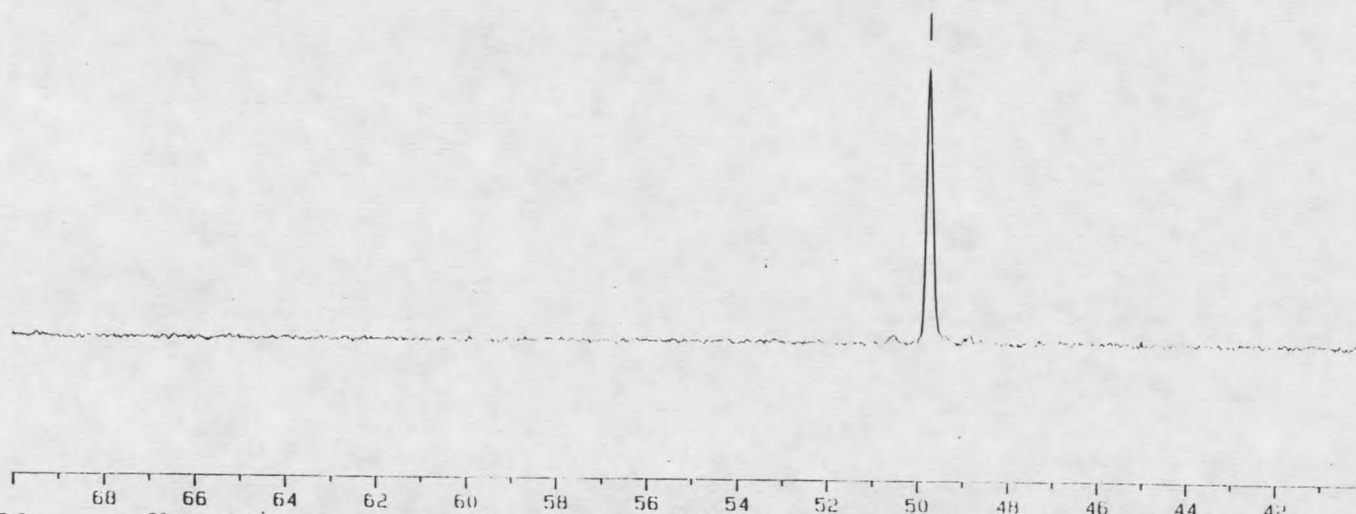
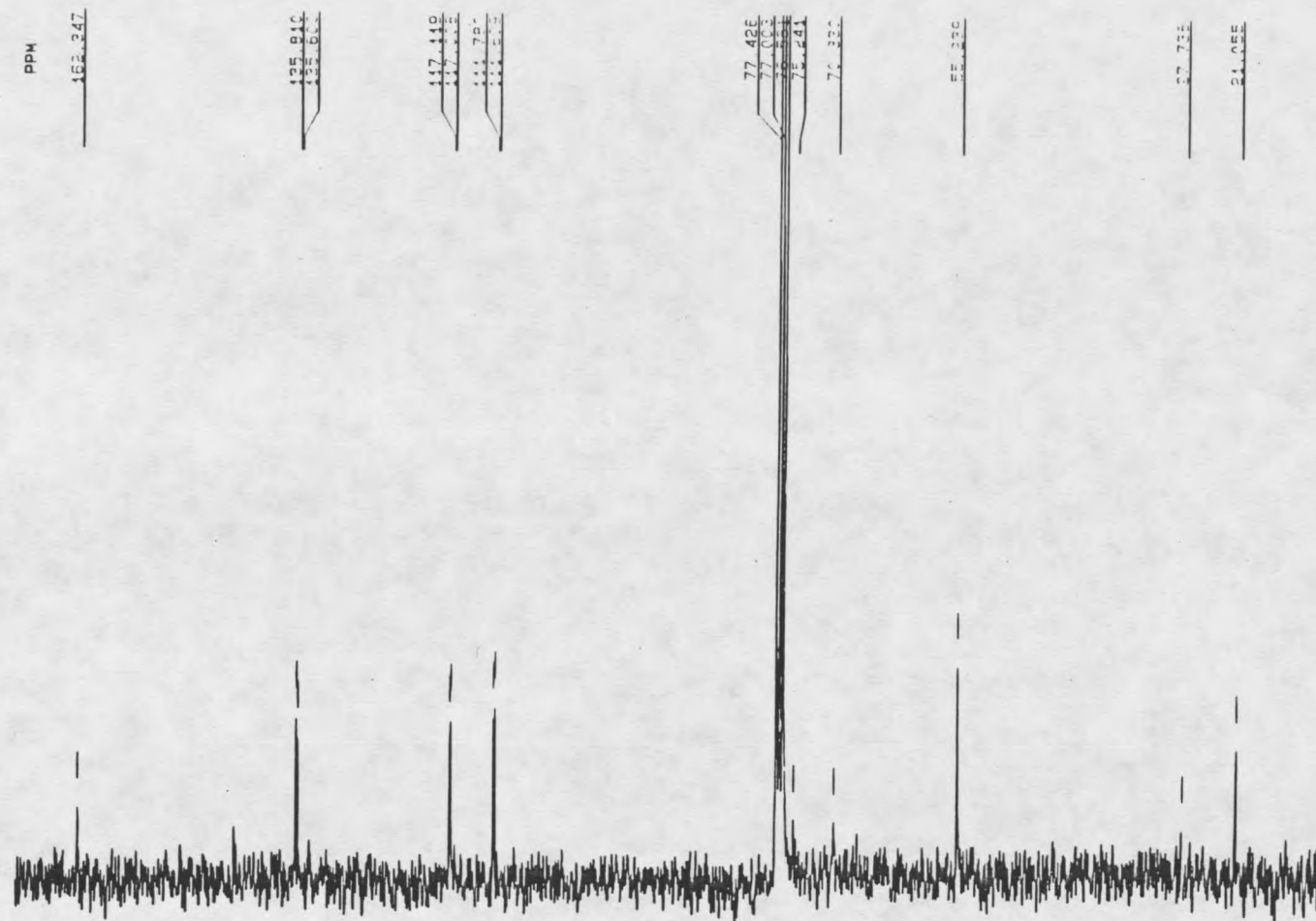


Figure 38. ^{31}P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)-N,N-dimethylaminophosphine (31)

Figure 40. ^{13}C NMR Spectrum of Bis(4-methoxy-2-methylphenyl)boronato phosphine (27c)



HERTZ

-2250.66
-2250.50

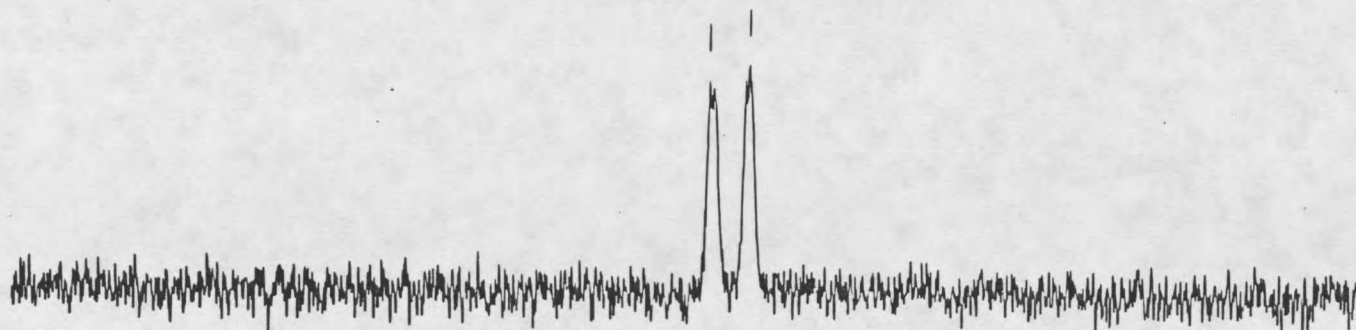


Figure 41. ^{31}P NMR Spectrum of Bis(4-methoxy-2-methylphenyl)boronate phosphine (27c)

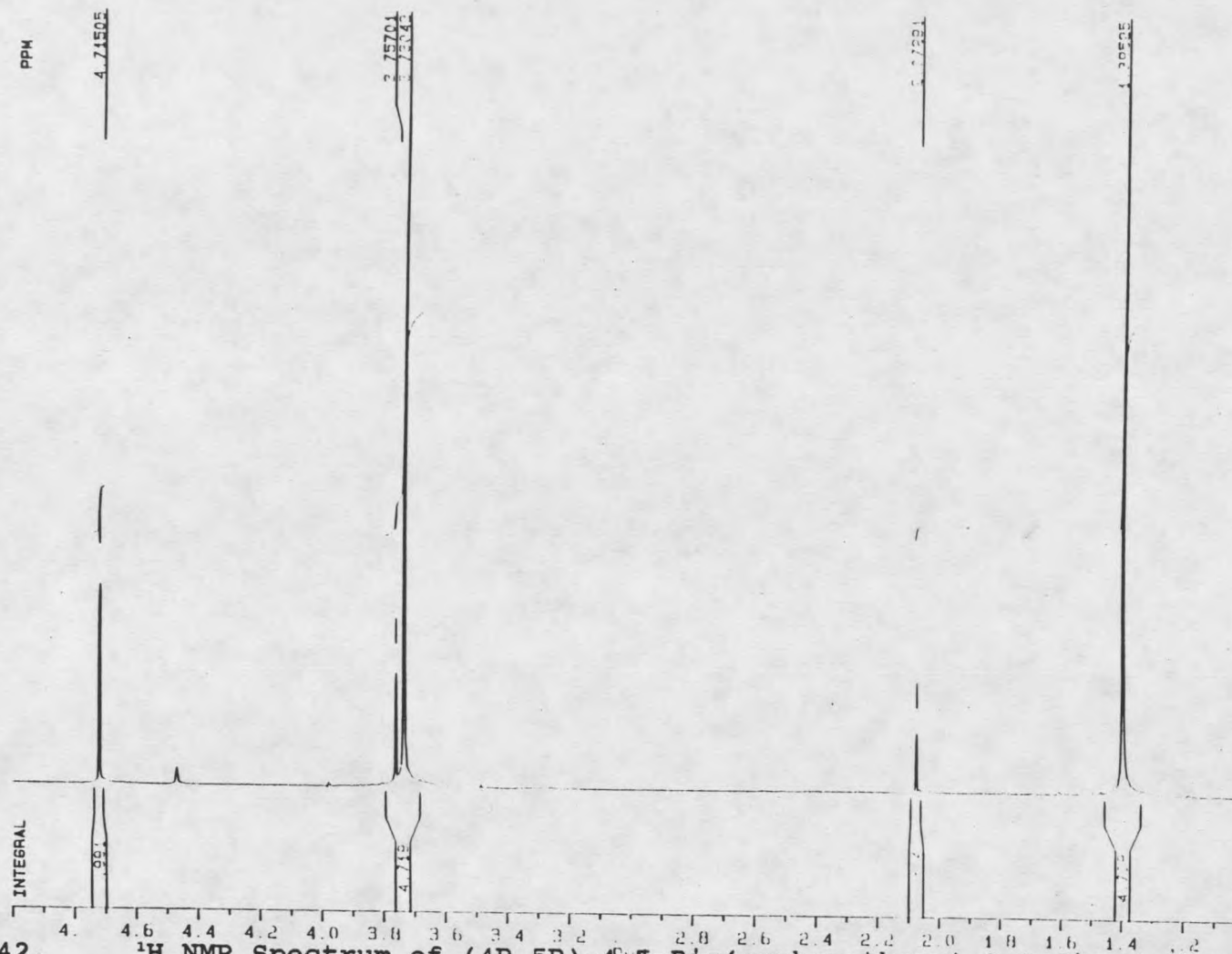


Figure 42. ¹H NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2,2-dimethyl-1,3-dioxolane (100a)

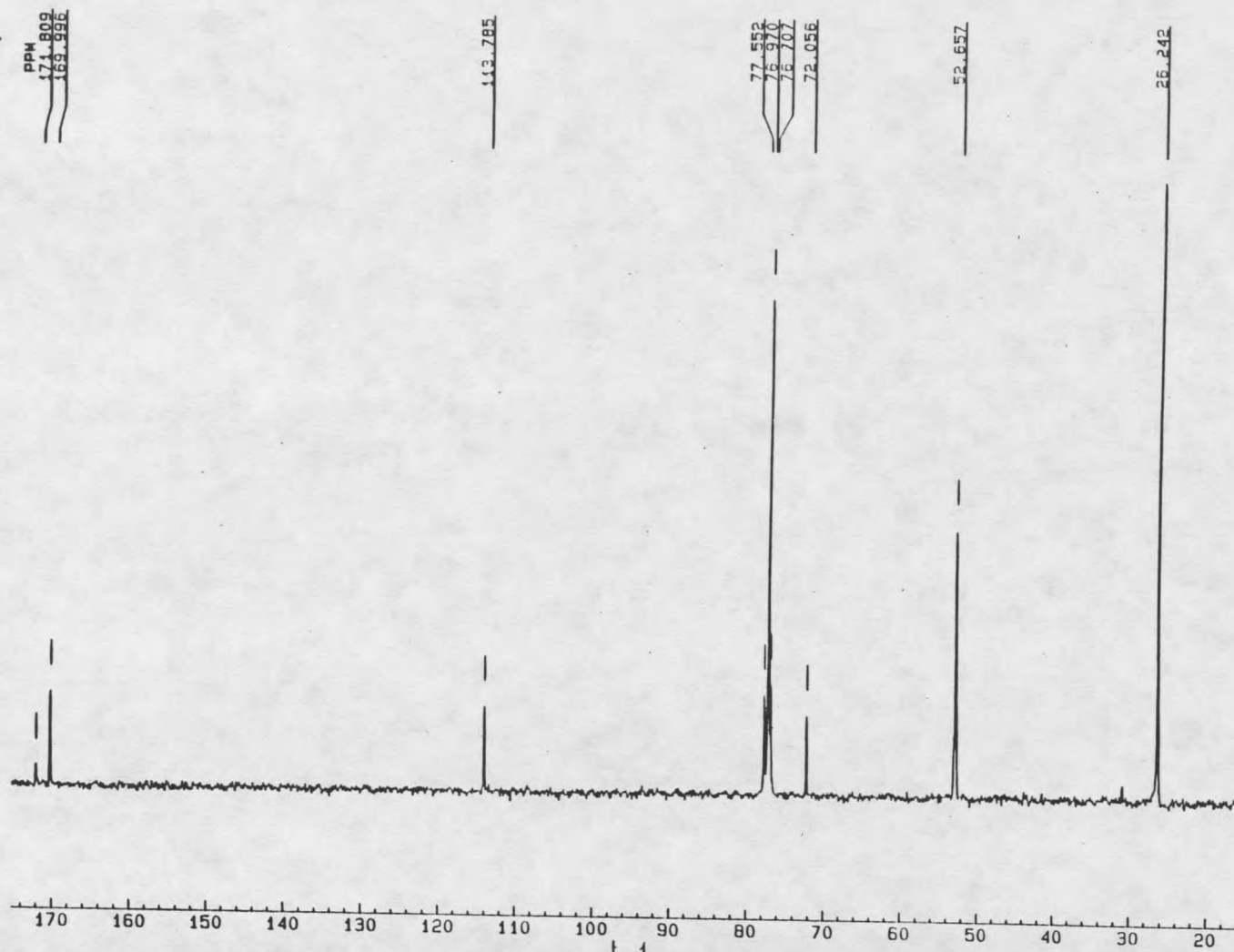


Figure 43. ^{13}C NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2,2-dimethyl-1,3-dioxolane (100a)

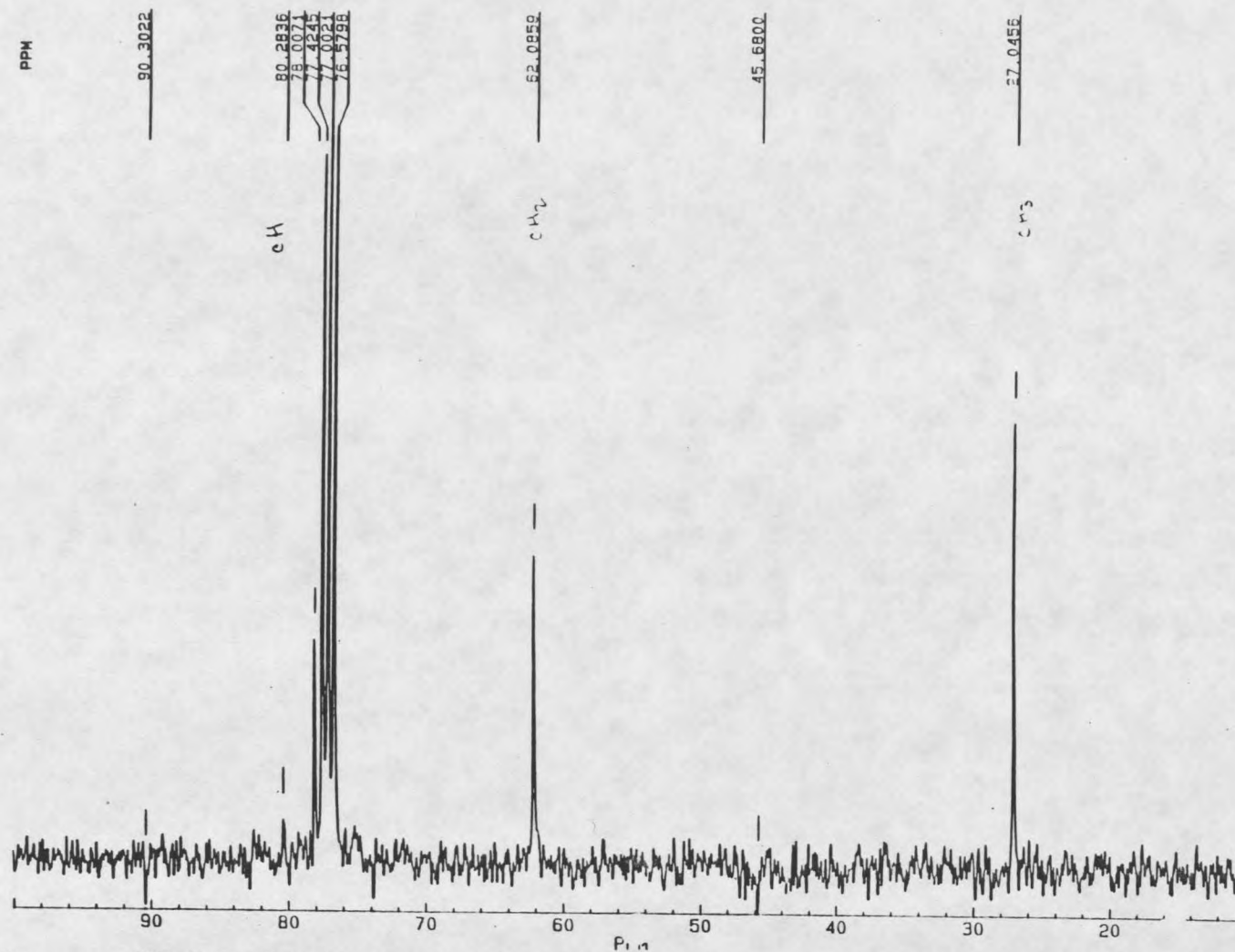


Figure 45. ¹³C NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (101a)

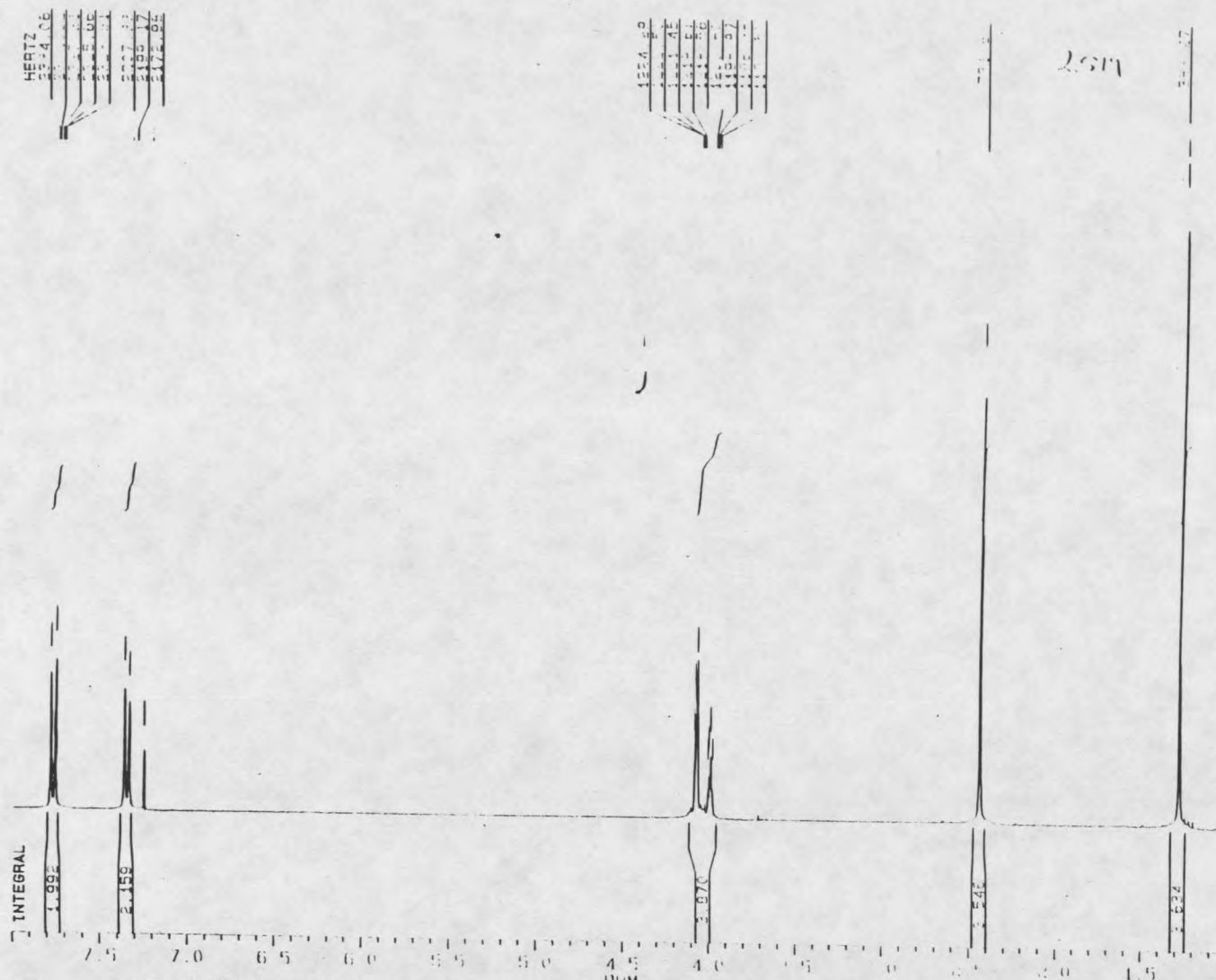


Figure 46. ^1H NMR Spectrum of (4S,5S)-4,5-Bis[(p-tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (6a)

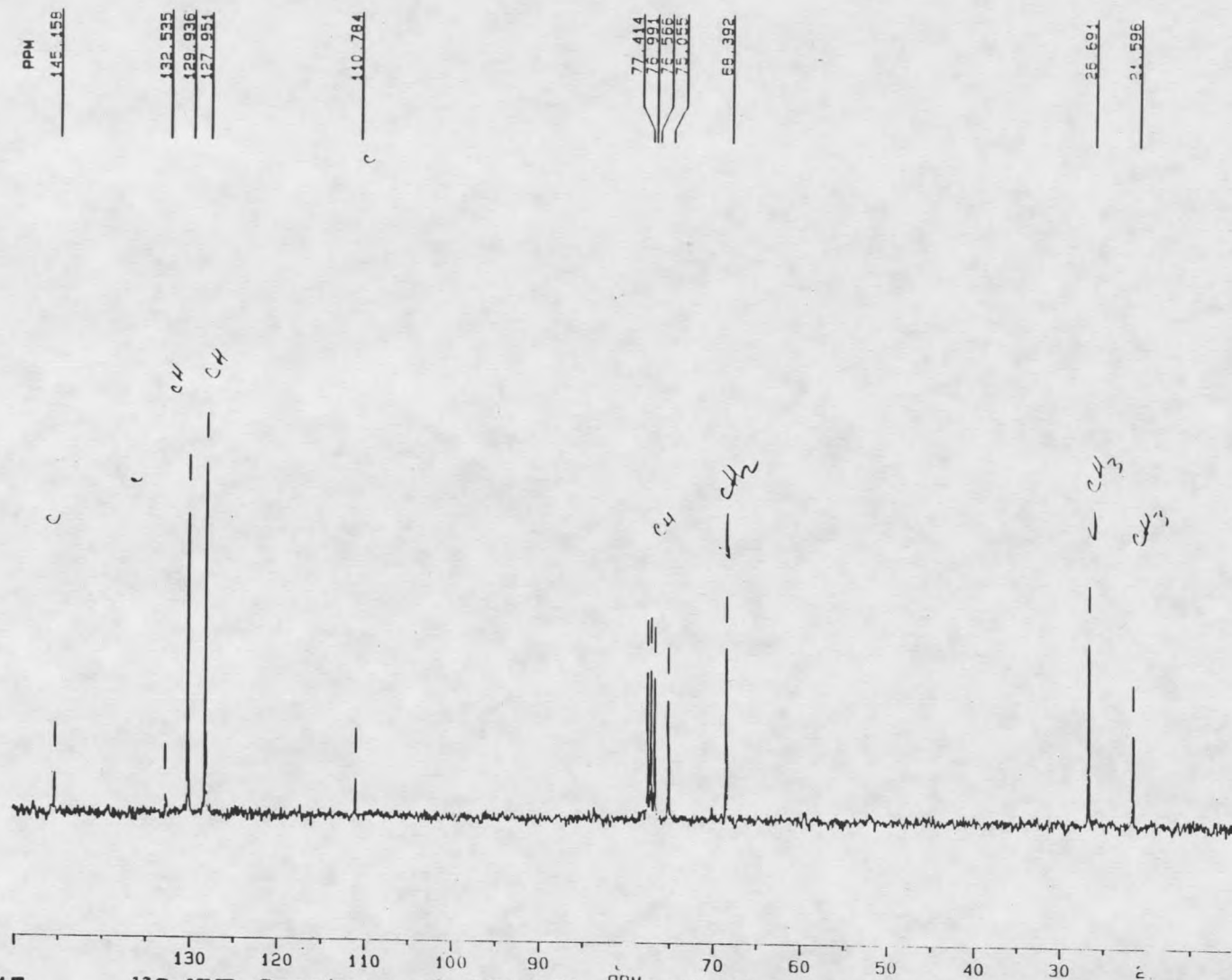


Figure 47. ^{13}C NMR Spectrum of (4S,5S)-4,5-Bis[(p-tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (6a)

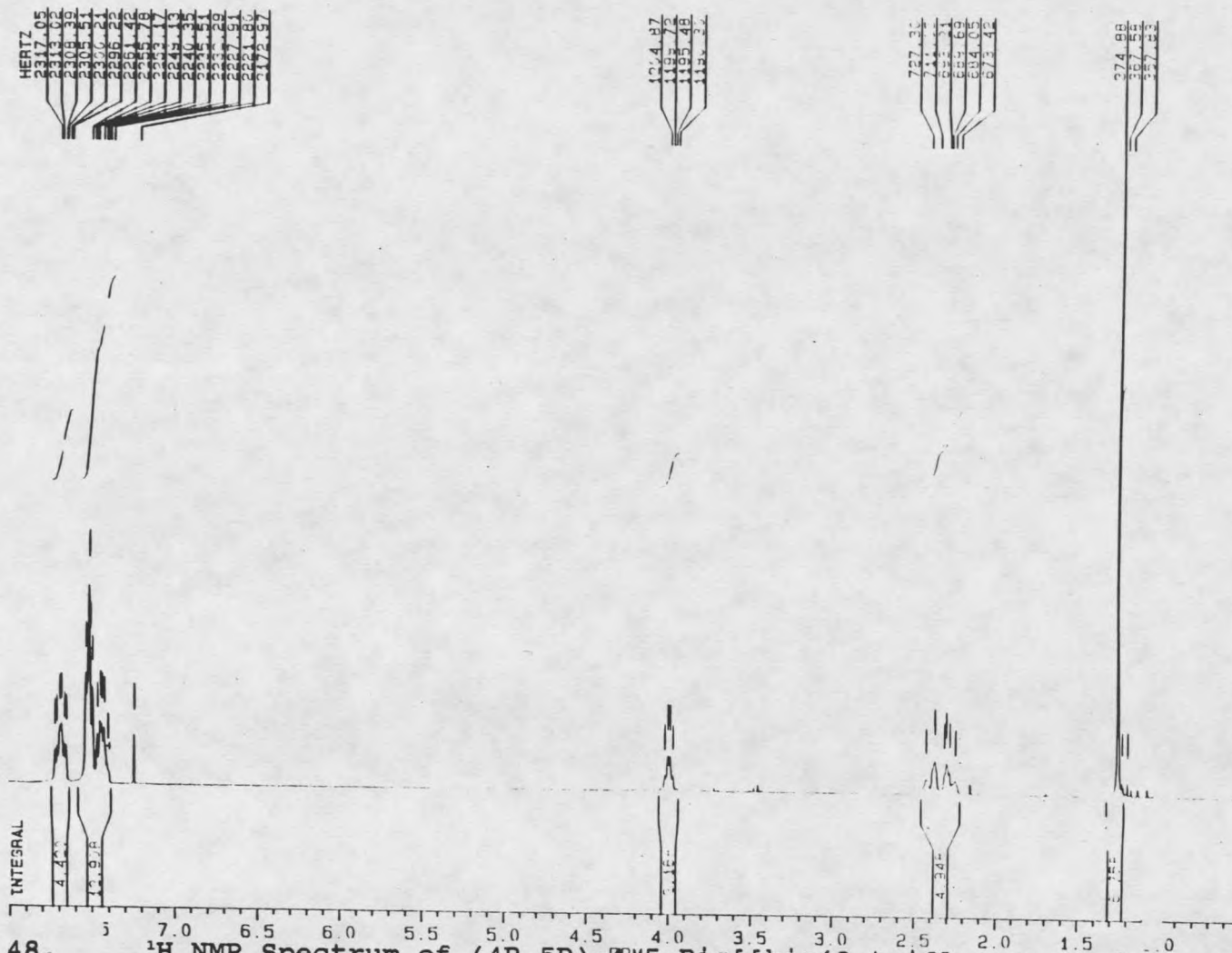


Figure 48. ^1H NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)

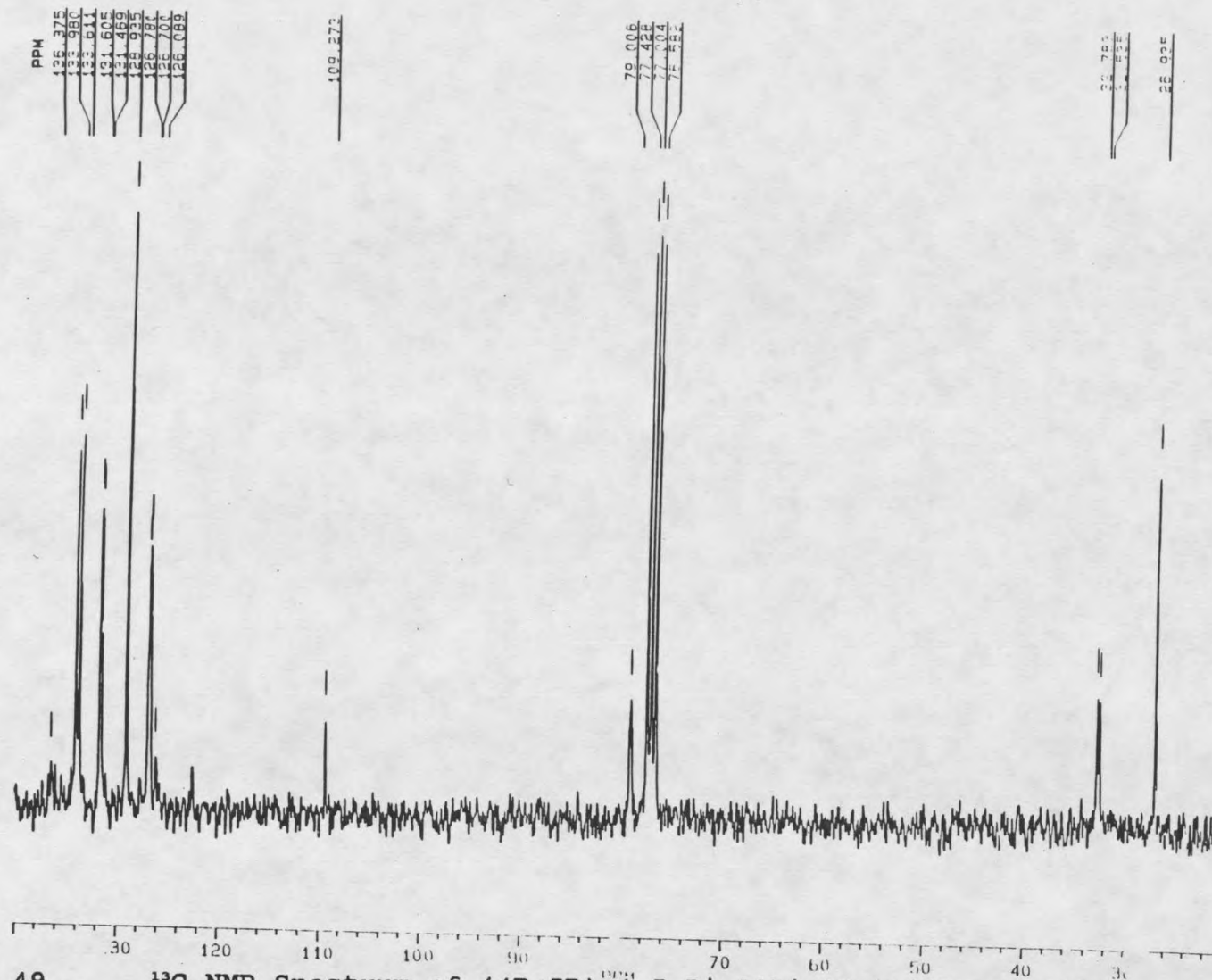


Figure 49.

^{13}C NMR Spectrum of (4R,5R)-4,5-bis[[bis(2-trifluoromethyl-phenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)



HERTZ

DATE 29-6-92

SF 202.458
SY 118.0
O1 -31536.360
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 16384
NS 32
TE 297

FW 150000
Q2 0.0
DP 63L P0

LB 0.0
GB 0.0
CX 25.00
CY 5.00
F1 -9.999P
F2 -39.995P
HZ/CM 242.920
PPM/CM 1.200
SR -31531.27

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100

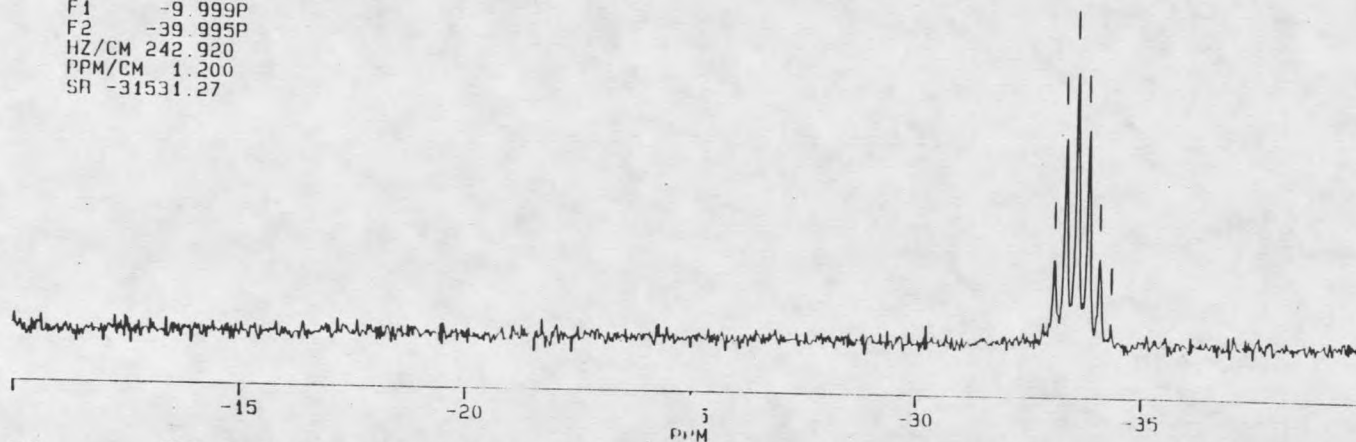


Figure 50. ^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3f)

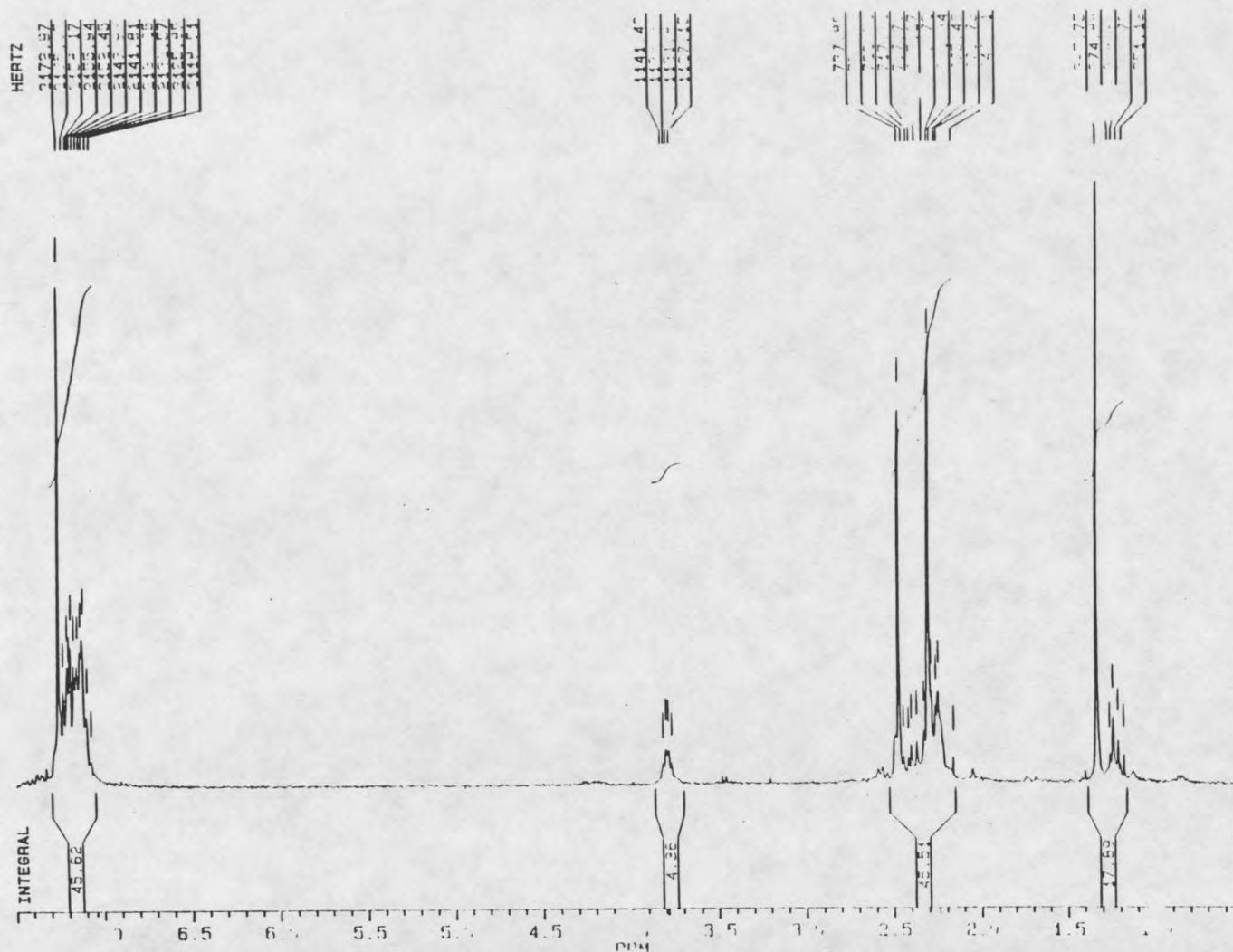


Figure 51. ^1H NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)

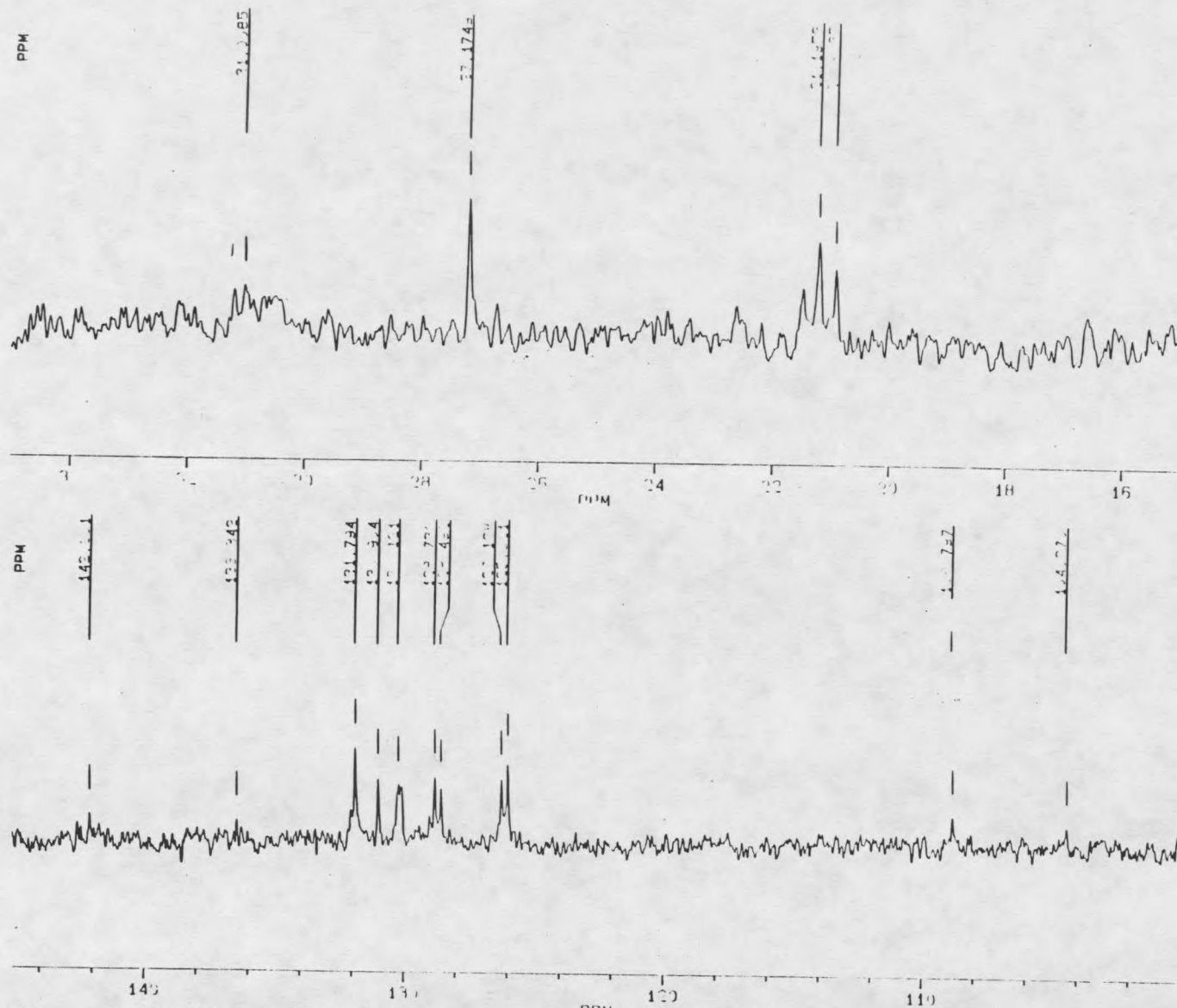
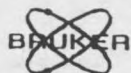


Figure 52. ^{13}C NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)



PPM

DATE 19-2-93

SF 202.459
SY 118.0
O1 -31378.686
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 8581
TE 297

FW 150000
Q2 0.0
DP 63L P0

LB 4.000
GB 0.0
CX 25.00
CY 5.00
F1 -4.995P
F2 -59.988P
HZ/CM 445.353
PPM/CM 2.200
SR -31379.55

-42.9284

180

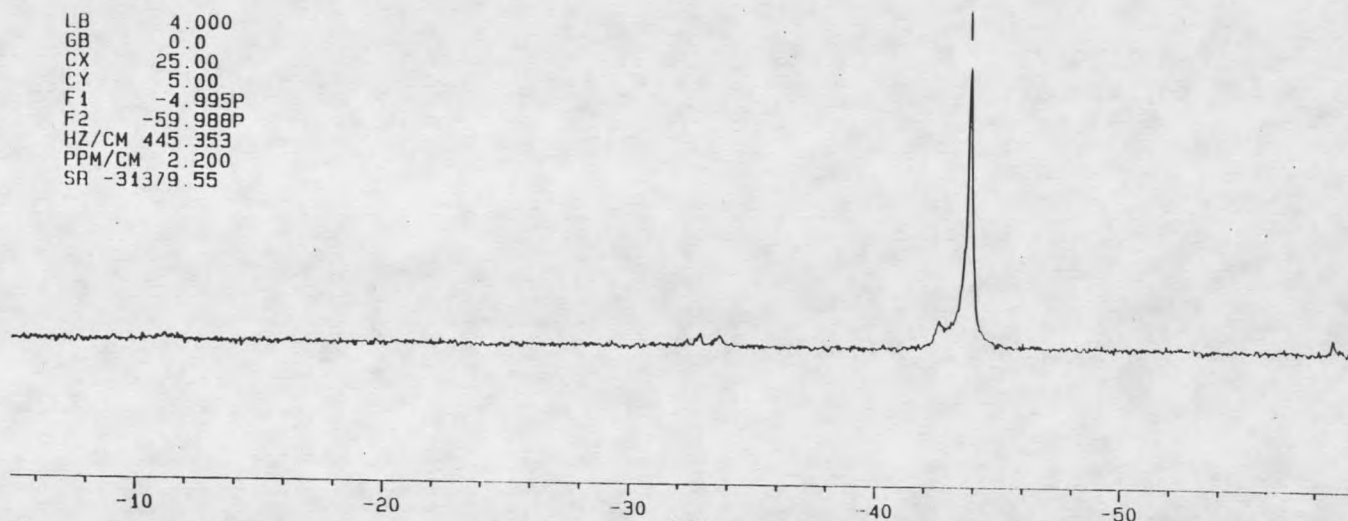


Figure 53.

³¹P NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3e)

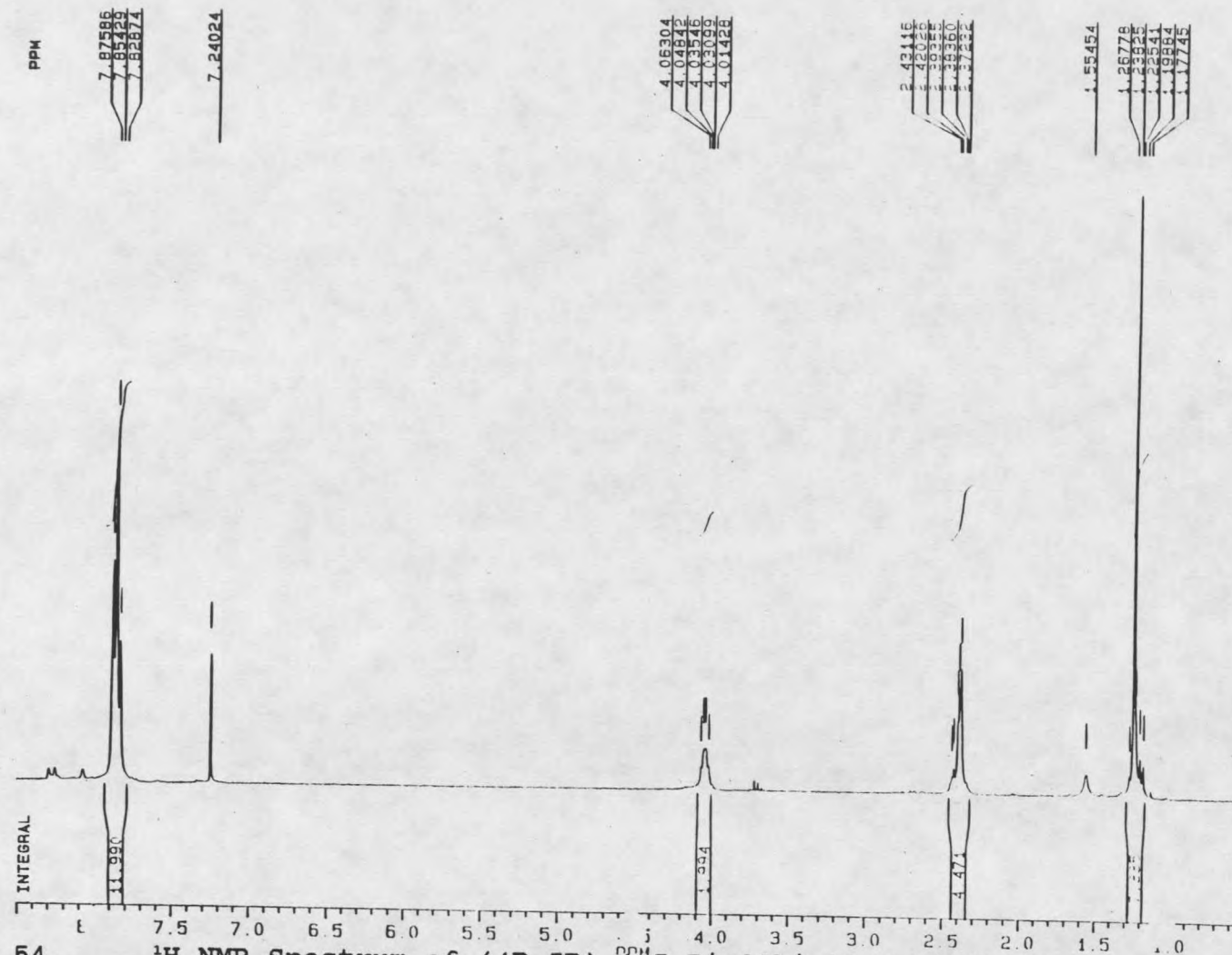


Figure 54. ^1H NMR Spectrum of (4R,5R)-2,5-Bis[[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)

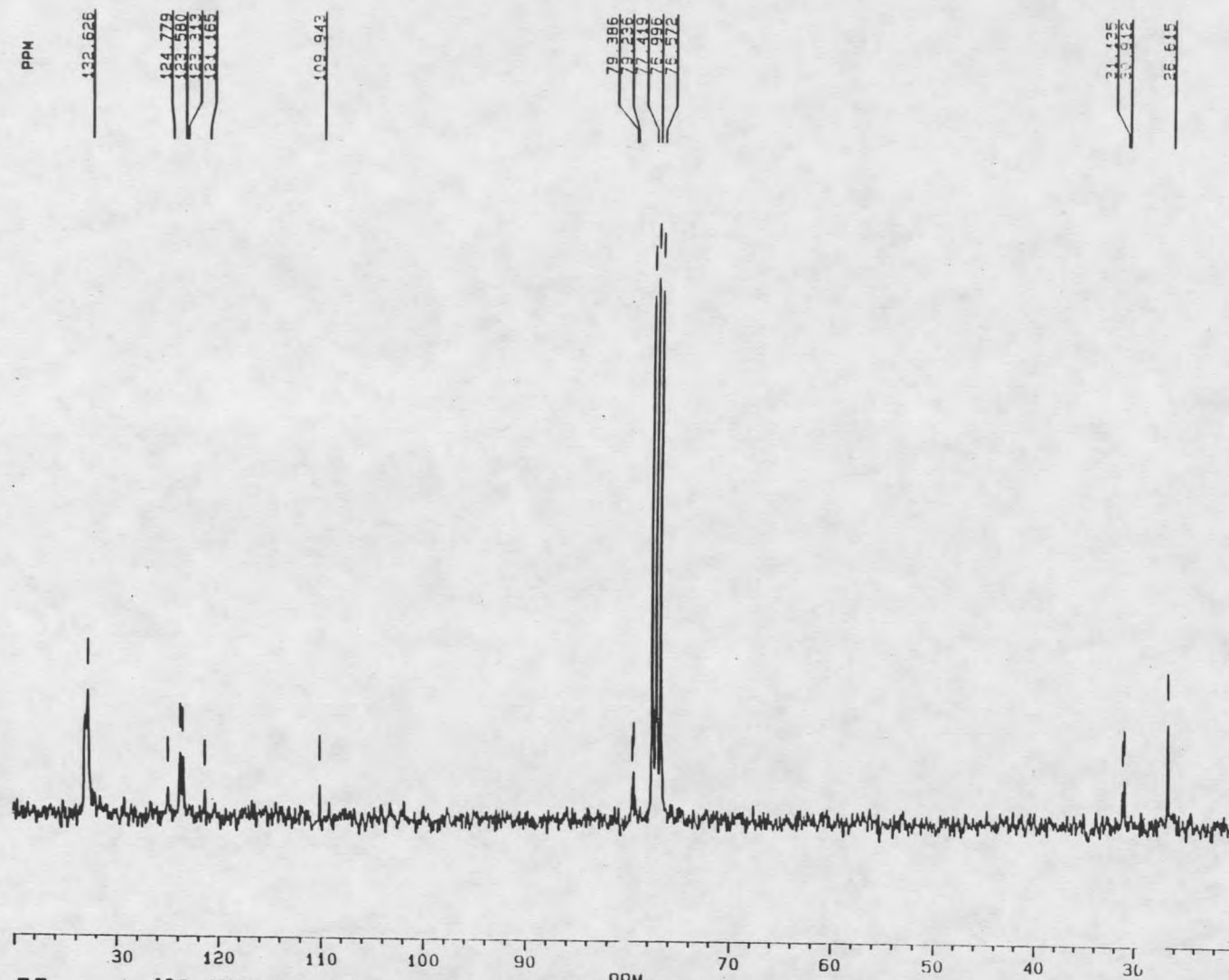


Figure 55.

^{13}C NMR Spectrum of (4R,5R)-4,5-Bis[[bis[3,5-bis(trifluoro-methyl)phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)



PPM

I124F.SER
ROW 0
DATE 24-11-92

SF 202.459
SY 118.0
O1 -31536.360
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 16
TE 297

FW 150000
O2 0.0
DP 63L PD

LB 5.000
GB 0.0
CX 25.00
CY 5.00
F1 10.003P
F2 -29.992P
HZ/CM 323.893
PPM/CM 1.600
SR -31415.16

-17.1819

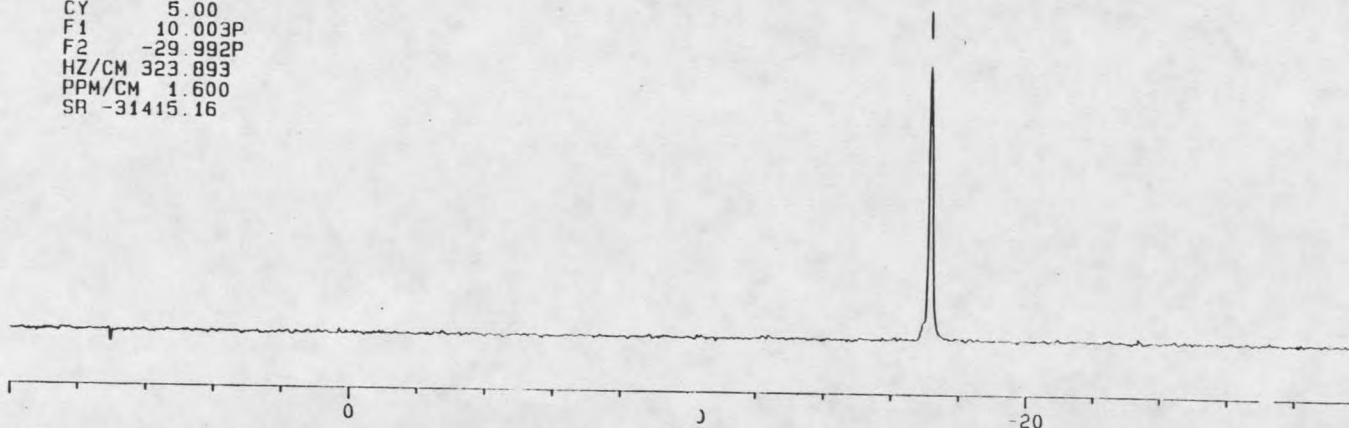
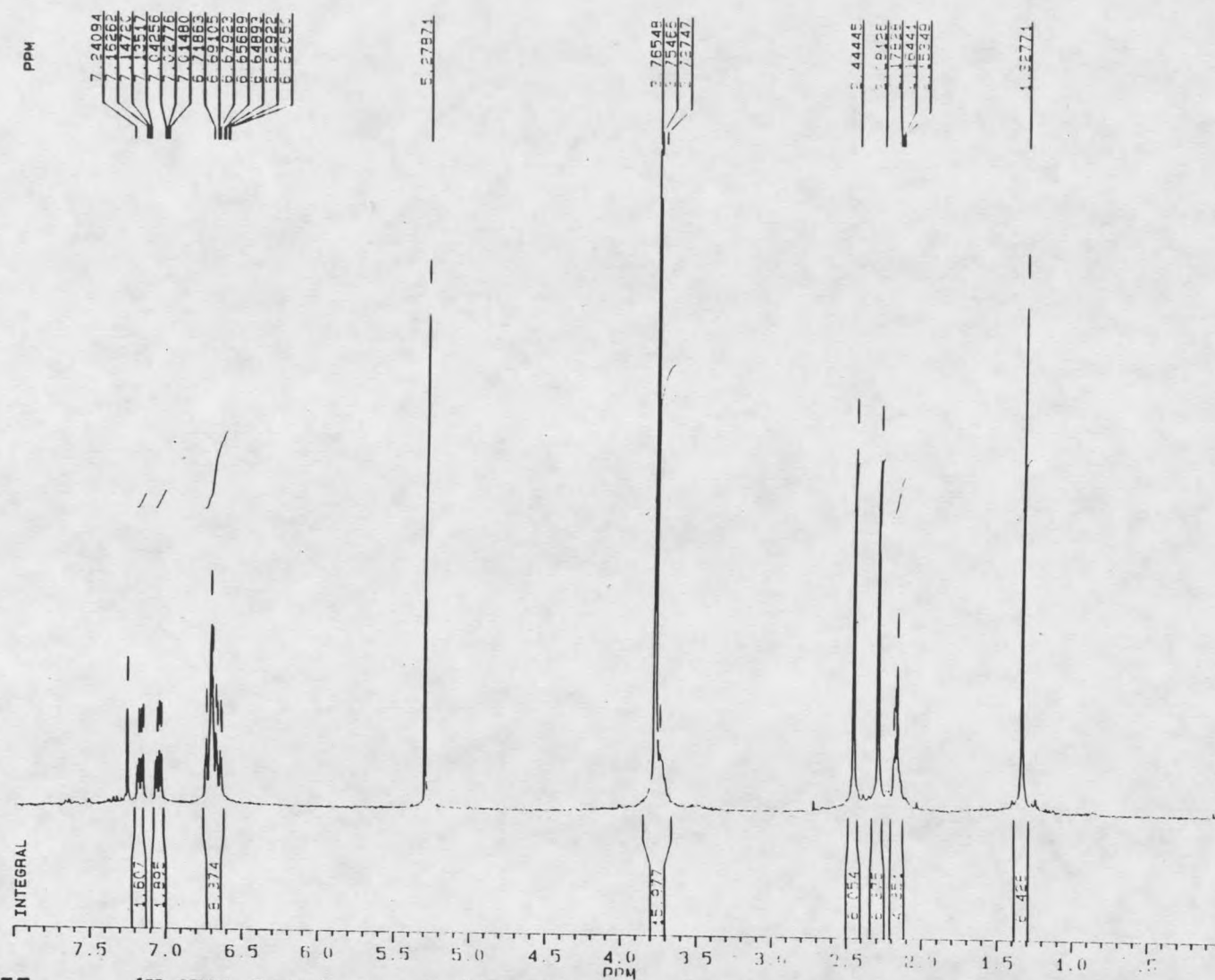


Figure 56. ^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3d)



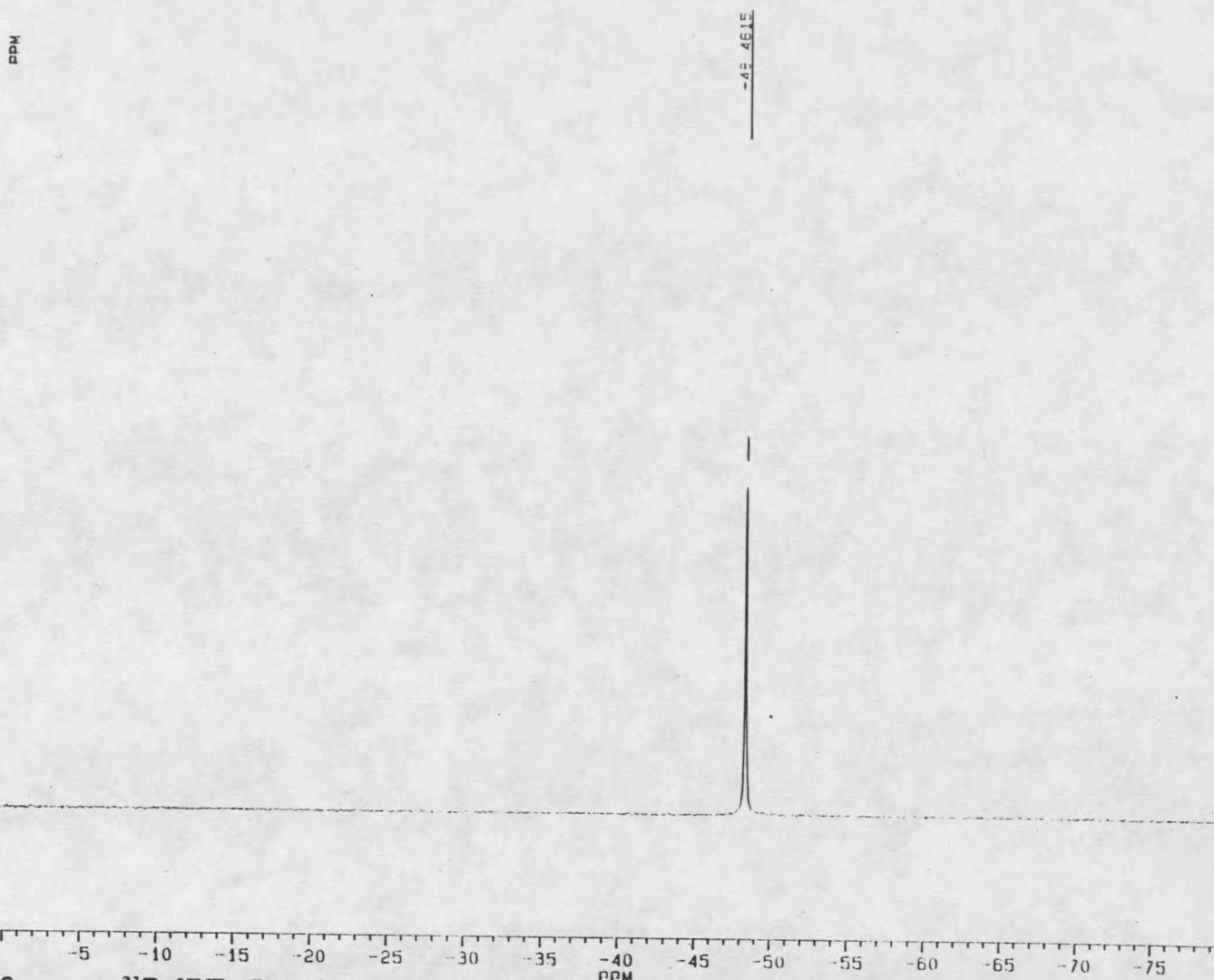


Figure 59.

^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[[bis(4-methoxy-2-methylphenyl)phosphino]methyl]-2,2-dimethyl-1,3-dioxolane (3h)

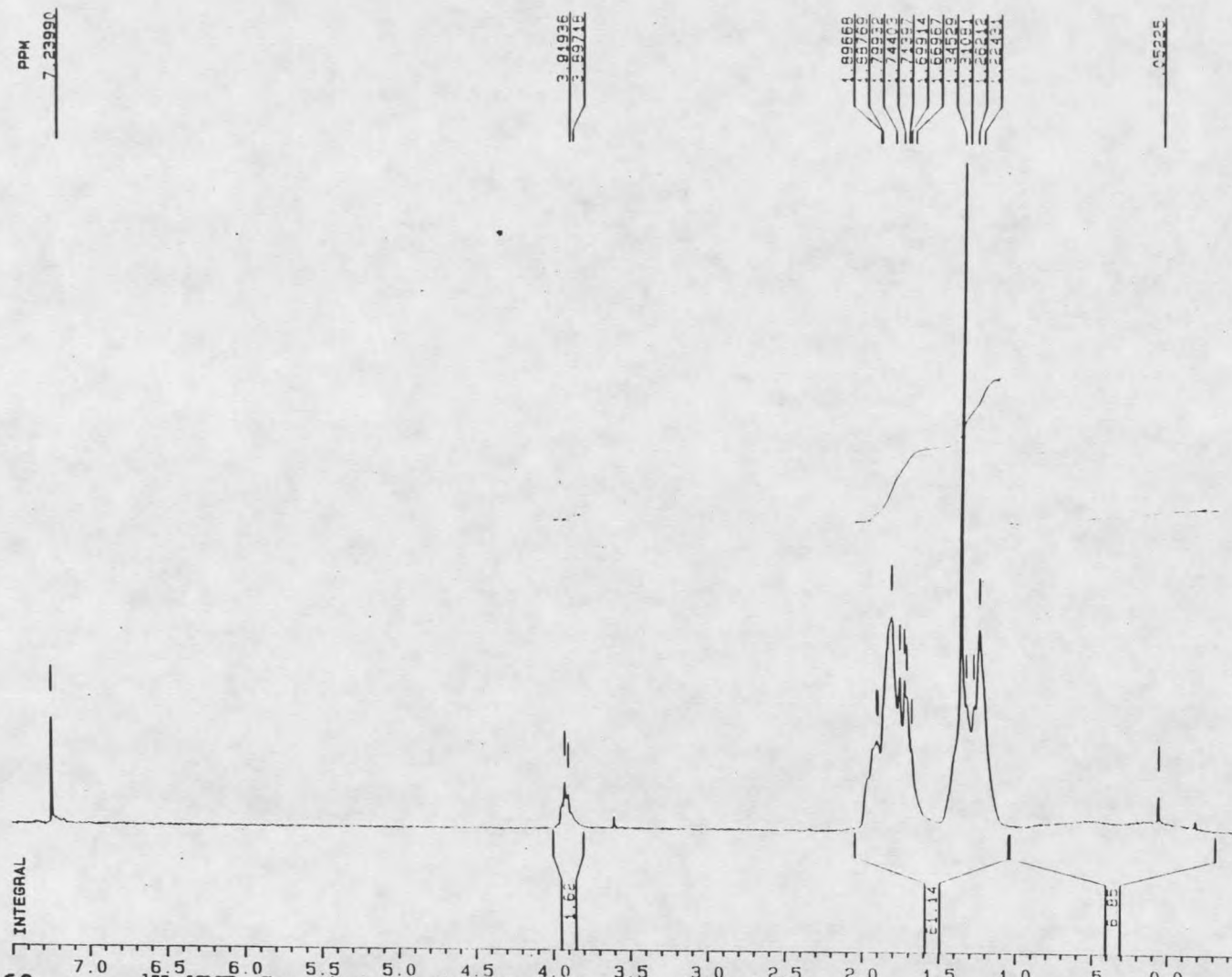
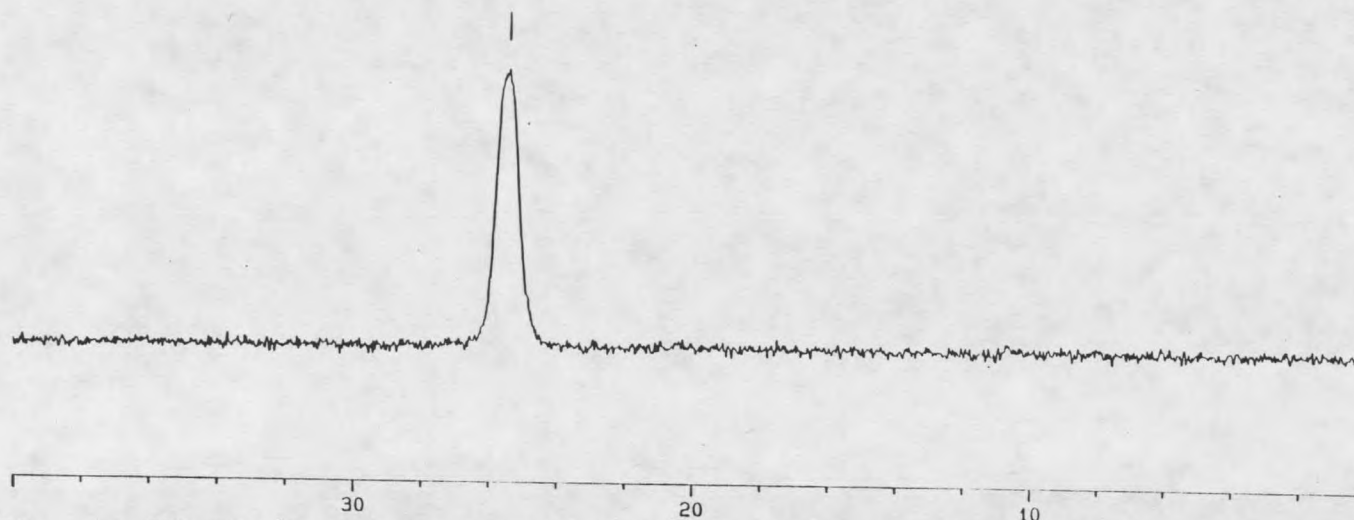


Figure 60. ^1H NMR Spectrum of (4R,5R)-4,5-Bis[(boronadicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33)

HERTZ

513.68



189

Figure 62. ^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[(boronatodicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (33)

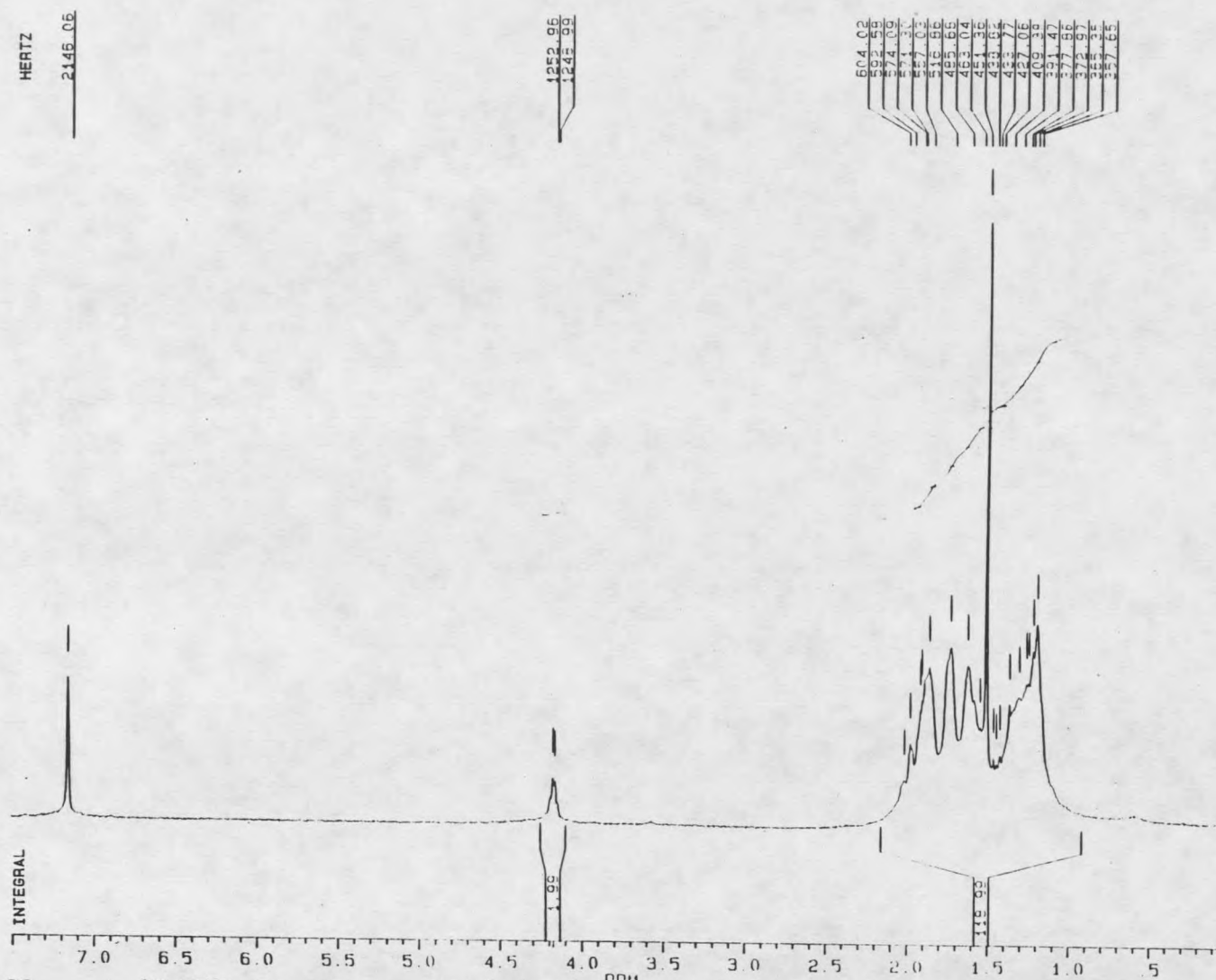


Figure 63. ^1H NMR Spectrum of (4R,5R)-4,5-Bis[(dicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (32)



PPM

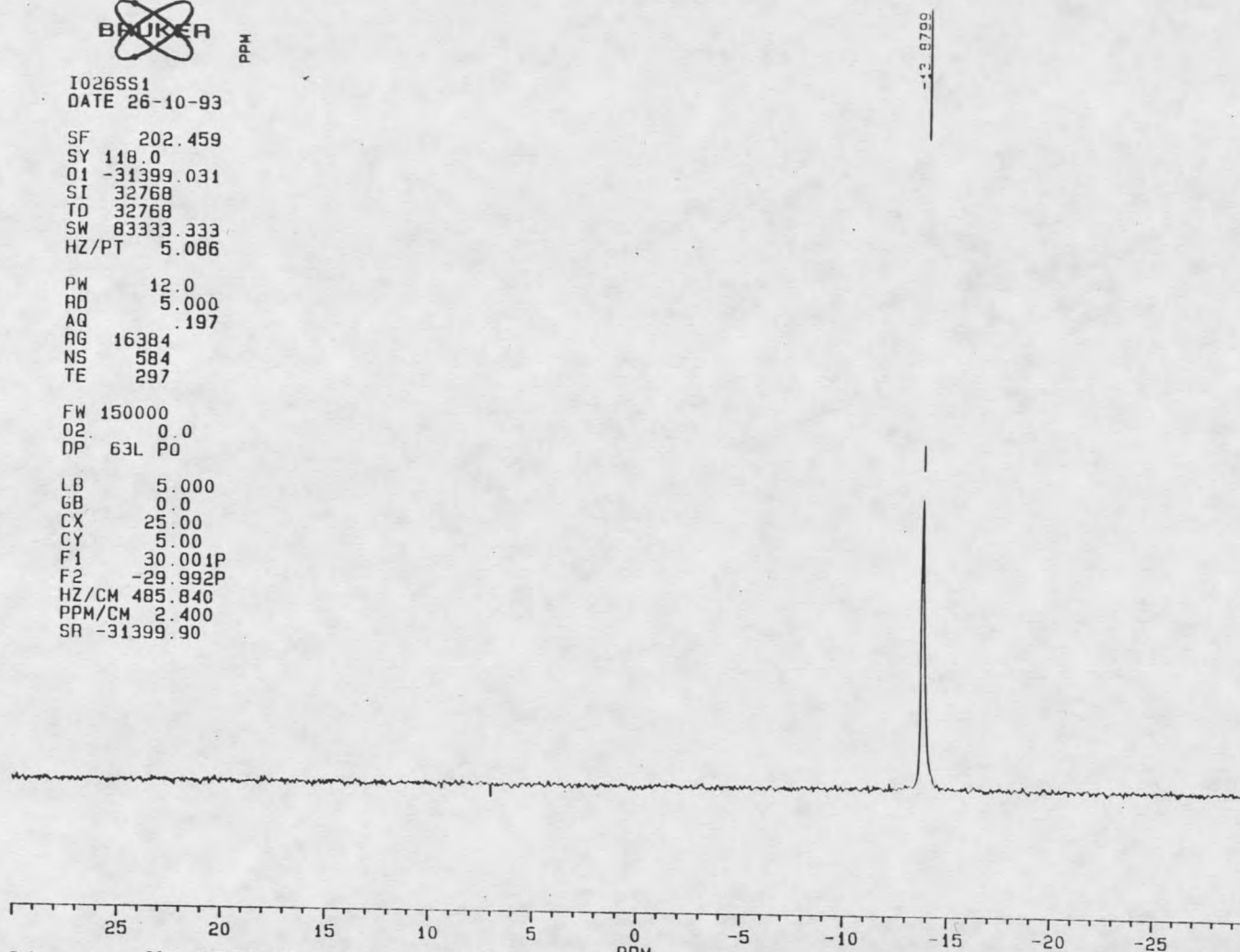
I026SS1
DATE 26-10-93

SF 202.459
SY 118.0
O1 -31399.031
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 16384
NS 584
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 5.000
GB 0.0
CX 25.00
CY 5.00
F1 30.001P
F2 -29.992P
HZ/CM 485.840
PPM/CM 2.400
SR -31399.90



191

Figure 64. ^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[(dicyclohexylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (32)

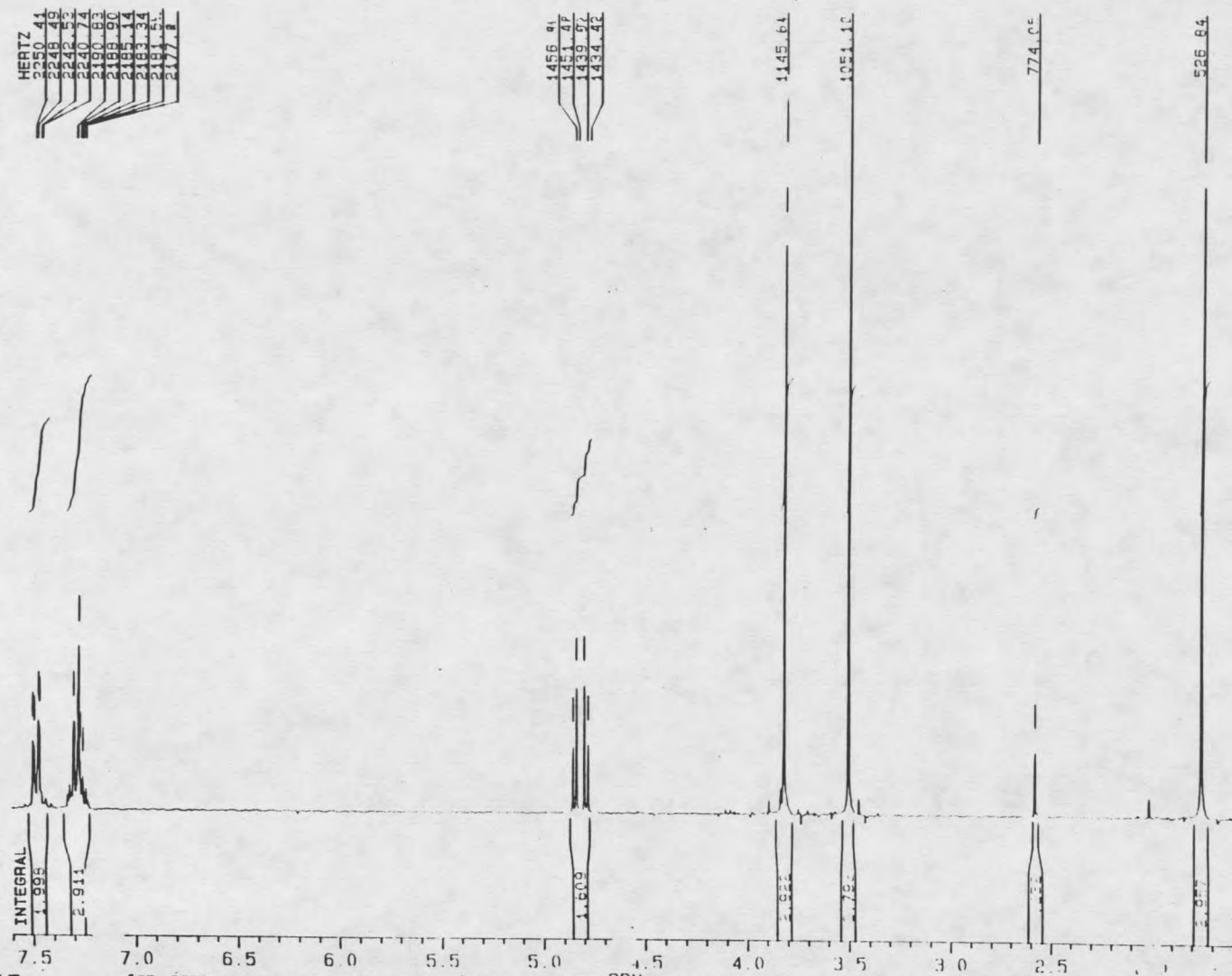
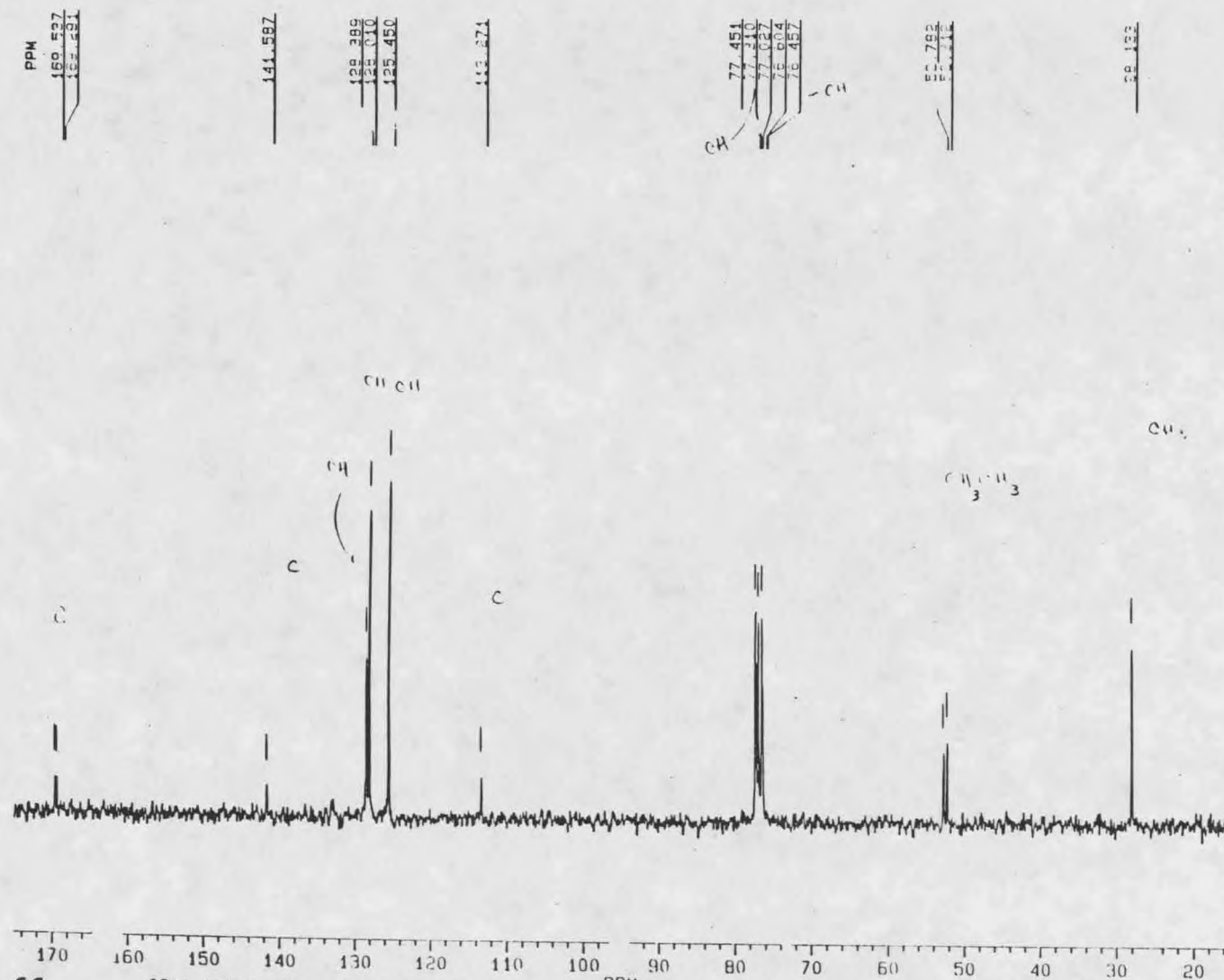


Figure 65.

^1H NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2-methyl-2-phenyl-1,3-dioxolane (100b)



193

Figure 66.

¹³C NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2-methyl-2-phenyl-1,3-dioxolane (100b)

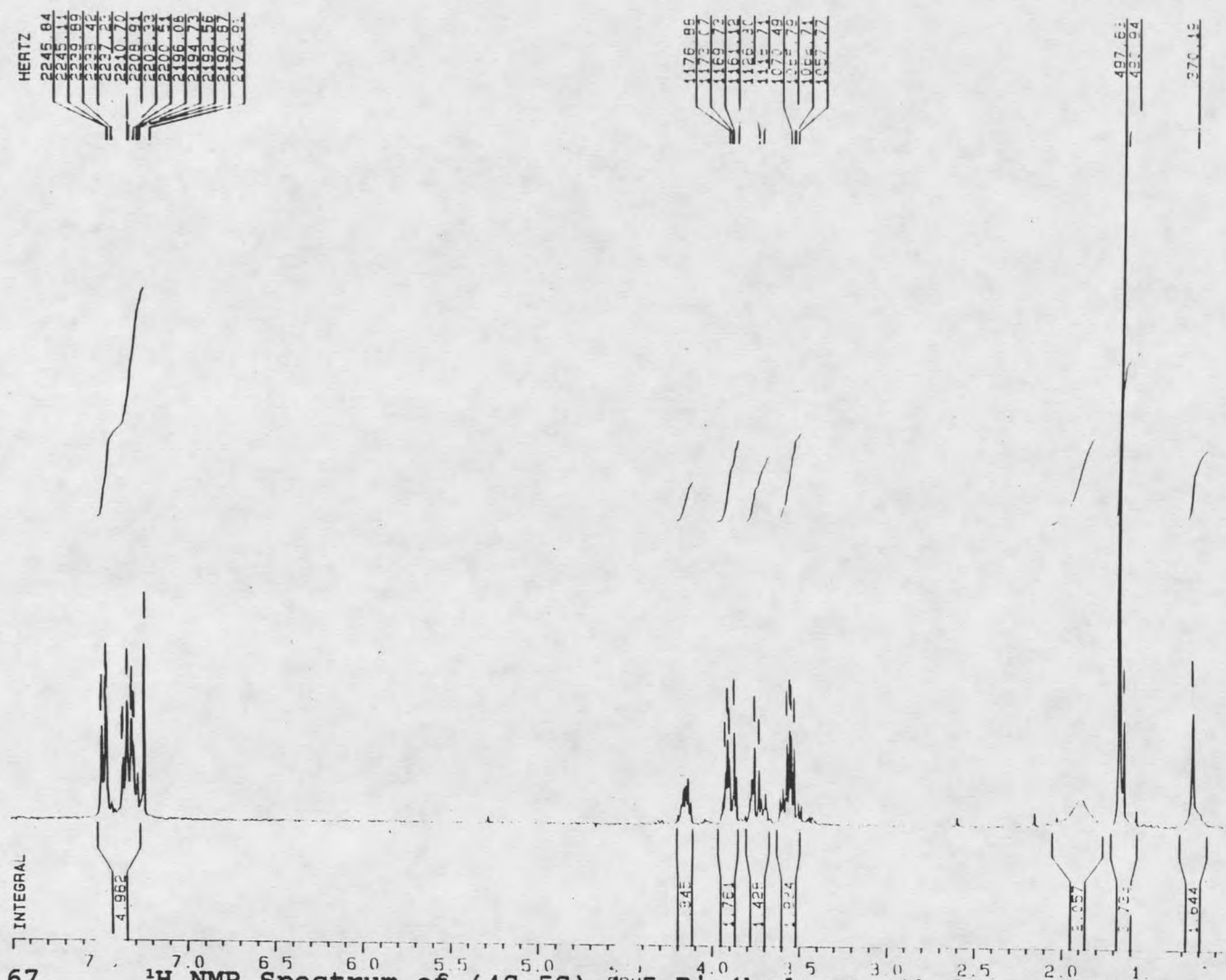


Figure 67. ^1H NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)

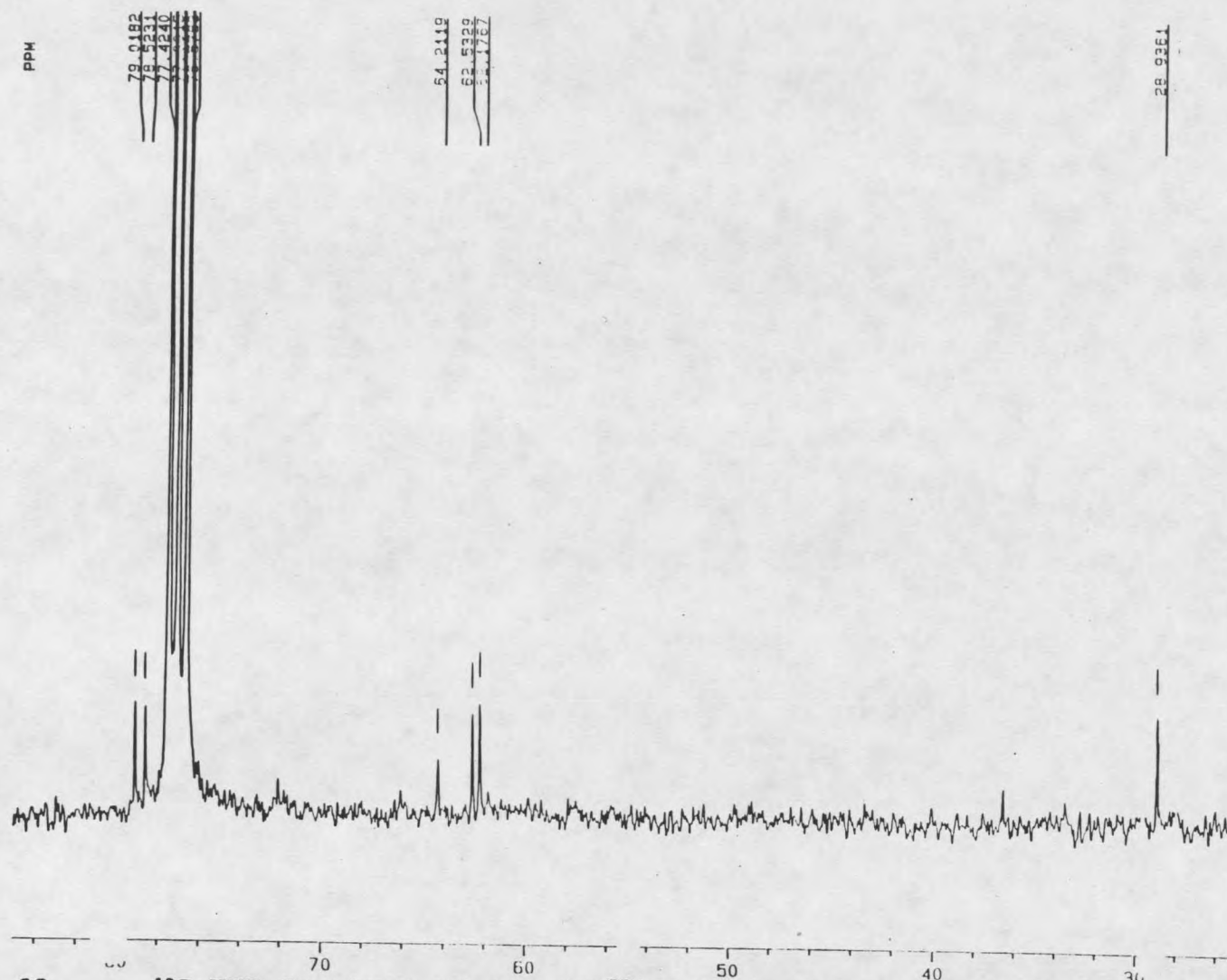


Figure 68. ¹³C NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)

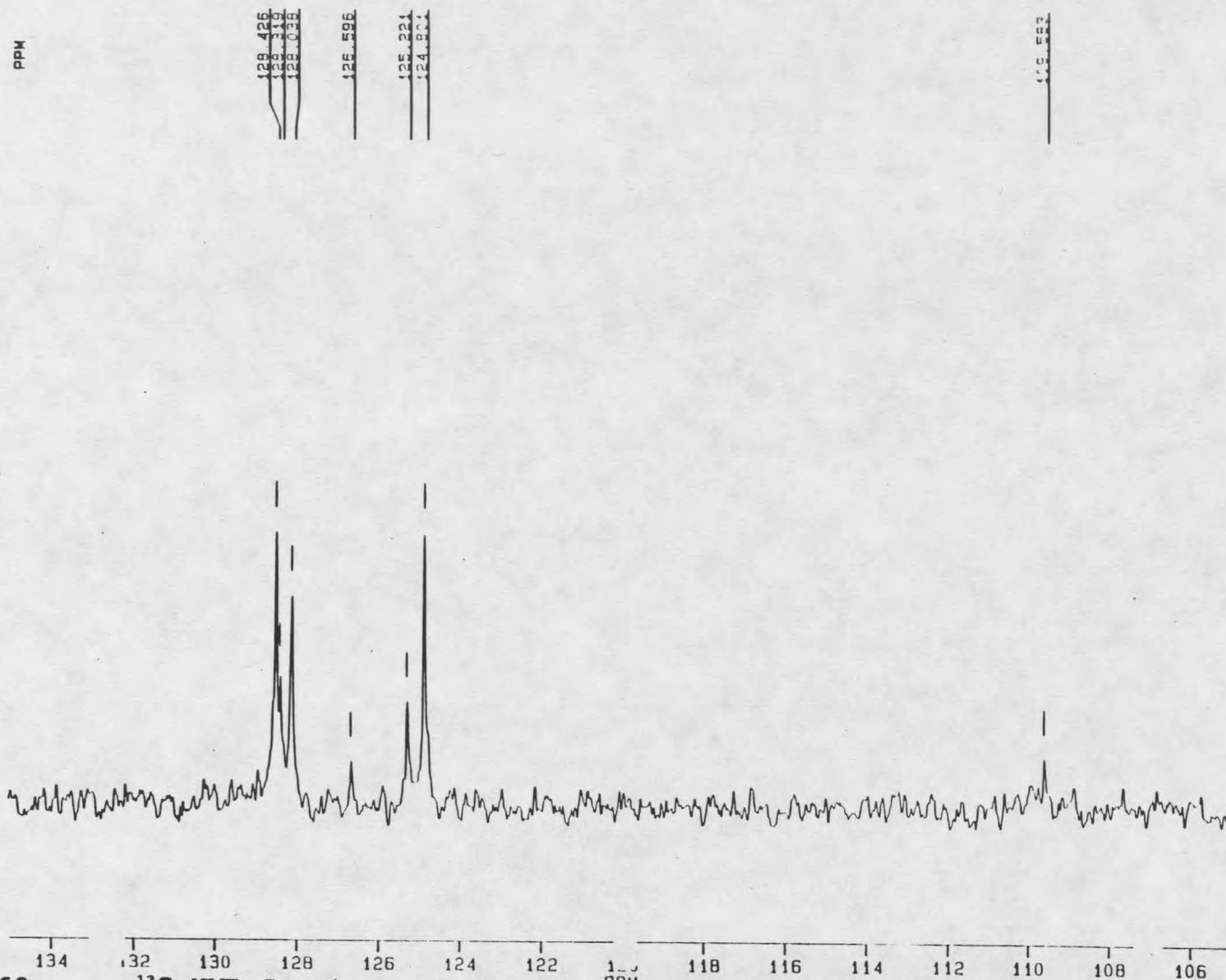
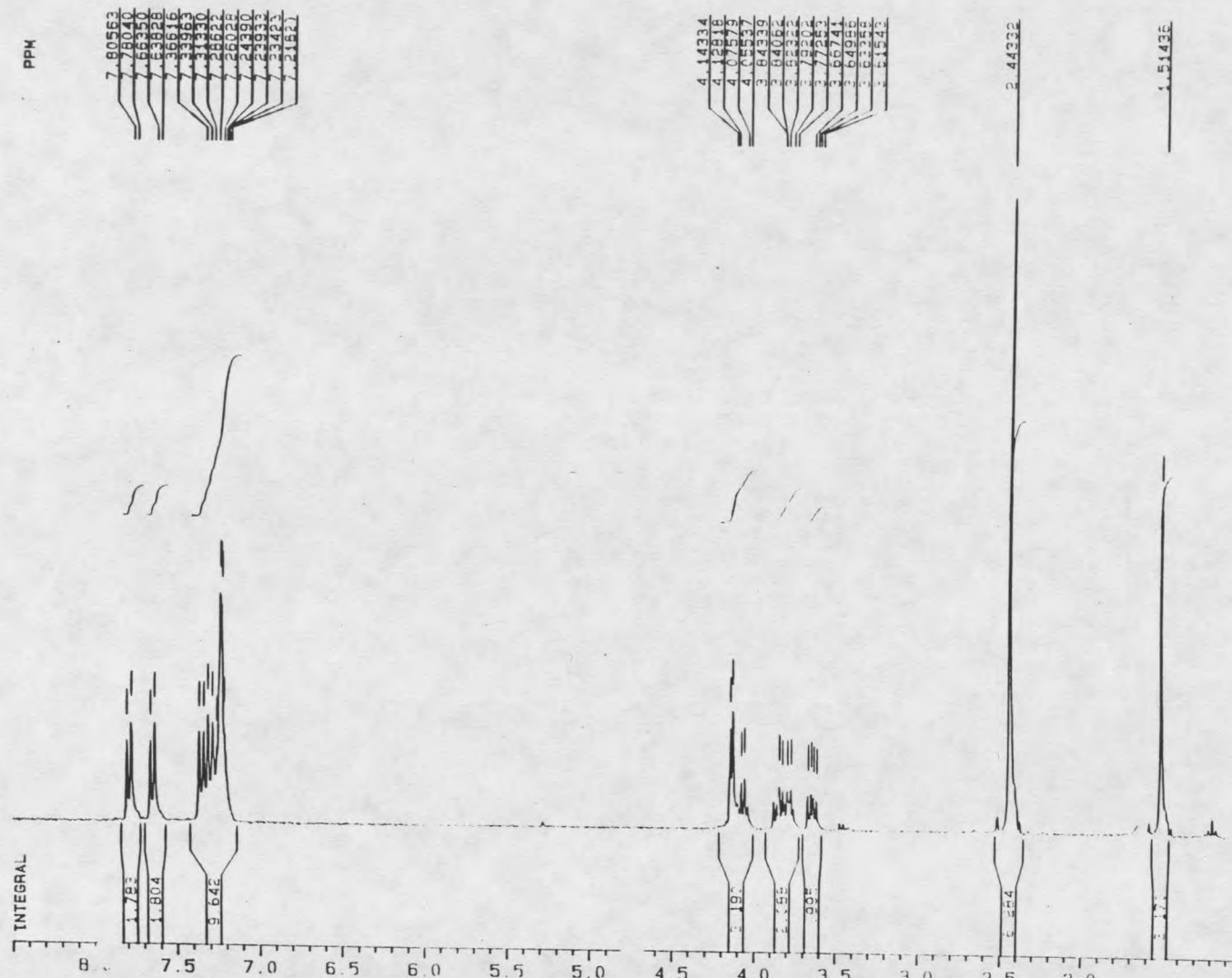


Figure 69.

^{13}C NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2-methyl-2-phenyl-1,3-dioxolane (101b)



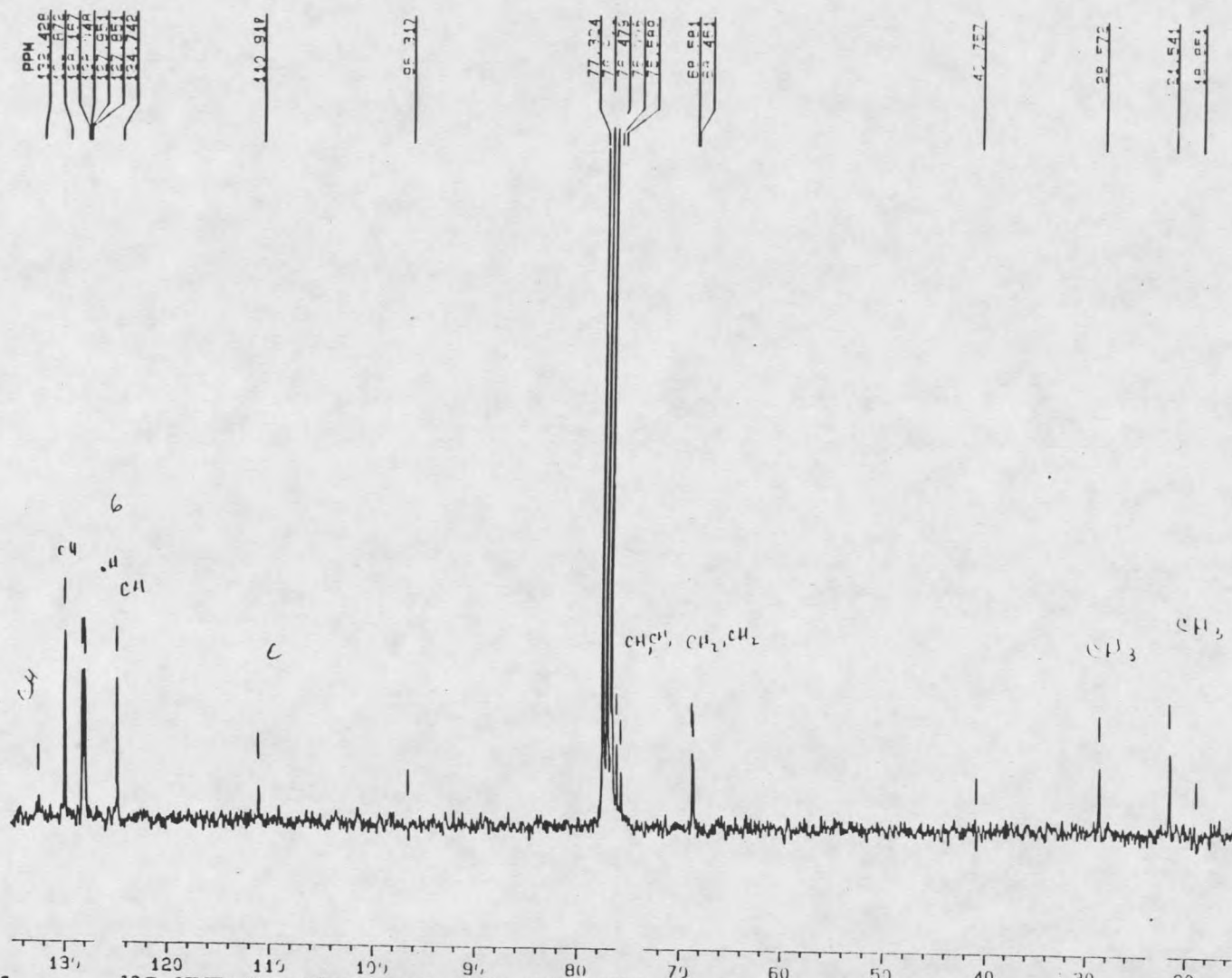


Figure 71.

¹³C NMR Spectrum of (4S,5S)-4,5-bis[(p-tosyloxy)methyl]-2-methyl-2-phenyl-1,3-dioxolane (6b)



HERTZ

DATE 18-2-93

SF 202.459
SY 118.0
O1 -31378.686
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 32
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 4.000
GB 0.0
CX 25.00
CY 5.00
F1 -9.994P
F2 -29.992P
HZ/CM 161.947
PPM/CM .800
SR -31379.55

-4652.53
-4708.20

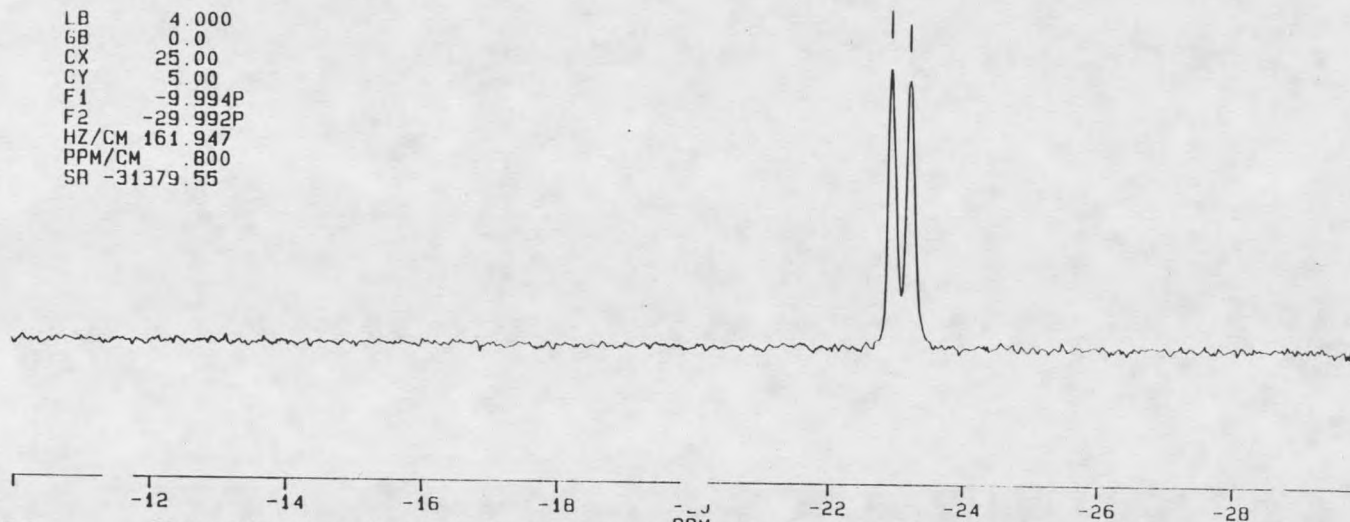


Figure 74.

³¹P NMR Spectrum of (4R,5R)-4,5-Bis[(diphenylphosphino)methyl]-2-methyl-2-phenyl-1,3-dioxolane (3b)

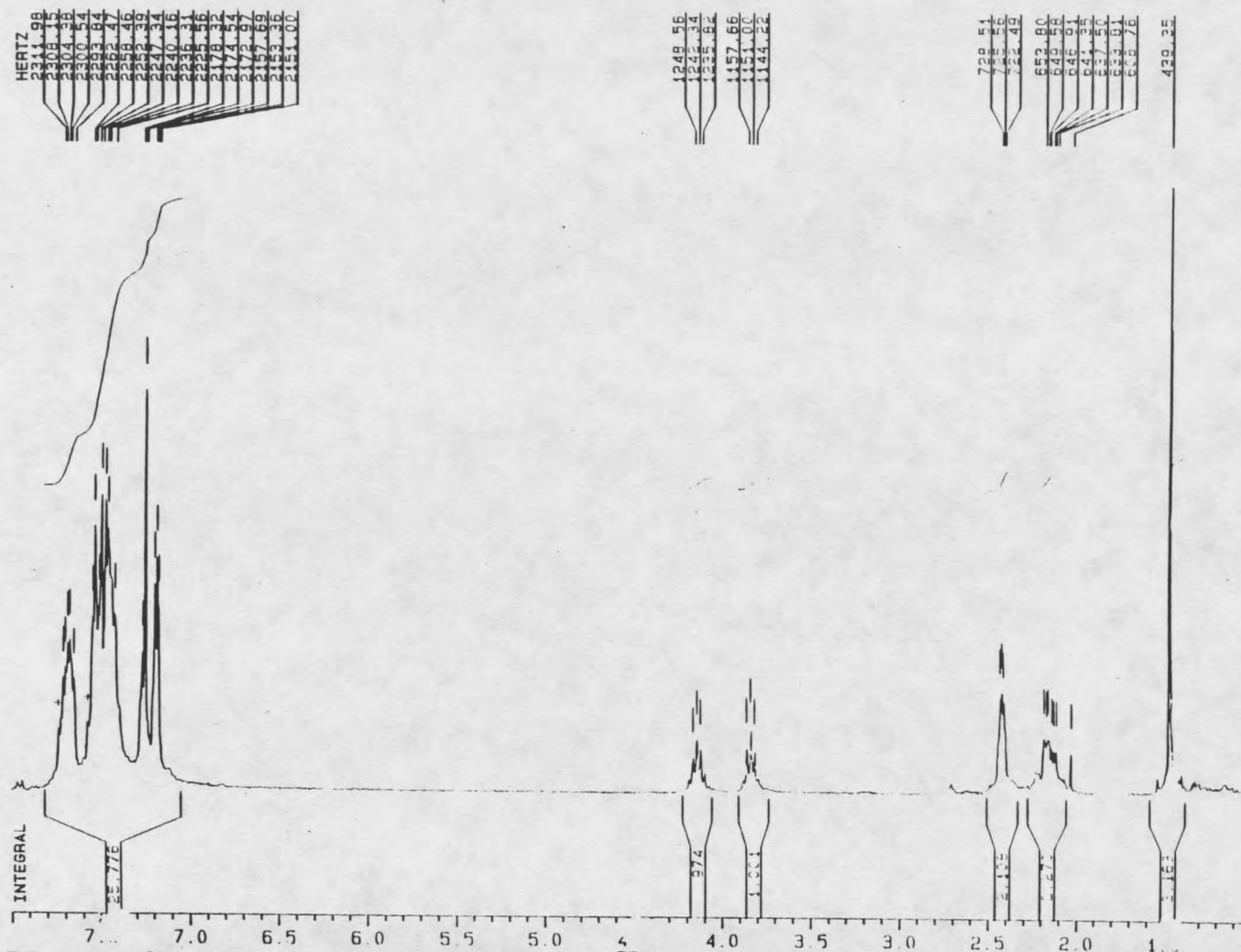


Figure 75. ^1H NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-trifluoromethylphenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g)



HERTZ

DATE 18-2-93

SF 202.459
SY 118.0
O1 -31378.686
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 338
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 4.000
GB 0.0
CX 25.00
CY 5.00
F1 -25.997P
F2 -35.971P
HZ/CM 80.770
PPM/CM .399
SR -31379.55

-6607.37
-6558.74
-6533.63
-6514.00
-6493.33
-6473.33
-6453.33
-6433.33
-6413.33
-6393.33

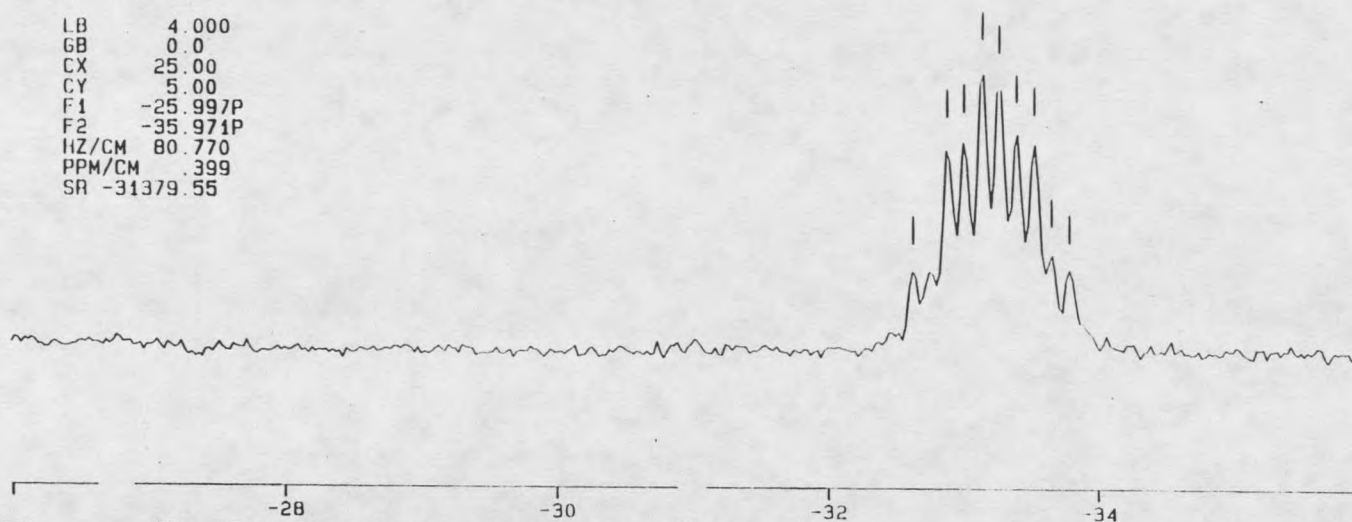


Figure 77.

^{31}P NMR Spectrum of (4R,5R)-4,5-Bis[[bis(2-trifluoromethyl-phenyl)phosphino]methyl]-2-methyl-2-phenyl-1,3-dioxolane (3g)

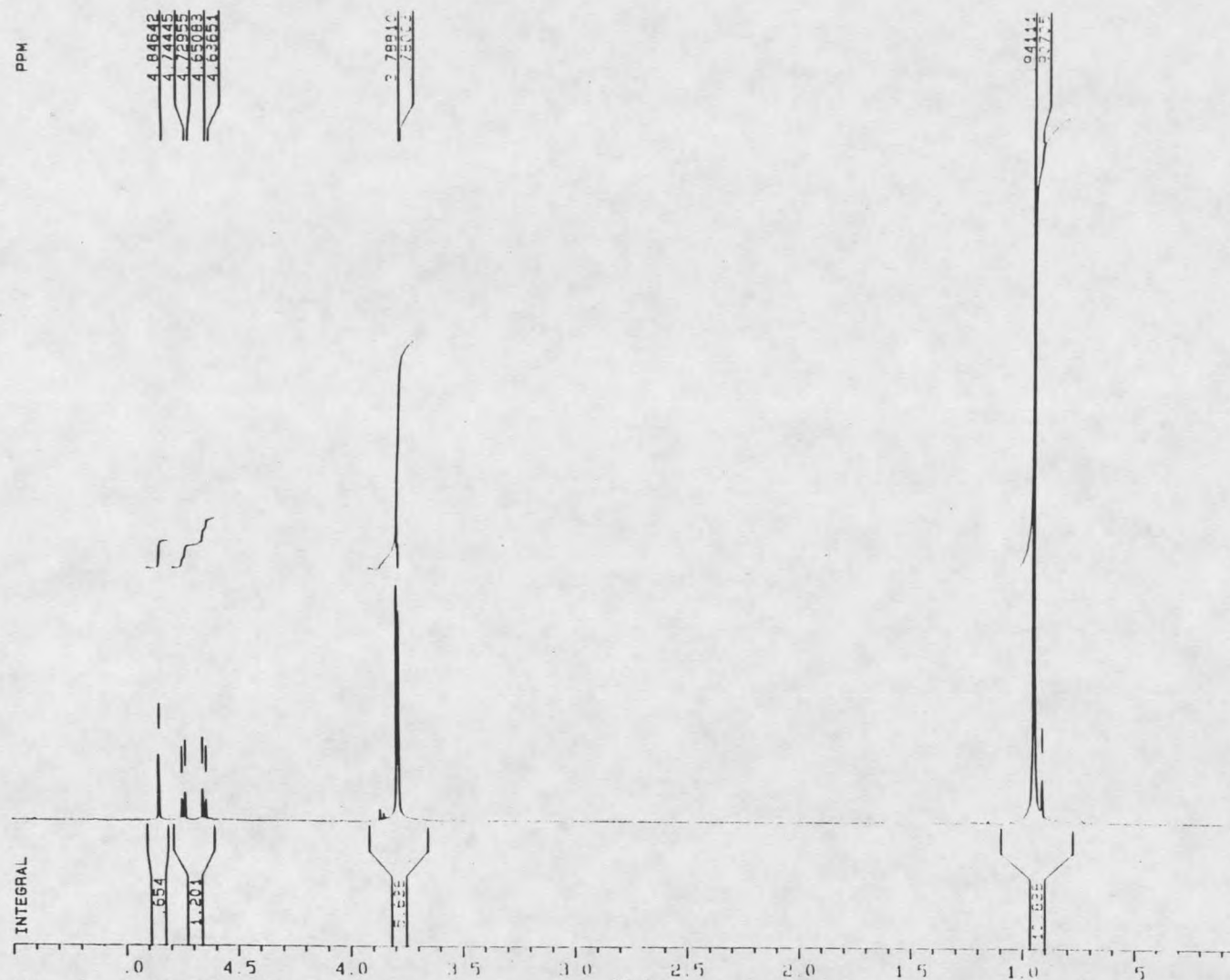


Figure 78. ¹H NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2-t-butyl-1,3-dioxolane (100c)

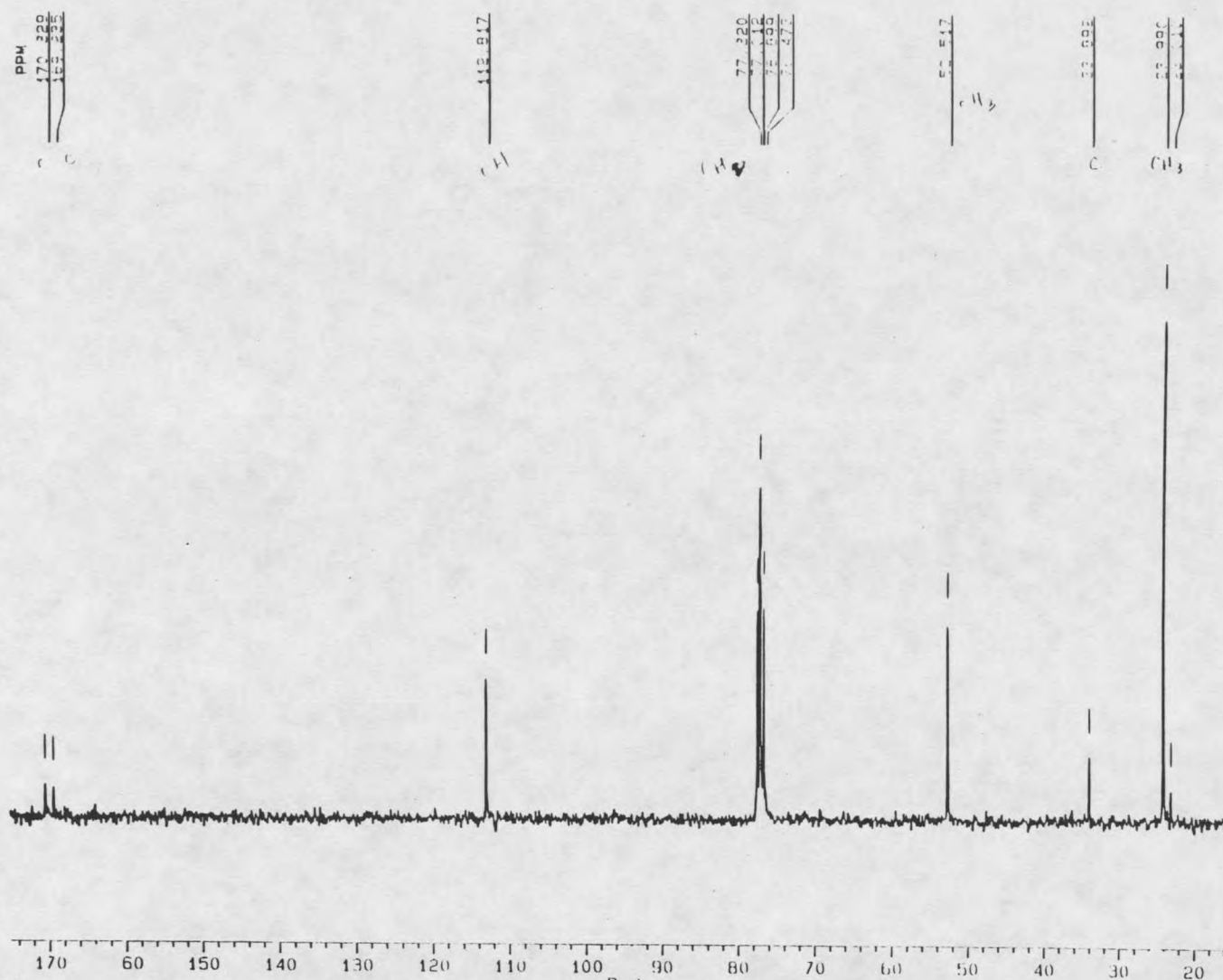


Figure 79. ^{13}C NMR Spectrum of (4R,5R)-4,5-Bis(carbomethoxy)-2-t-butyl-1,3-dioxolane (100c)



Figure 80. ^1H NMR Spectrum of (4S,5S)-4,5-Bis(hydroxymethyl)-2-t-butyl-1,3-dioxolane (101c)

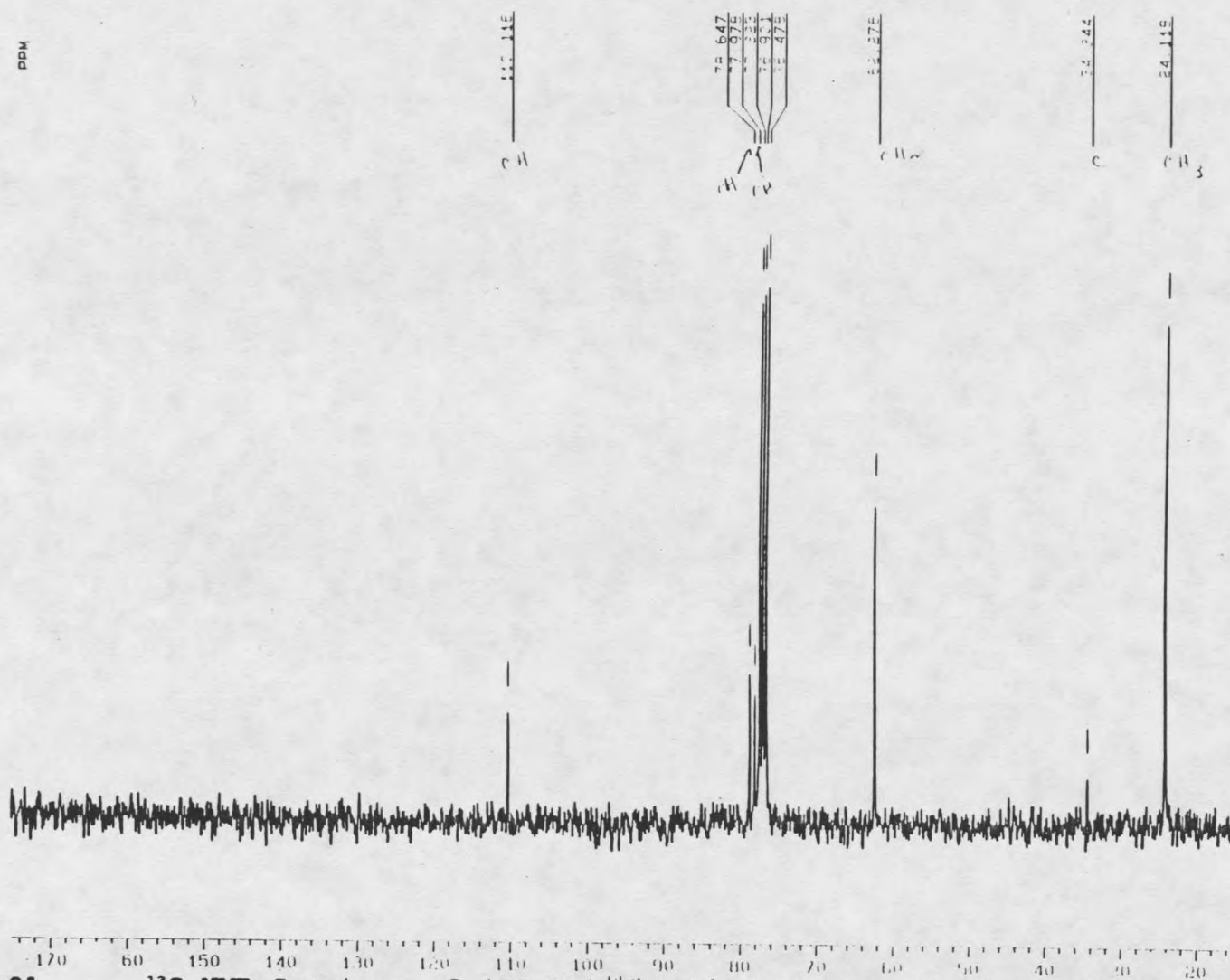


Figure 81. ^{13}C NMR Spectrum of (4S,5S)-4',5-Bis(hydroxymethyl)-2-t-butyl-1,3-dioxolane (101c)

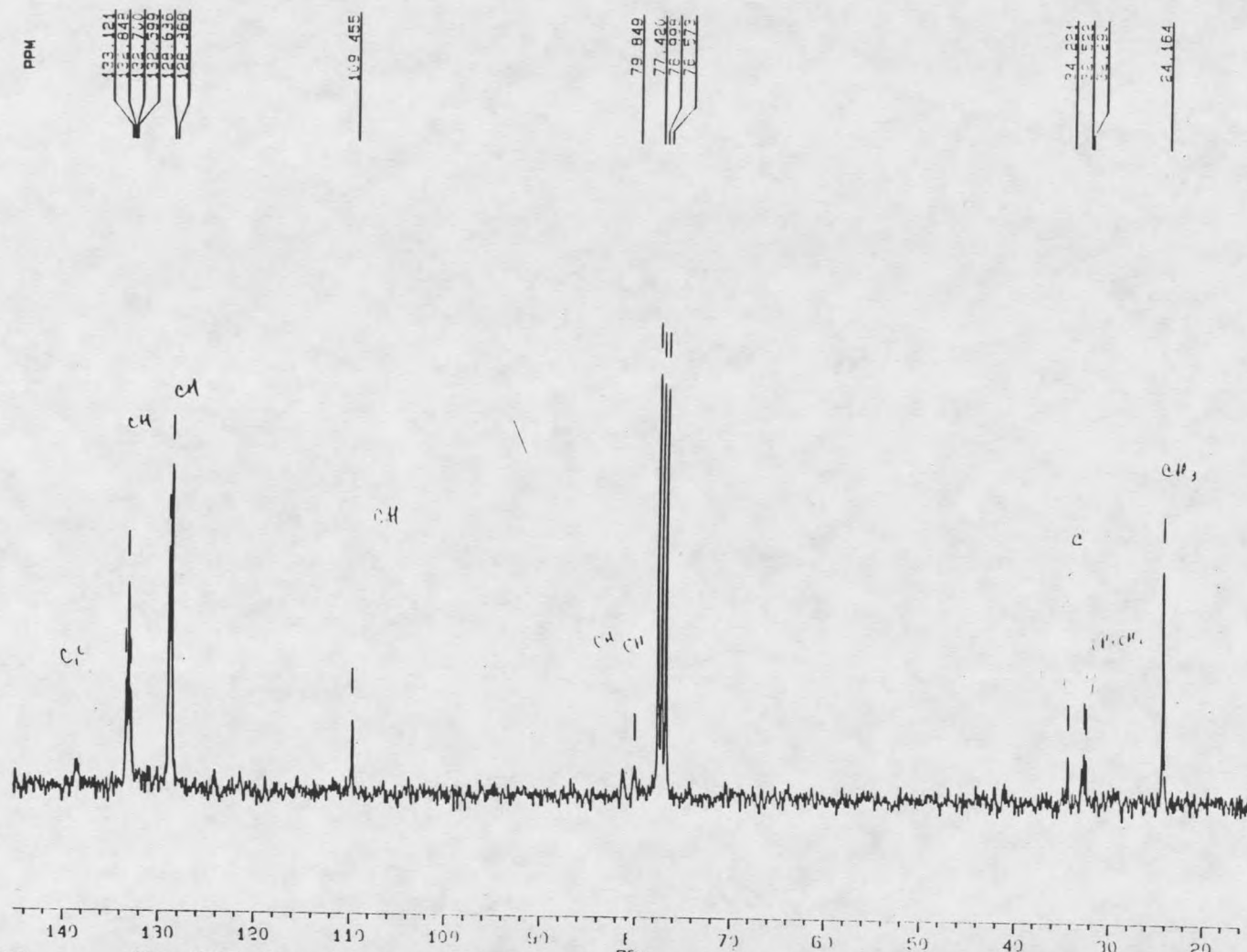


Figure 85. ¹³C NMR Spectrum of (4R,5R)-4,5-Bis[(diphenylphosphino)methyl]-2-t-Butyl-1,3-dioxolane (3c)



HERTZ

DATE 19-2-93

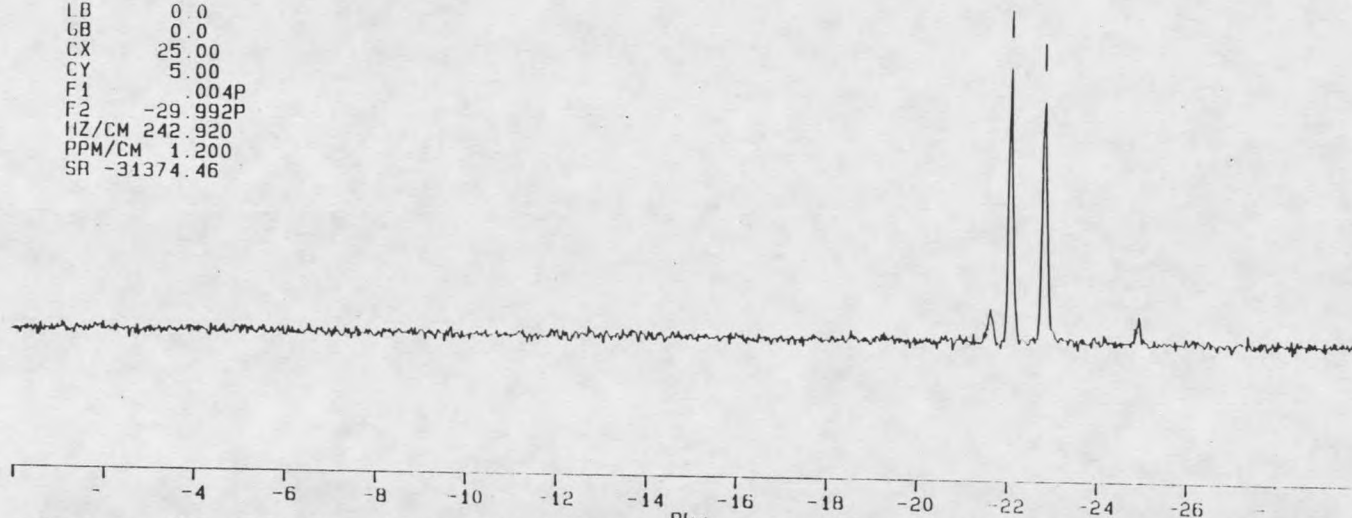
SF 202.459
SY 118.0
O1 -31373.600
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 435
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 0.0
GB 0.0
CX 25.00
CY 5.00
F1 .004P
F2 -29.992P
HZ/CM 242.920
PPM/CM 1.200
SR -31374.46

-4474.05
-4626.17



213

Figure 86. ³¹P NMR Spectrum of (4R,5R)-4,5-Bis[(diphenylphosphino)methyl]-2-t-Butyl-1,3-dioxolane (3c)

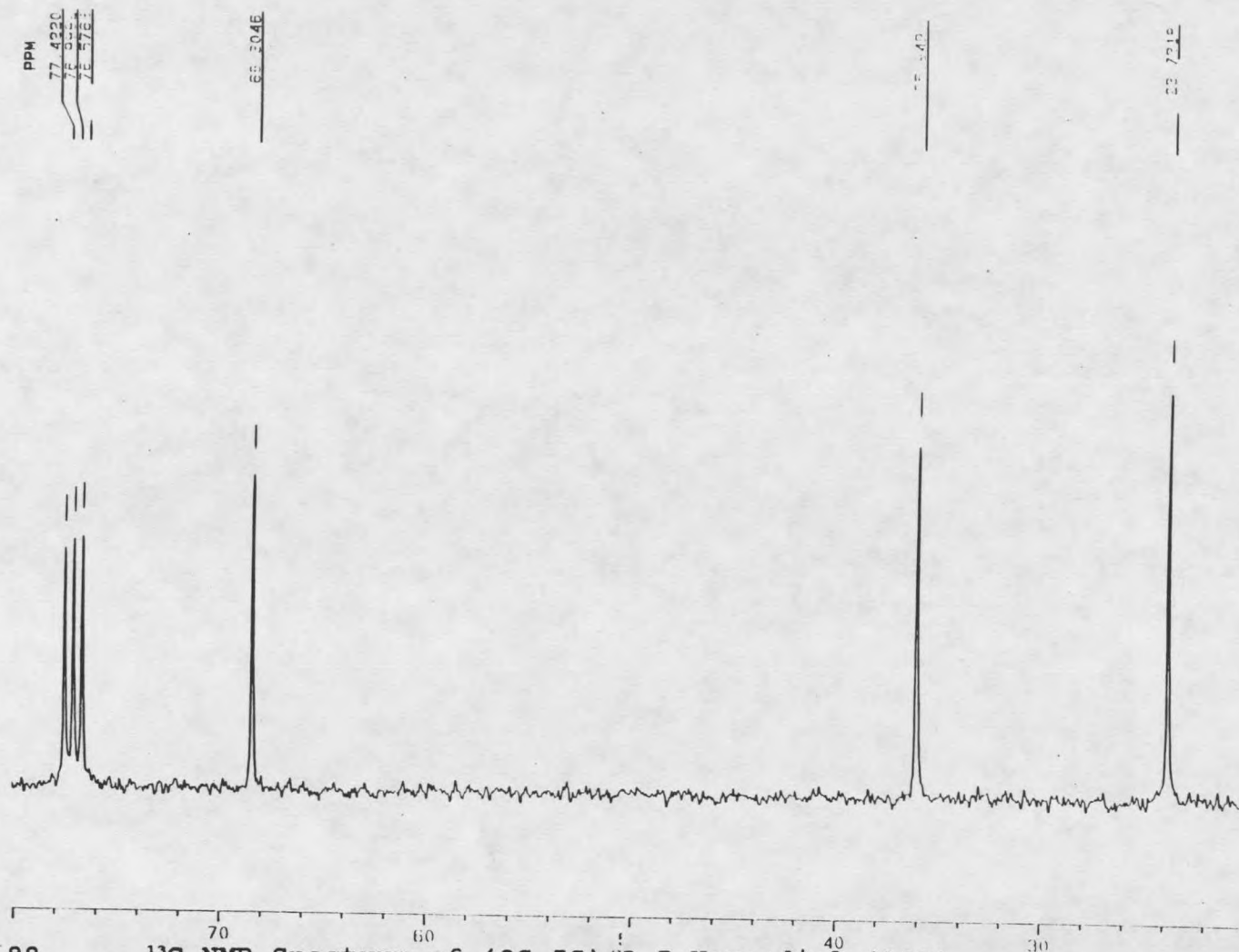
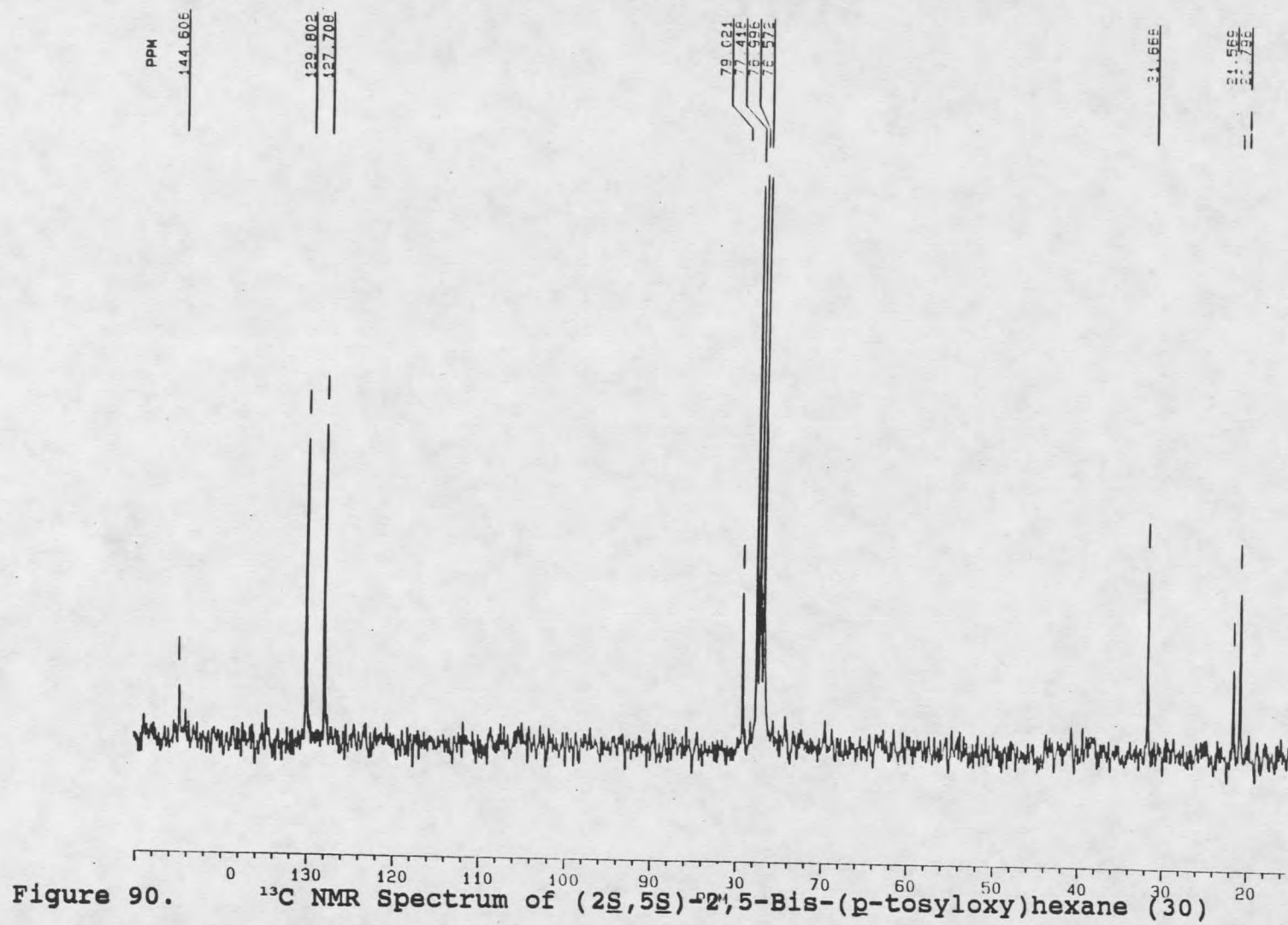


Figure 88. ^{13}C NMR Spectrum of (2S,5S)-2,5-Hexandiol (102)



ppm

-1.93495

220

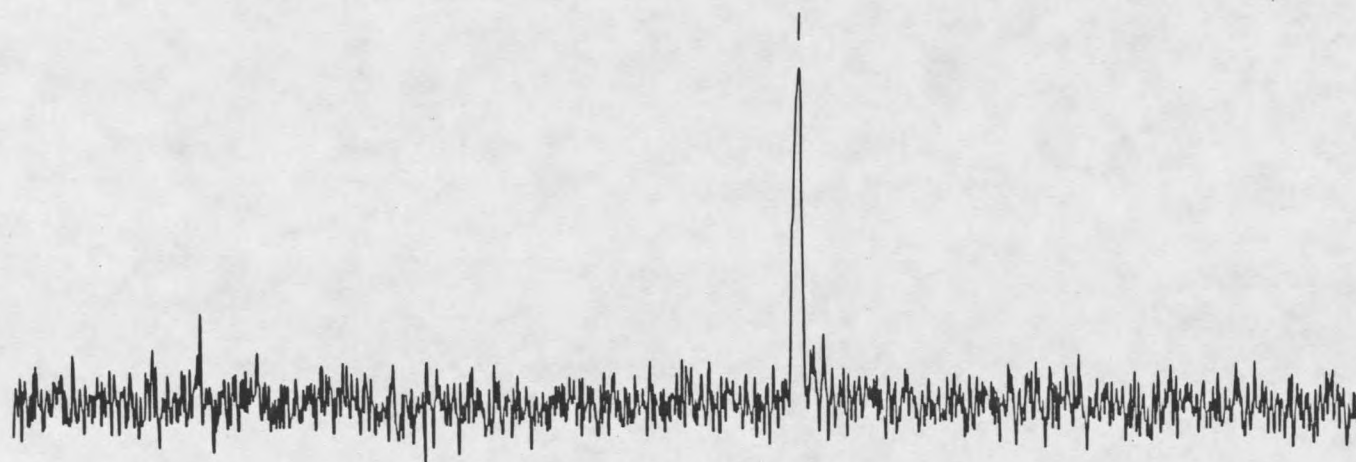


Figure 93. ^{31}P NMR Spectrum of (2R,5R)-2,5-Bis(diphenylphosphino)hexane (21b)

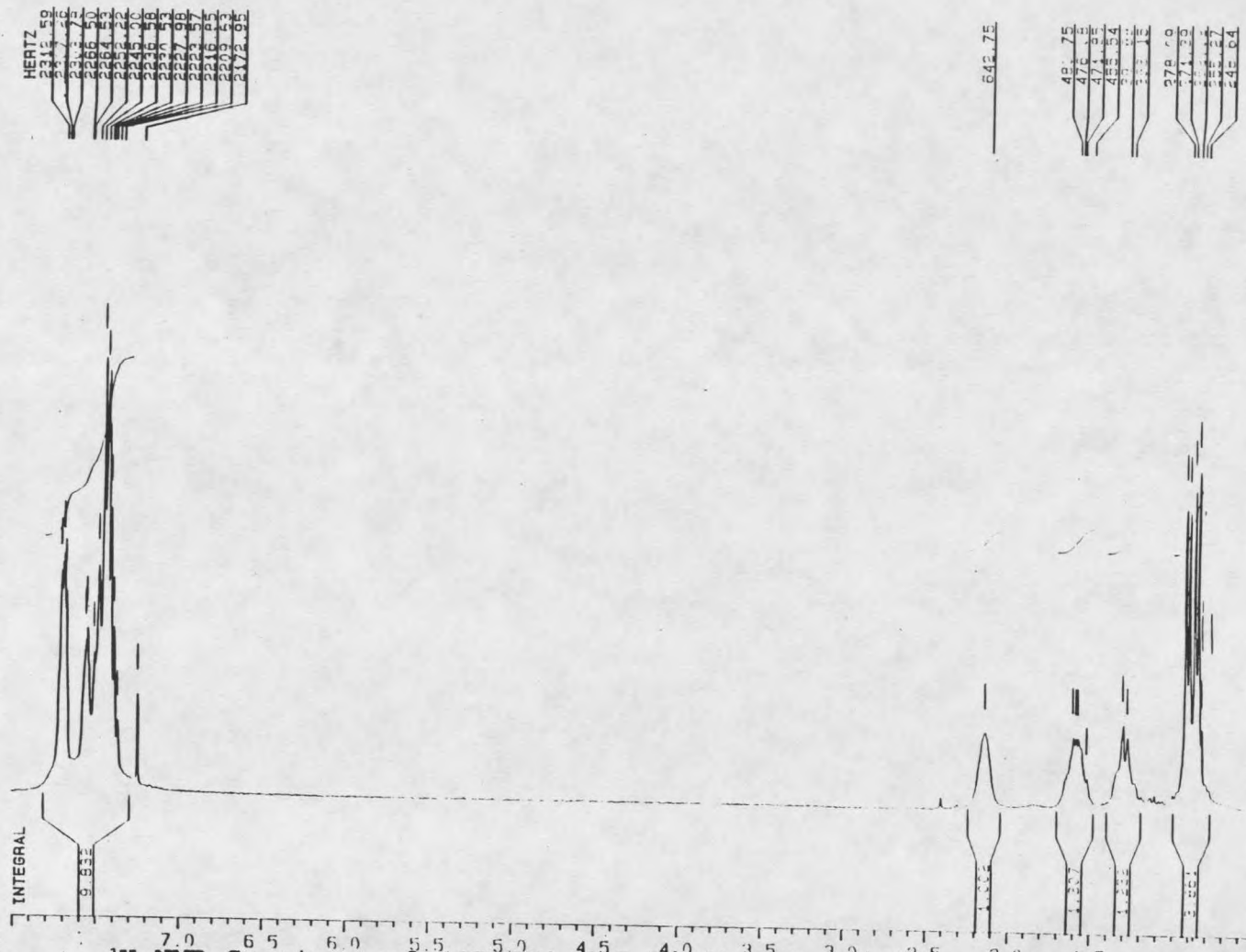
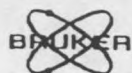


Figure 94. ^1H NMR Spectrum of (2R,5R)-2,5-Bis[bis(2-trifluoromethylphenyl)phosphino]hexane (15a)





HERTZ

DATE 18-2-93

SF 202.459
SY 118.0
O1 -31378.686
SI 32768
TD 32768
SW 83333.333
HZ/PT 5.086

PW 12.0
RD 5.000
AQ .197
RG 8192
NS 1716
TE 297

FW 150000
O2 0.0
DP 63L P0

LB 4.000
GB 0.0
CX 25.00
CY 5.00
F1 -9.994P
F2 -24.993P
HZ/CM 121.460
PPM/CM .600
SR -31379.55

-4110.65
-4154.75



Figure 96. ^{31}P NMR Spectrum of (2R,5R)-2,5-Bis[bis(2-trifluoromethylphenyl)phosphino]hexane (15a)

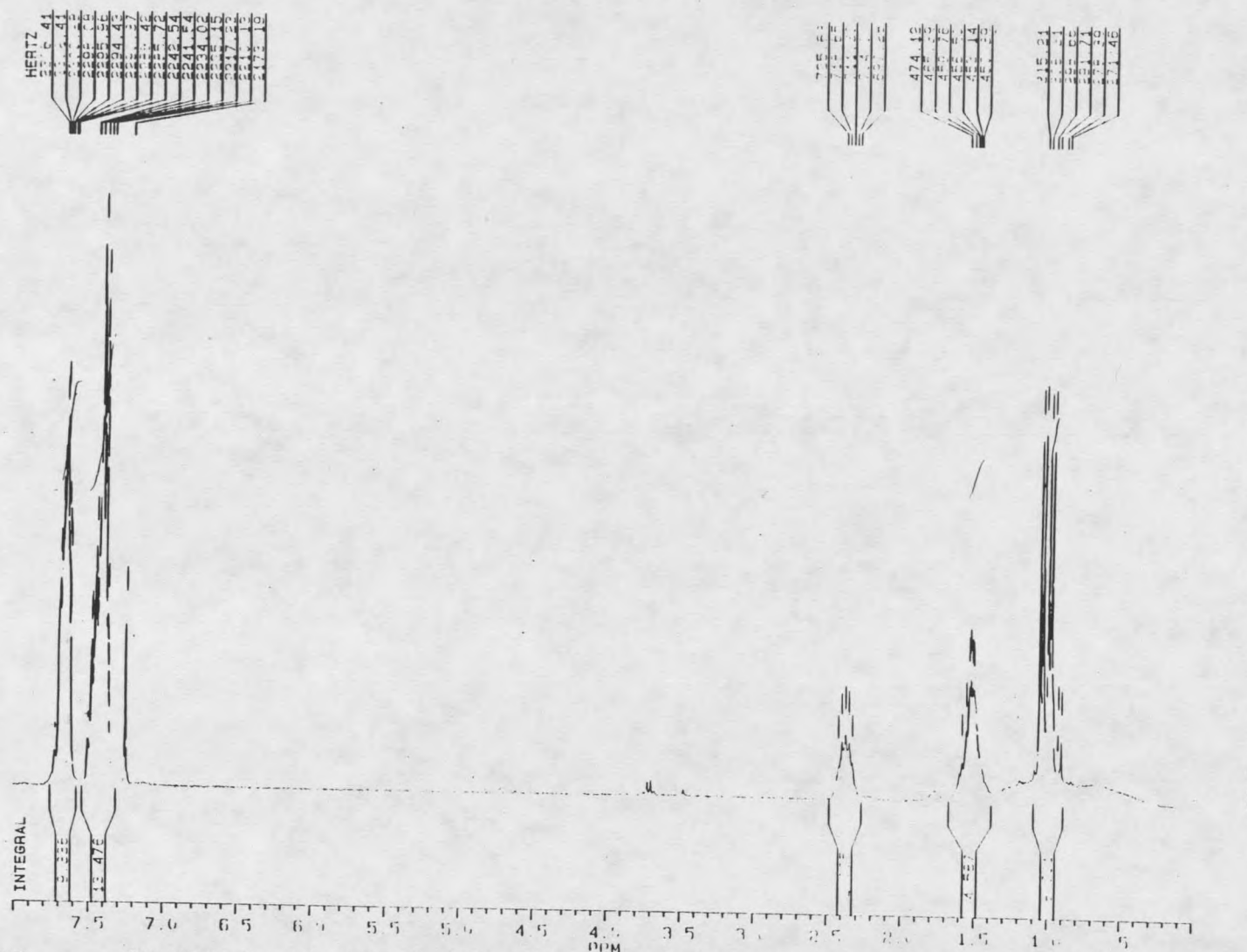
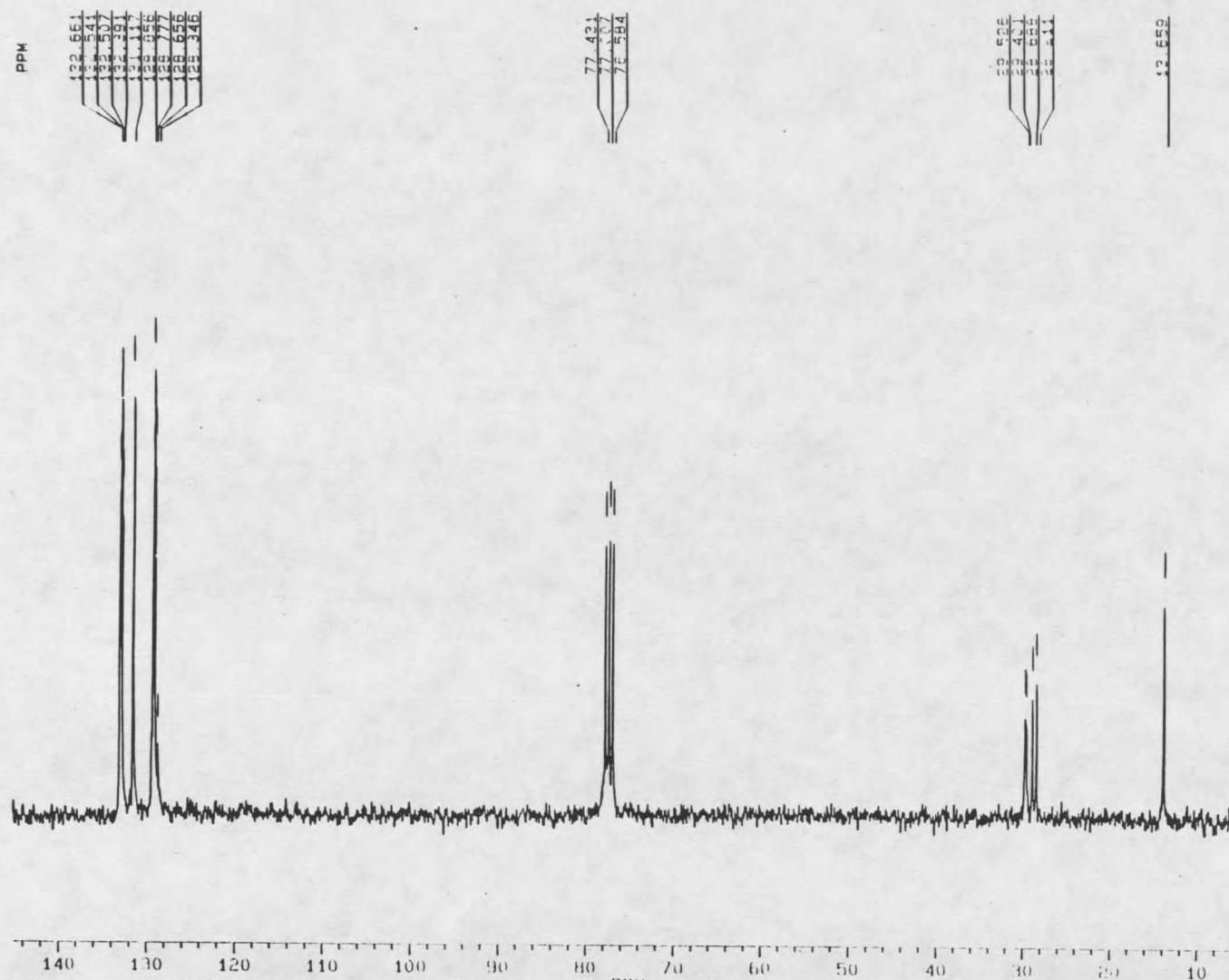


Figure 97. ^1H NMR Spectrum of (2R,5R)-2,5-Bis(boronato-diphenylphosphino)hexane (26b)



PPM

70
60
50
40
30
20
10
0

226

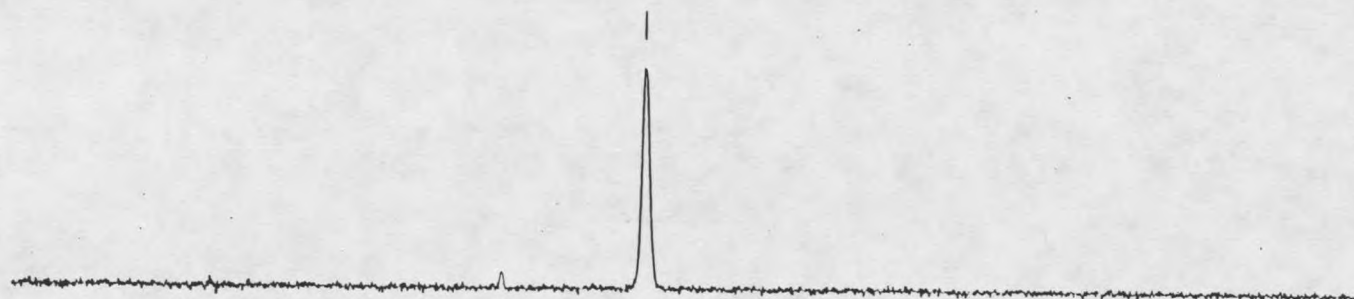


Figure 99. ^{31}P NMR Spectrum of $(2\text{R},5\text{R})$ - ^{31}P -2,5-Bis(boronato-diphenylphosphino)hexane (26b)

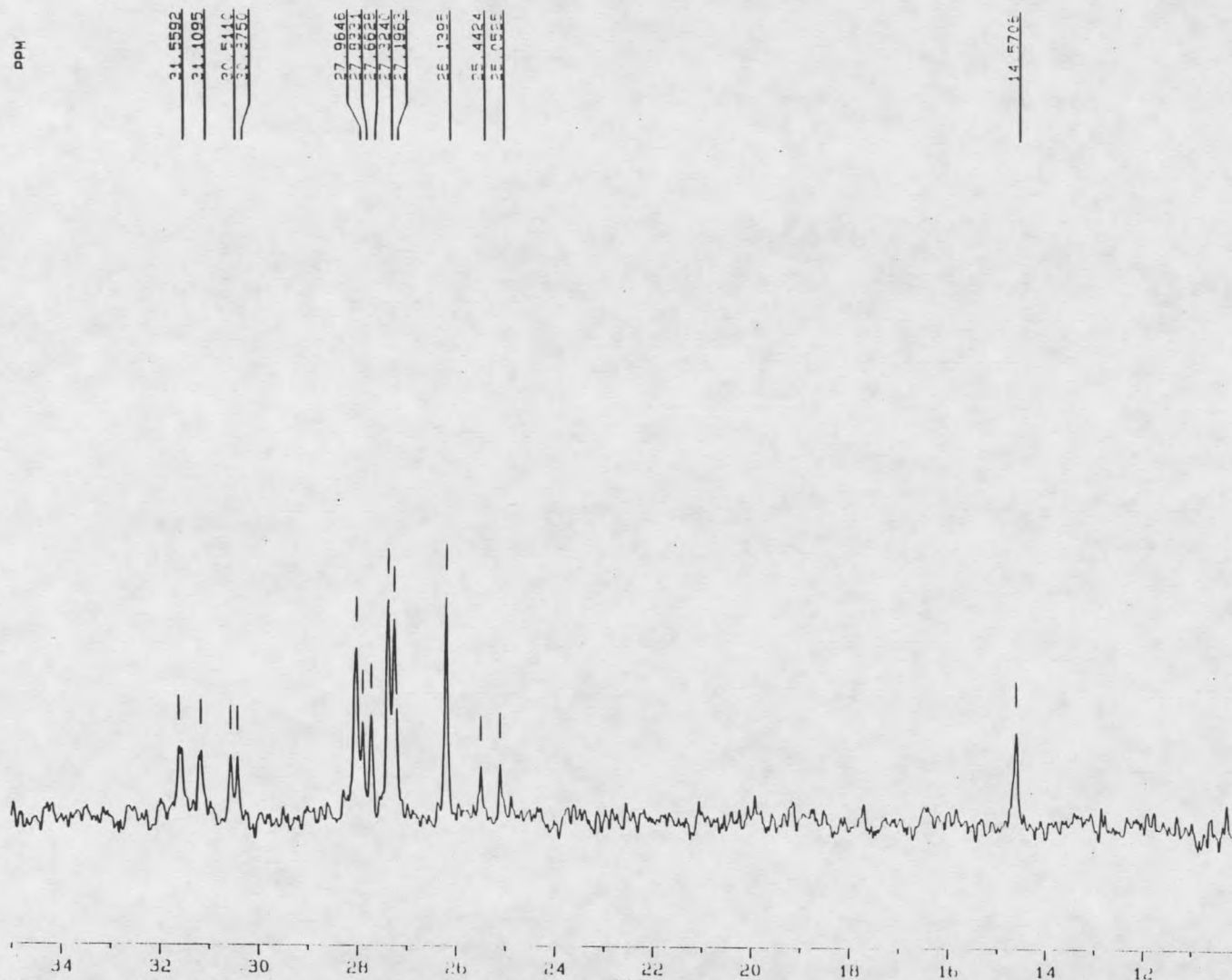
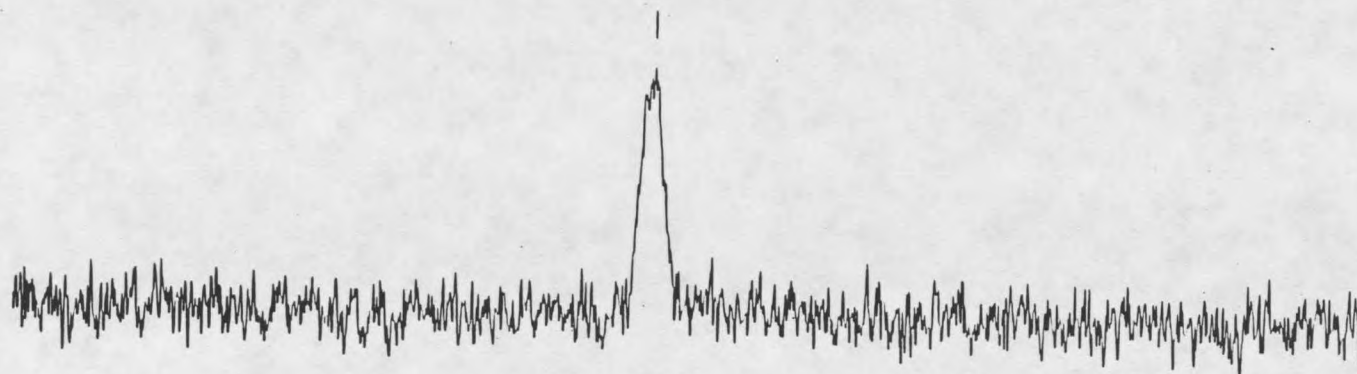


Figure 101. ^{13}C NMR Spectrum of (2R,5R)-2,5-Bis(boronato dicyclohexylphosphino)hexane (26a)

Mod

30112



229

Figure 102. ^{31}P NMR Spectrum of (2R,5R)-2,5-Bis(boronato dicyclohexylphosphino)hexane (26a)

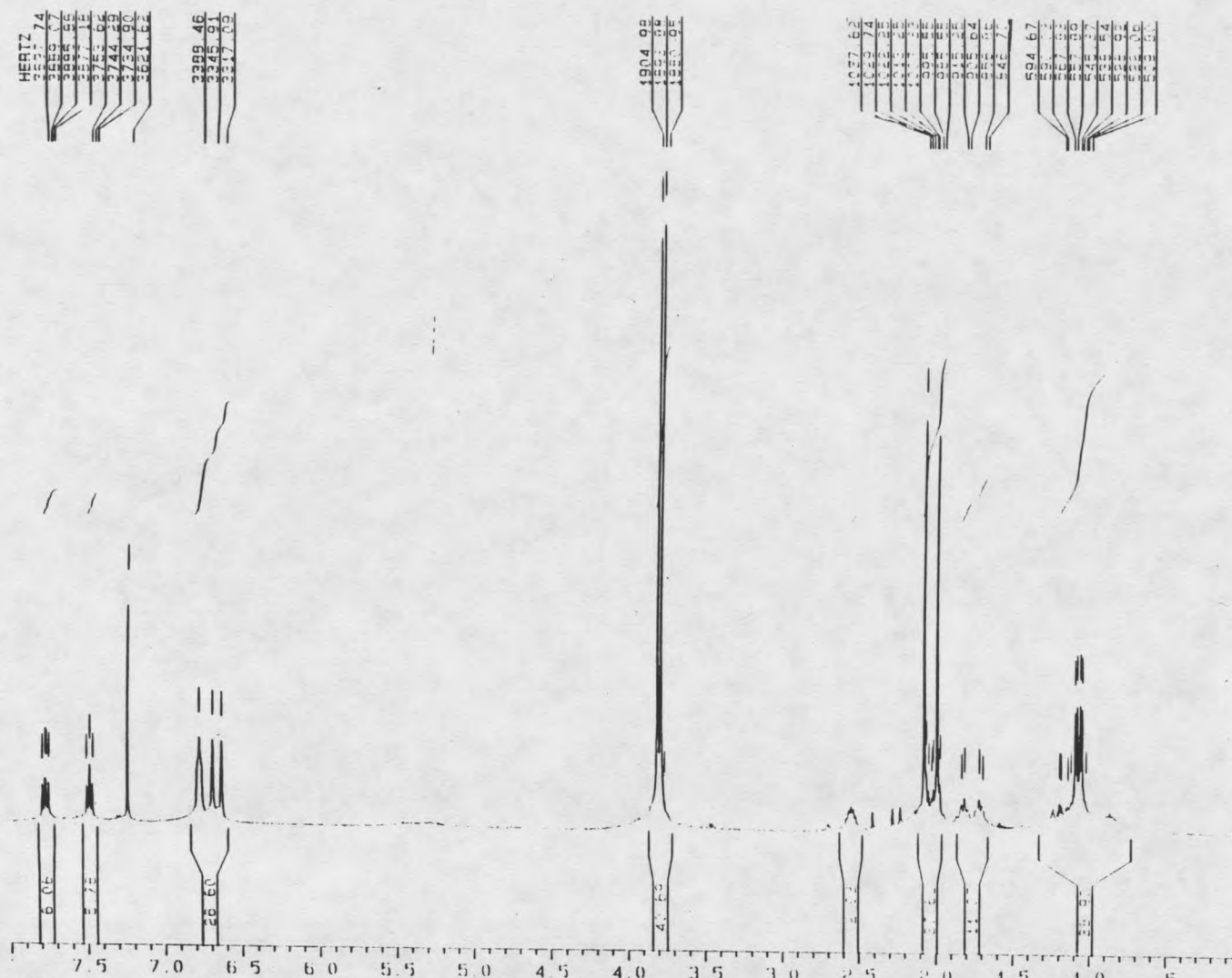


Figure 103. ^1H NMR Spectrum of (2R,2R)-2,5-Bis[boronato-Bis(4-methoxy-2-methylphenyl)phosphino]hexane (26c)

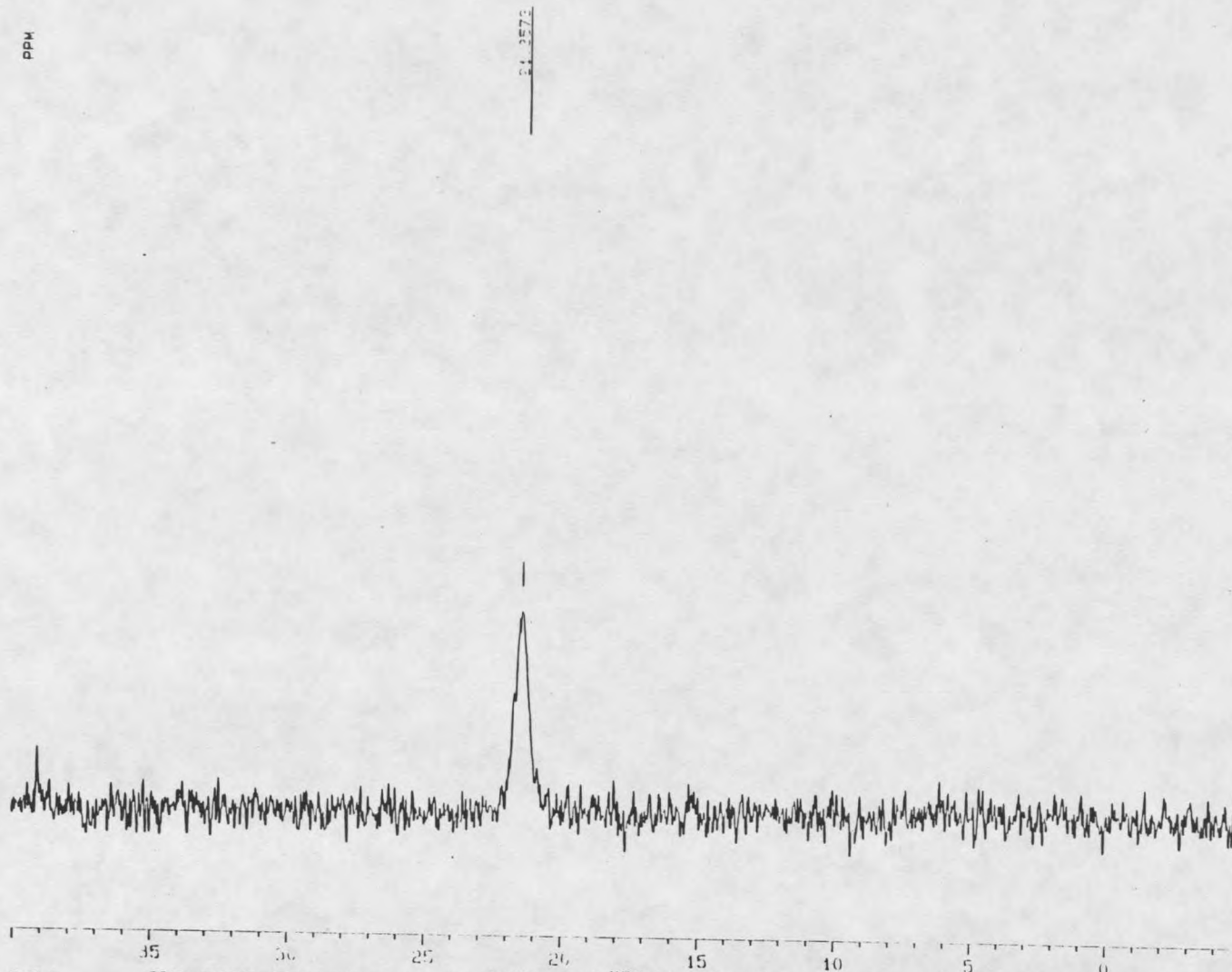


Figure 104. ^{31}P NMR Spectrum of (2R,2R)-2,5-Bis[boronato-Bis(4-methoxy-2-methylphenyl)phosphino]hexane (26c)

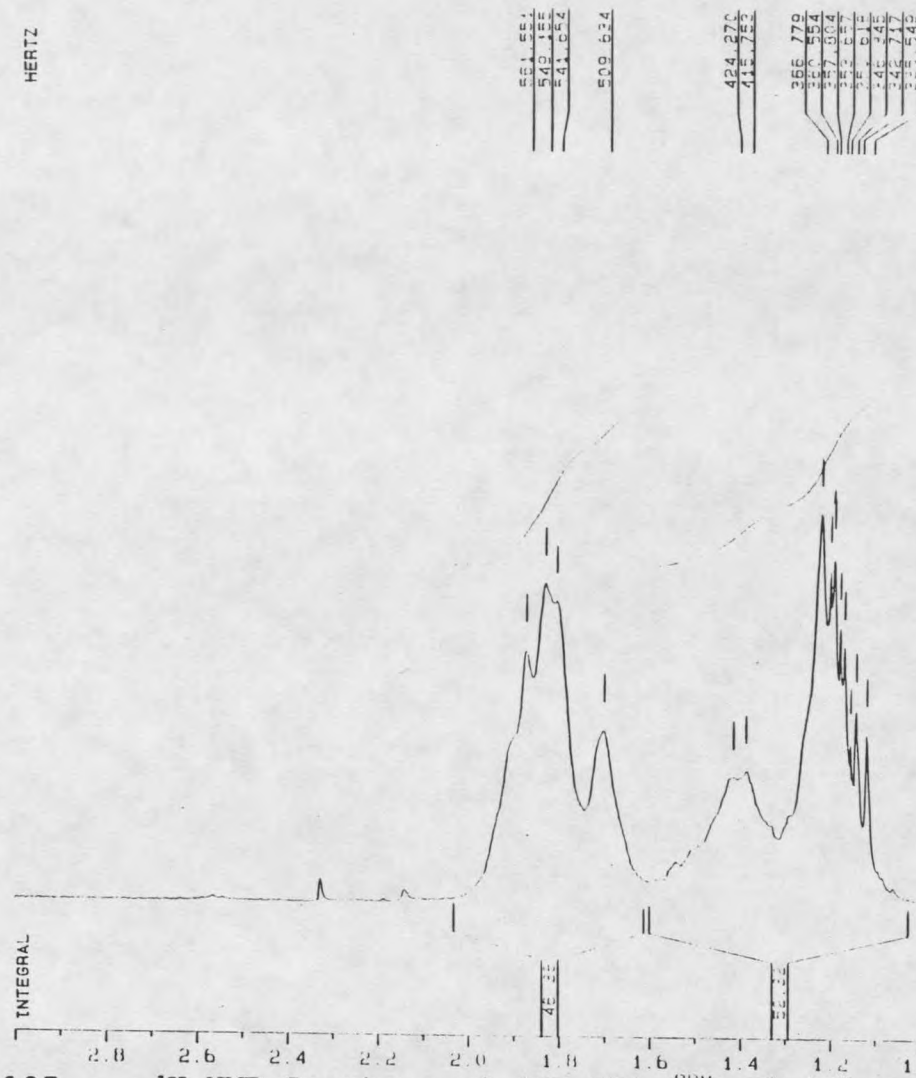


Figure 105. ^1H NMR Spectrum of (2R,5R)-2,5-Bis(dicyclohexylphosphino)hexane (21a)

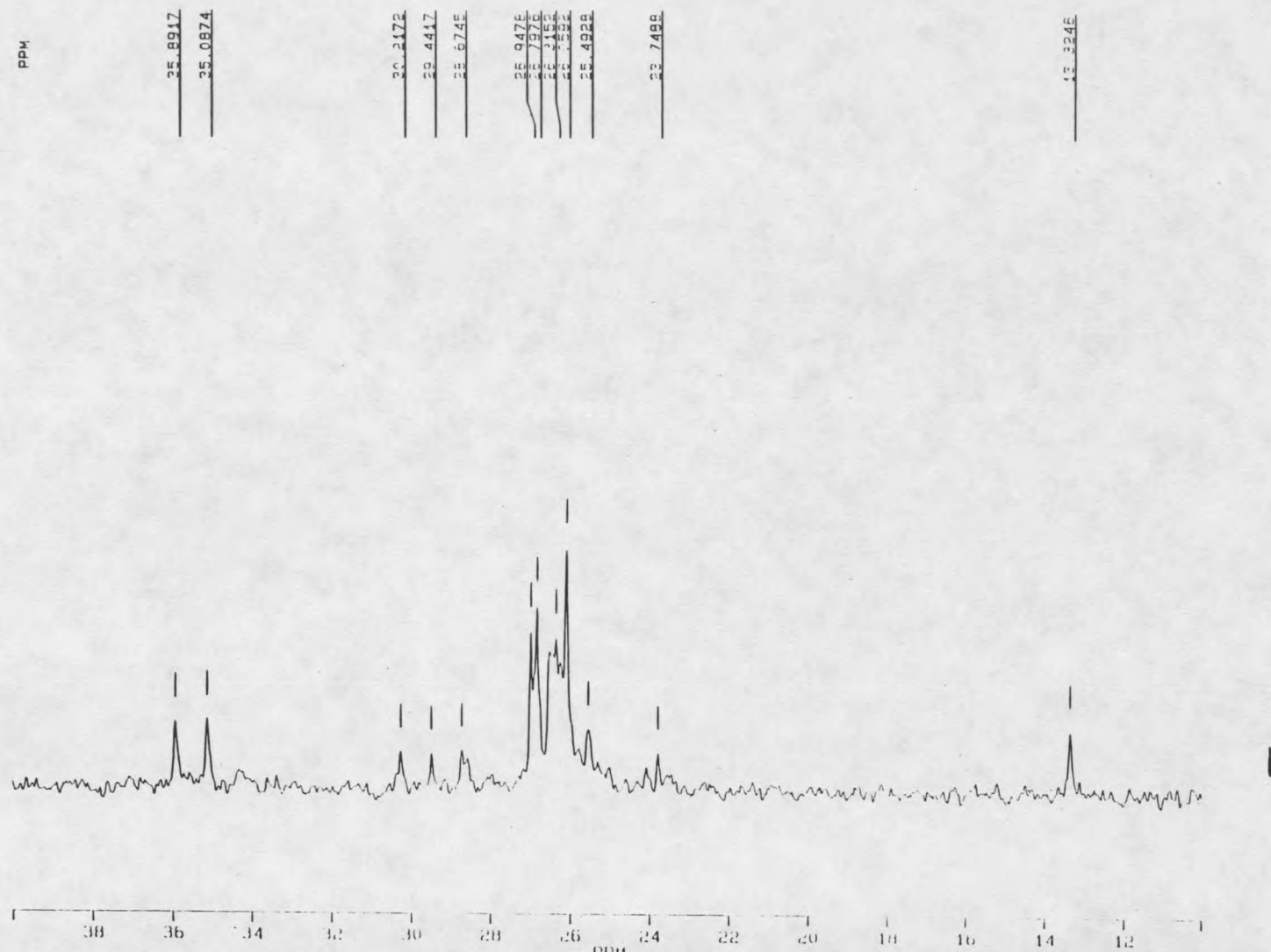


Figure 106. ^{13}C NMR Spectrum of (2R,5R)-2,5-Bis(dicyclohexylphosphino)hexane (21a)

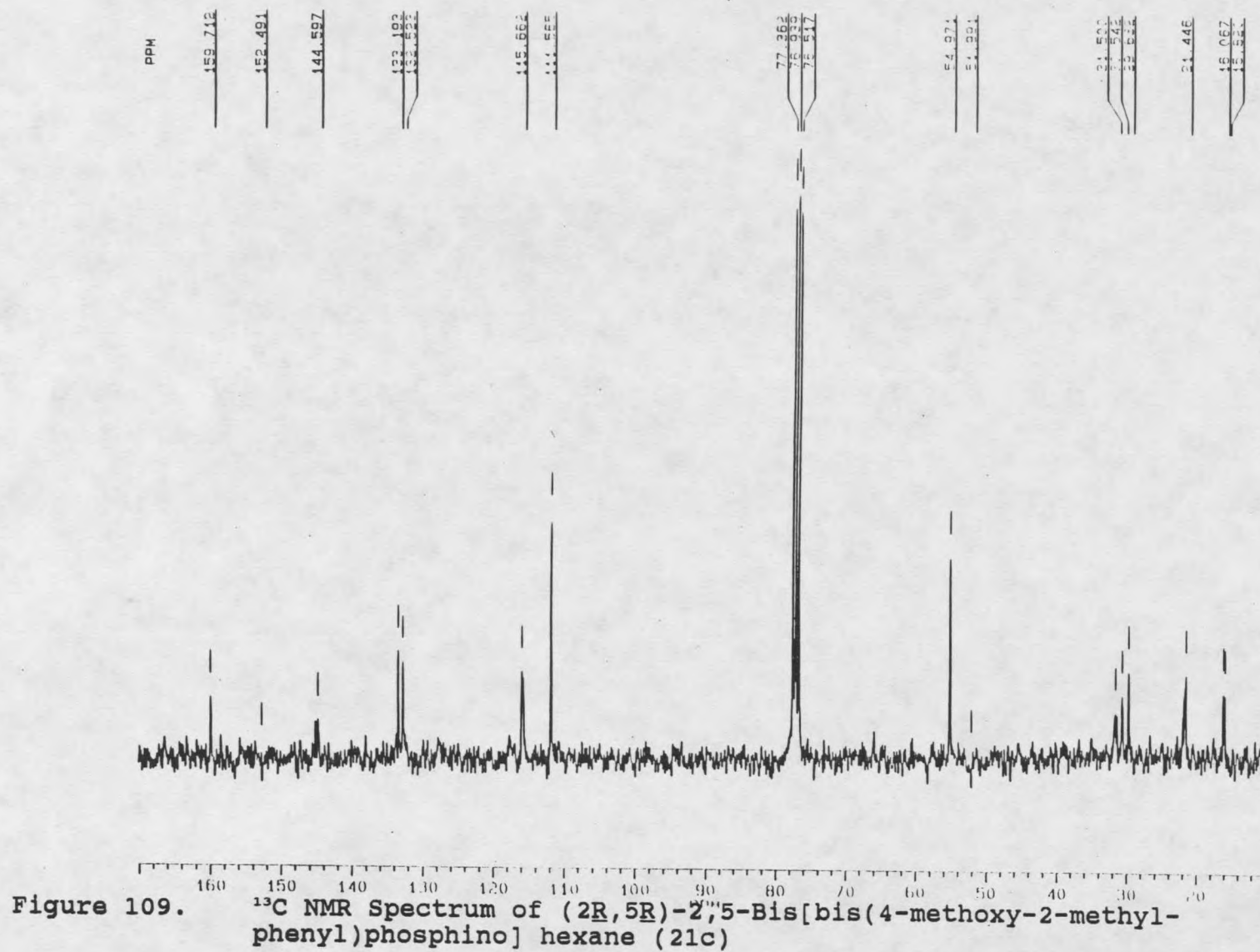
ppm

11.0667

234



Figure 107. ^{31}P NMR Spectrum of (2R,5R)-2,5-Bis(dicyclohexylphosphino)hexane (21a)



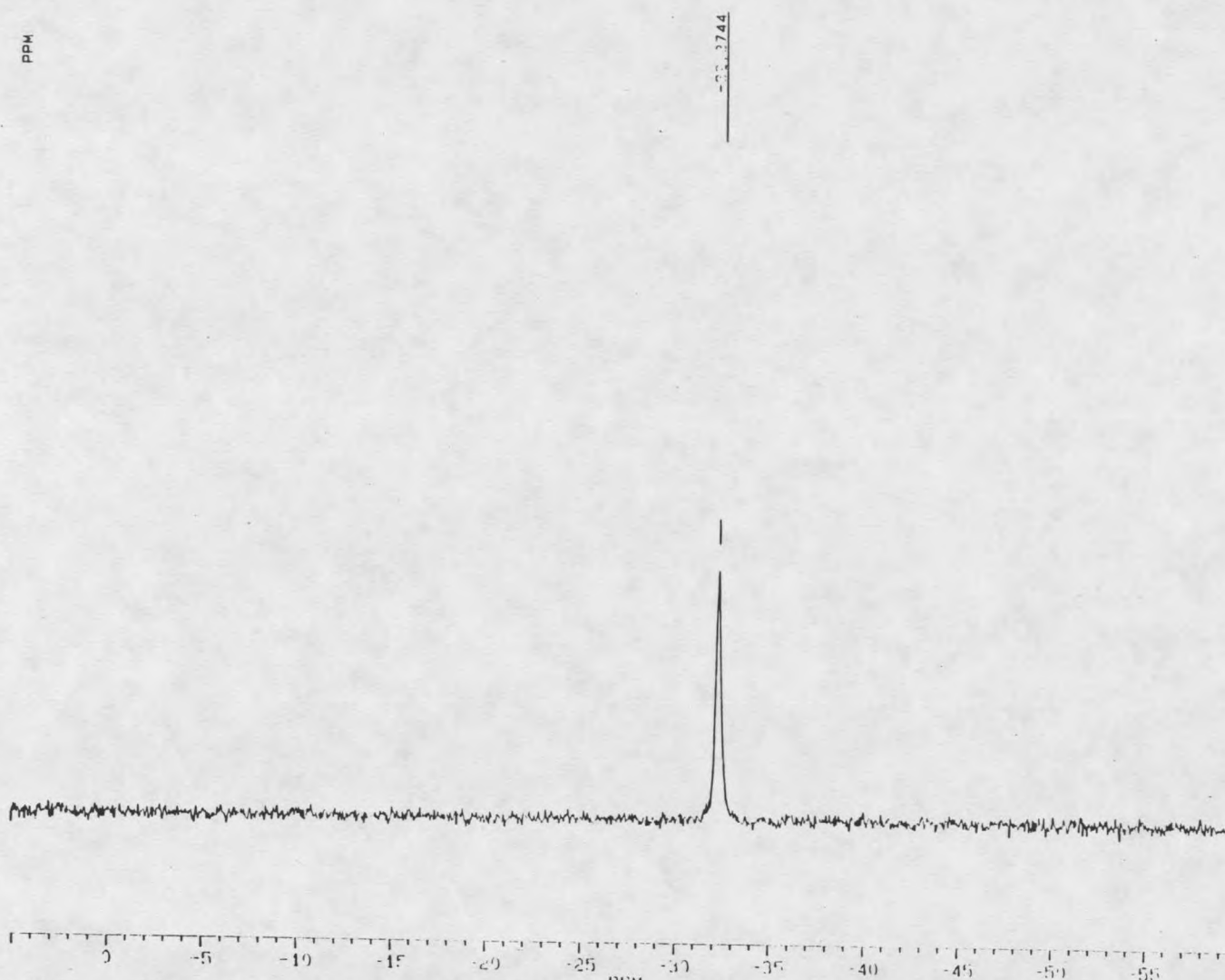


Figure 110. ^{31}P NMR Spectrum of (2R,5R)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino] hexane (21c)

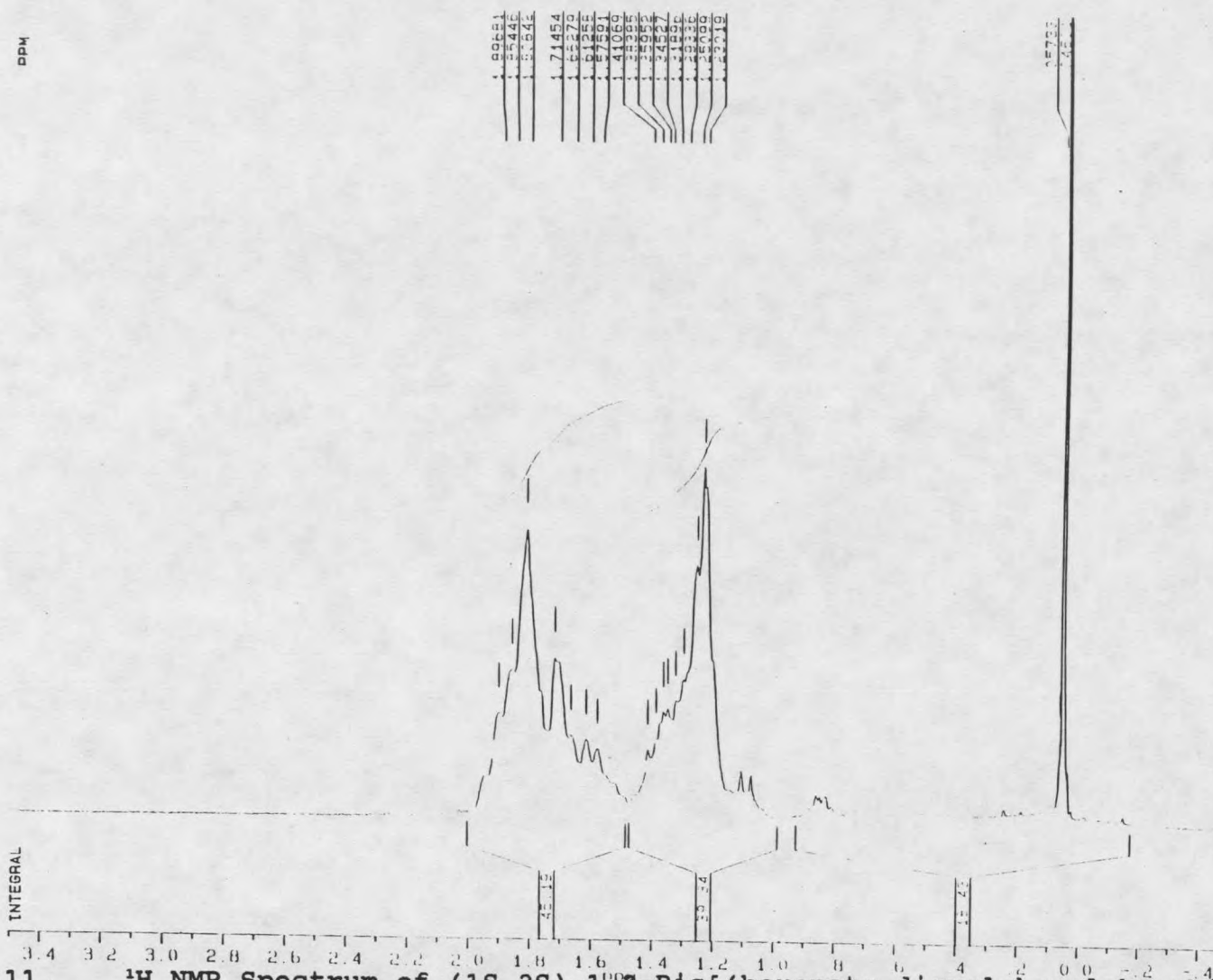


Figure 111. ^1H NMR Spectrum of (1S,2S)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl]cyclohexane (25a)

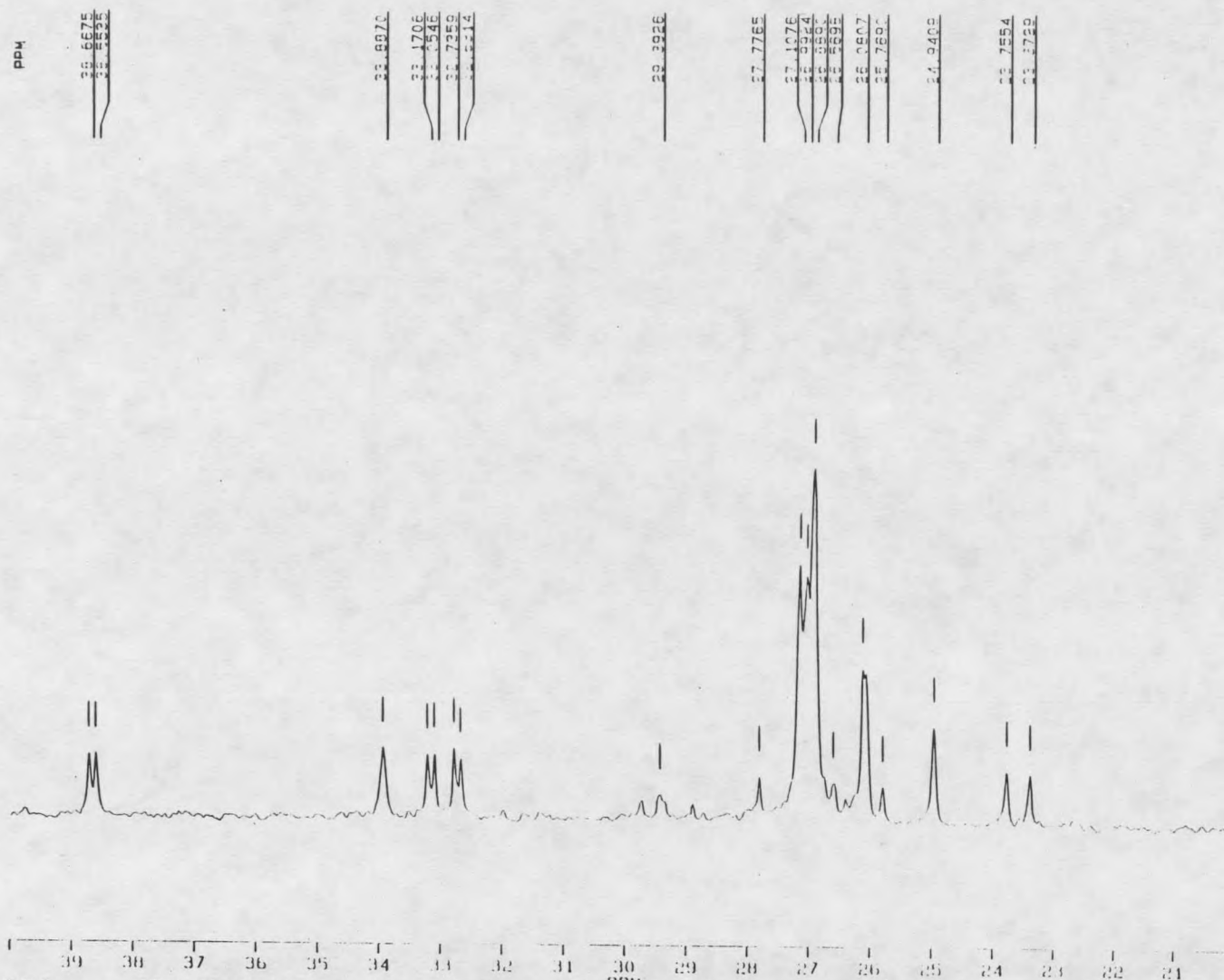


Figure 112. ^{13}C NMR Spectrum of (1*S*,2*S*)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl] cyclohexane (25a)

ppm

2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
14.0
14.5
15.0
15.5
16.0
16.5
17.0
17.5
18.0
18.5
19.0
19.5
20.0
20.5
21.0
21.5
22.0
22.5
23.0
23.5
24.0
24.5
25.0
25.5
26.0
26.5
27.0
27.5
28.0
28.5
29.0
29.5
30.0
30.5
31.0
31.5
32.0
32.5
33.0
33.5
34.0
34.5
35.0
35.5
36.0
36.5
37.0
37.5
38.0
38.5
39.0
39.5
40.0
40.5
41.0
41.5
42.0
42.5
43.0
43.5
44.0
44.5
45.0
45.5
46.0
46.5
47.0
47.5
48.0
48.5
49.0
49.5
50.0
50.5
51.0
51.5
52.0
52.5
53.0
53.5
54.0
54.5
55.0
55.5
56.0
56.5
57.0
57.5
58.0
58.5
59.0
59.5
60.0
60.5
61.0
61.5
62.0
62.5
63.0
63.5
64.0
64.5
65.0
65.5
66.0
66.5
67.0
67.5
68.0
68.5
69.0
69.5
70.0
70.5
71.0
71.5
72.0
72.5
73.0
73.5
74.0
74.5
75.0
75.5
76.0
76.5
77.0
77.5
78.0
78.5
79.0
79.5
80.0
80.5
81.0
81.5
82.0
82.5
83.0
83.5
84.0
84.5
85.0
85.5
86.0
86.5
87.0
87.5
88.0
88.5
89.0
89.5
90.0
90.5
91.0
91.5
92.0
92.5
93.0
93.5
94.0
94.5
95.0
95.5
96.0
96.5
97.0
97.5
98.0
98.5
99.0
99.5
100.0

240

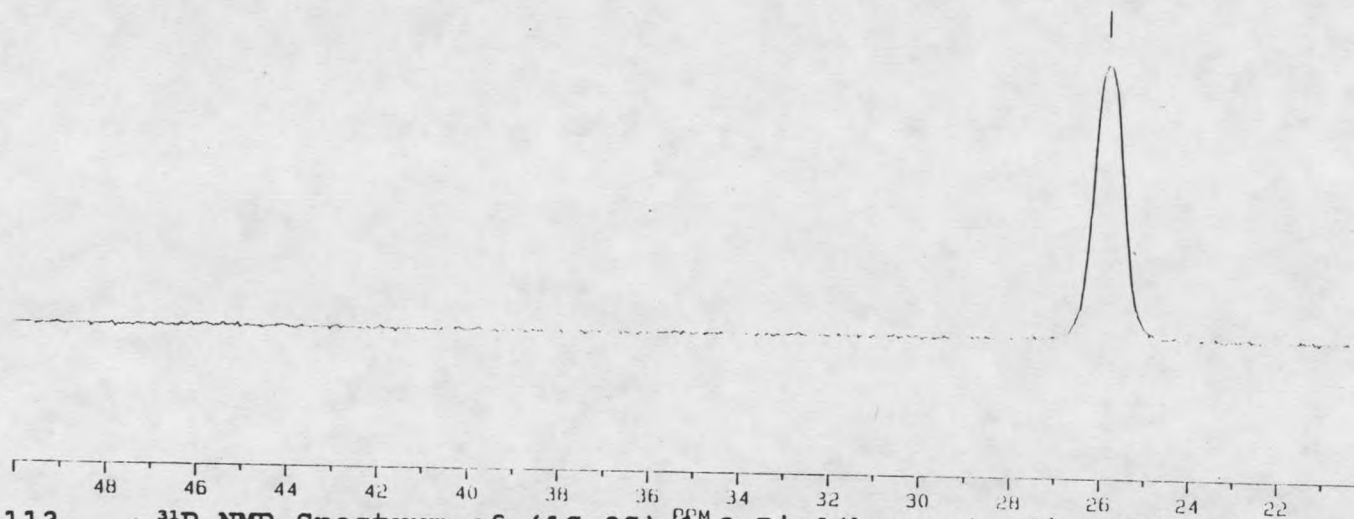


Figure 113. ^{31}P NMR Spectrum of (1S,2S)-1,2-Bis[(boronato-dicyclohexylphosphino)methyl] cyclohexane (25a)

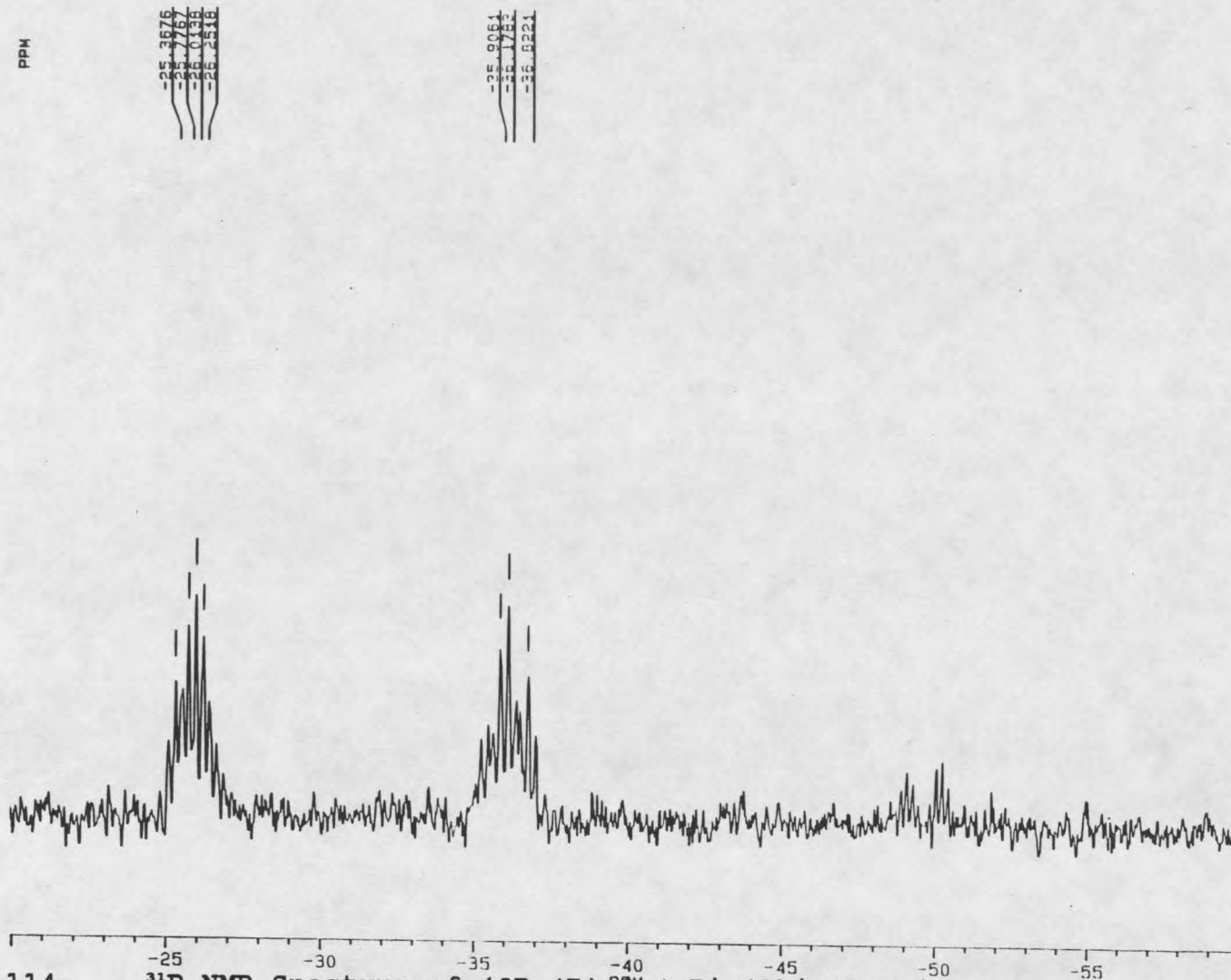


Figure 114.

³¹P NMR Spectrum of (2R,4R)-2,4-bis([bis(2-trifluoro-
methylphenyl)phosphino]pentane (16a)

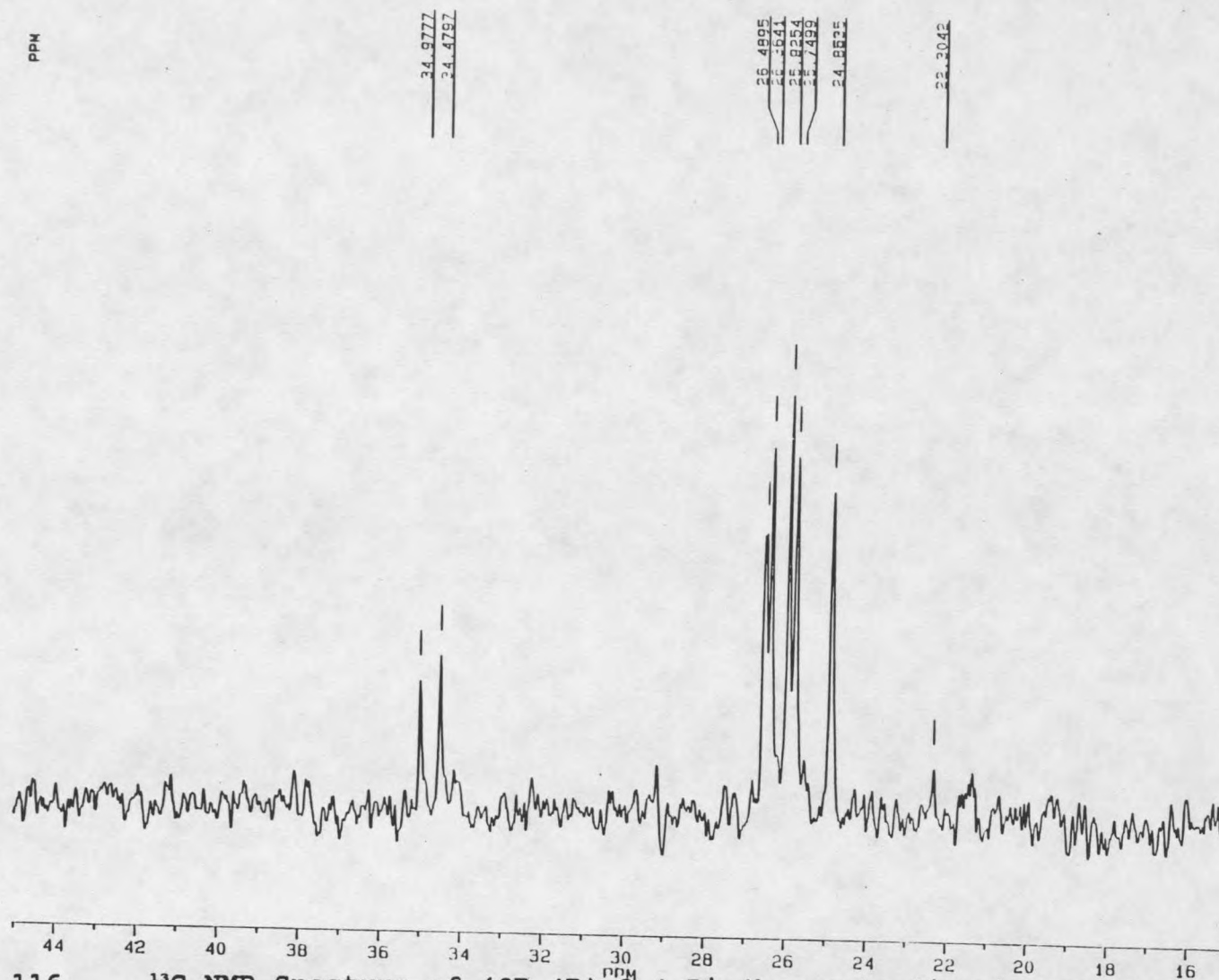


Figure 116. ^{13}C NMR Spectrum of (2R,4R)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24)

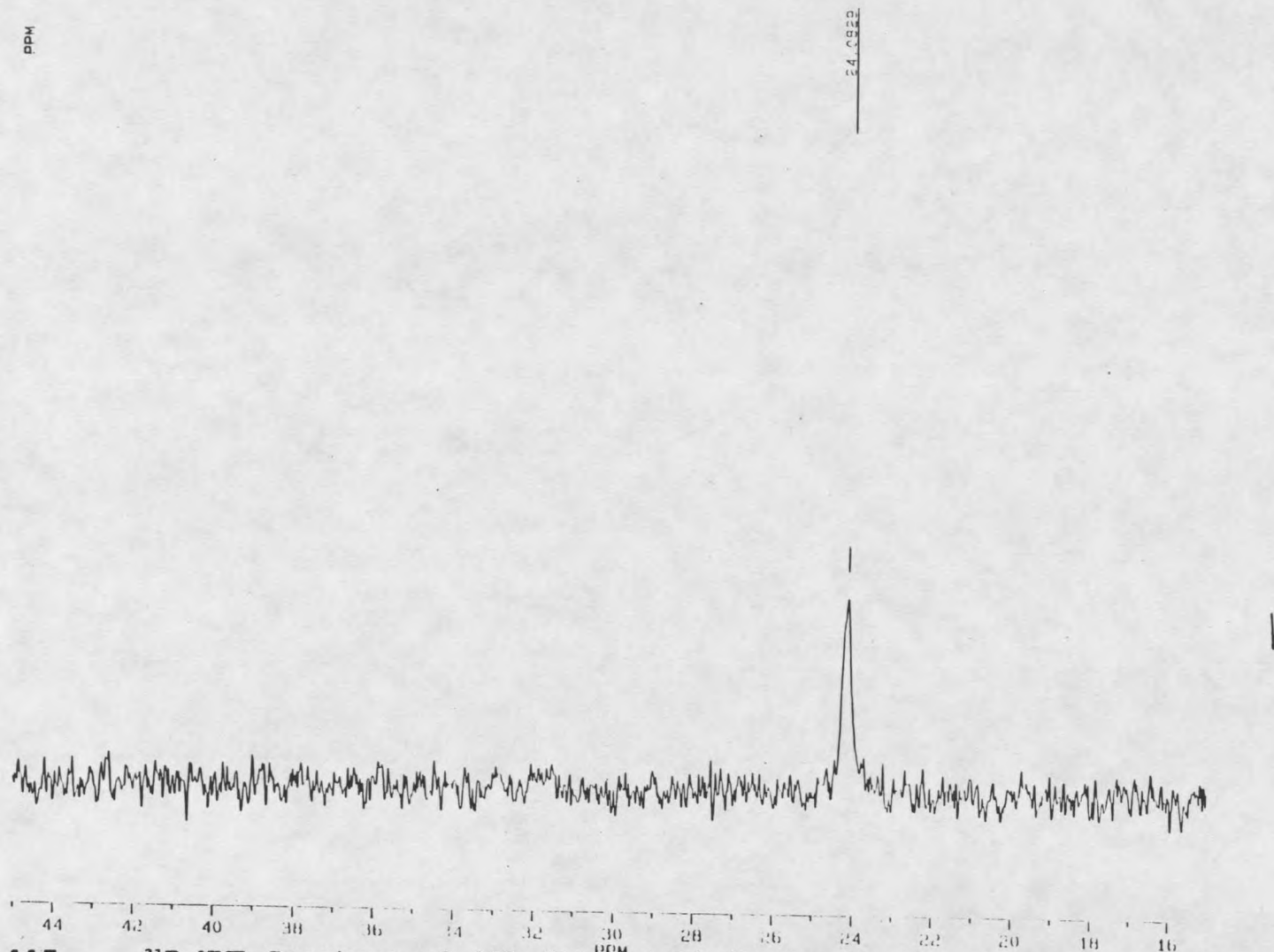


Figure 117. ^{31}P NMR Spectrum of (2R,4R)-2,4-Bis(boronato-dicyclohexylphosphino)pentane (24)

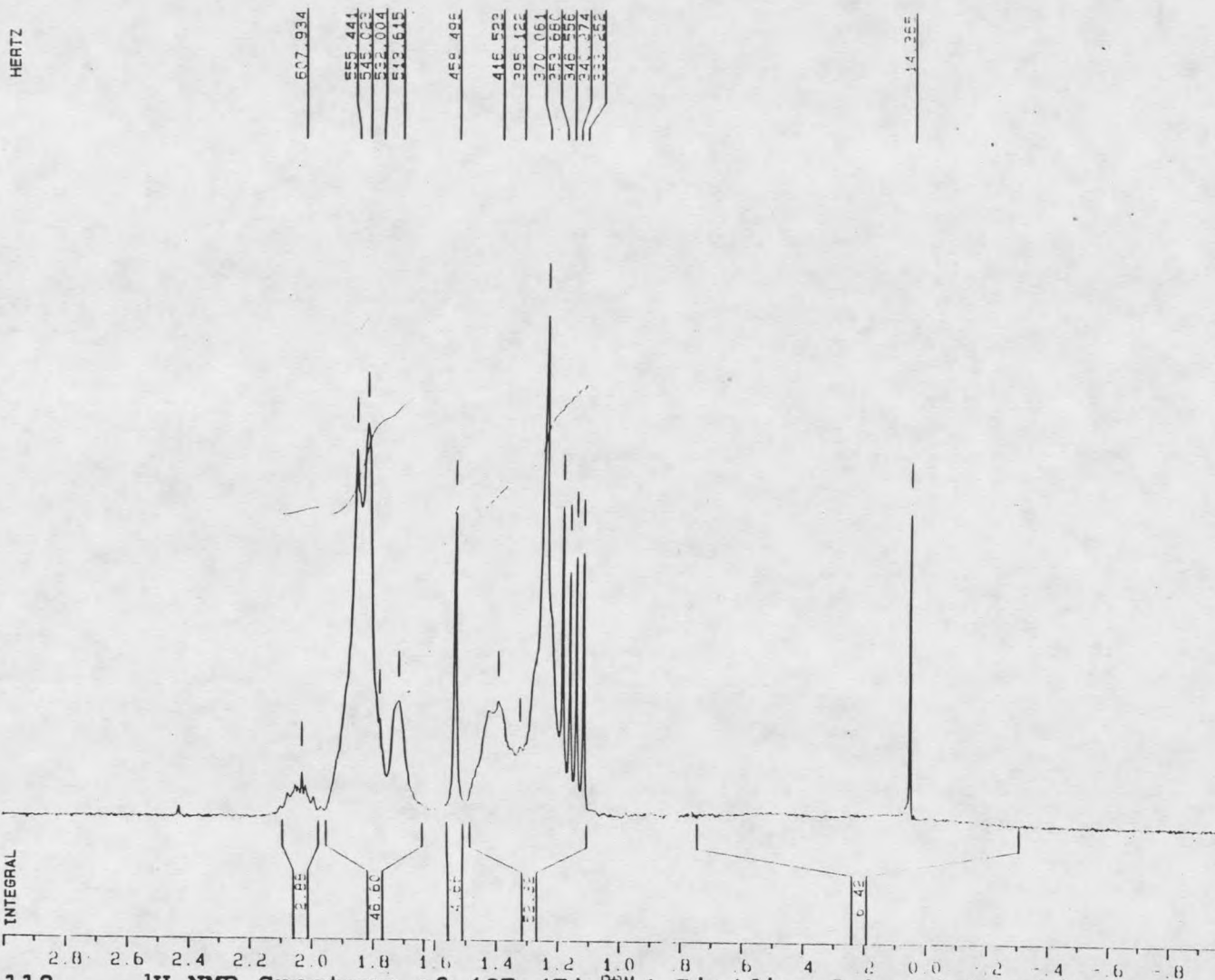


Figure 118. ¹H NMR Spectrum of (2R,4R)-2,4-Bis(dicyclohexylphosphino)pentane (19)

ppm

100
80
60
40
20
0

246

Figure 119. ^{31}P NMR Spectrum of (2R,4R)-2,4-Bis(dicyclohexylphosphino)pentane (19)

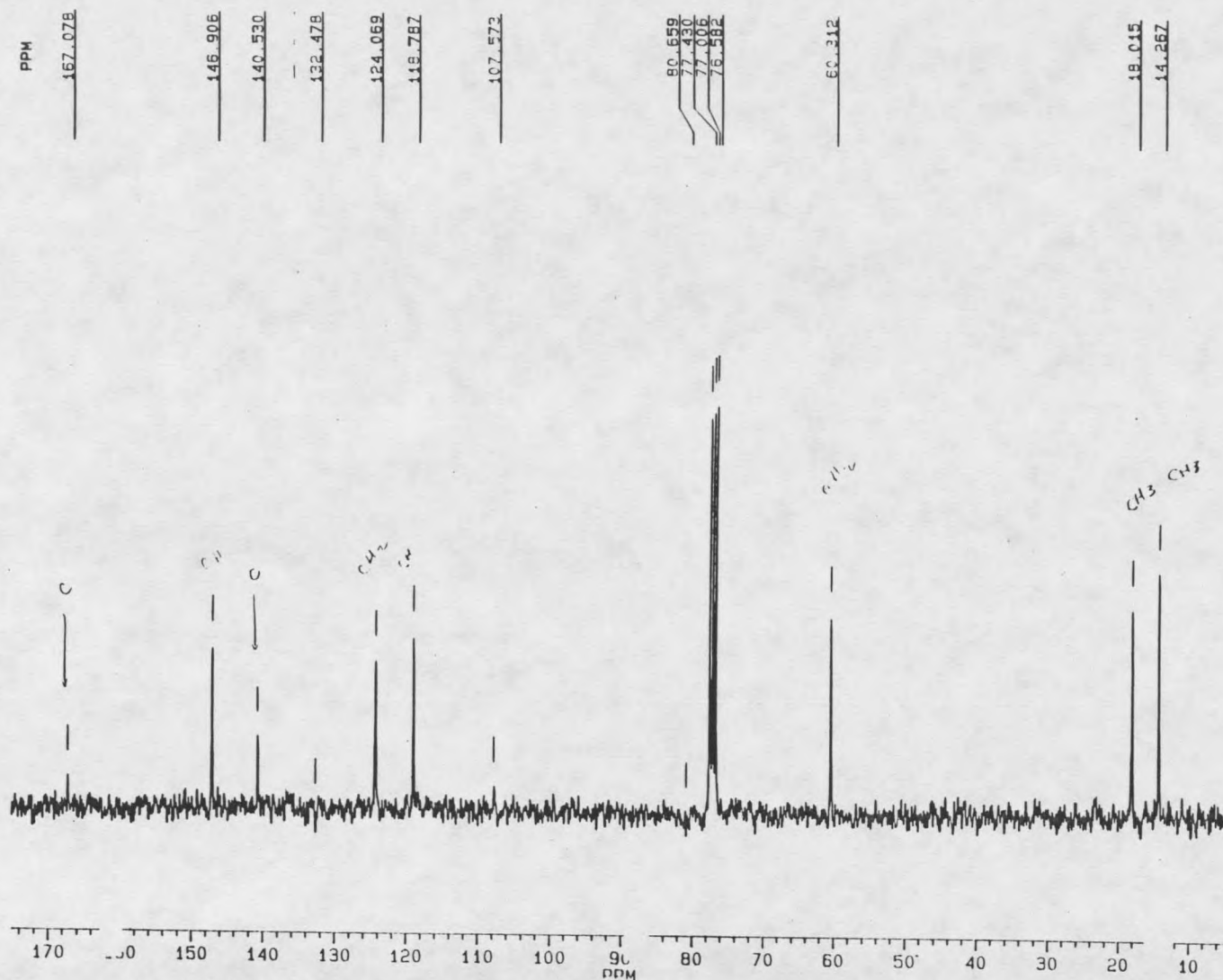


Figure 121. ¹³C NMR Spectrum of Ethyl-4-methyl-2(E),4-pentadienoate (103)

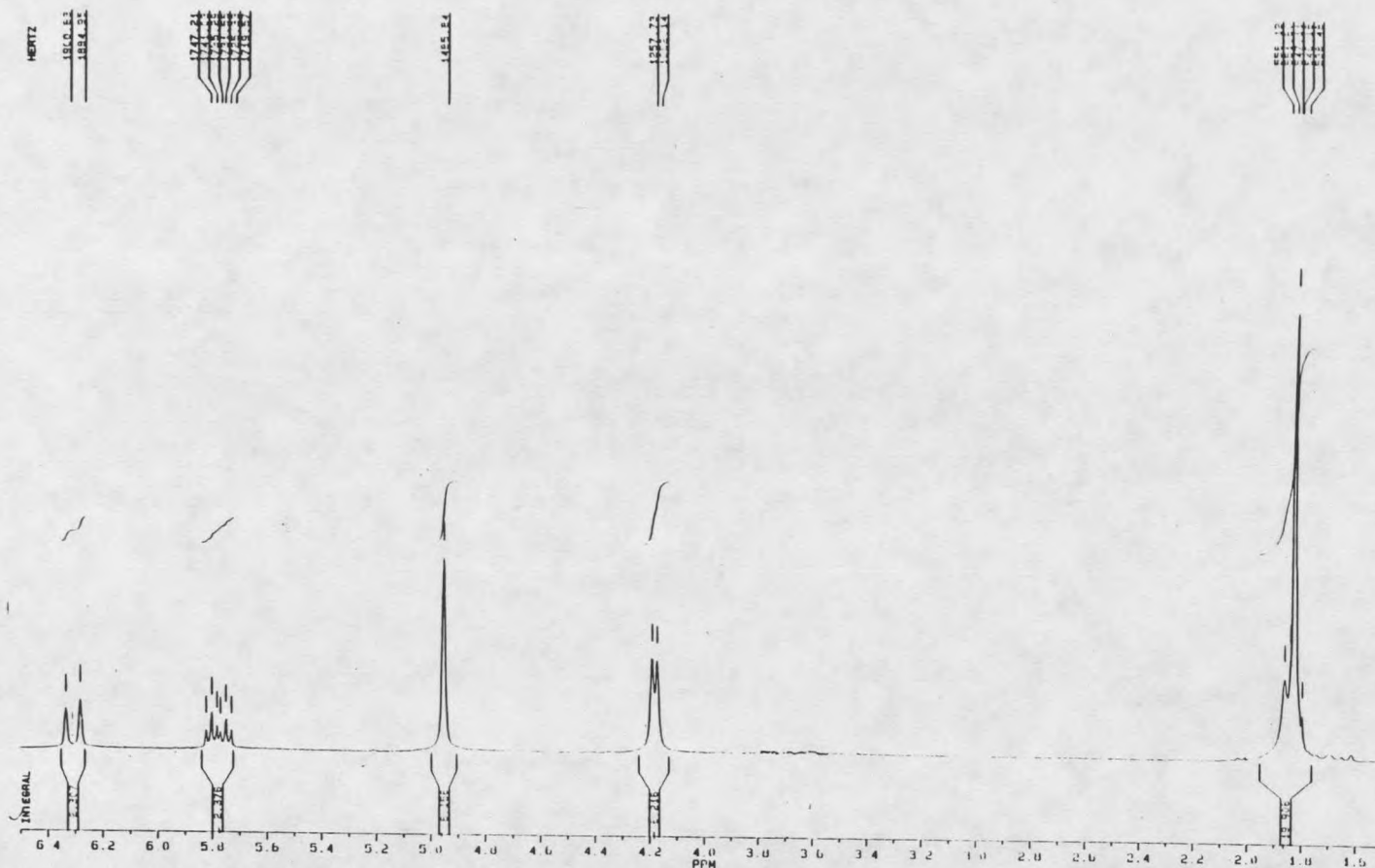


Figure 122. ^1H NMR Spectrum of 4-Methyl-2(E),4-pentadien-1-ol (104)

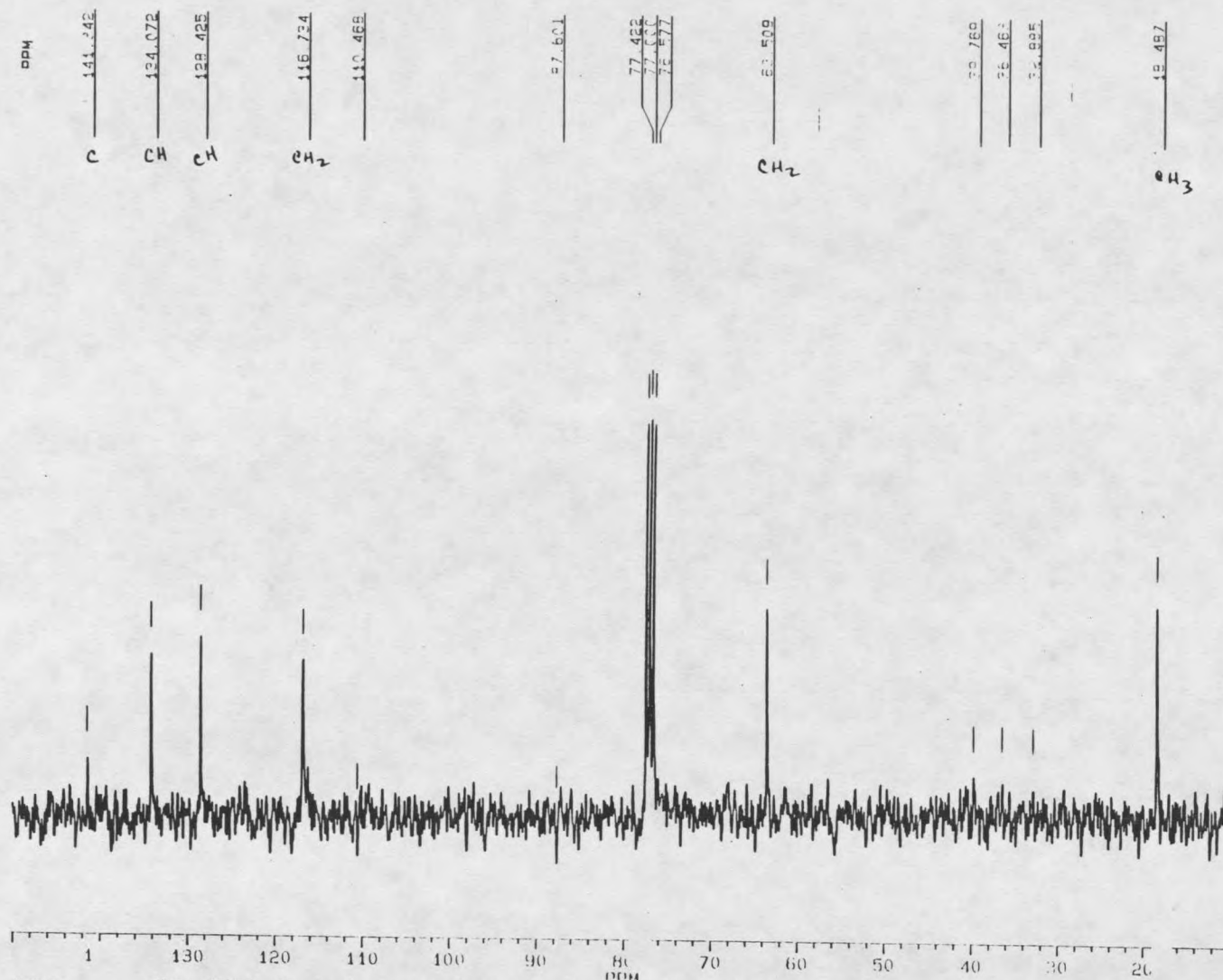


Figure 123. ¹³C NMR Spectrum of 4-Methyl-2(E),4-pentadien-1-ol (104)

4

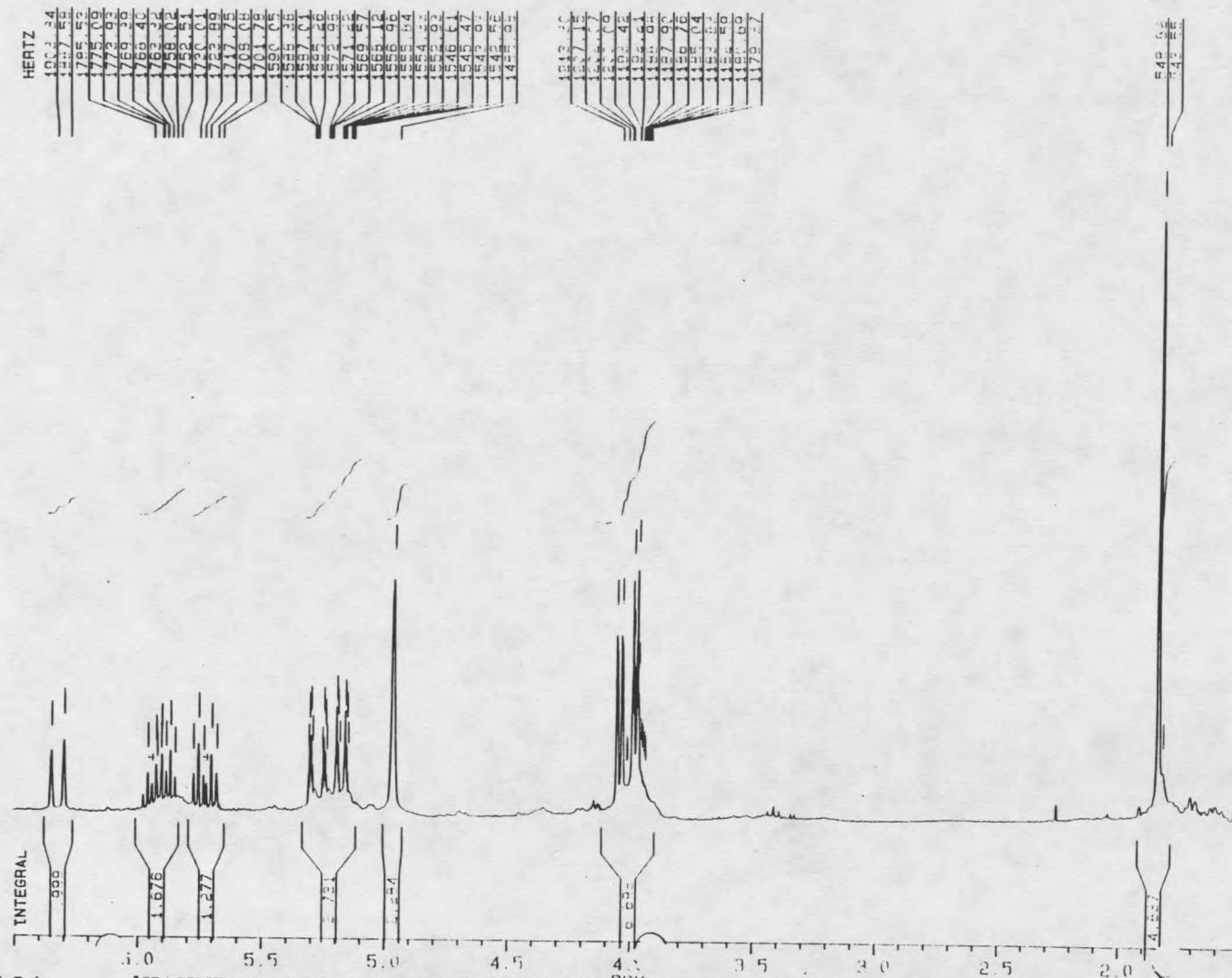


Figure 124. ^1H NMR Spectrum of 8-Methyl-4-oxo-1,6(E),8-nonatriene (7a)

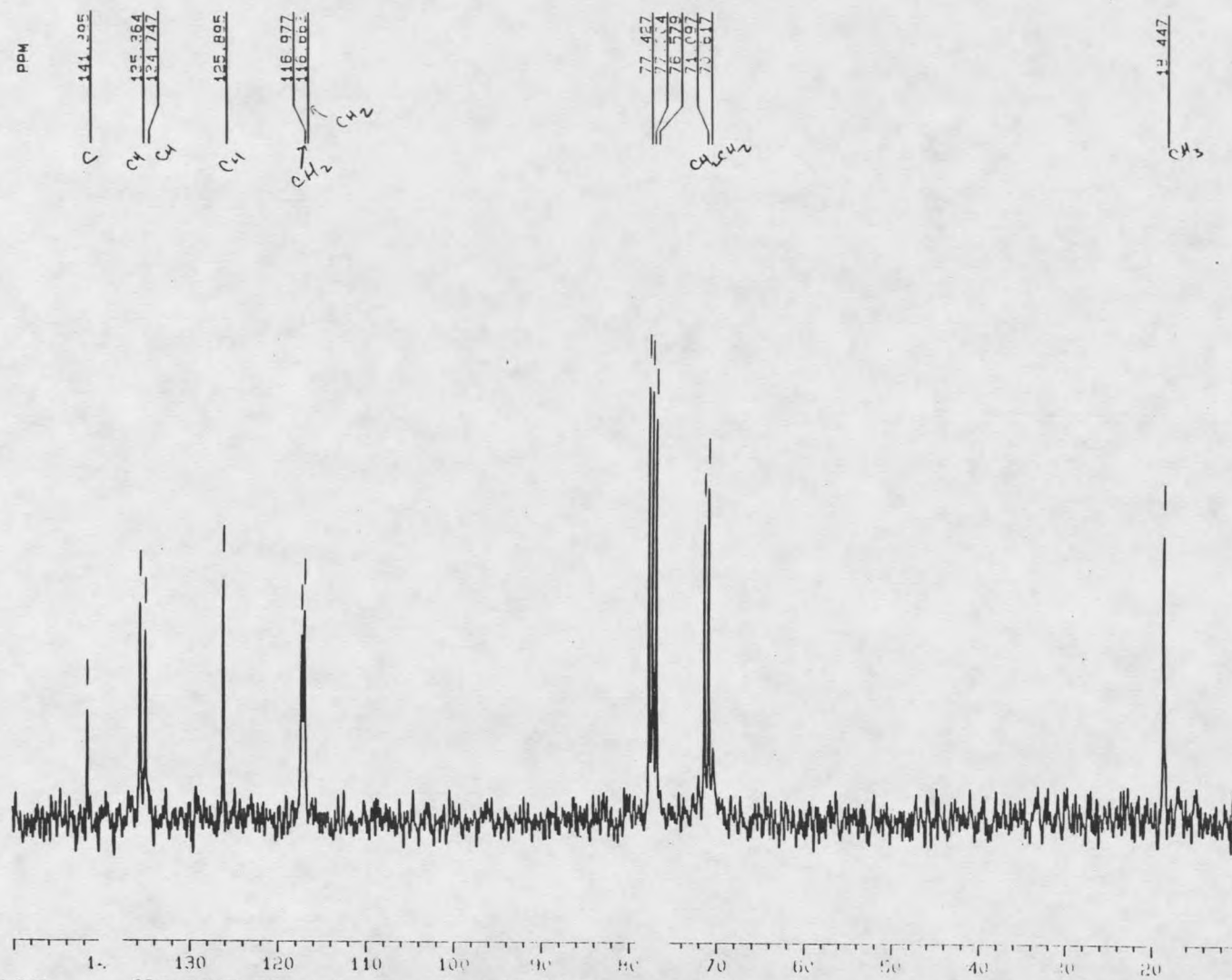
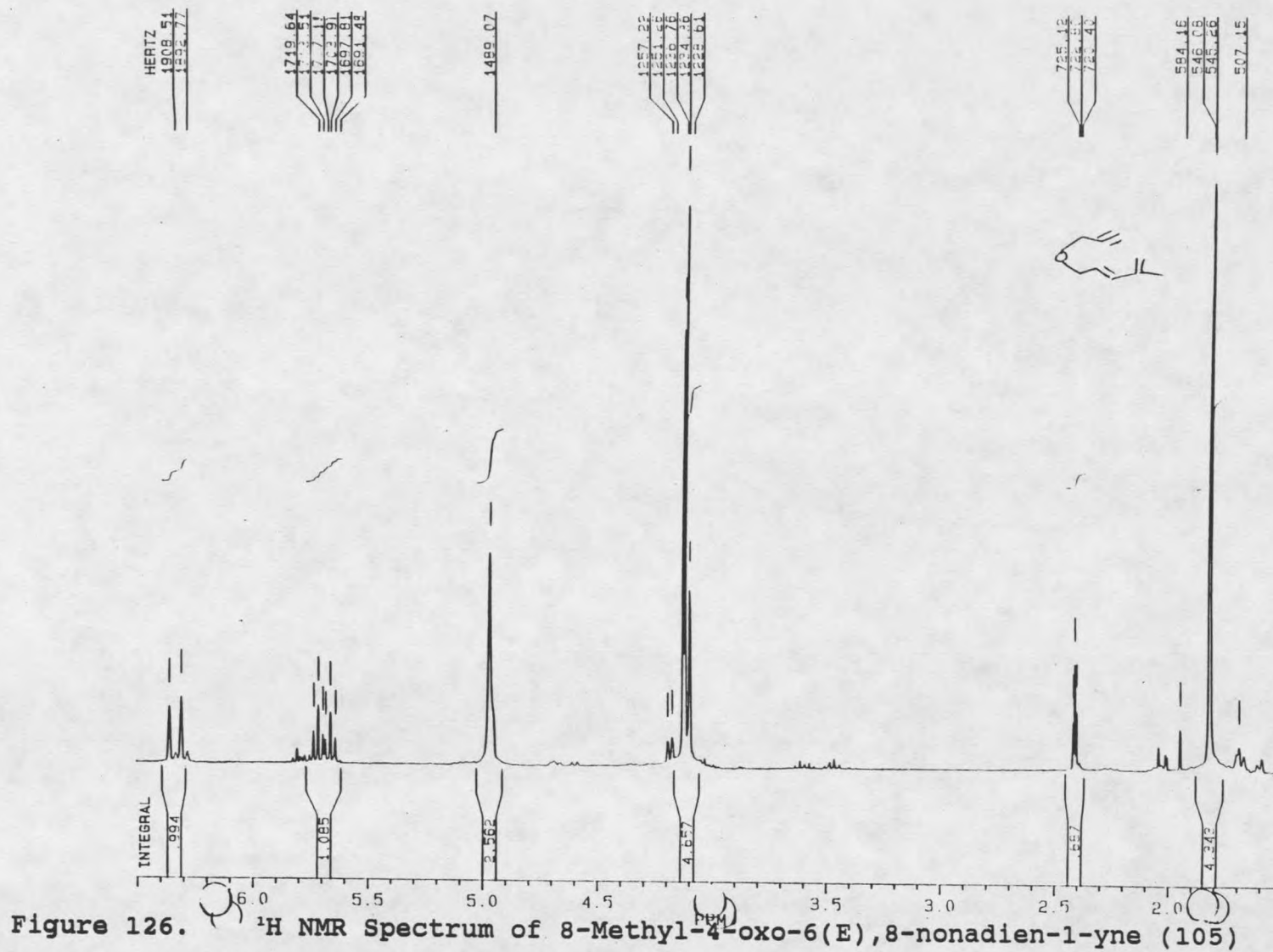


Figure 125. ^{13}C NMR Spectrum of 8-Methyl-4-oxo-1,6(E),8-nonatriene (7a)



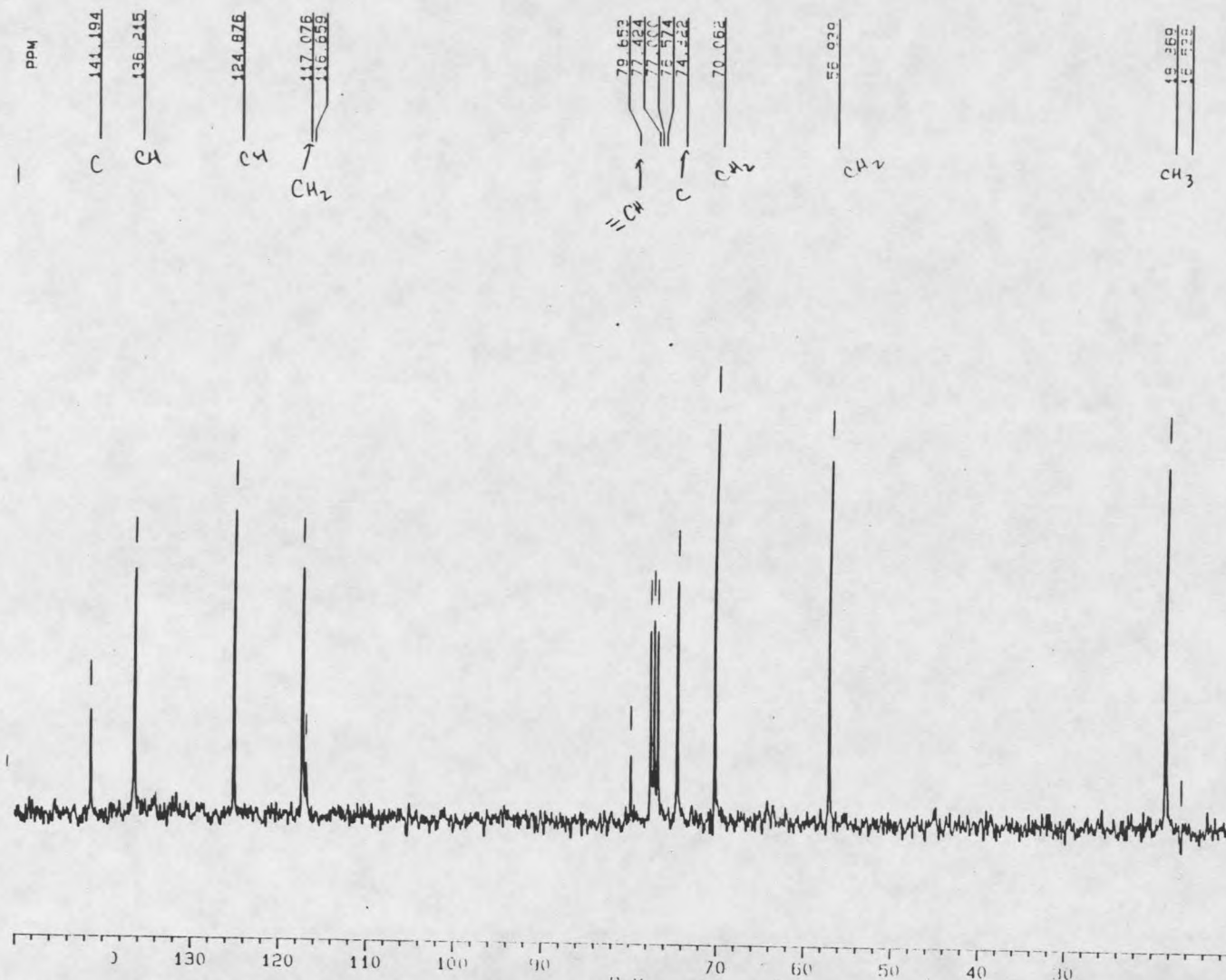
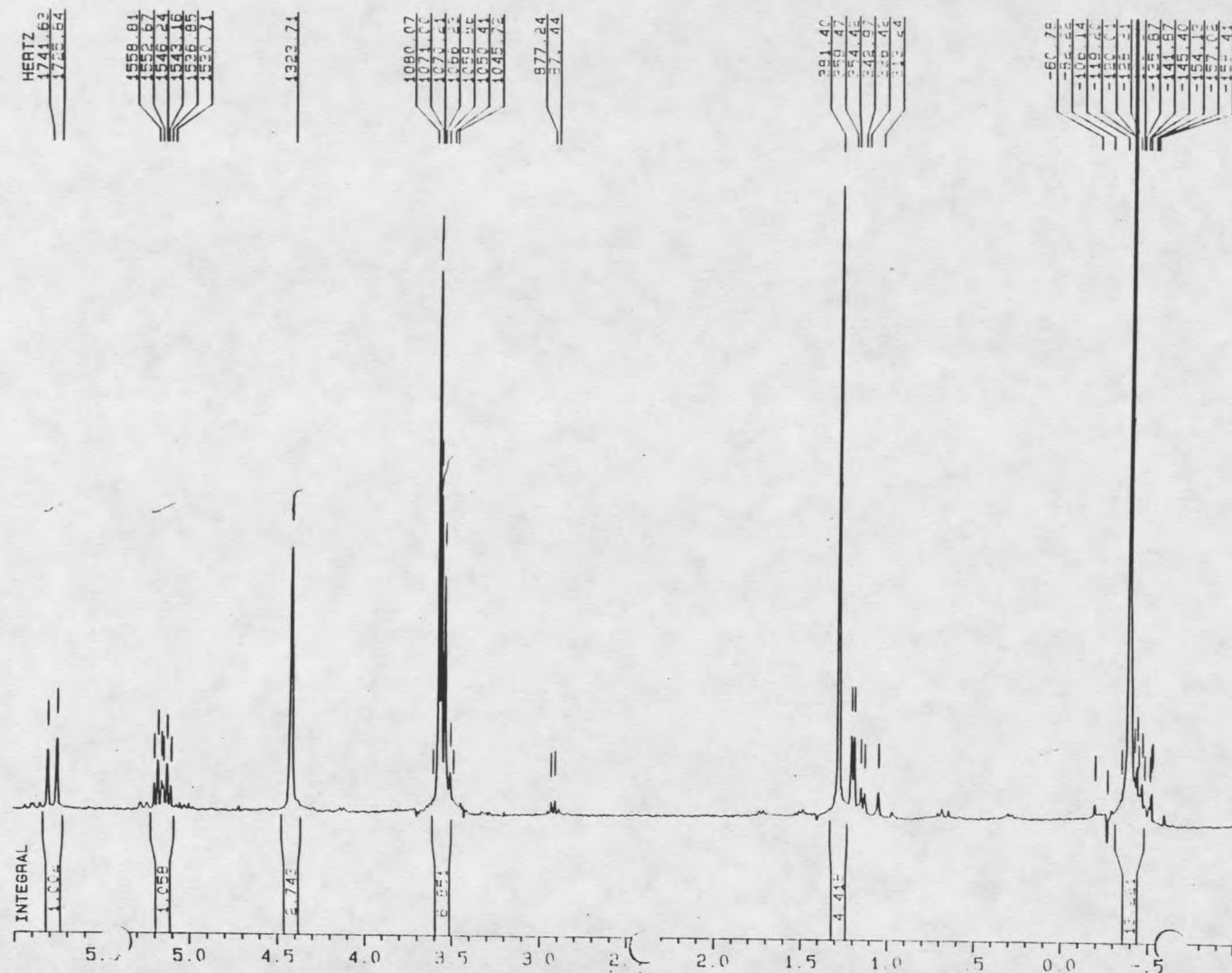


Figure 127. ^{13}C NMR Spectrum of 8-Methyl-4-oxo-6(E),8-nonadien-1-yne (105)



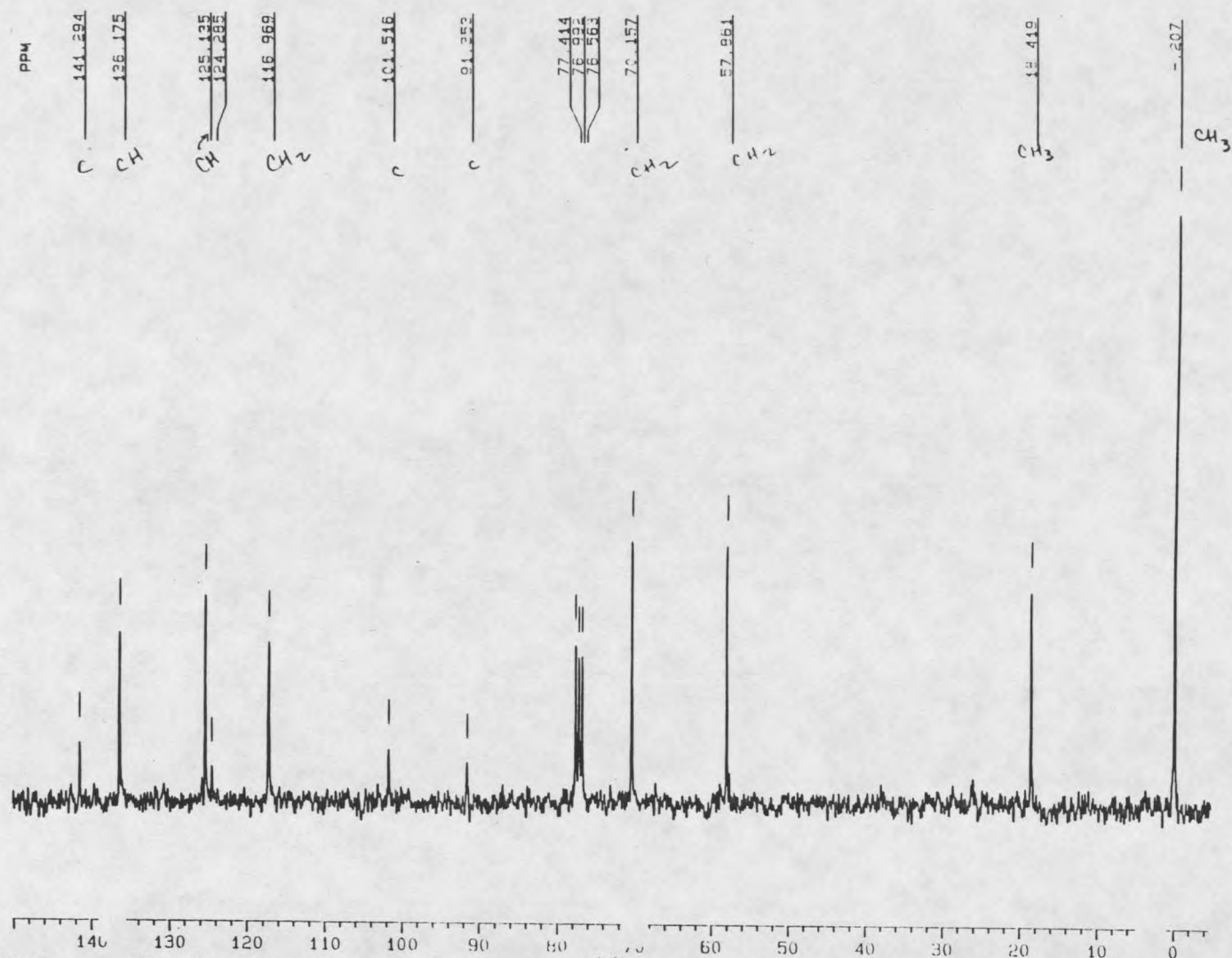


Figure 129.

¹³C NMR Spectrum of 8-Methyl-4-oxo-1-(trimethylsilyl)-6(E),8-nonadien-1-yne (10)

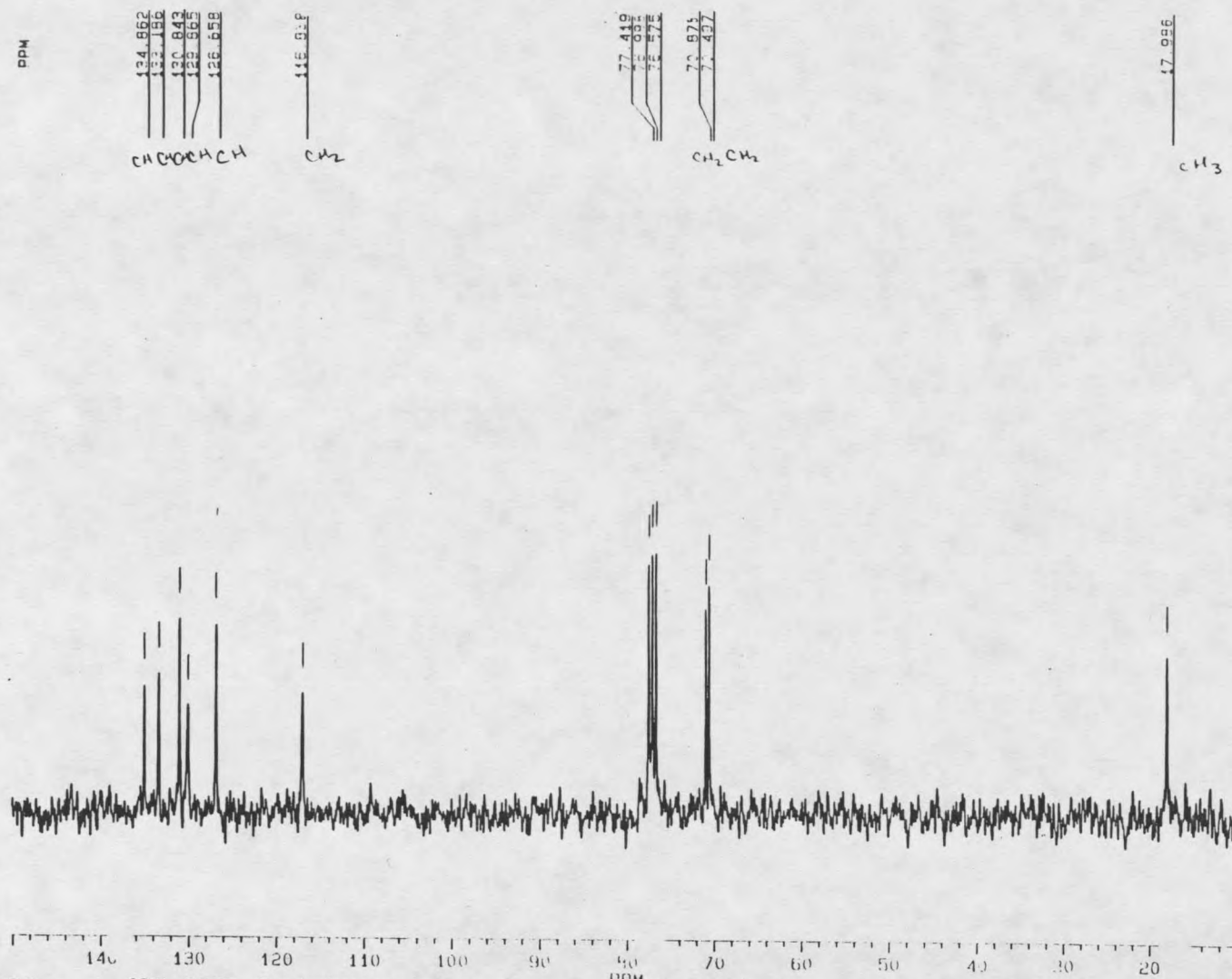


Figure 131. ¹³C NMR Spectrum of 4-Oxo-1,6(E),8(E)-decatriene (7c)

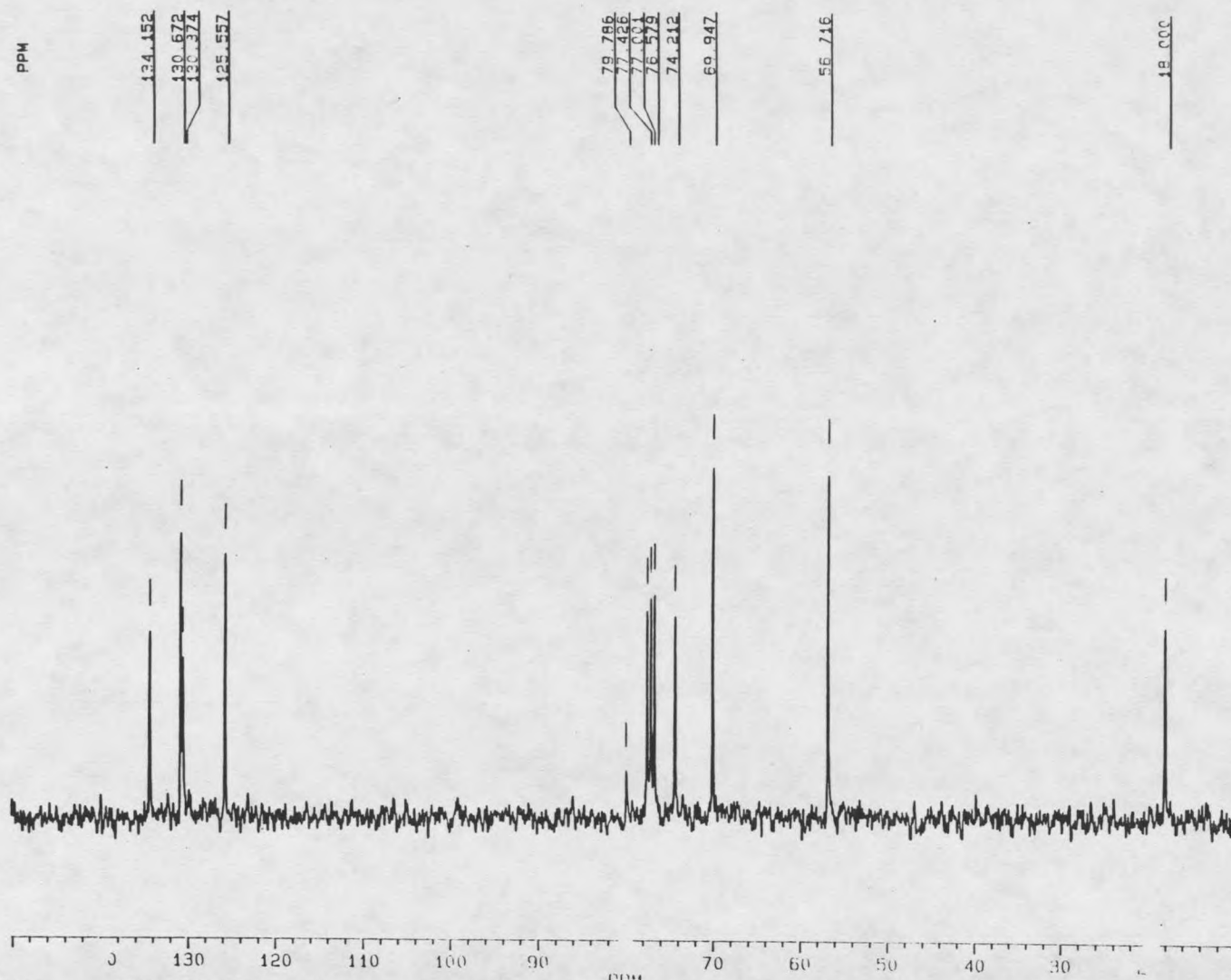


Figure 133. ¹³C NMR Spectrum of 4-Oxo-6(E),8(E)-decadien-1-yne (1)

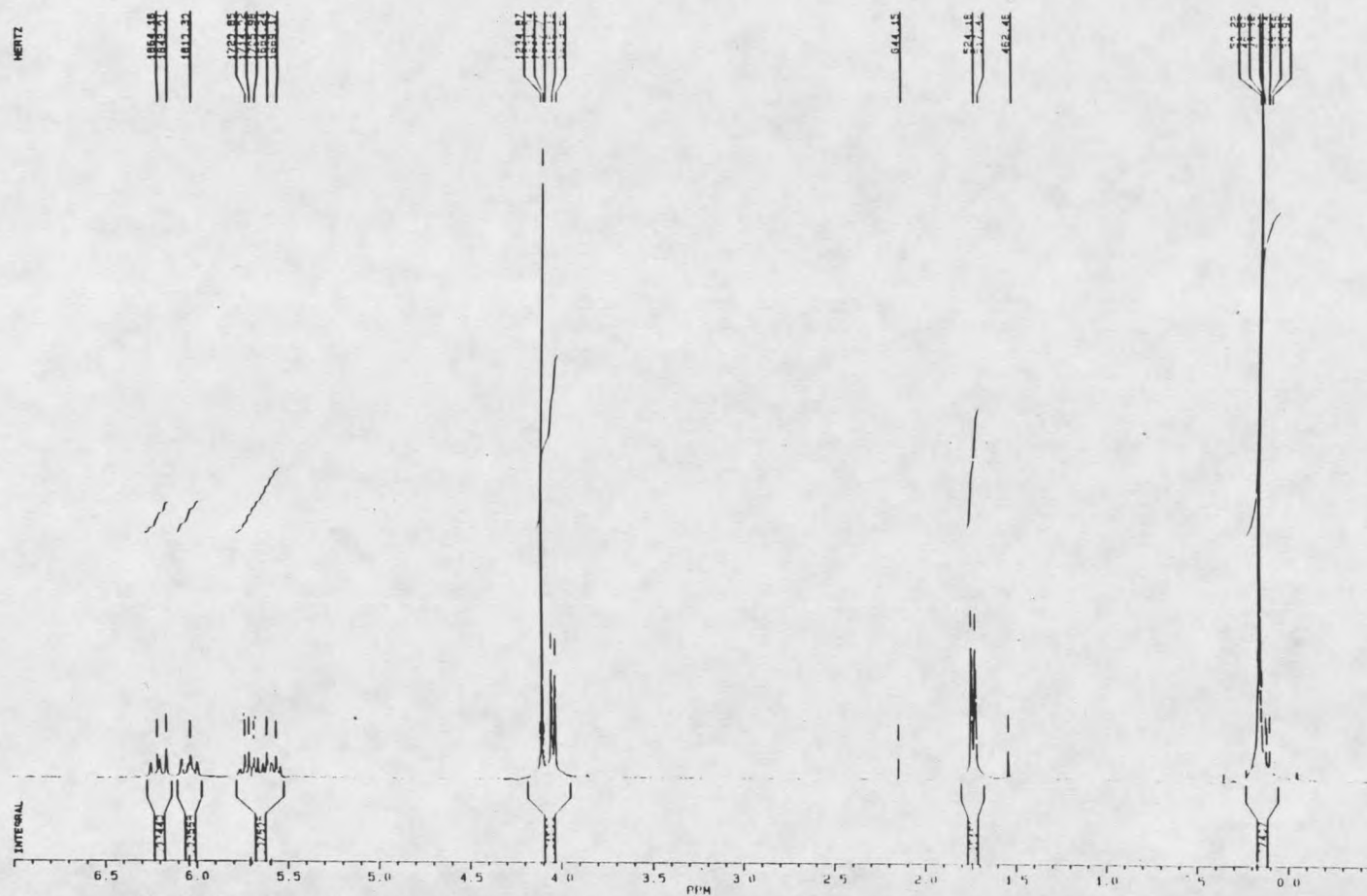


Figure 134. ^1H NMR Spectrum of 4-Oxo-1-(trimethylsilyl)-6(E),8(E)-decadien-1-yne (106)

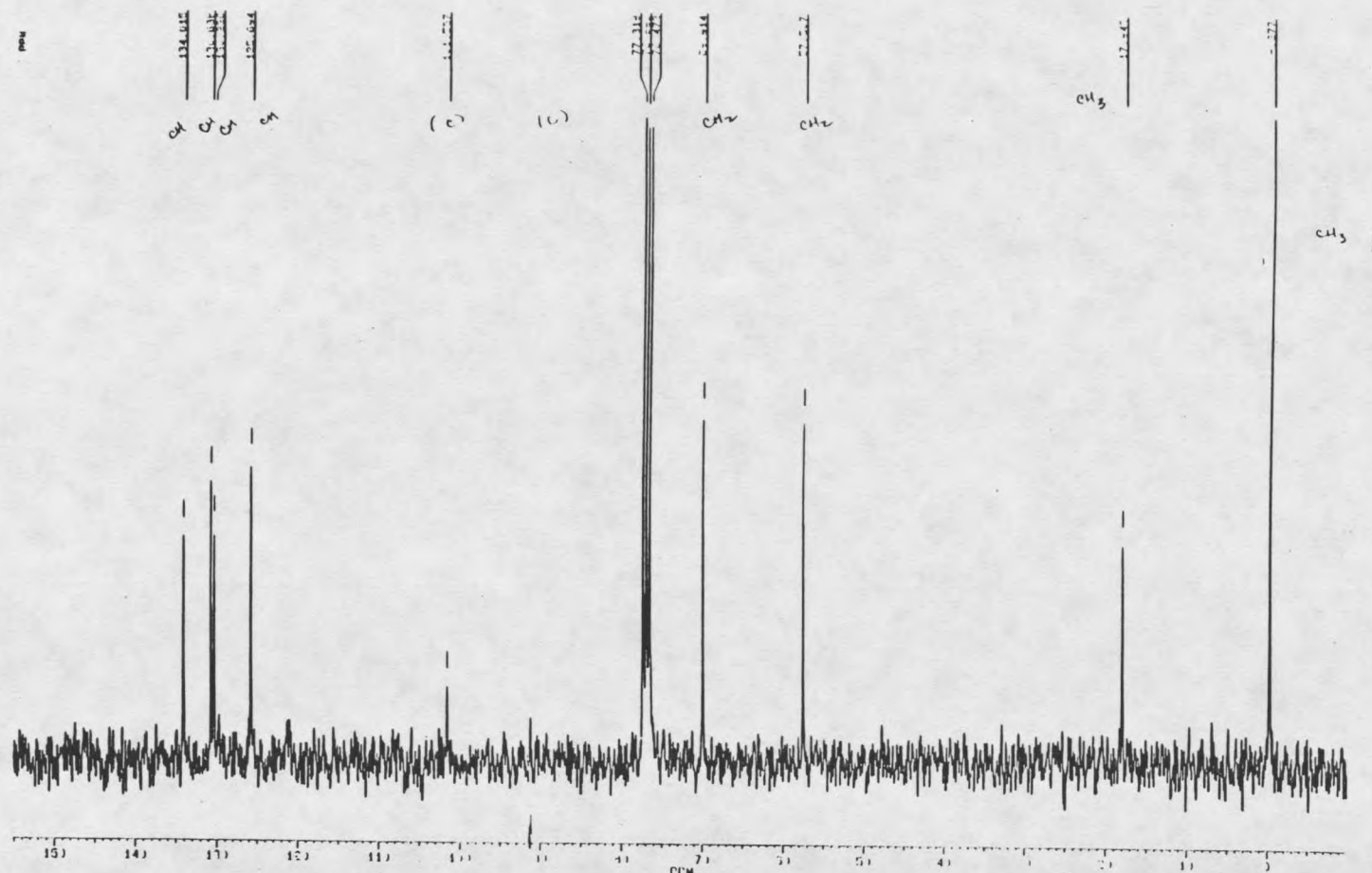


Figure 135. ¹³C NMR Spectrum of 4-Oxo-1-(trimethylsilyl)-6(E),8(E)-decadien-1-yne (106)

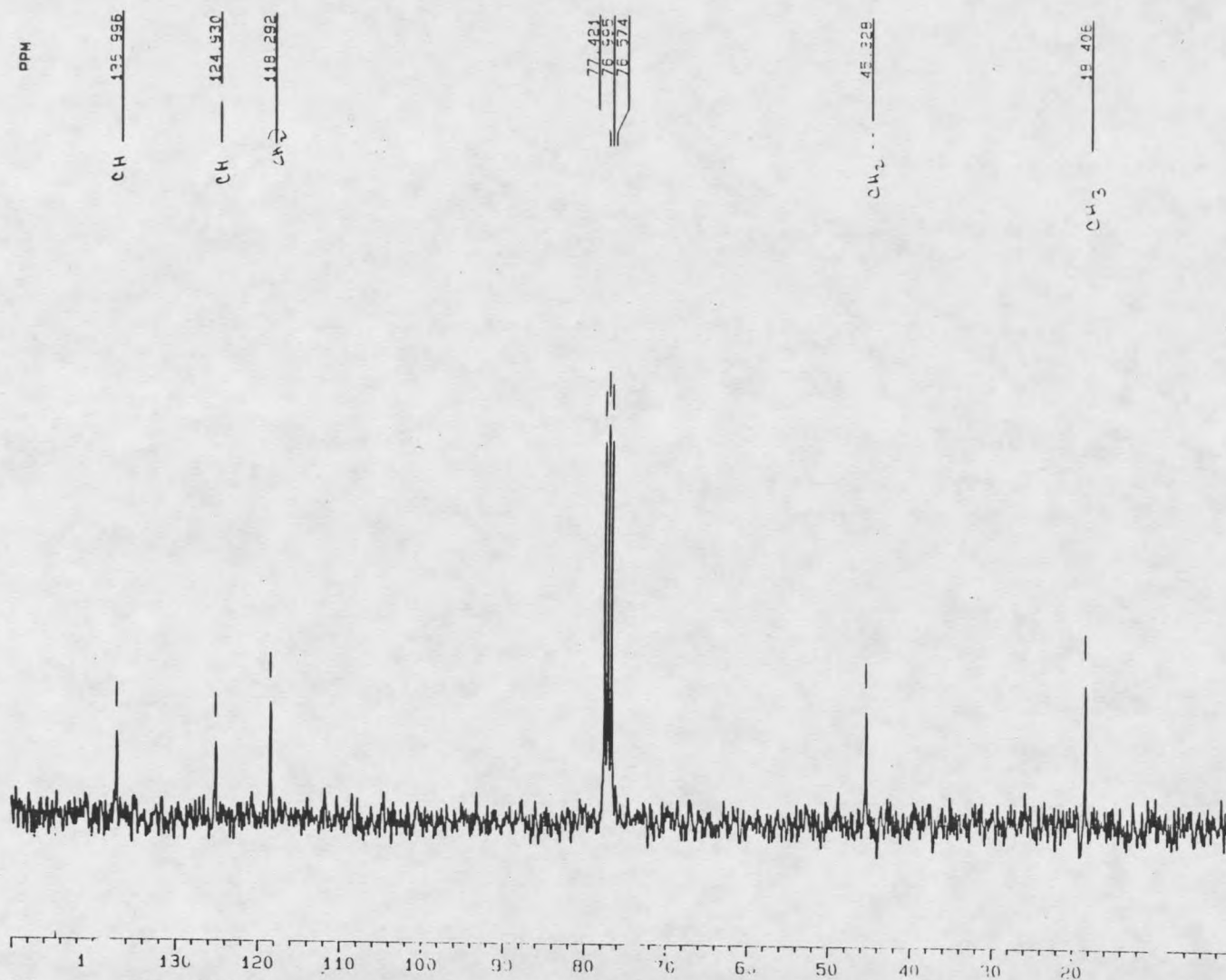


Figure 137. ¹³C NMR Spectrum of 1-Chloro-4-methyl-2(E),4-pentadiene (107)

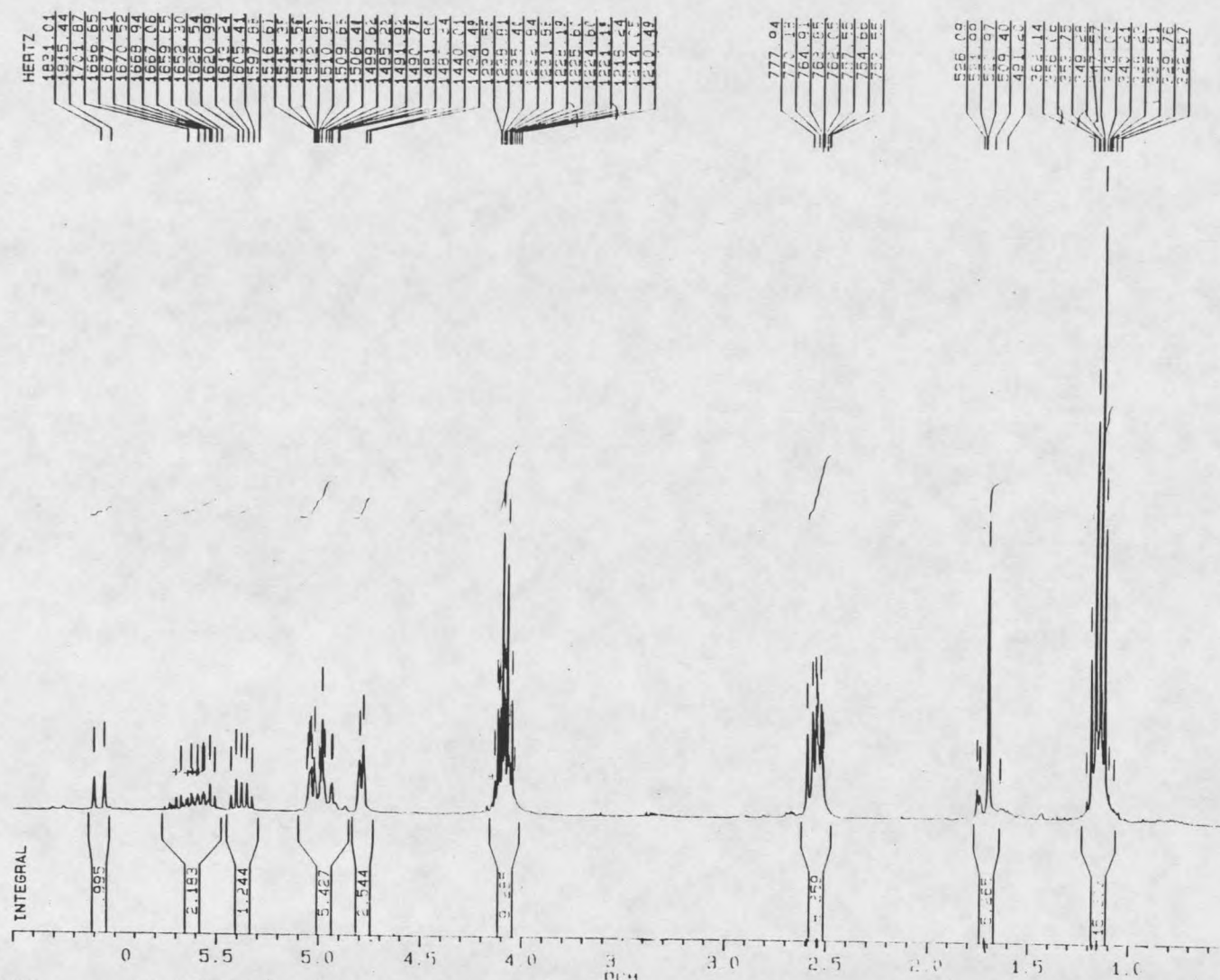
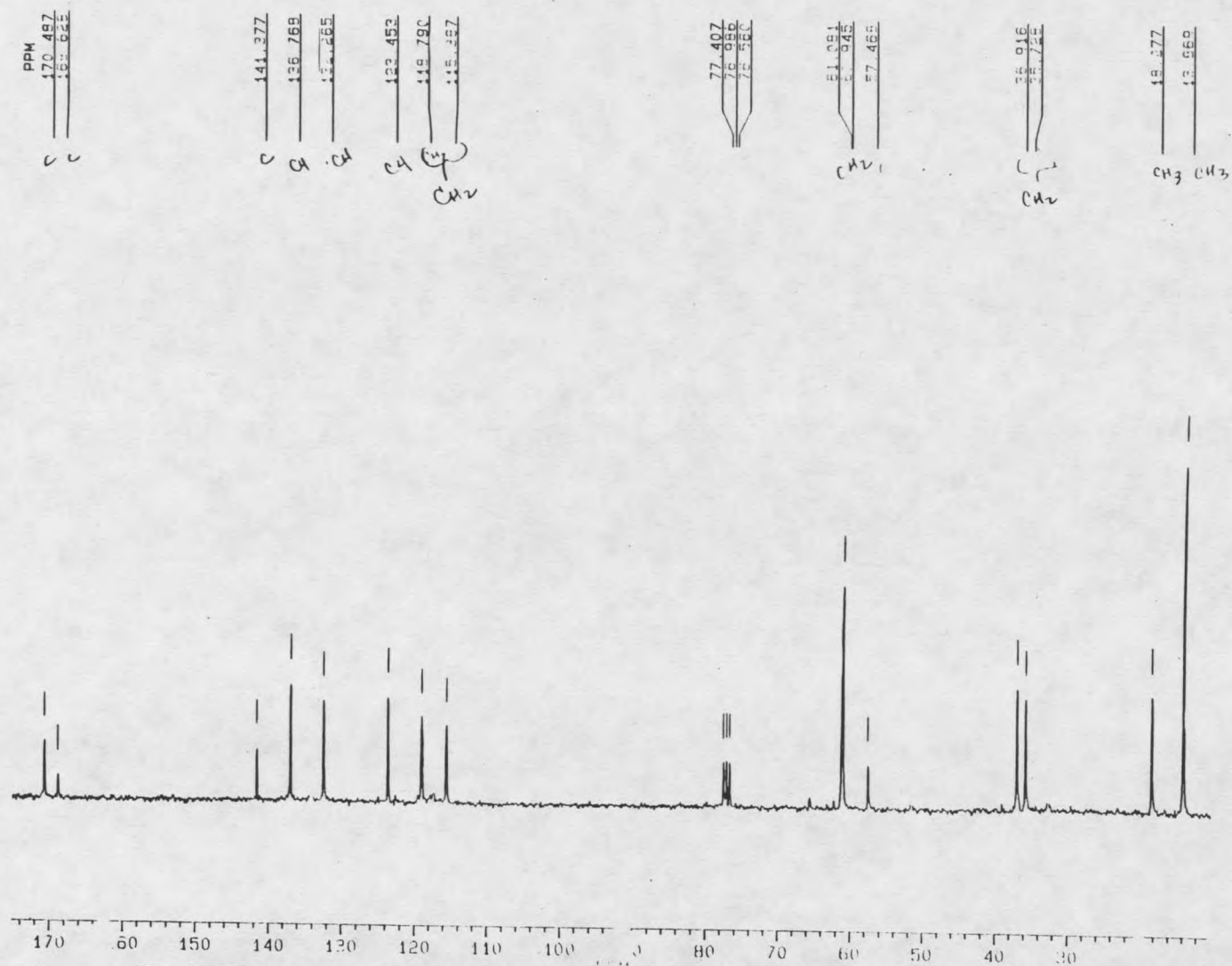


Figure 138. ^1H NMR Spectrum of 4,4-Bis(carboethoxy)-8-methyl-1,6(E),8-nonatriene (108)



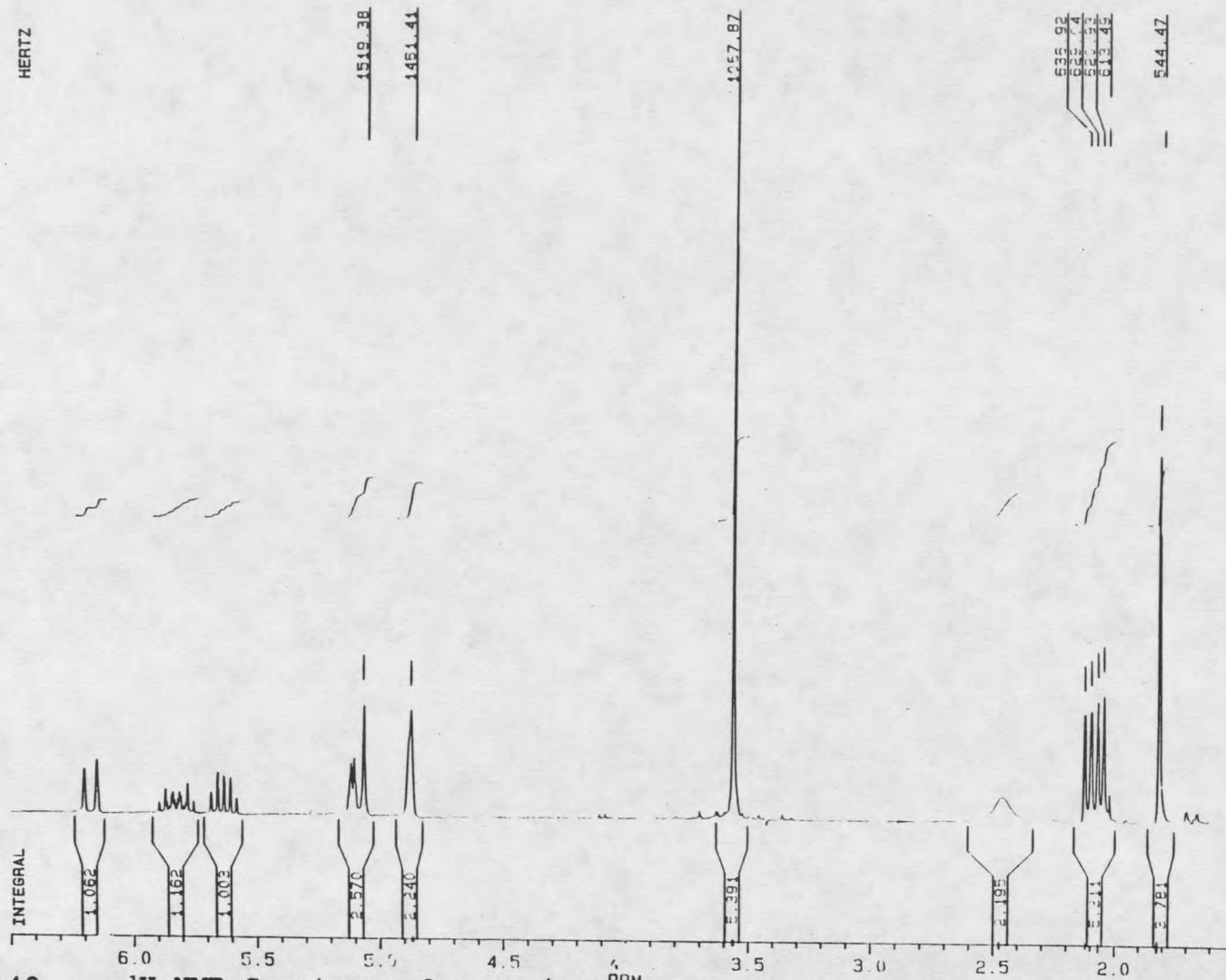


Figure 140. ^1H NMR Spectrum of 4,4-Bis(hydroxymethyl)-8-methyl-1,6(E),8-nonatriene (109)

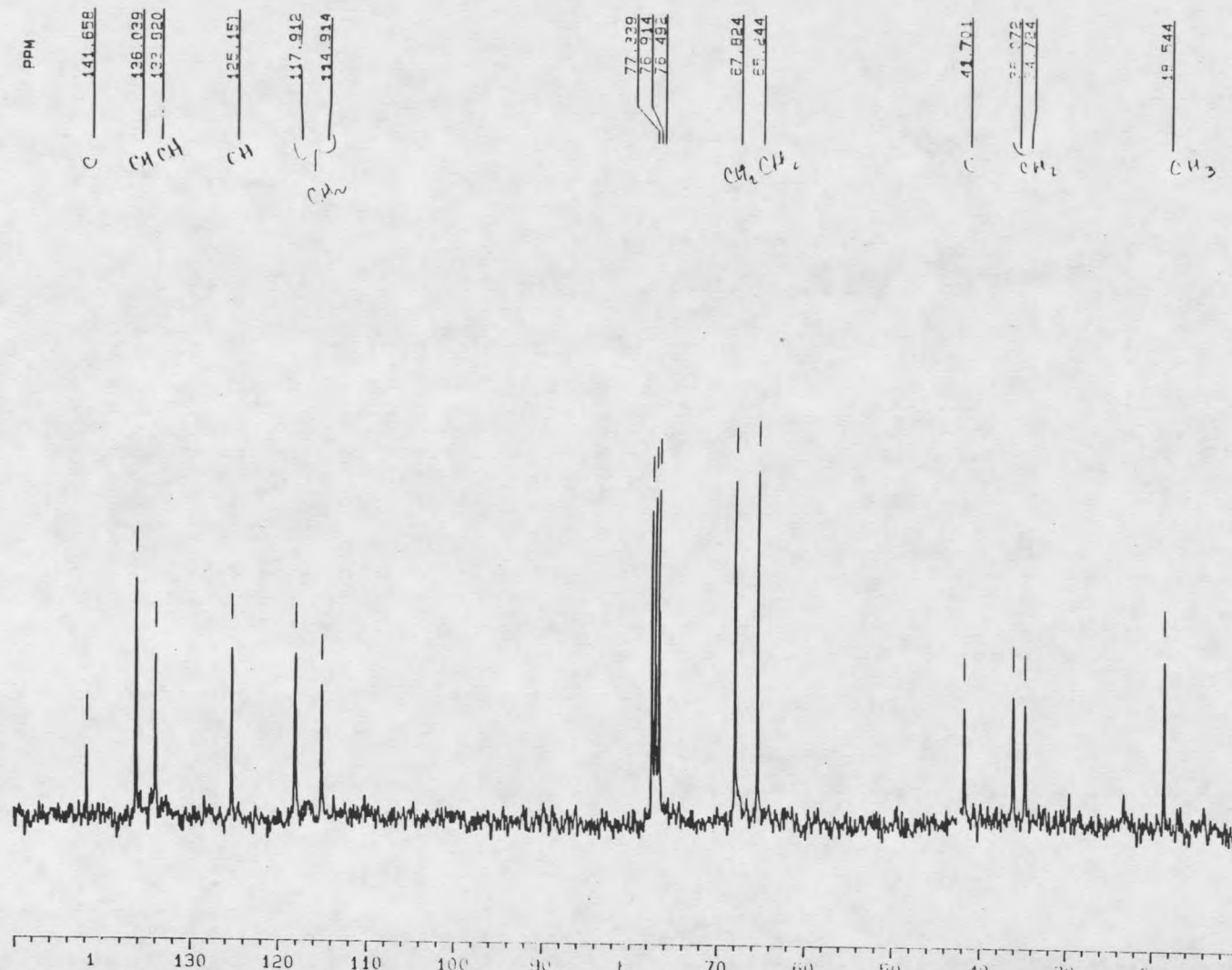


Figure 141. ¹³C NMR Spectrum of 4,4-Bis(hydroxymethyl)-8-methyl-1,6(E),8-nonatriene (109)

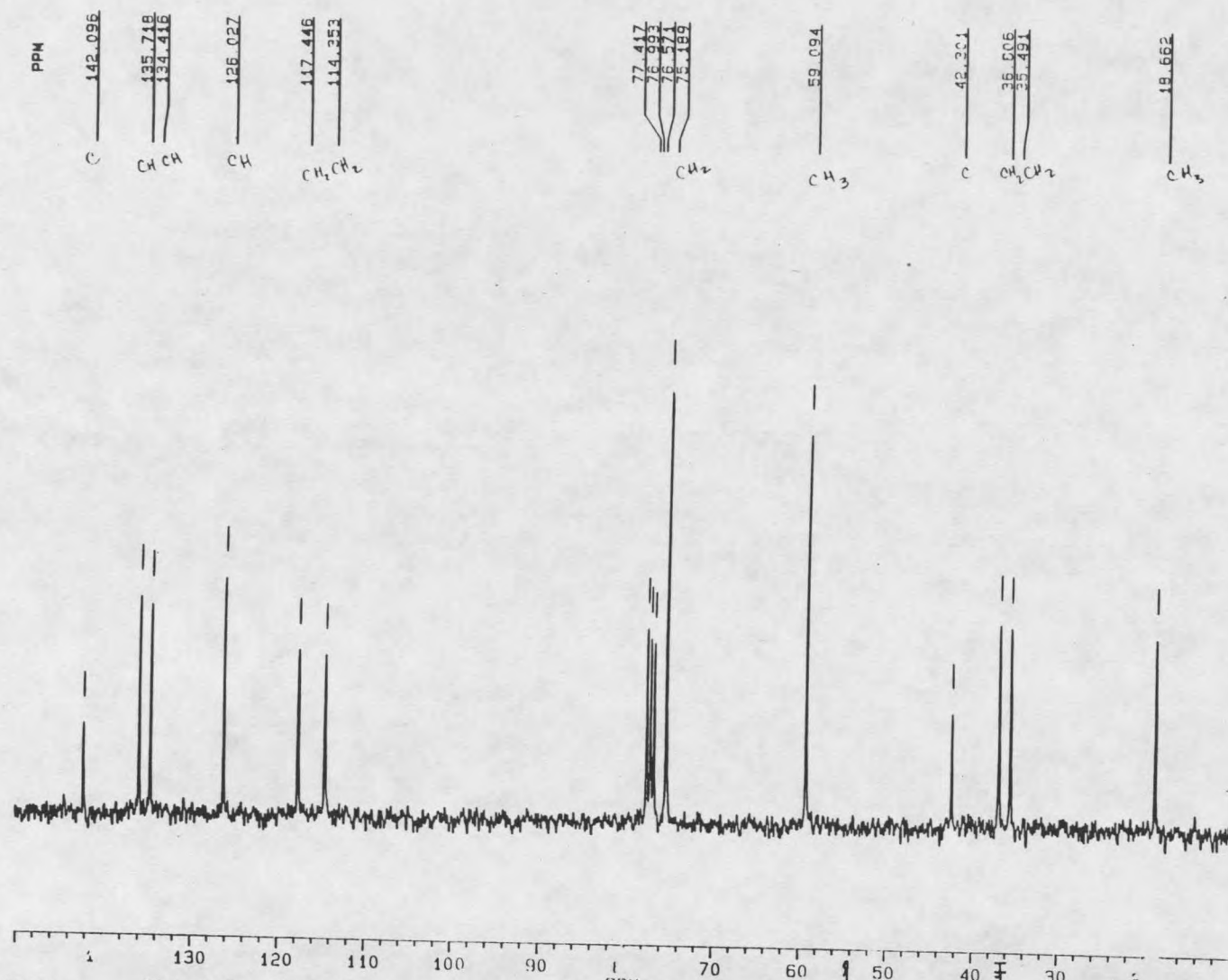


Figure 143. ¹³C NMR Spectrum of 4,4-Bis(methoxymethyl)-8-methy-1,6(E),8-nonatriene (7b)

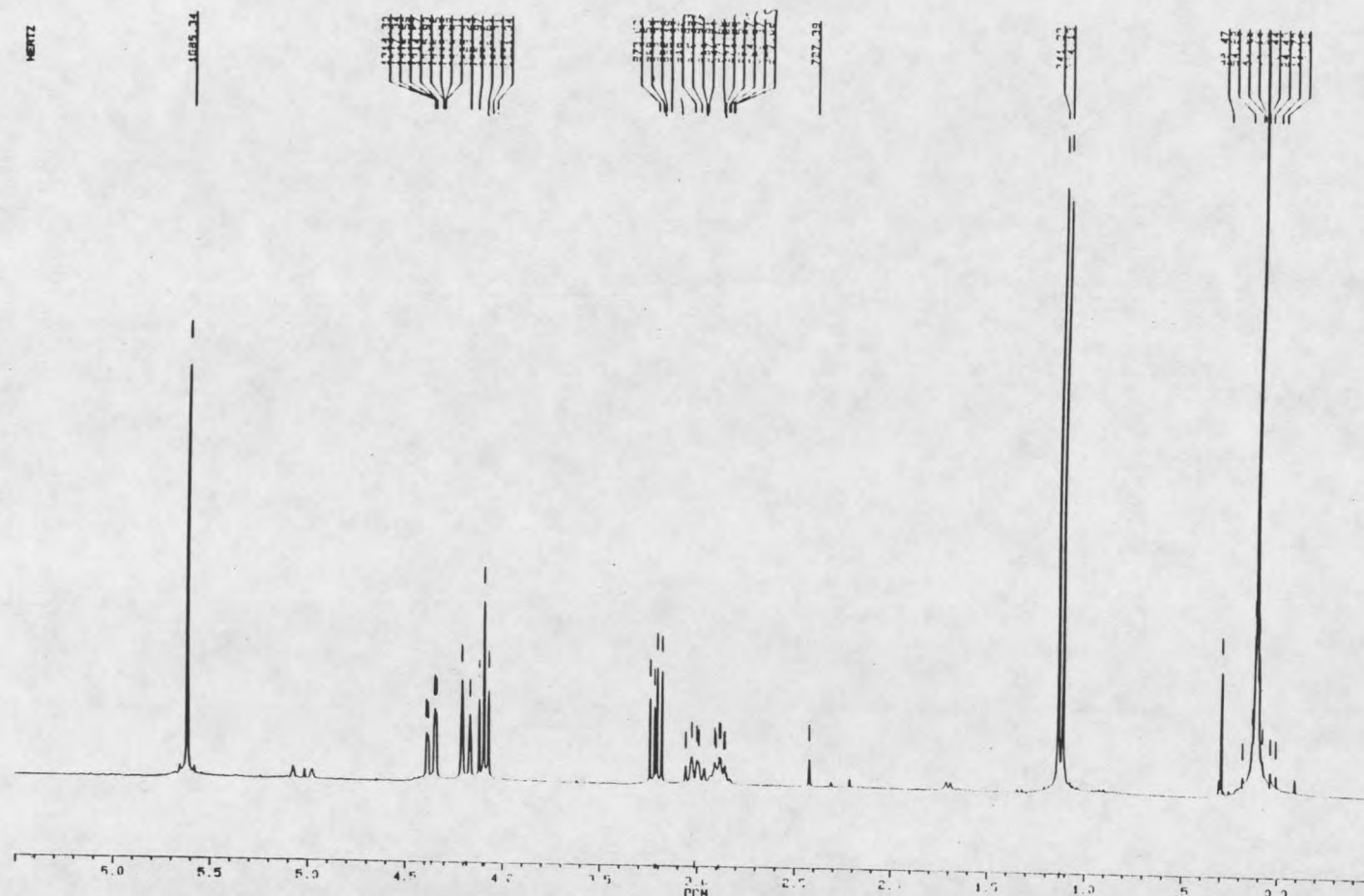


Figure 144. ^1H NMR Spectrum of 1,3,5 α ,7 $\alpha\beta$ -Tetrahydro-5-methyl-4-(trimethylsilyl)-isobenzofuran (110)

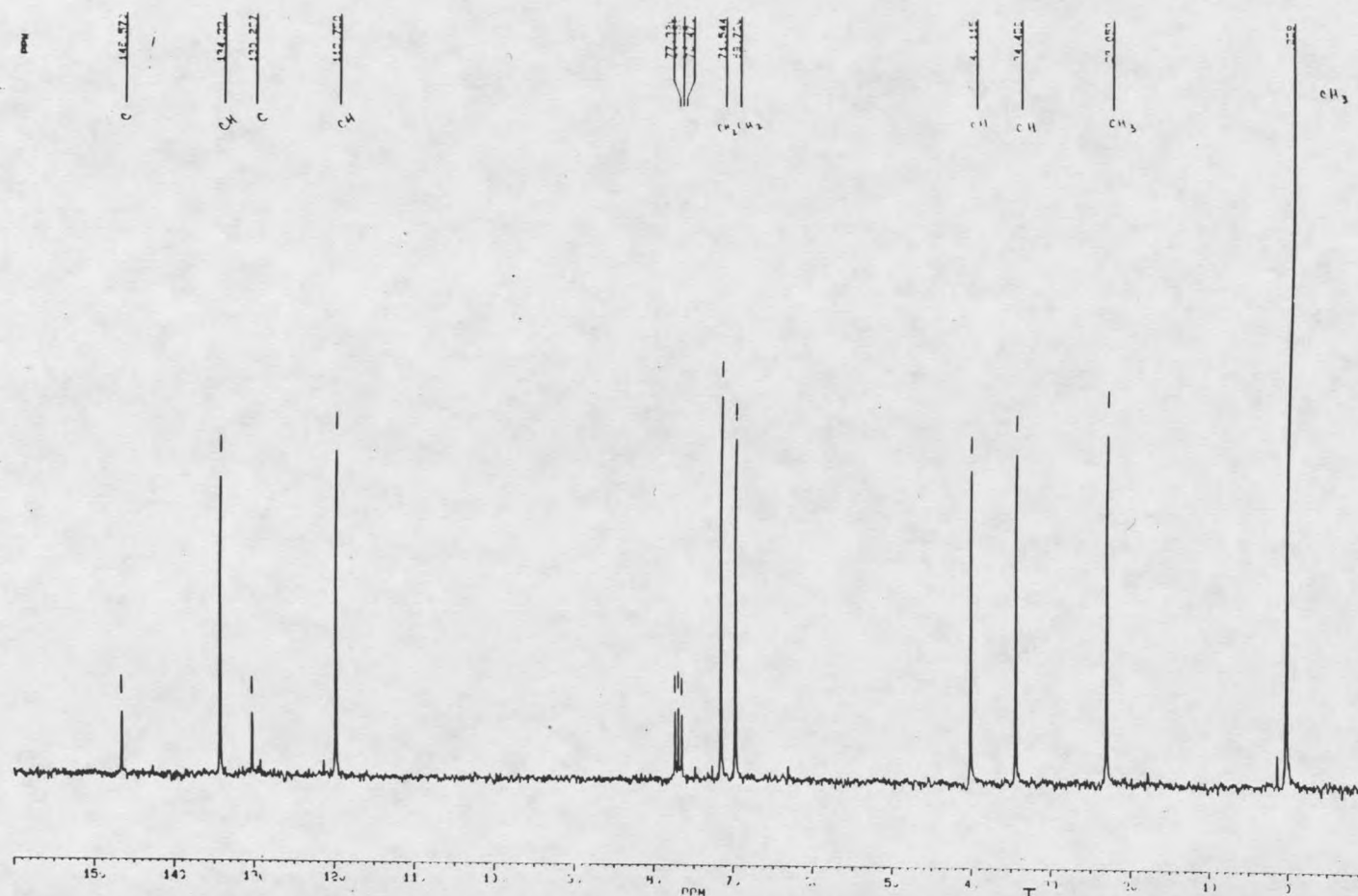


Figure 145. ¹³C NMR Spectrum of 1,3,5α,7αβ-Tetrahydro-5-methyl-4-(trimethylsilyl)-isobenzofuran (110)

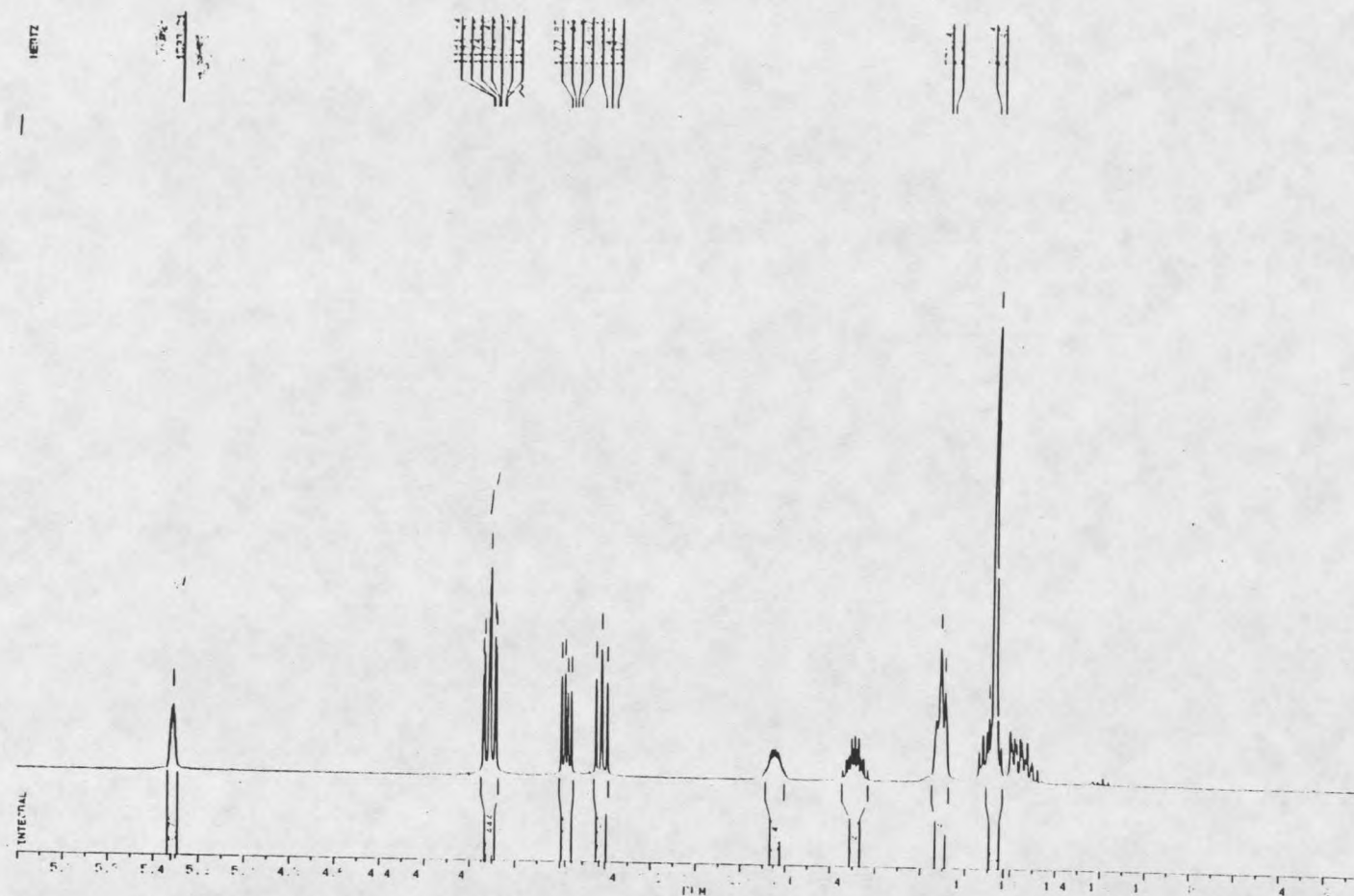


Figure 146. ^1H NMR Spectrum of 1,3,3a β ,6,7,7a β -hexahydro-5-methylisobenzo-furan (8a)

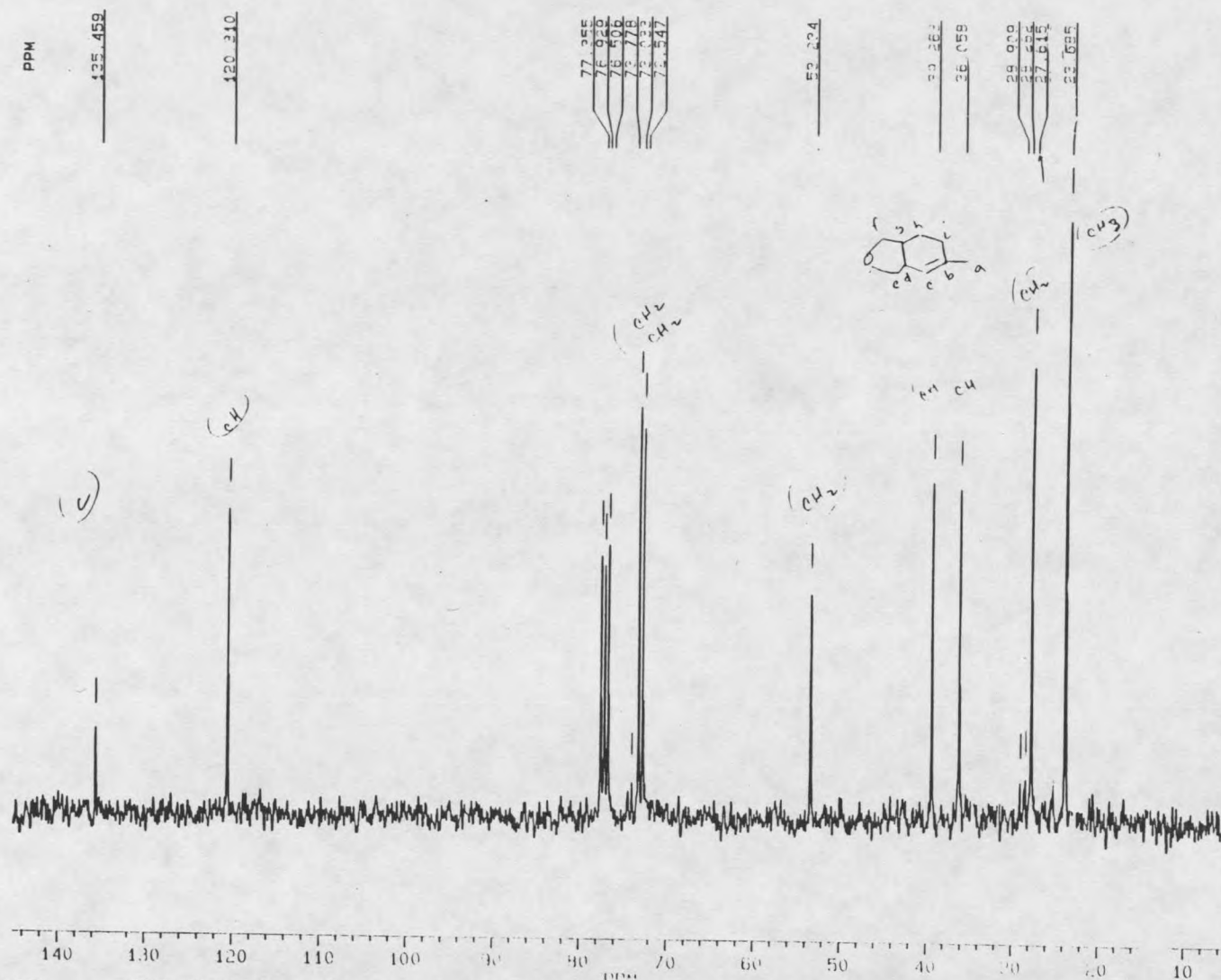


Figure 147. ^{13}C NMR Spectrum of 1,3,3aβ,6,7,7aβ-hexahydro-5-methylisobenzo-furan (8a)

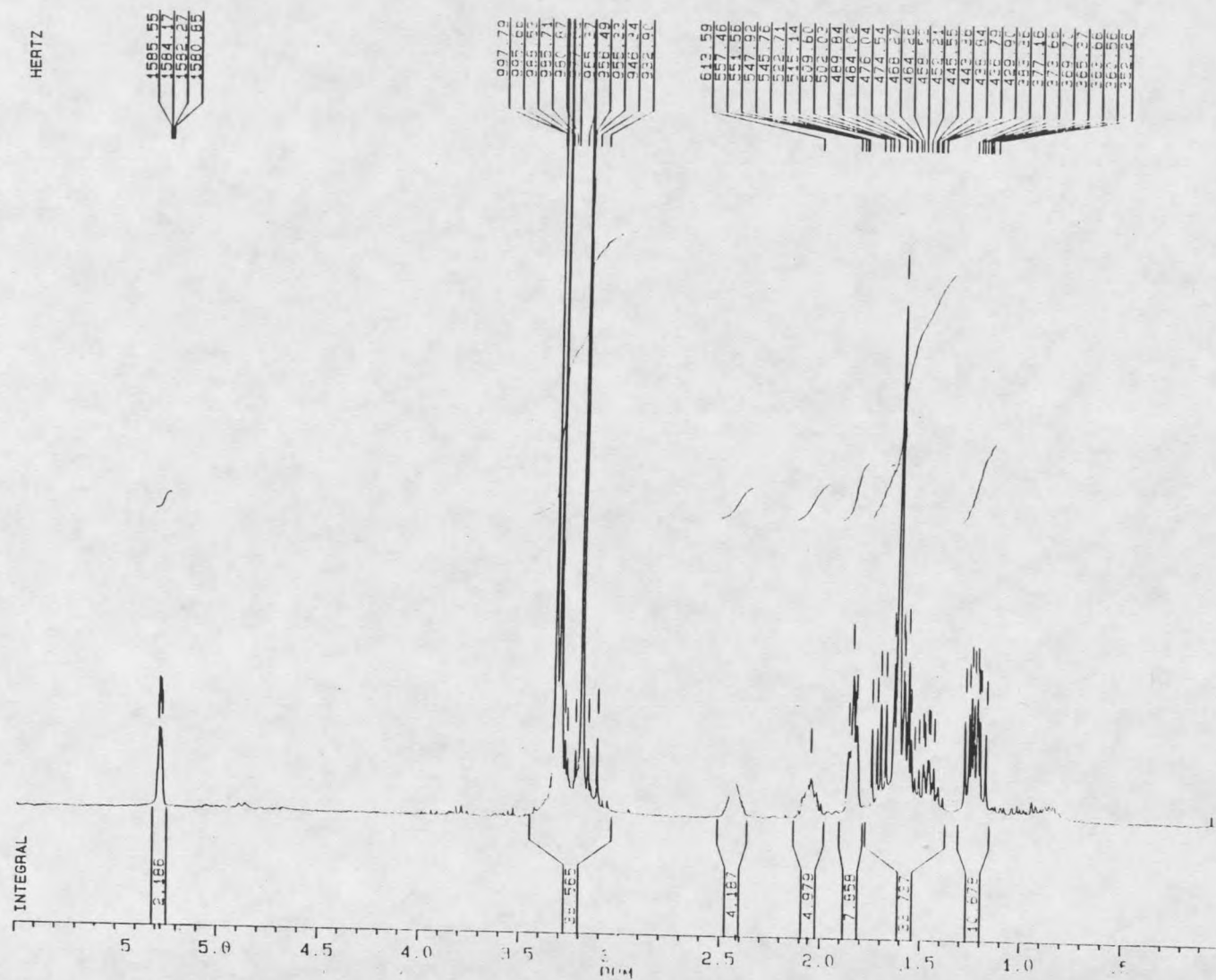


Figure 148. ^1H NMR Spectrum of 3a β ,6,7,7a β -Tetrahydro-2,2-bis(methoxy-methyl)-5-methylindan (8b)

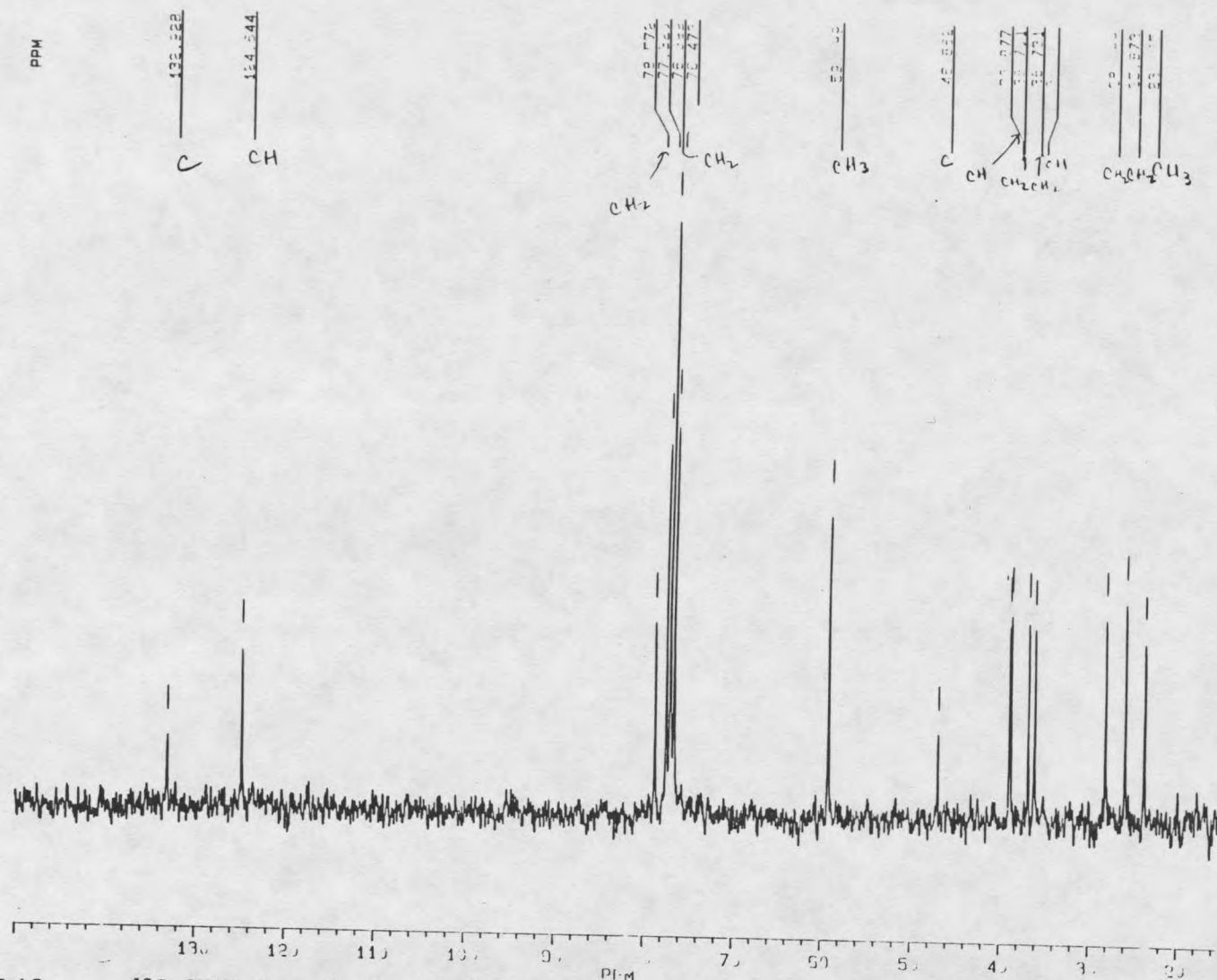


Figure 149. ¹³C NMR Spectrum of 3aβ,6,7,7aβ-Tetrahydro-2,2-bis(methoxy-methyl)-5-methylindan (8b)

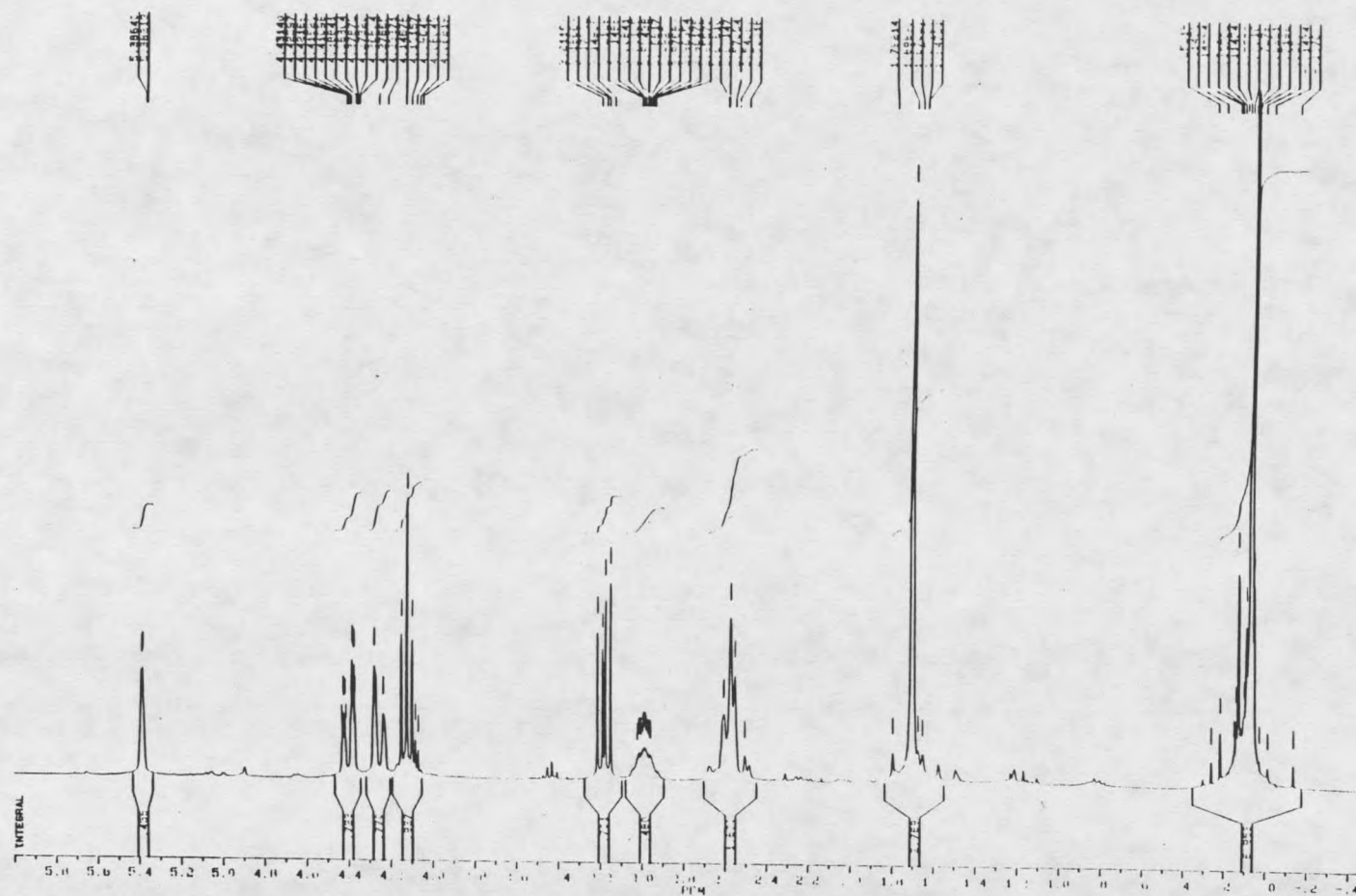


Figure 150. ^1H NMR Spectrum of 1,3,5,7a β -Tetrahydro-6-methyl-4-(tri-methylsilyl)isobenzofuran (11)

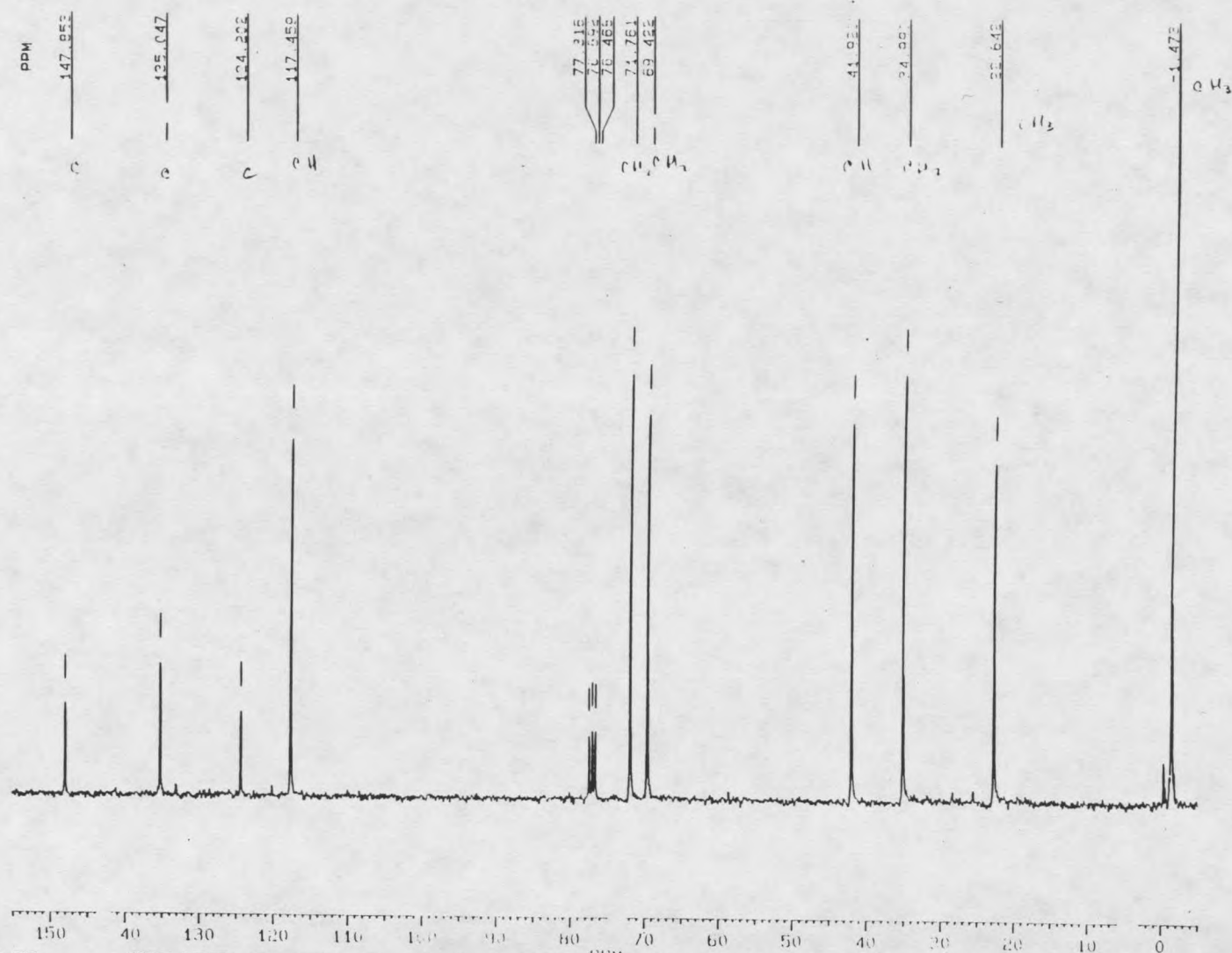


Figure 151. ¹³C NMR Spectrum of 1,3,5,7aβ-Tetrahydro-6-methyl-4-(tri-methylsilyl)isobenzofuran (11)

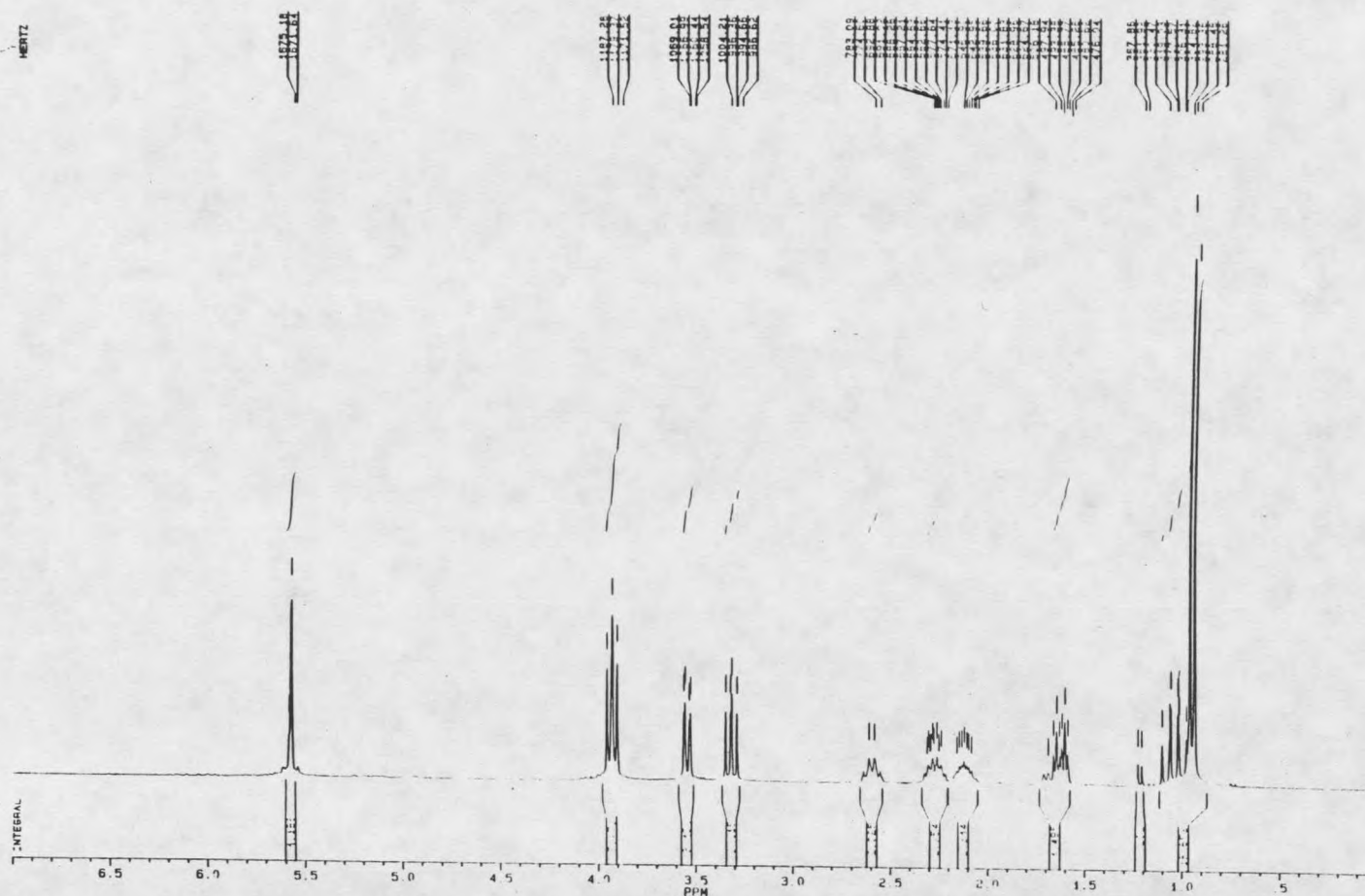


Figure 152. ^1H NMR Spectrum of 1,3,3a β ,4,5 α ,7a β -hexahydro-5-methyliso-benzofuran (8c)

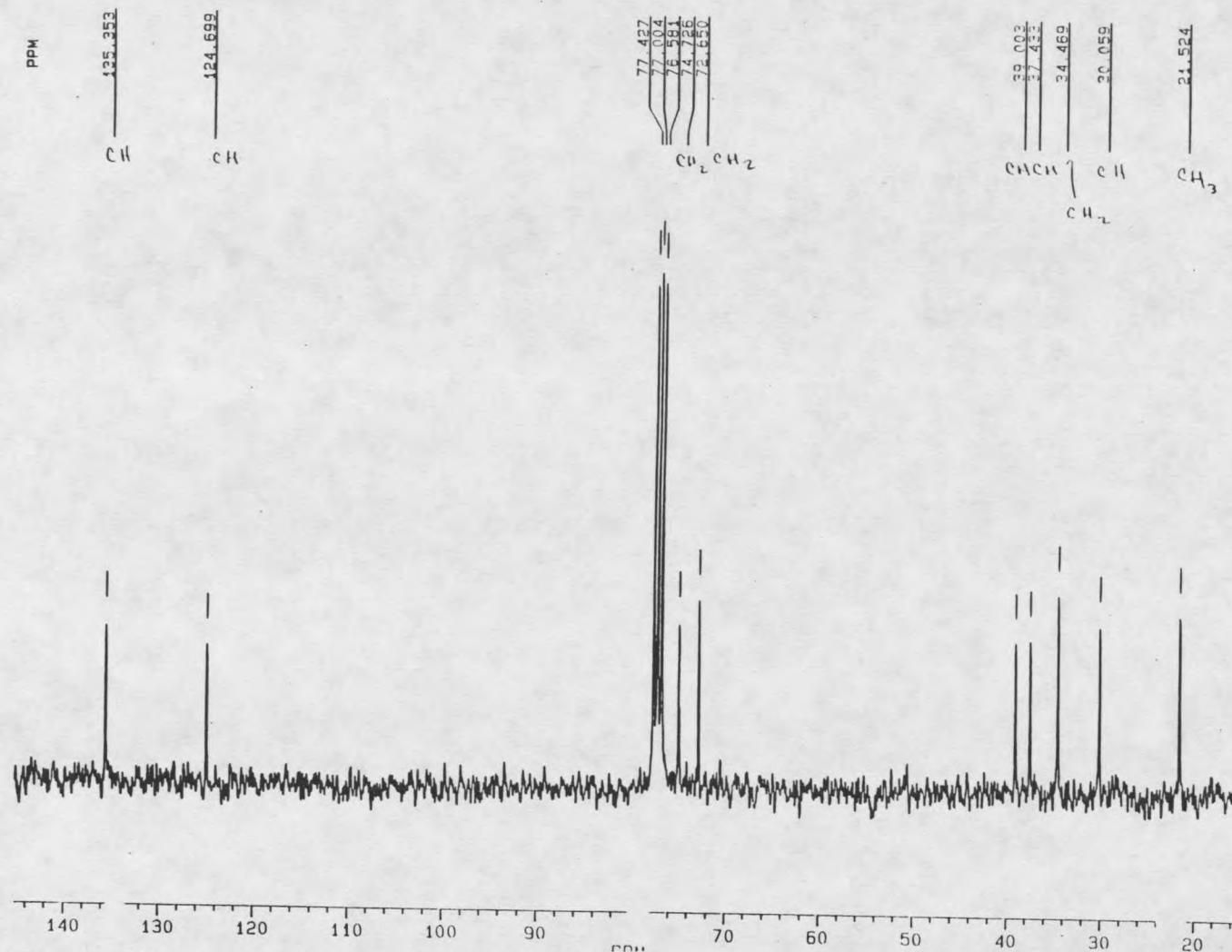


Figure 153. ¹³C NMR Spectrum of 1,3,3aβ,4,5α,7aβ-hexahydro-5-methyliso-benzofuran (8c)

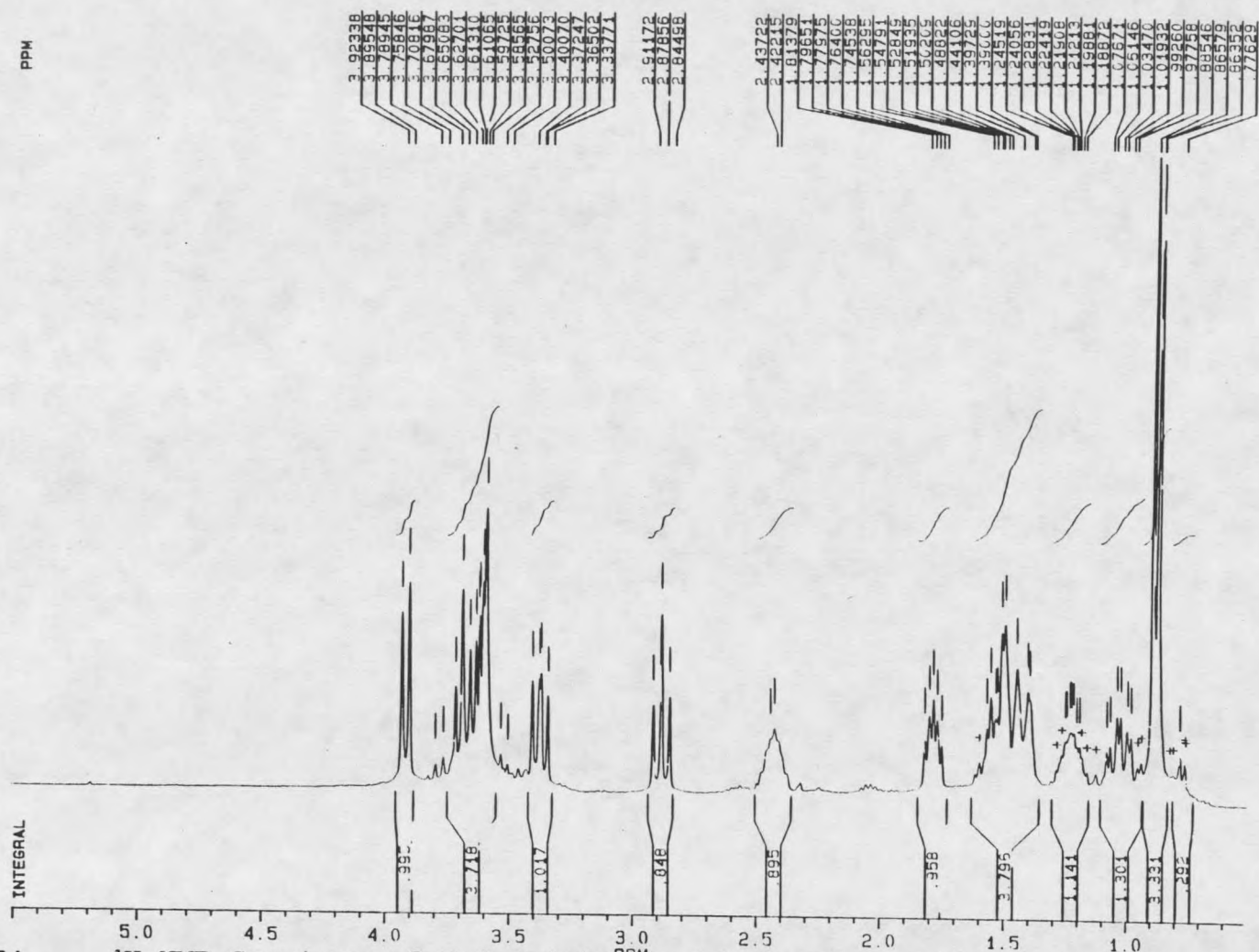


Figure 154. ^1H NMR Spectrum of 7a β -Octahydro-4-hydroxy-5-methylisobenzofuran (9a)

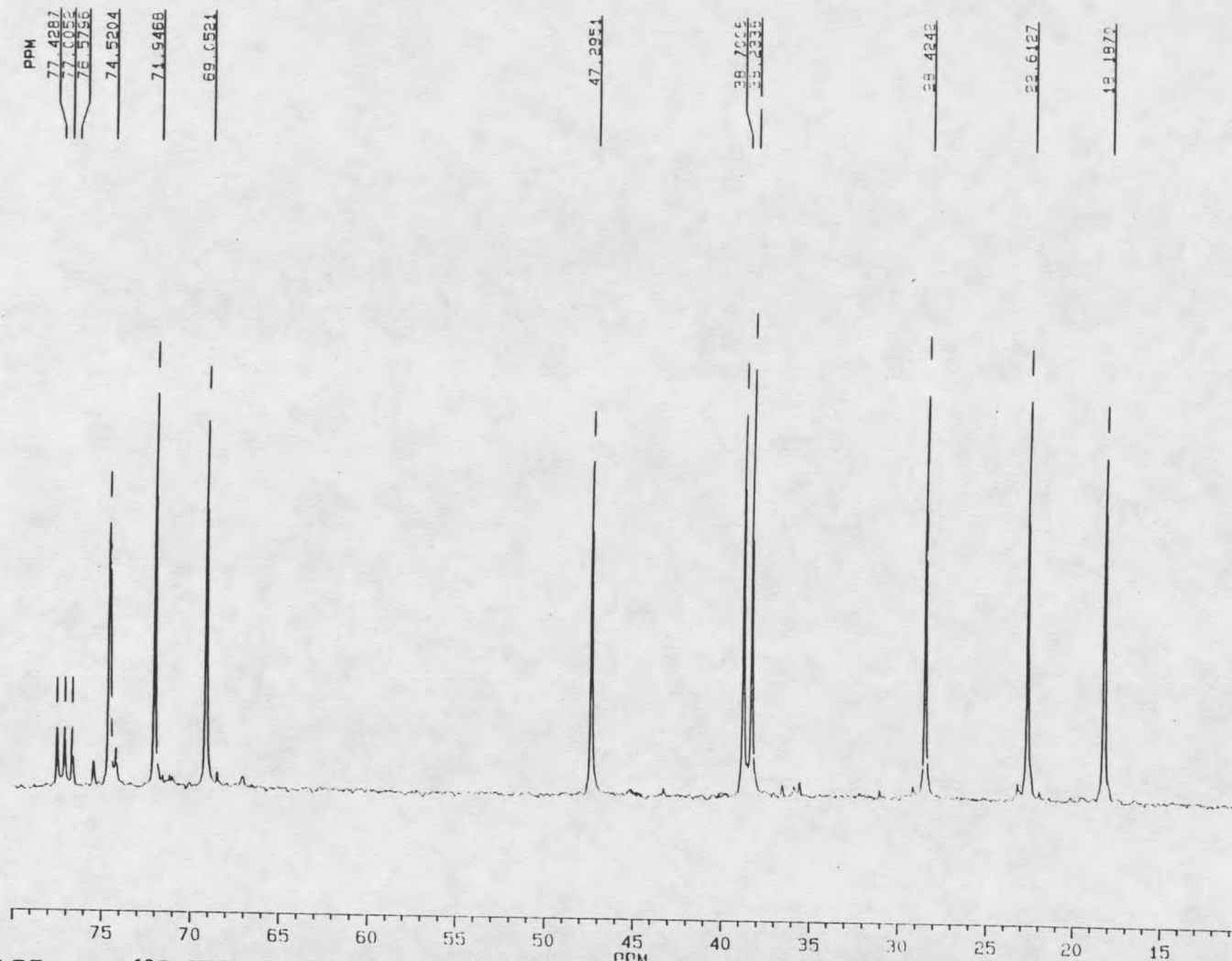


Figure 155. ^{13}C NMR Spectrum of 7a β -Octahydro-4-hydroxy-5-methylisobenzofuran (9a)

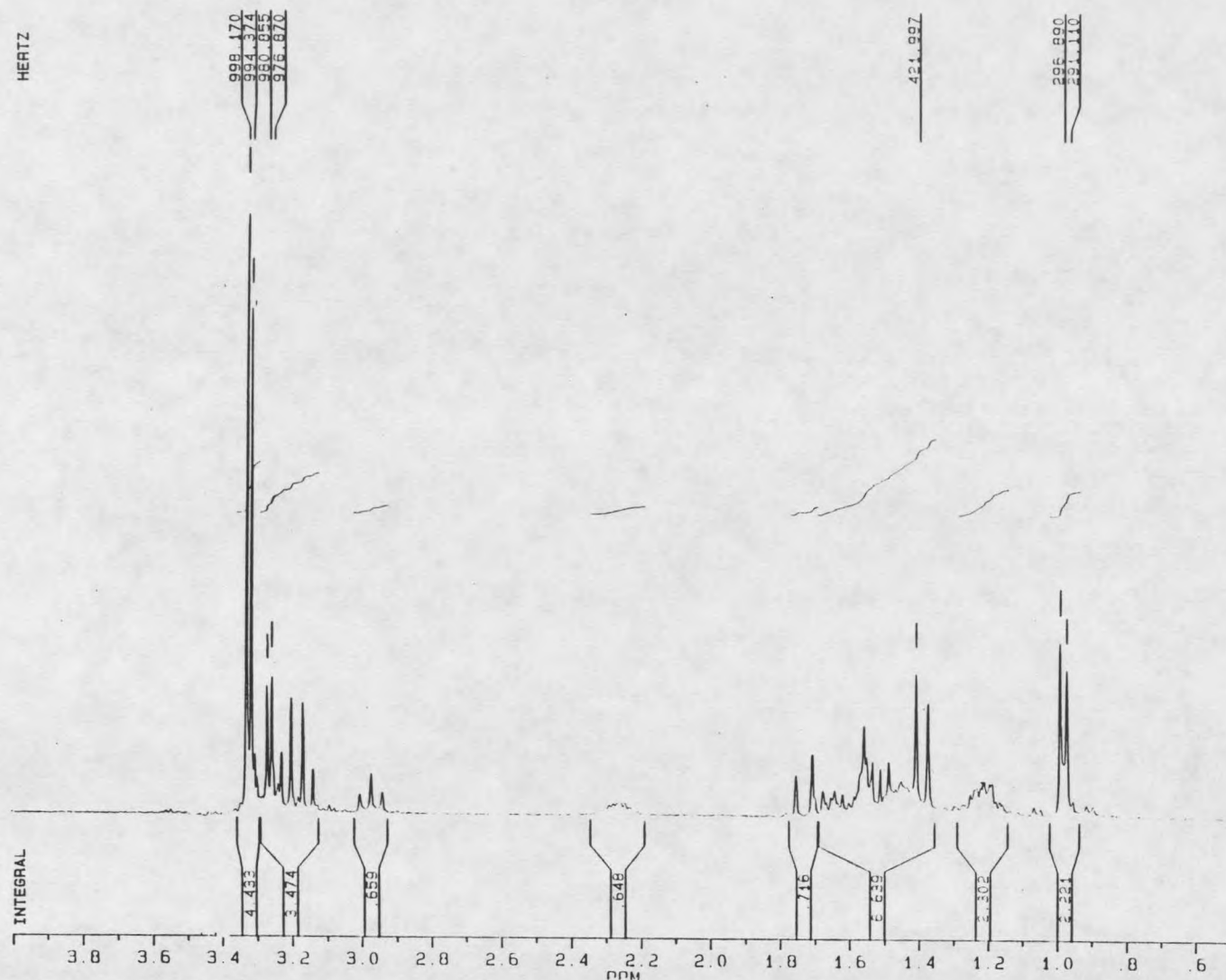


Figure 156. ^1H NMR Spectrum of $3a\beta, 4\alpha, 5\beta, 6, 7, 7a\beta$ -Hexahydro-4-hydroxy-2,2-bis(methoxymethyl)-5-methylindan (9b)

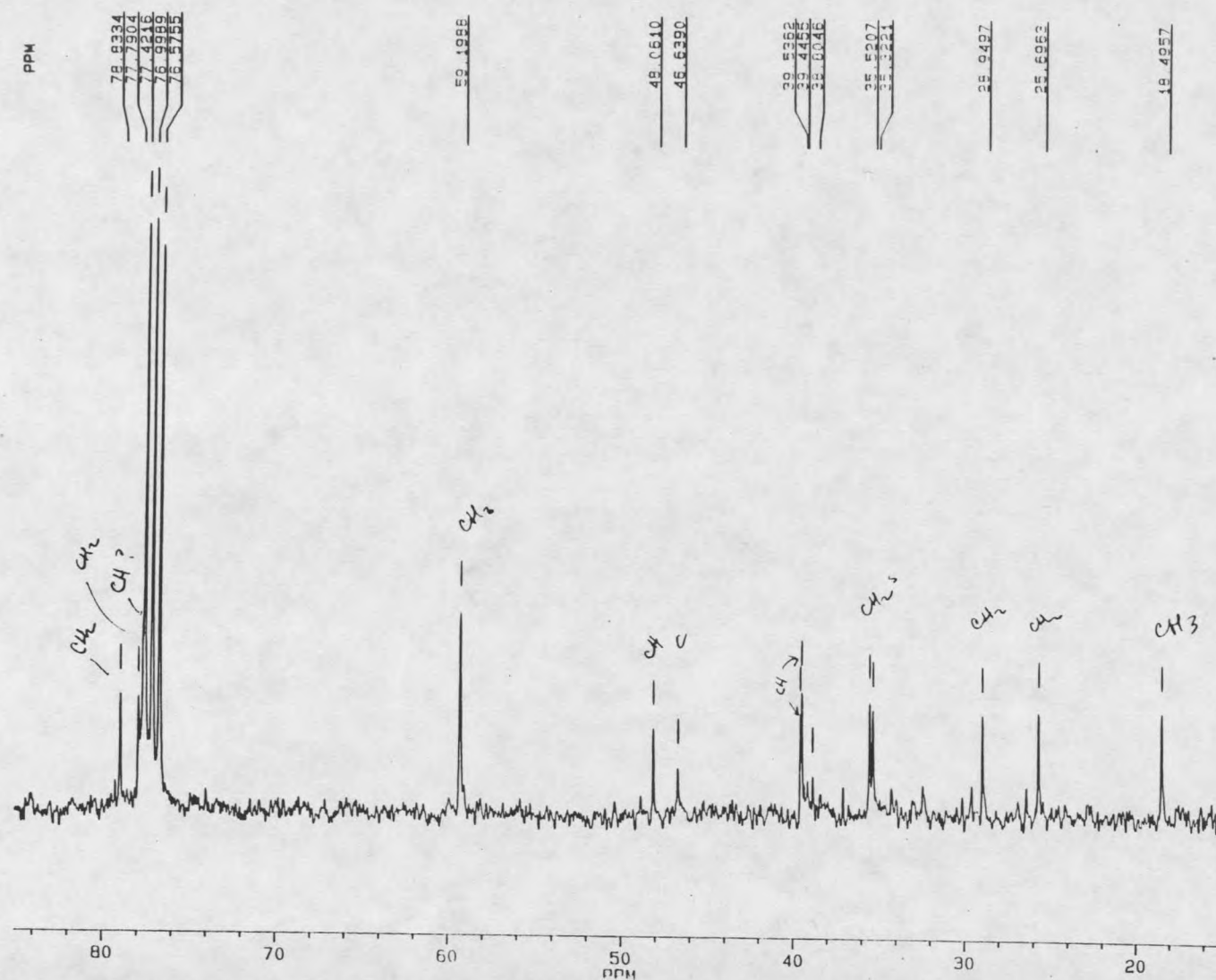


Figure 157. ^{13}C NMR Spectrum of 3a β ,4 α ,5 β ,6,7,7a β -Hexahydro-4-hydroxy-2,2-bis(methoxymethyl)-5-methylindan (9b)

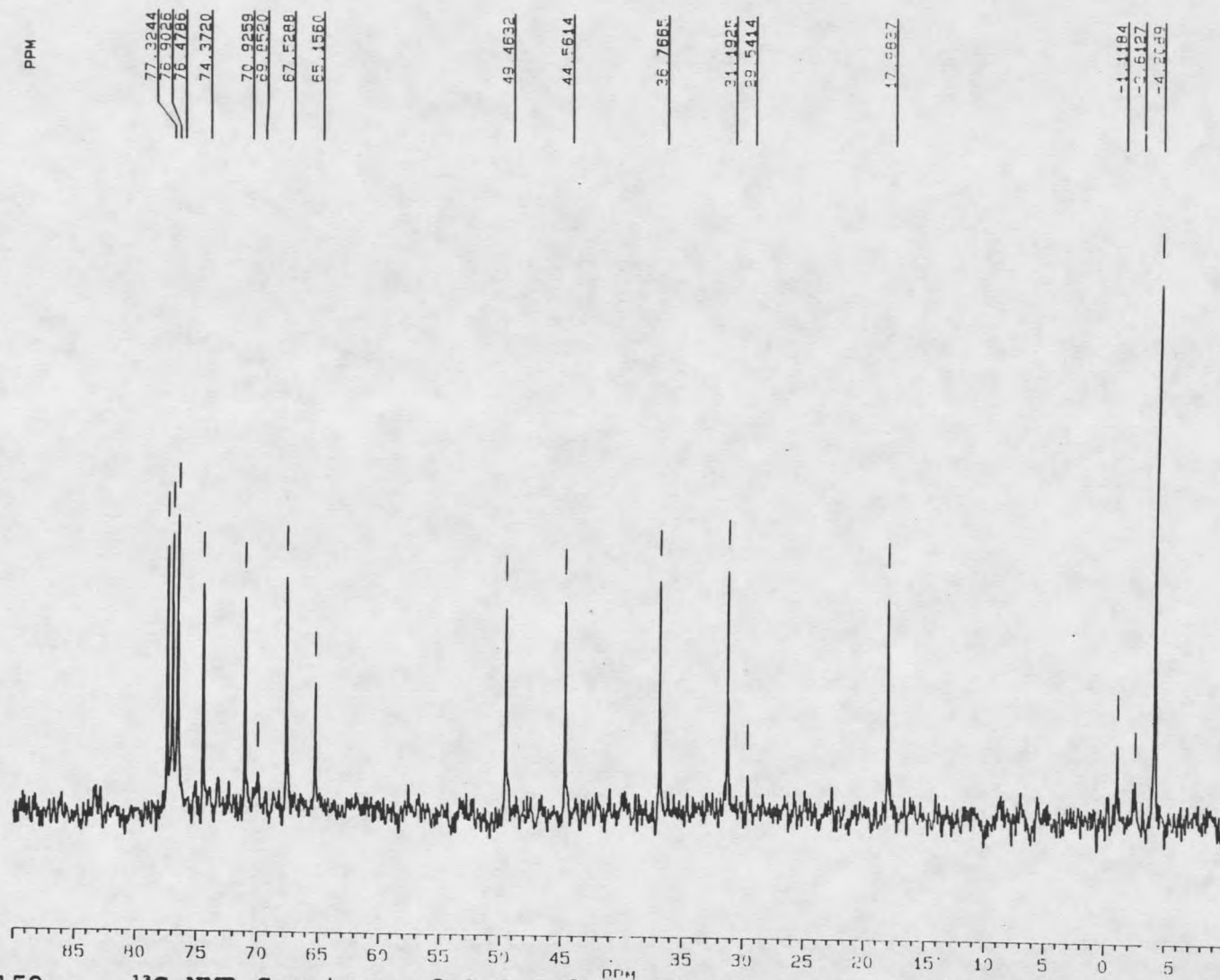


Figure 159. ^{13}C NMR Spectrum of 1,3,3a β ,4 α ,5 β ,6-Hexahydro-4-hydroxy-5-methyl-7-(trimethylsilyl)isobenzofuran (12)

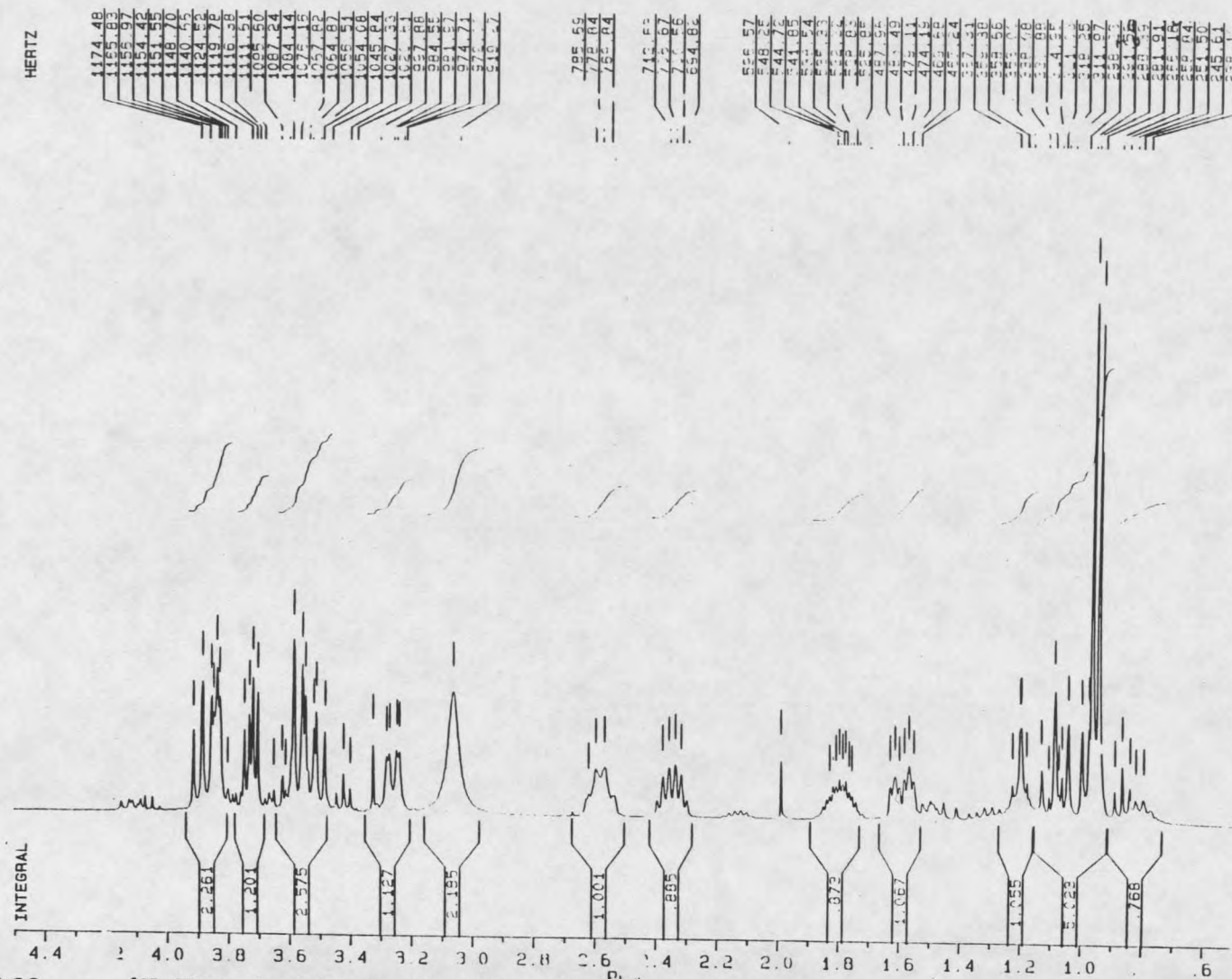


Figure 160. ¹H NMR Spectrum of 1,3,3aβ,4α,5α,6β,7,7aβ-Octahydro-4,5-bis(hydroxy)-6-methylisobenzofuran (9c)

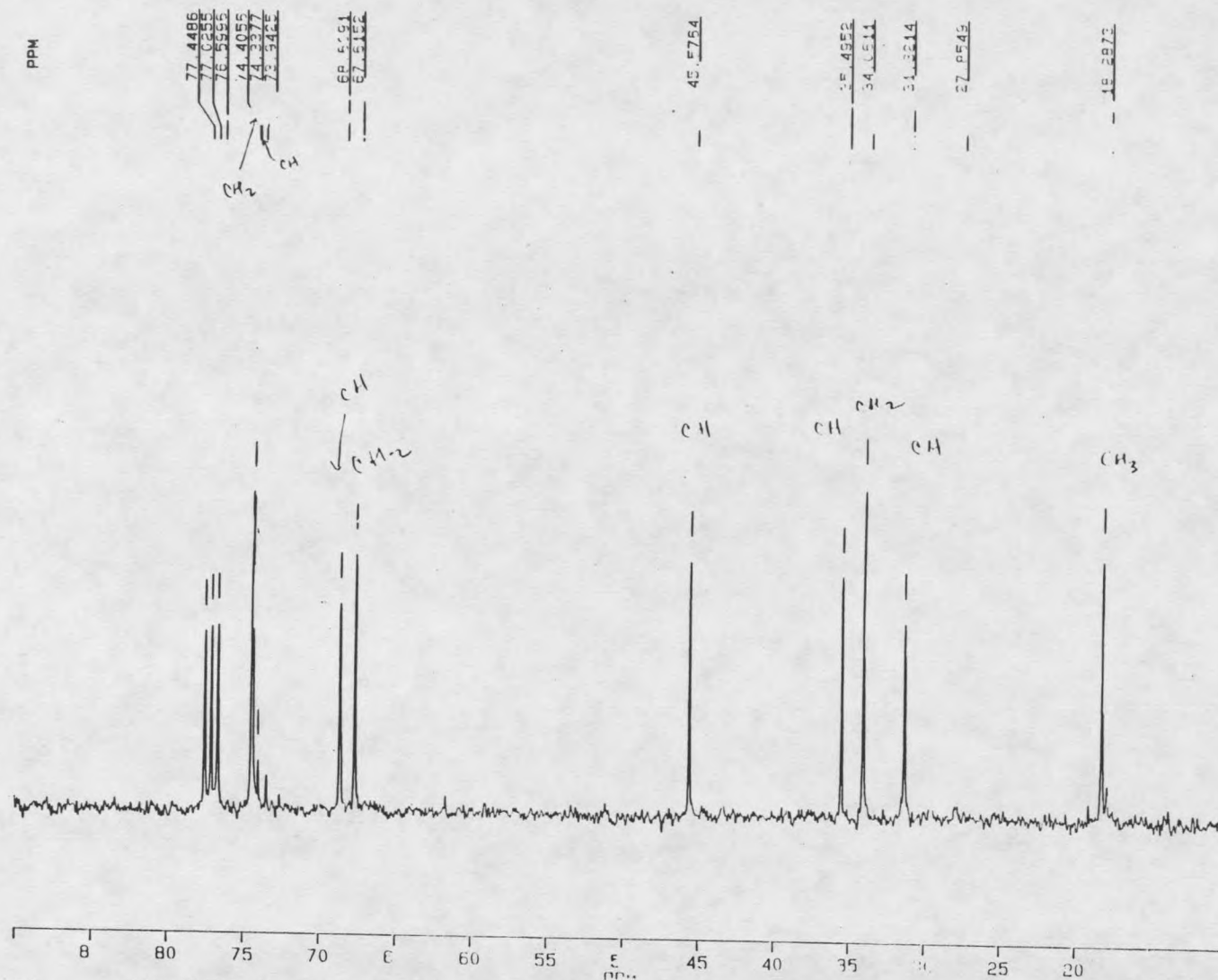


Figure 161. ¹³C NMR Spectrum of 1,3,3aβ,4α,5α,6β,7,7aβ-Octahydro-4,5-bis(hydroxy)-6-methylisobenzofuran (9c)

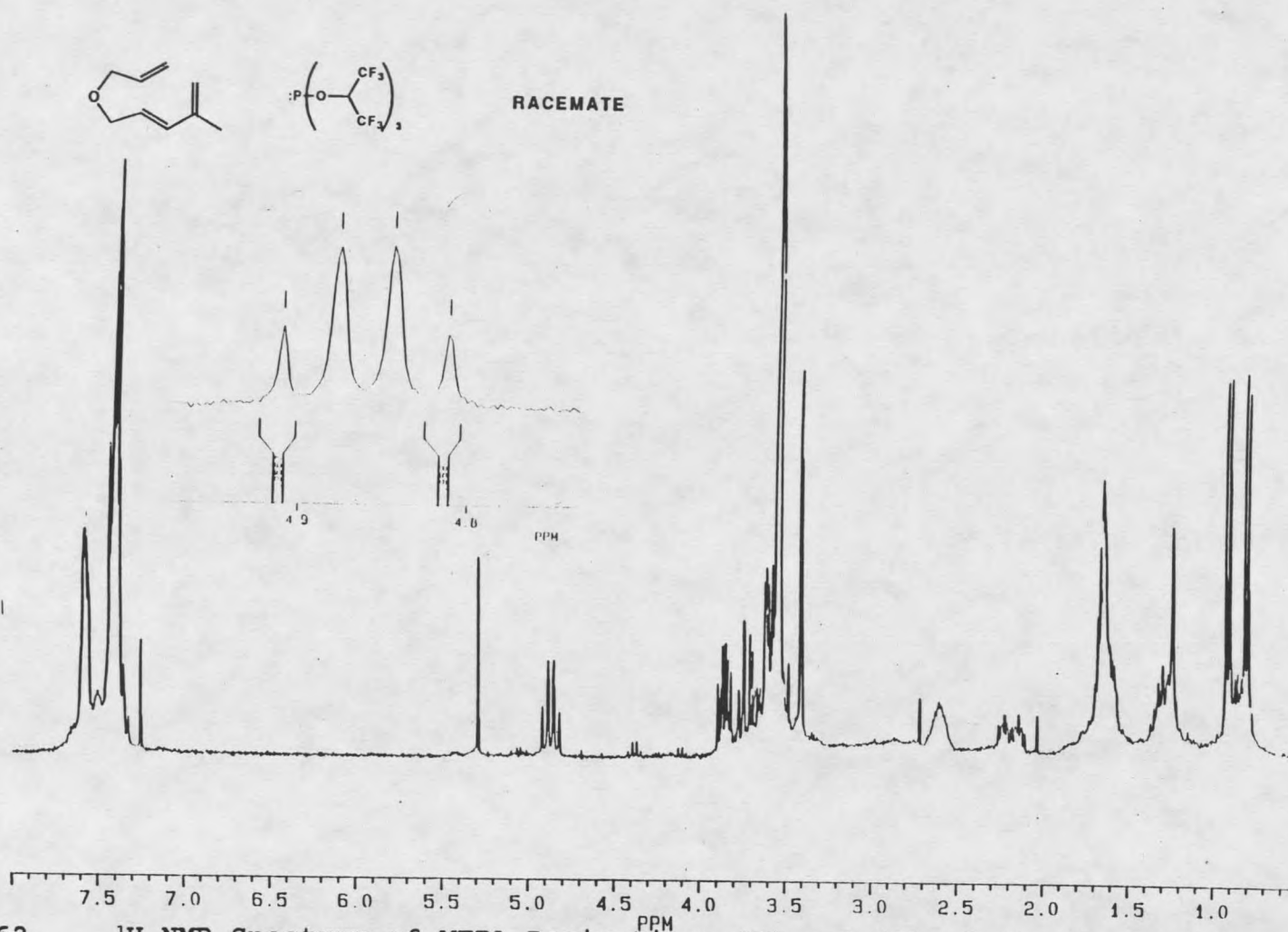


Figure 162. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Racemate)

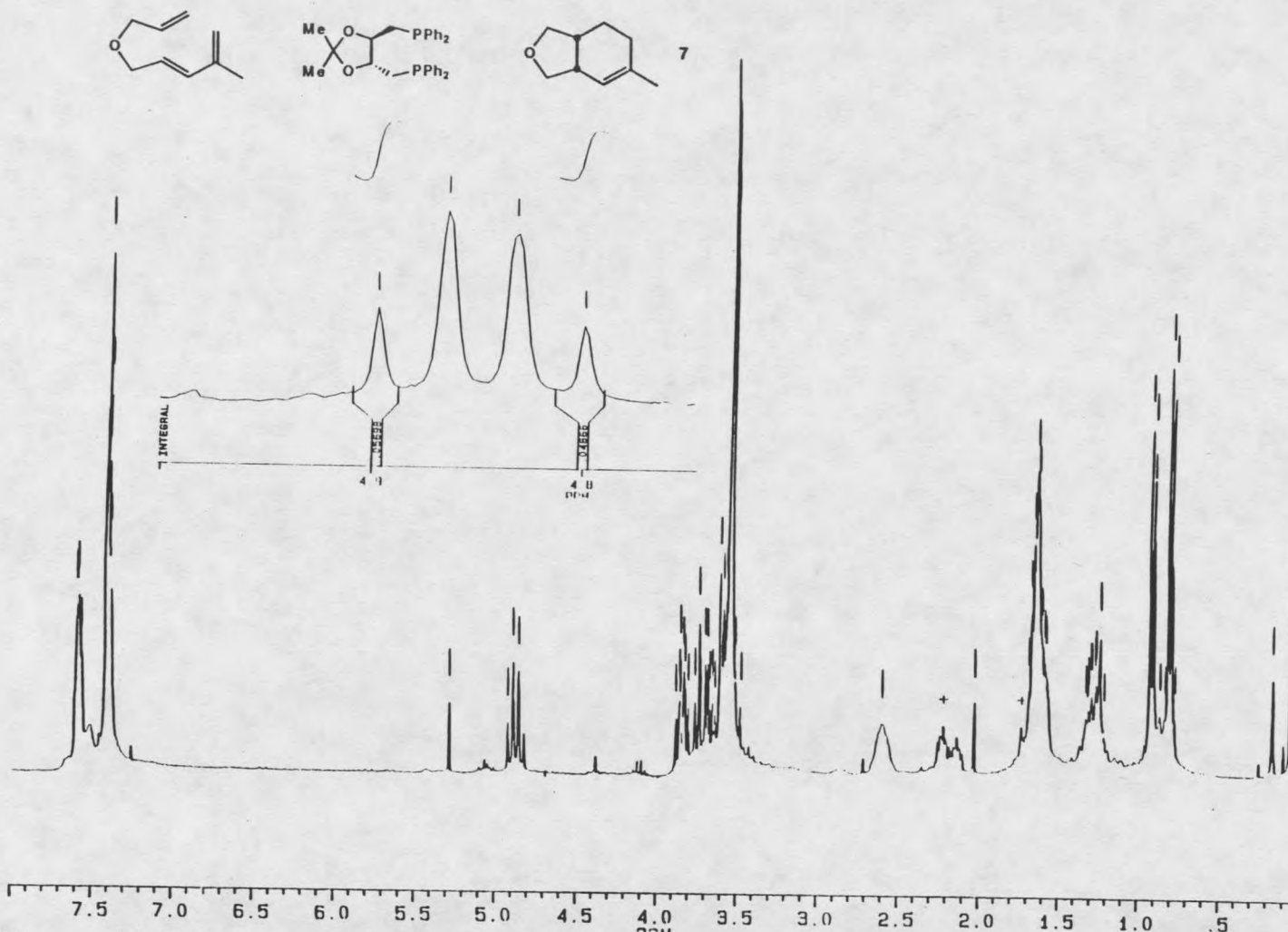


Figure 163. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3a)

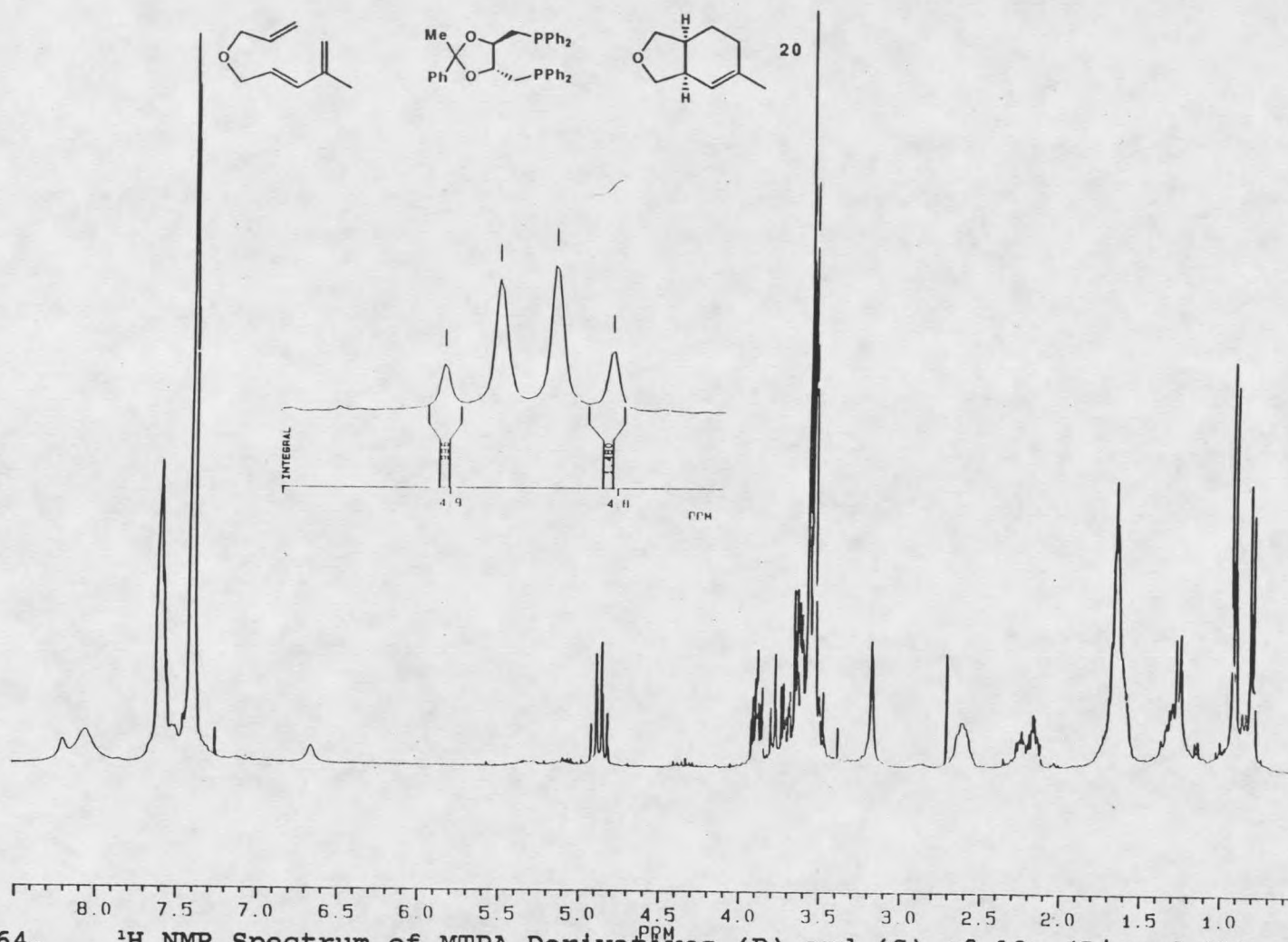


Figure 164. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3b)

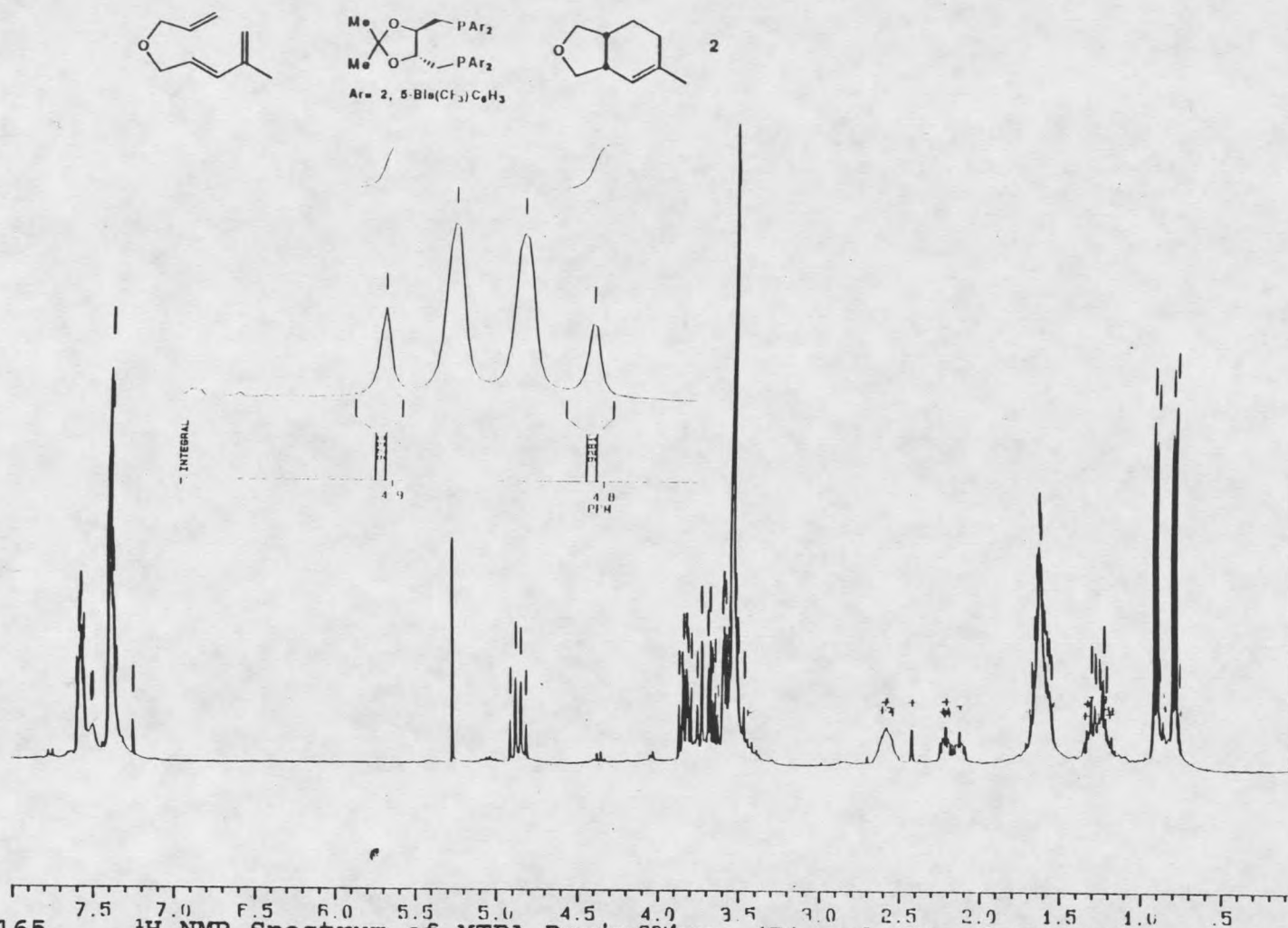


Figure 165. ¹H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3c)

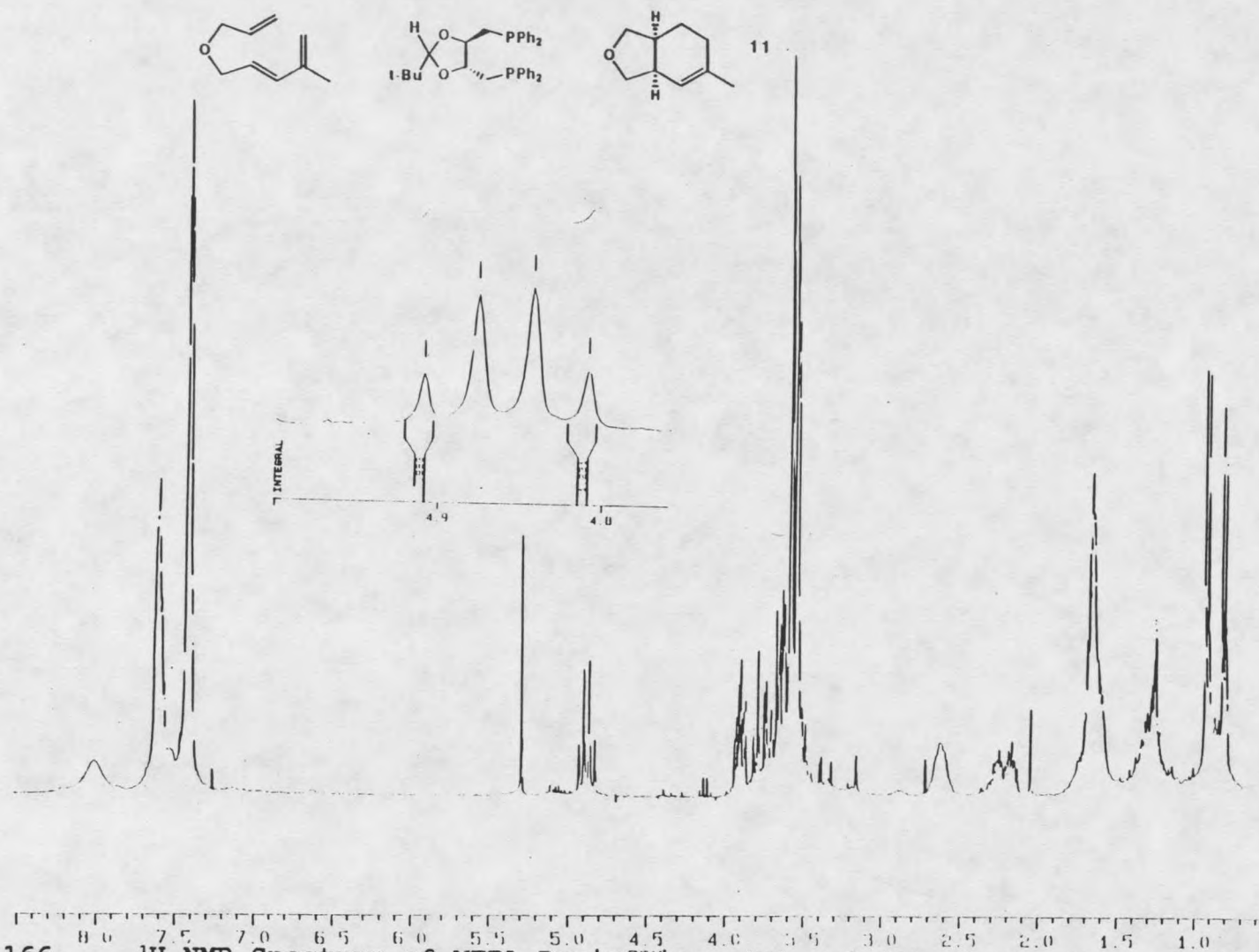


Figure 166. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3d)

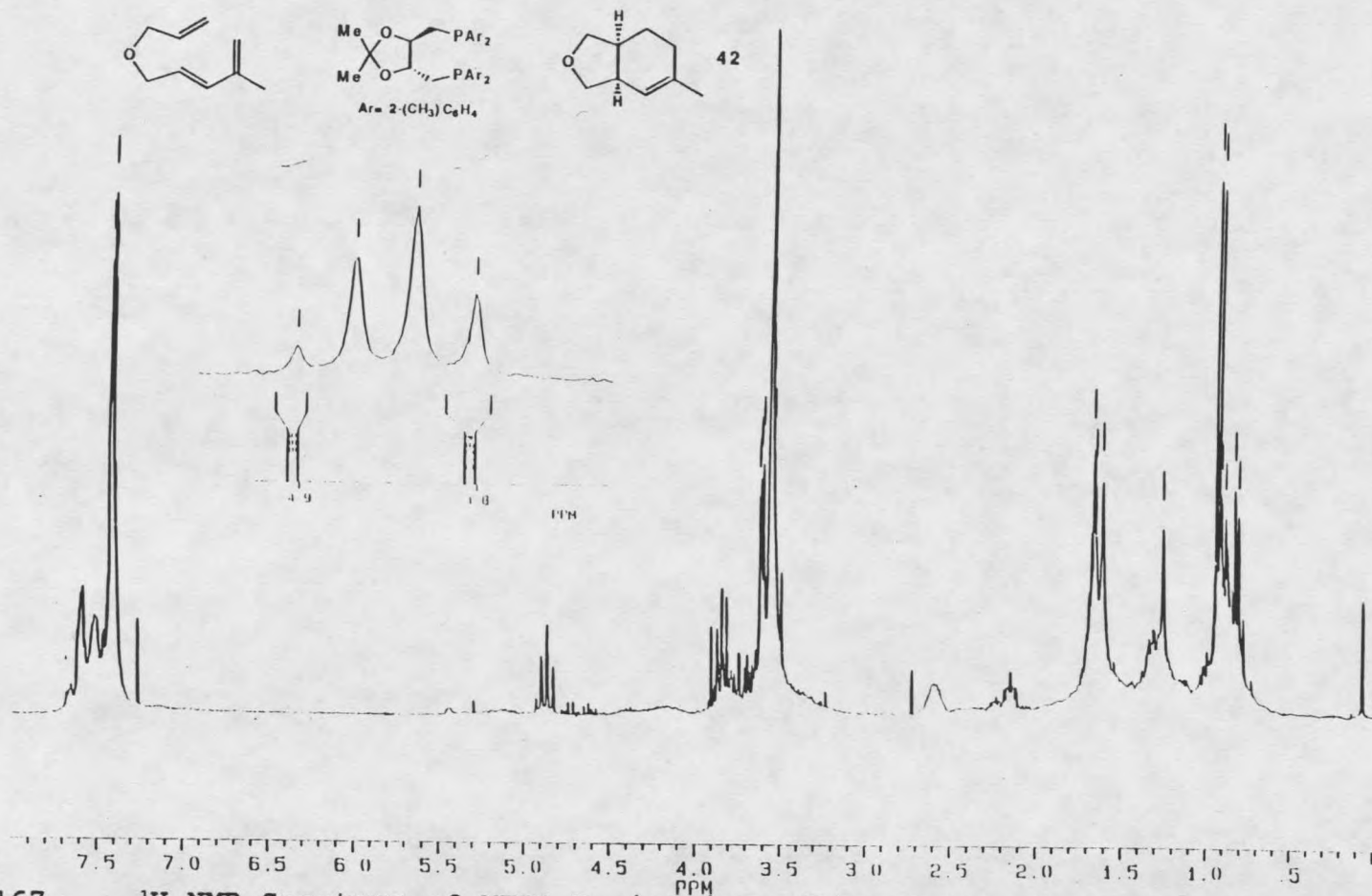


Figure 167. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3e)

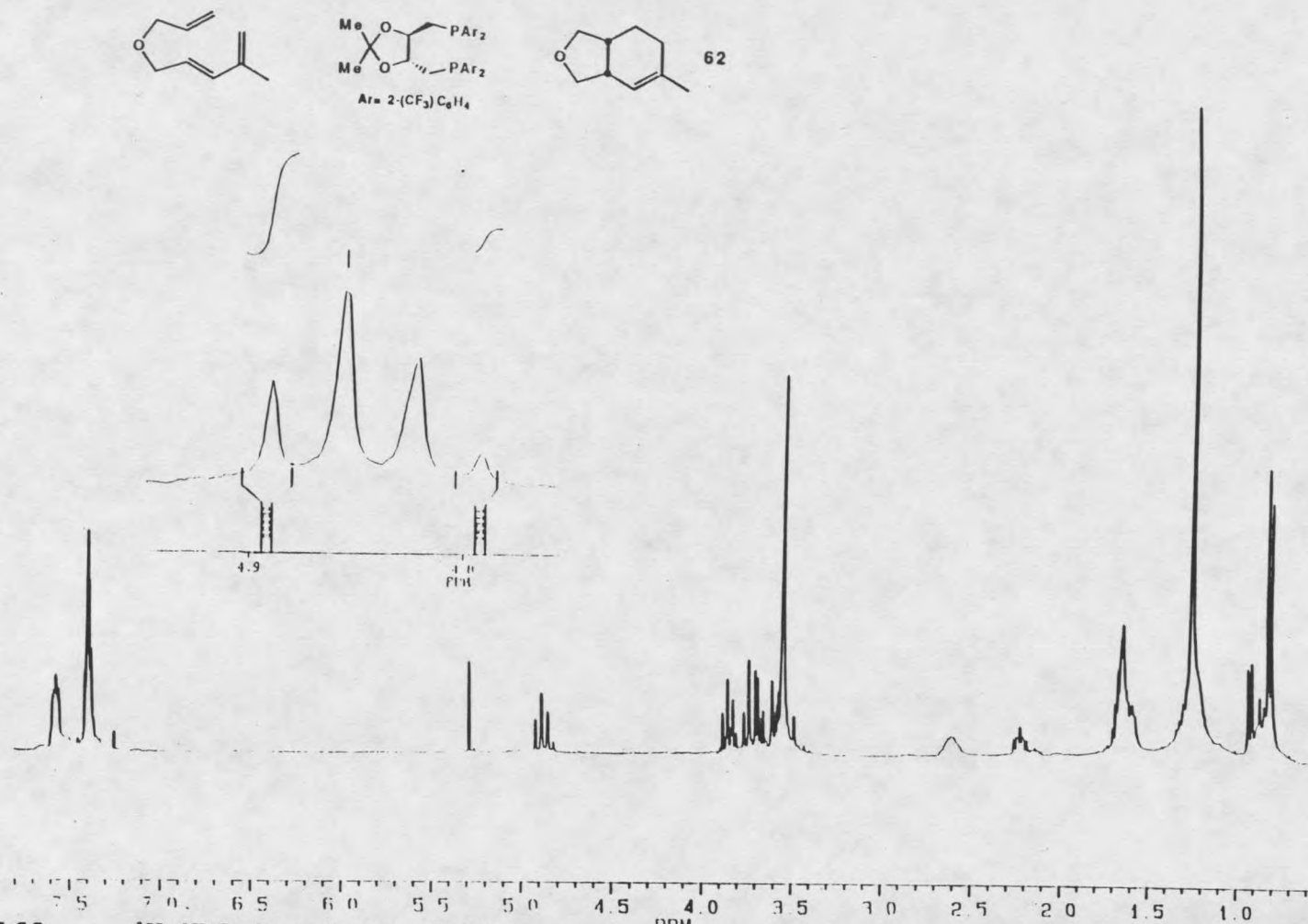


Figure 168. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3f)

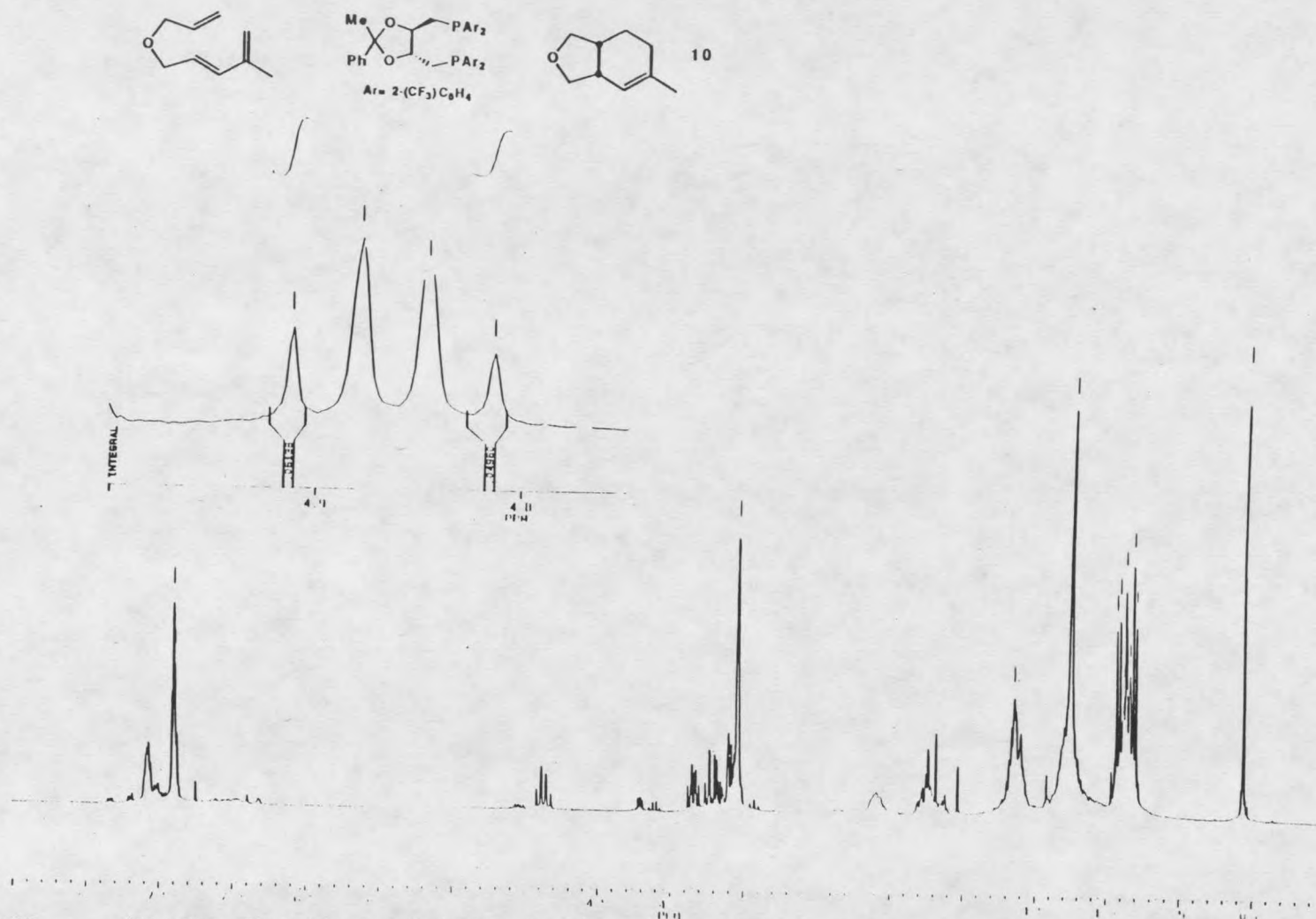


Figure 169. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 3g)

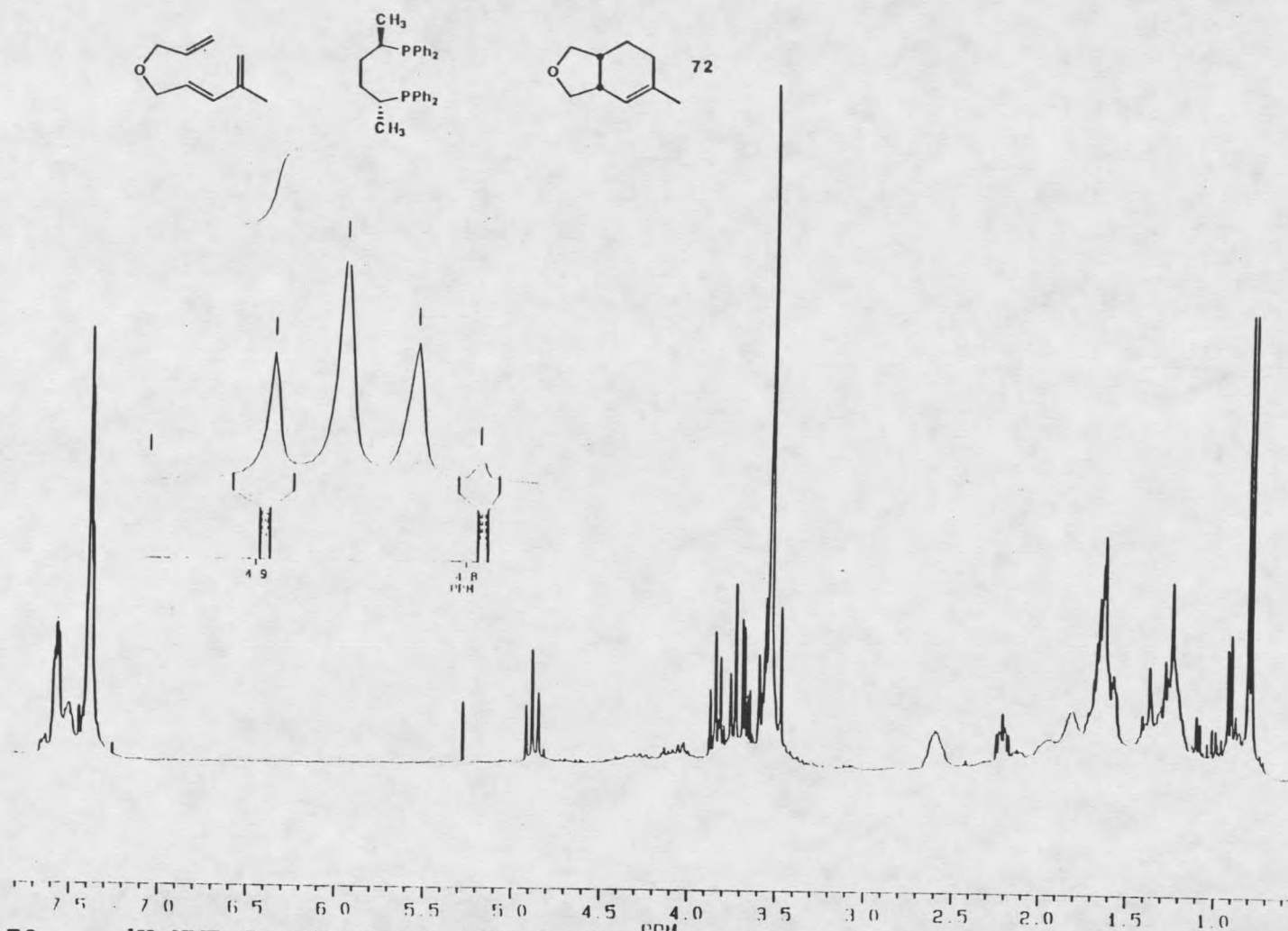


Figure 170. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13a (Ligand 21b)

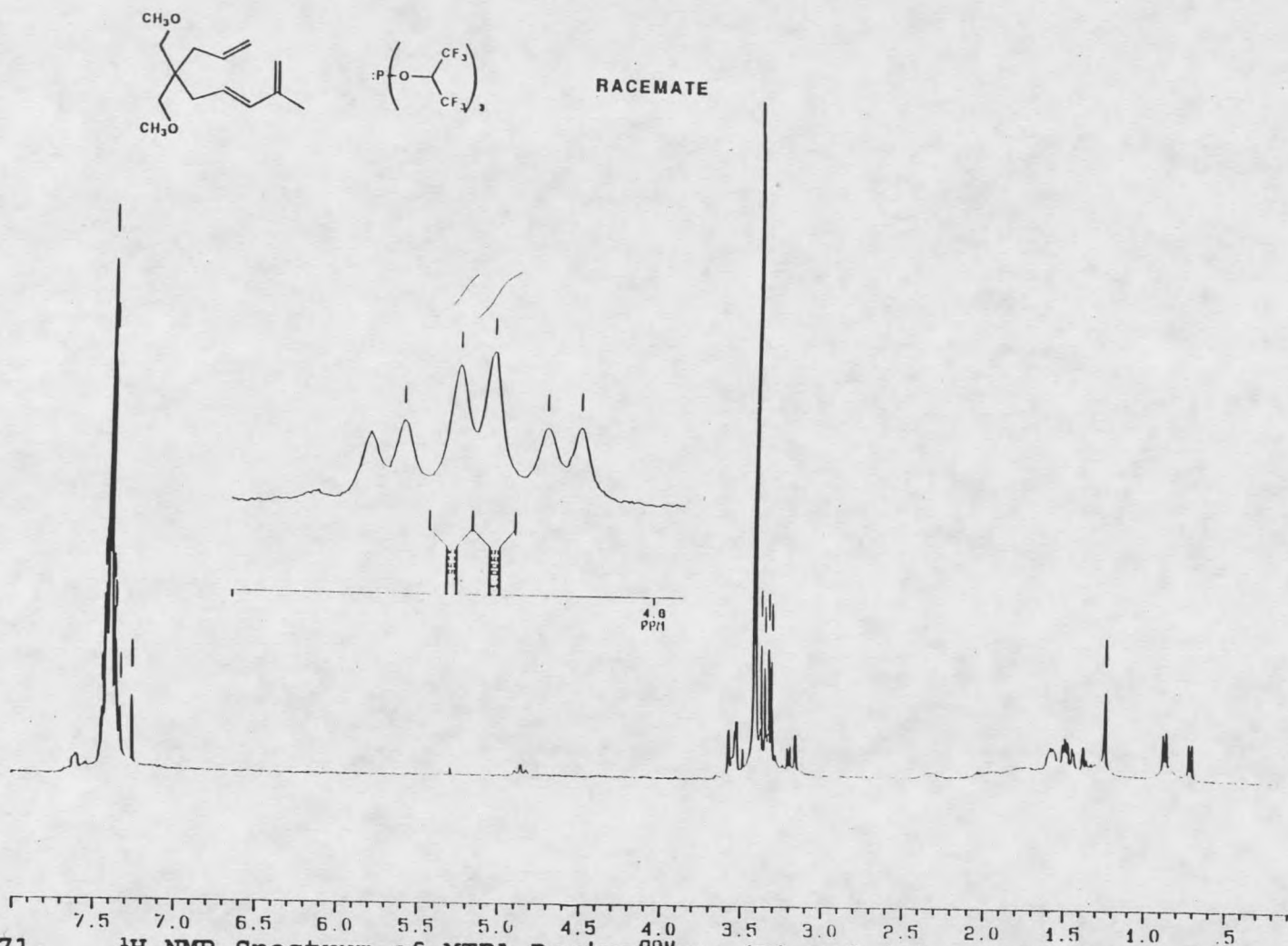


Figure 171. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13b (Racemate)

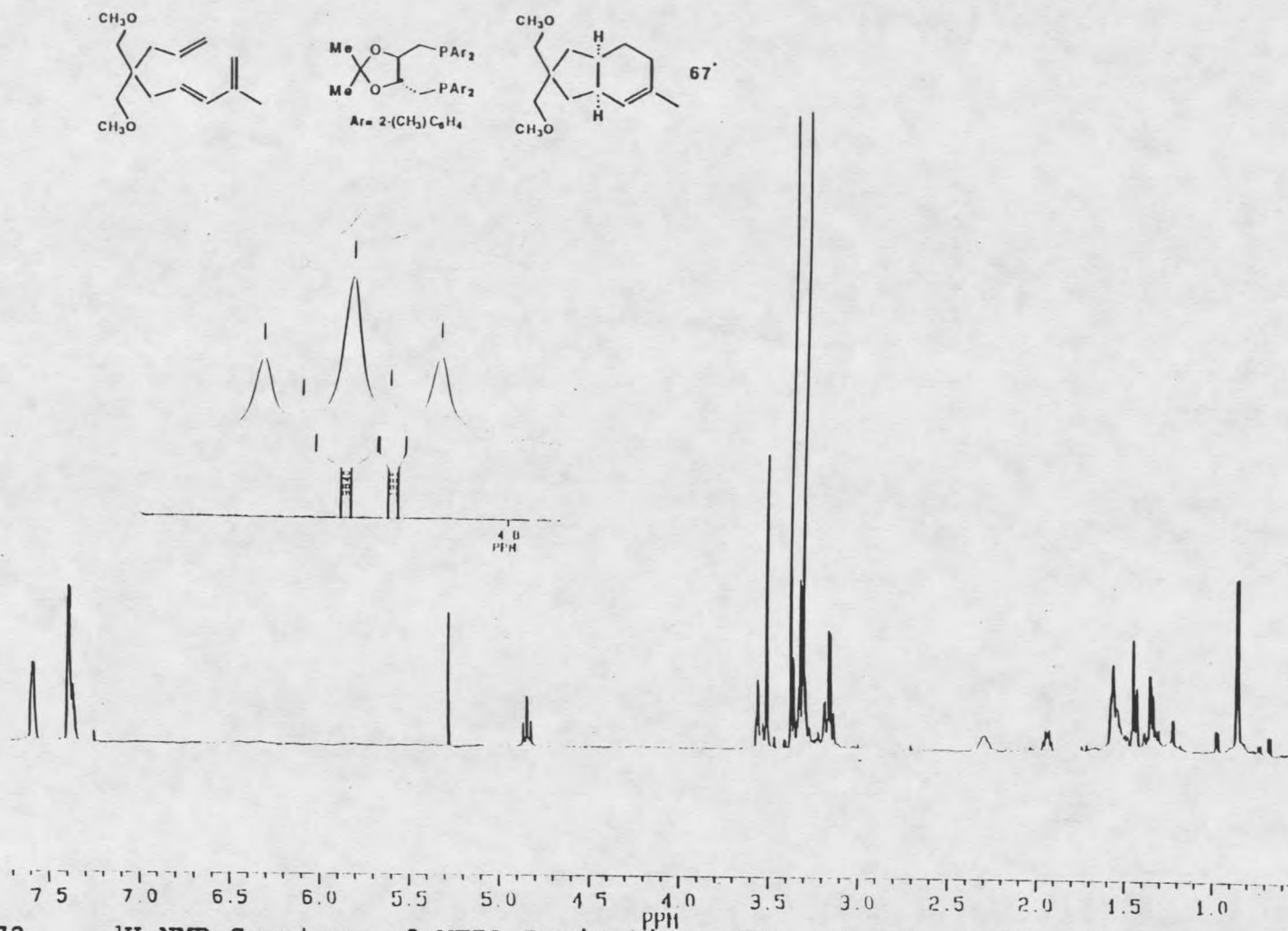


Figure 173. ^{1}H NMR Spectrum of MTPA Derivatives (R) and (S) of 13b (Ligand 3e)

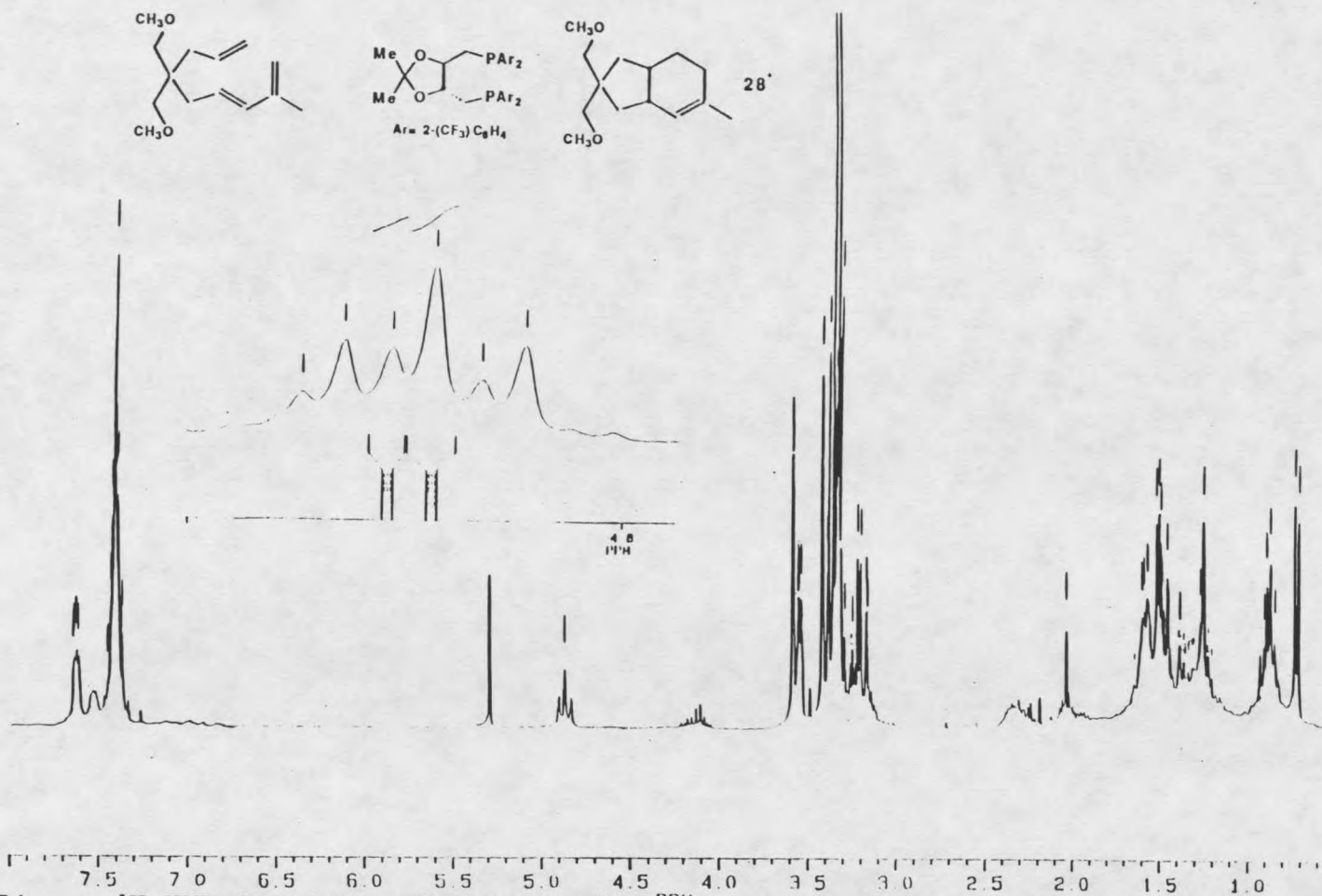


Figure 174. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13b (Ligand 3f)

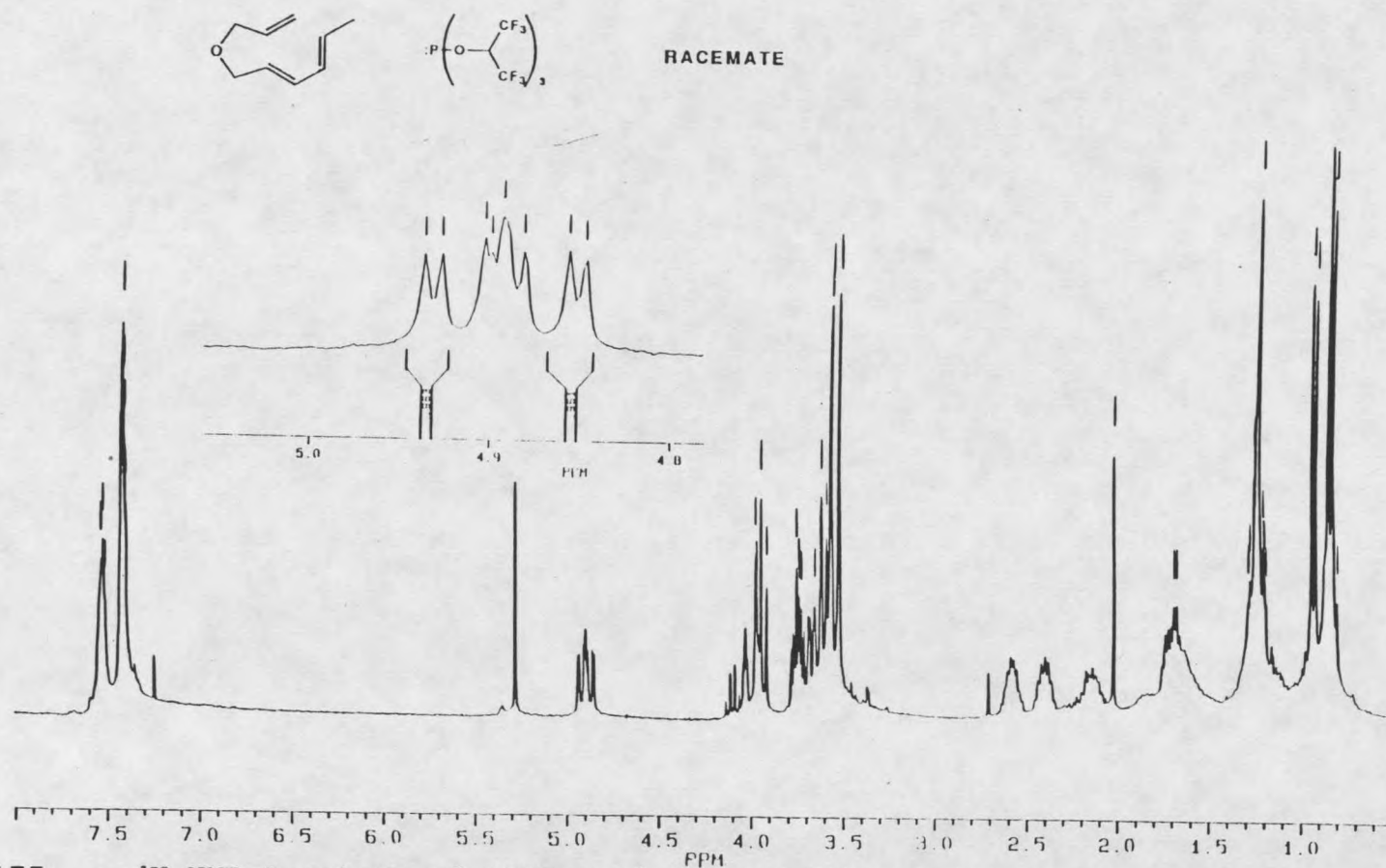


Figure 175. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13c (Racemate)

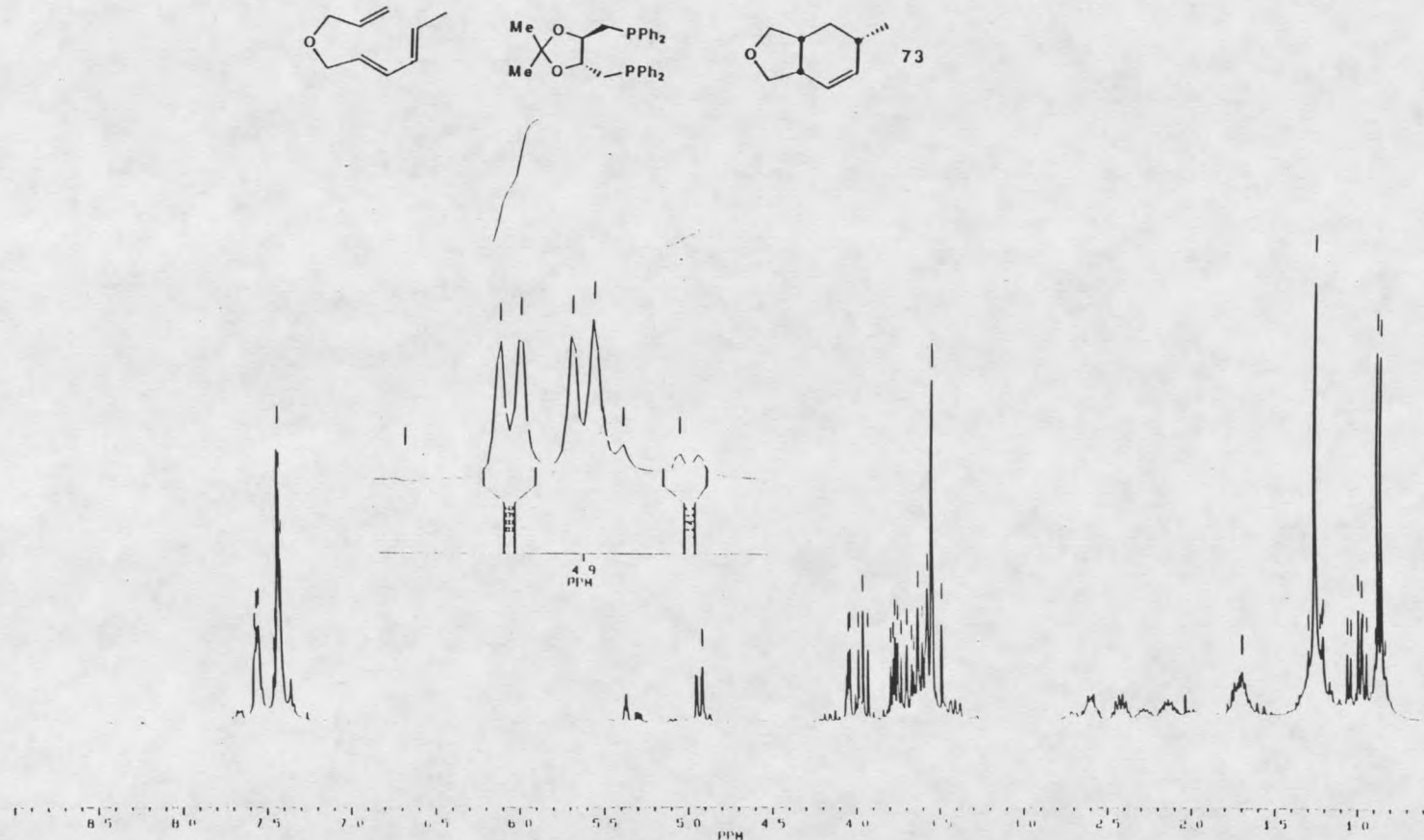


Figure 176. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13c (Ligand 3a)

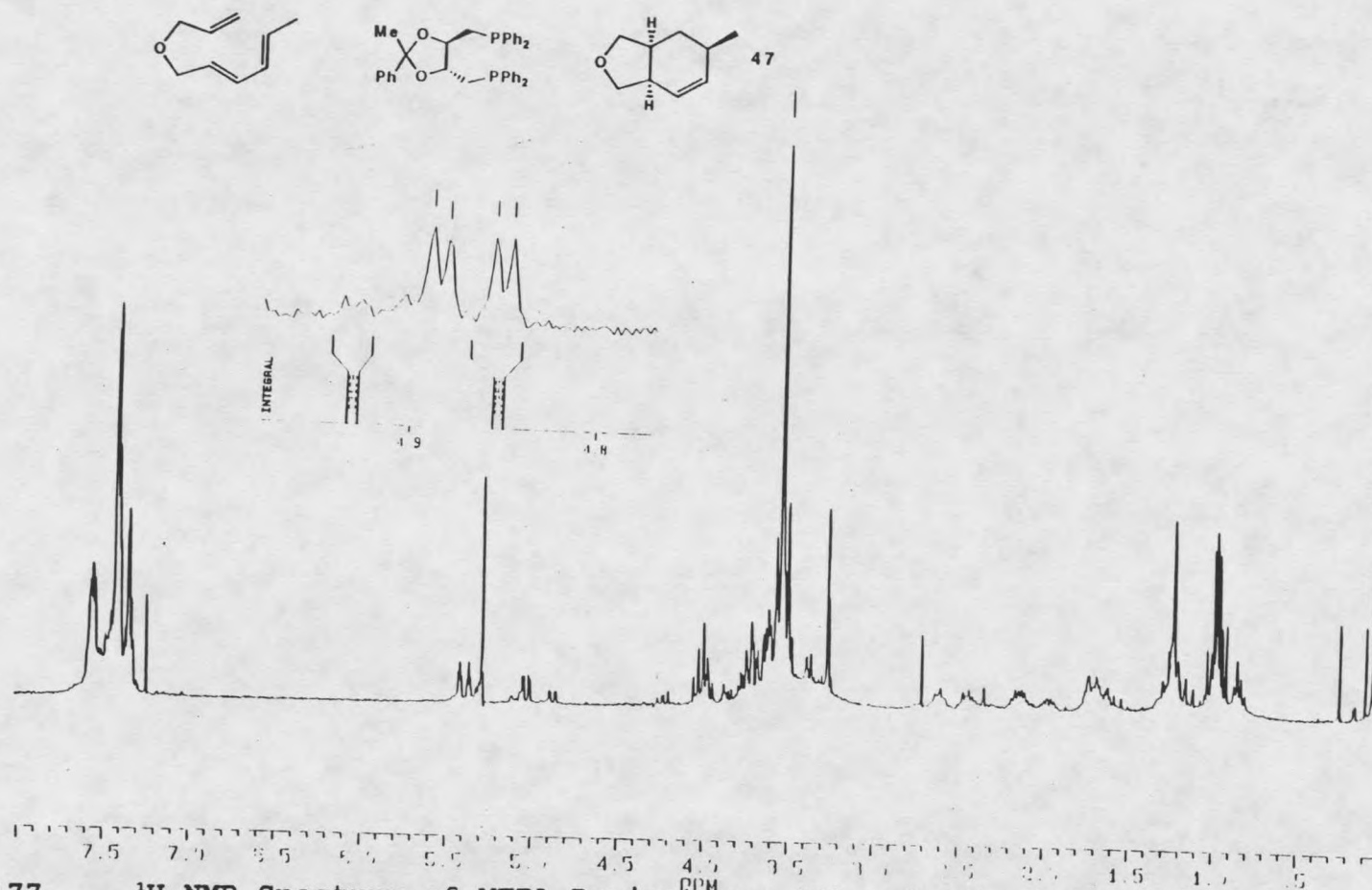


Figure 177. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13c (Ligand 3b)

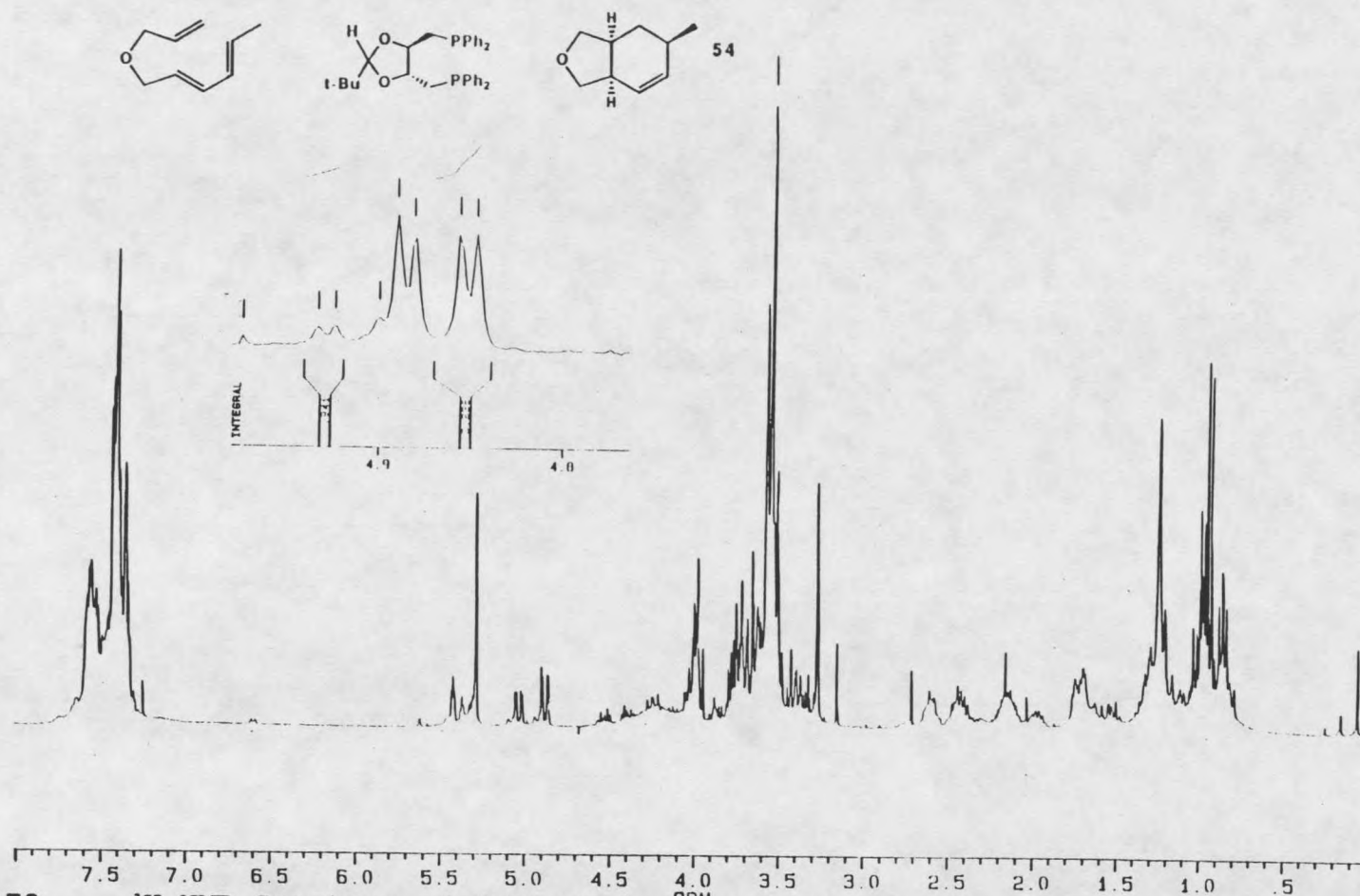


Figure 178. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13c (Ligand 3c)

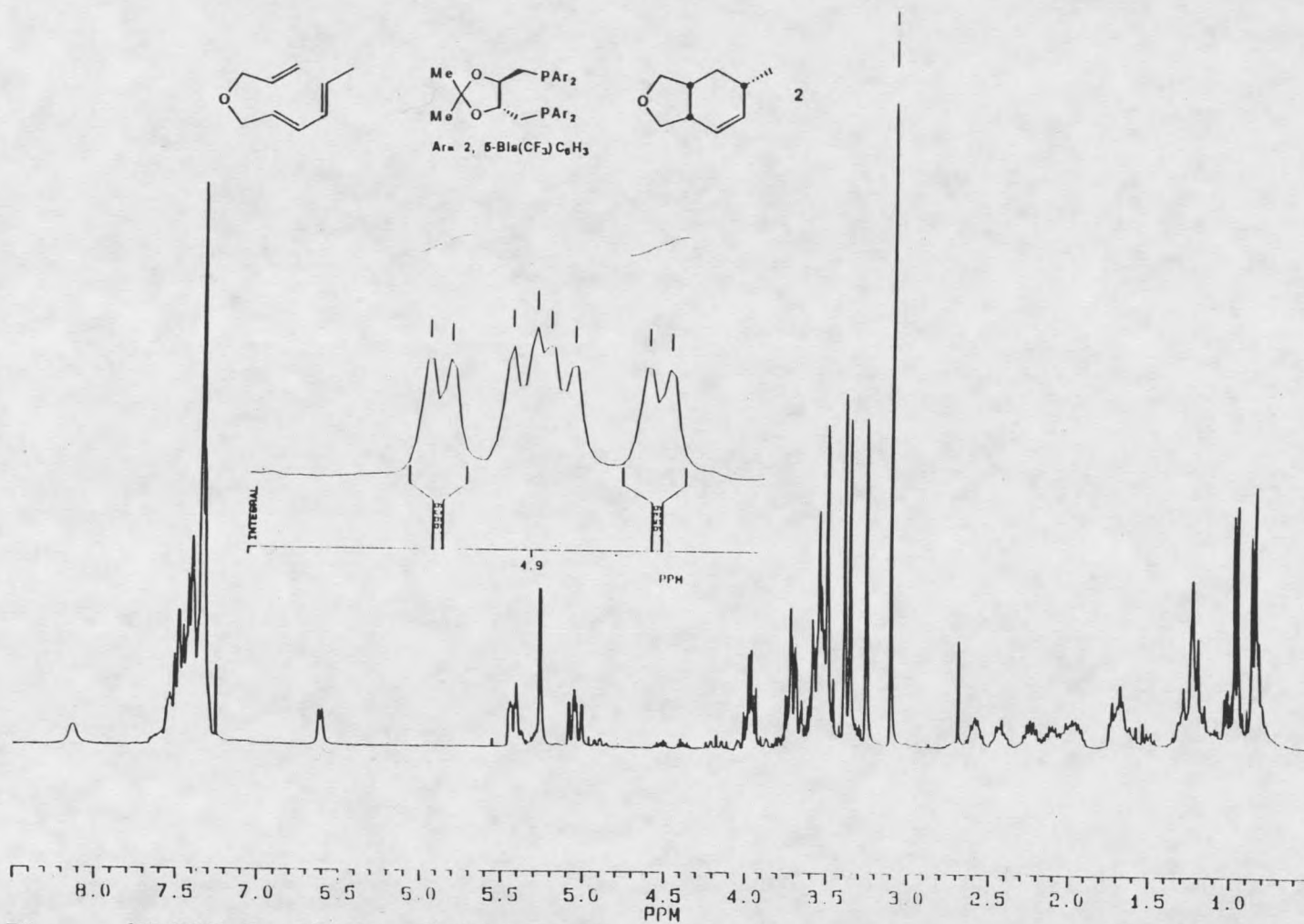


Figure 179. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 13c (Ligand 3d)

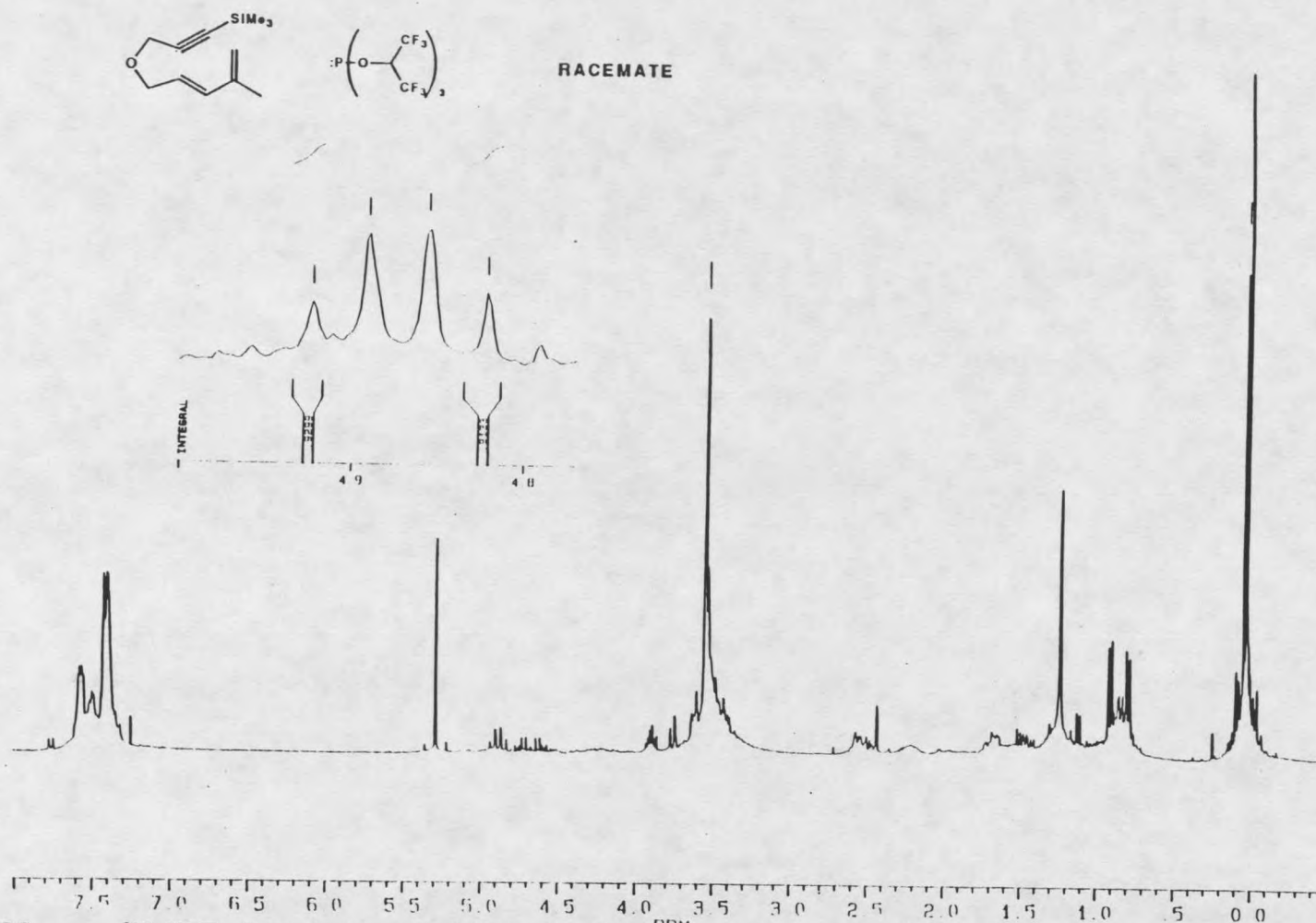


Figure 180. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Racemate)

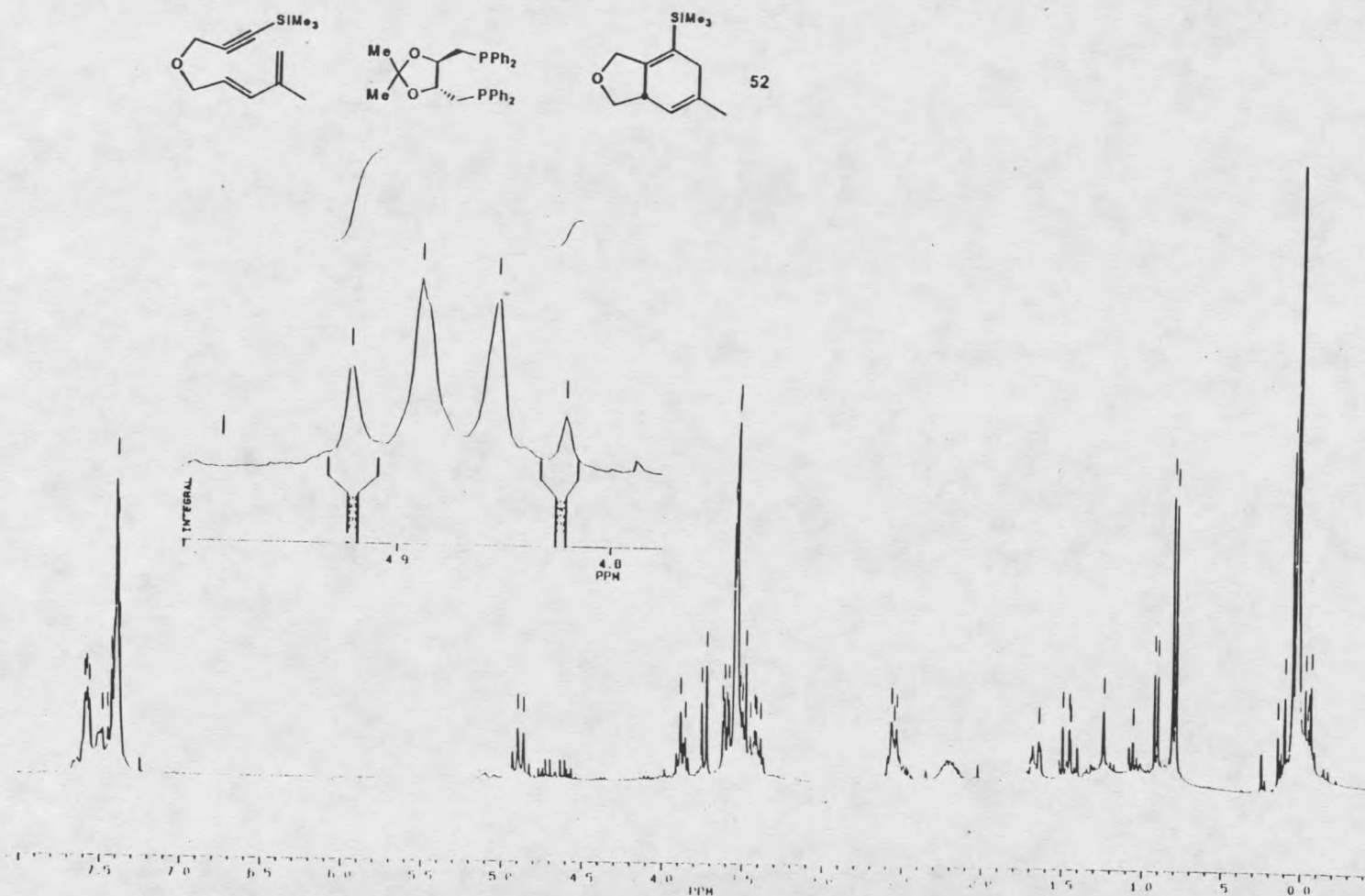


Figure 181. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Ligand 3a)

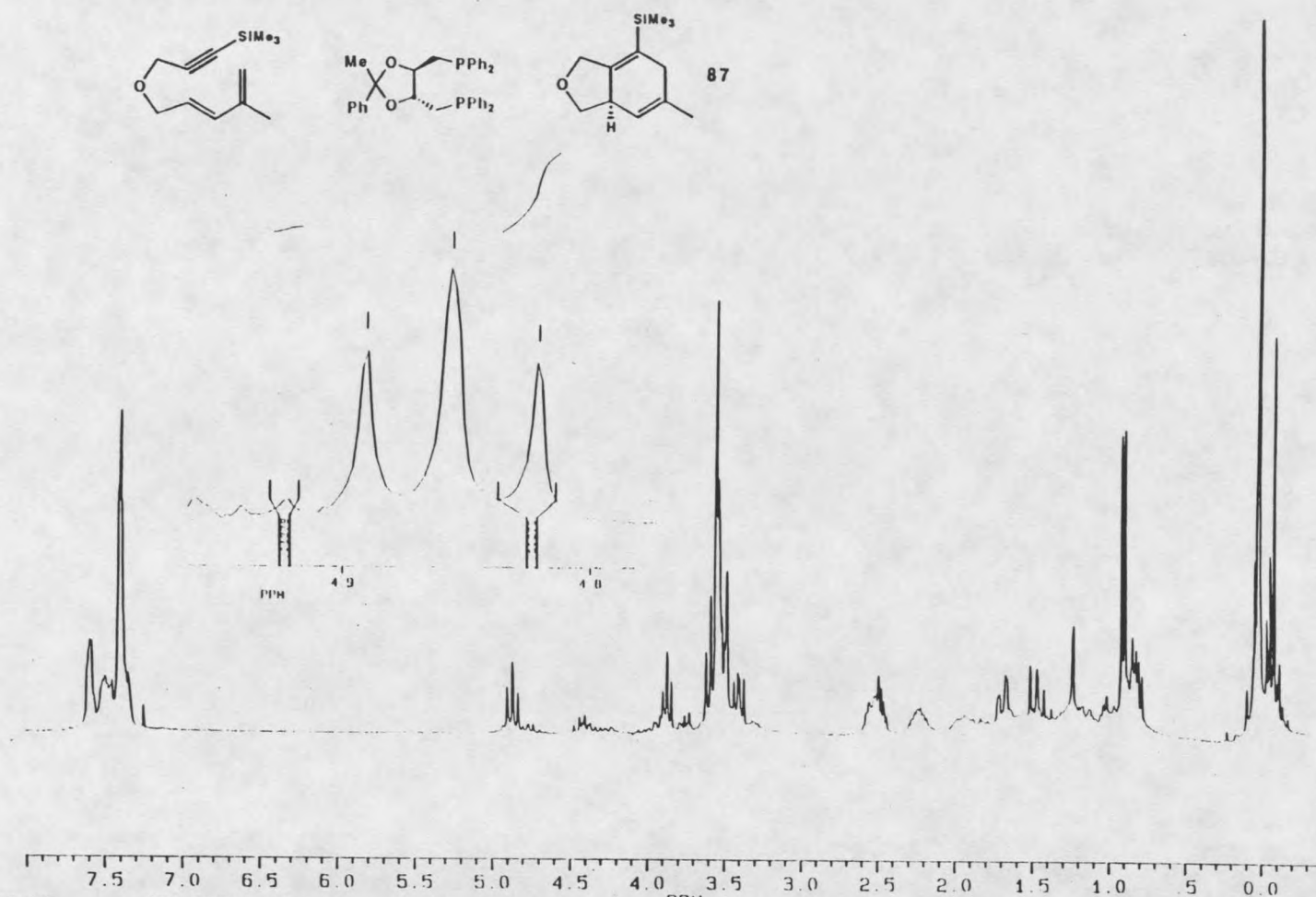


Figure 182. ¹H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Ligand 3b)

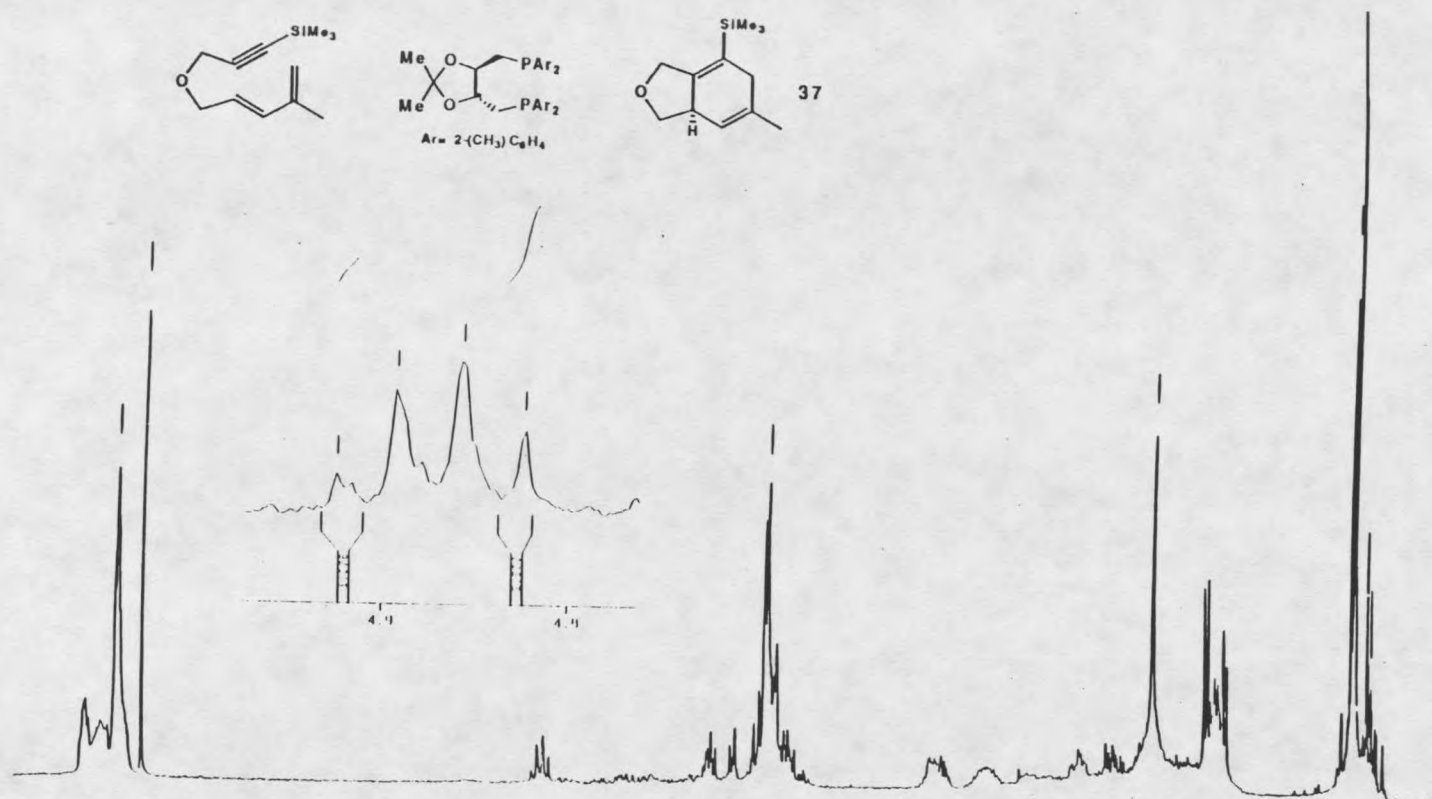


Figure 183. ¹H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Ligand 3e)

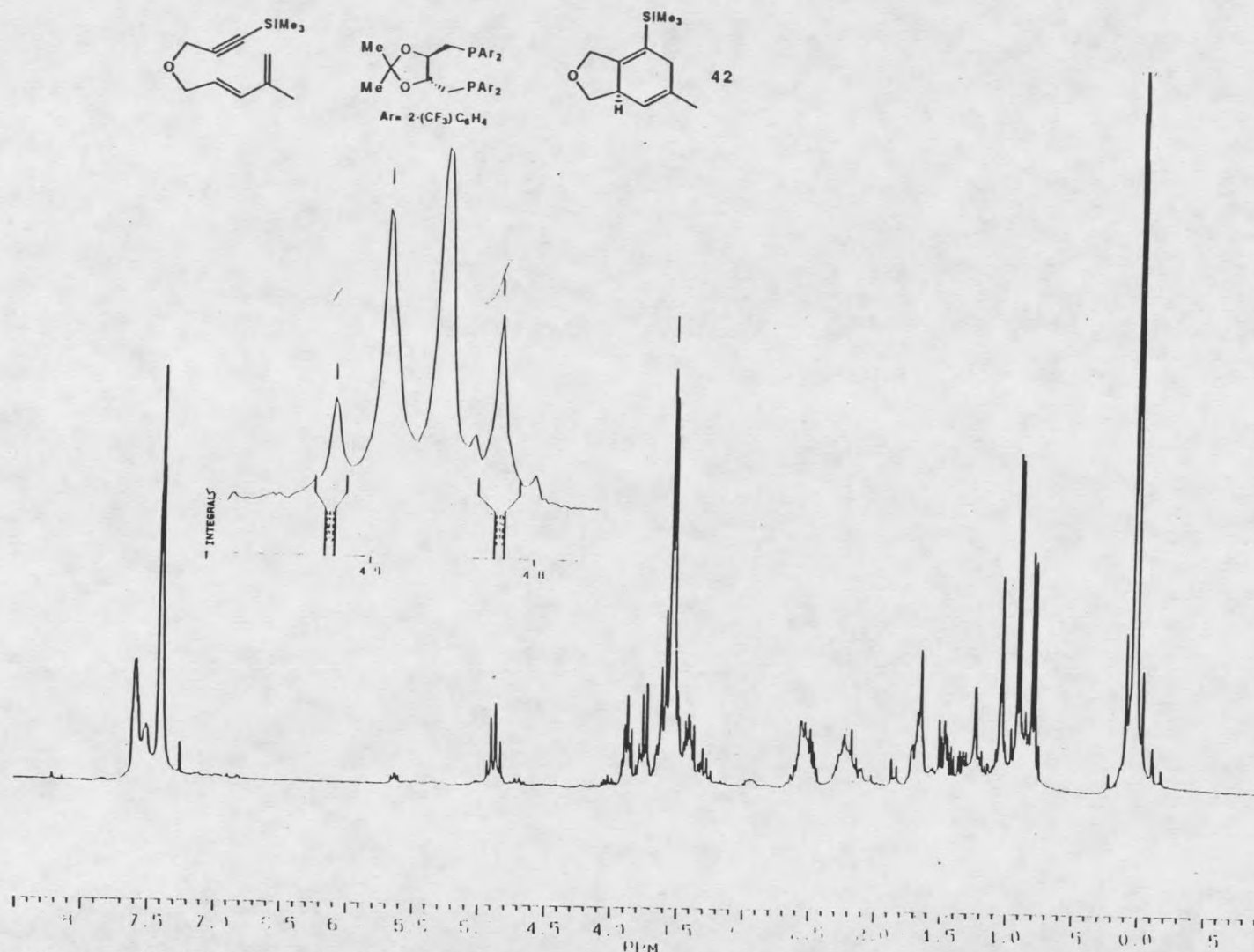


Figure 184. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Ligand 3f)

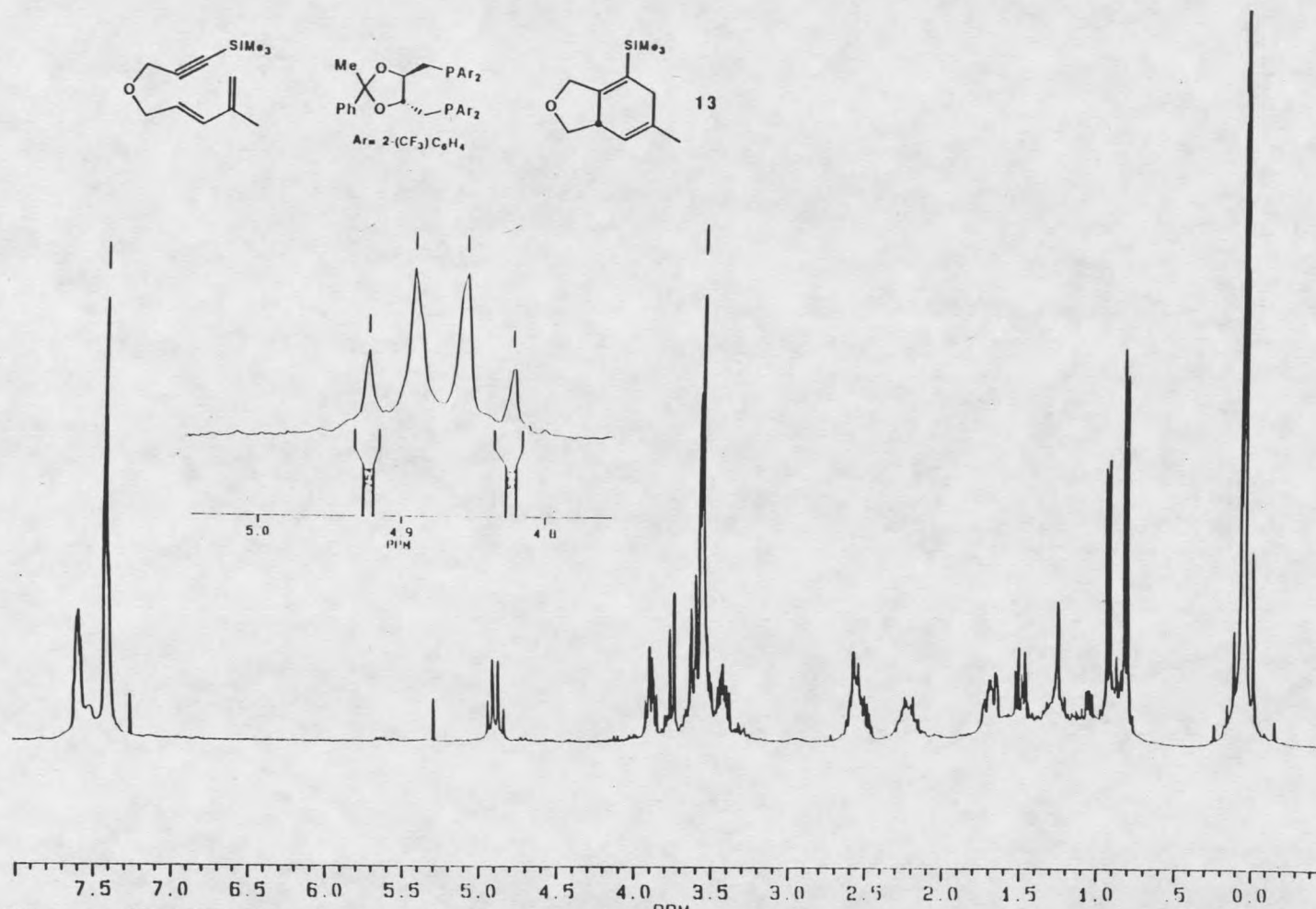
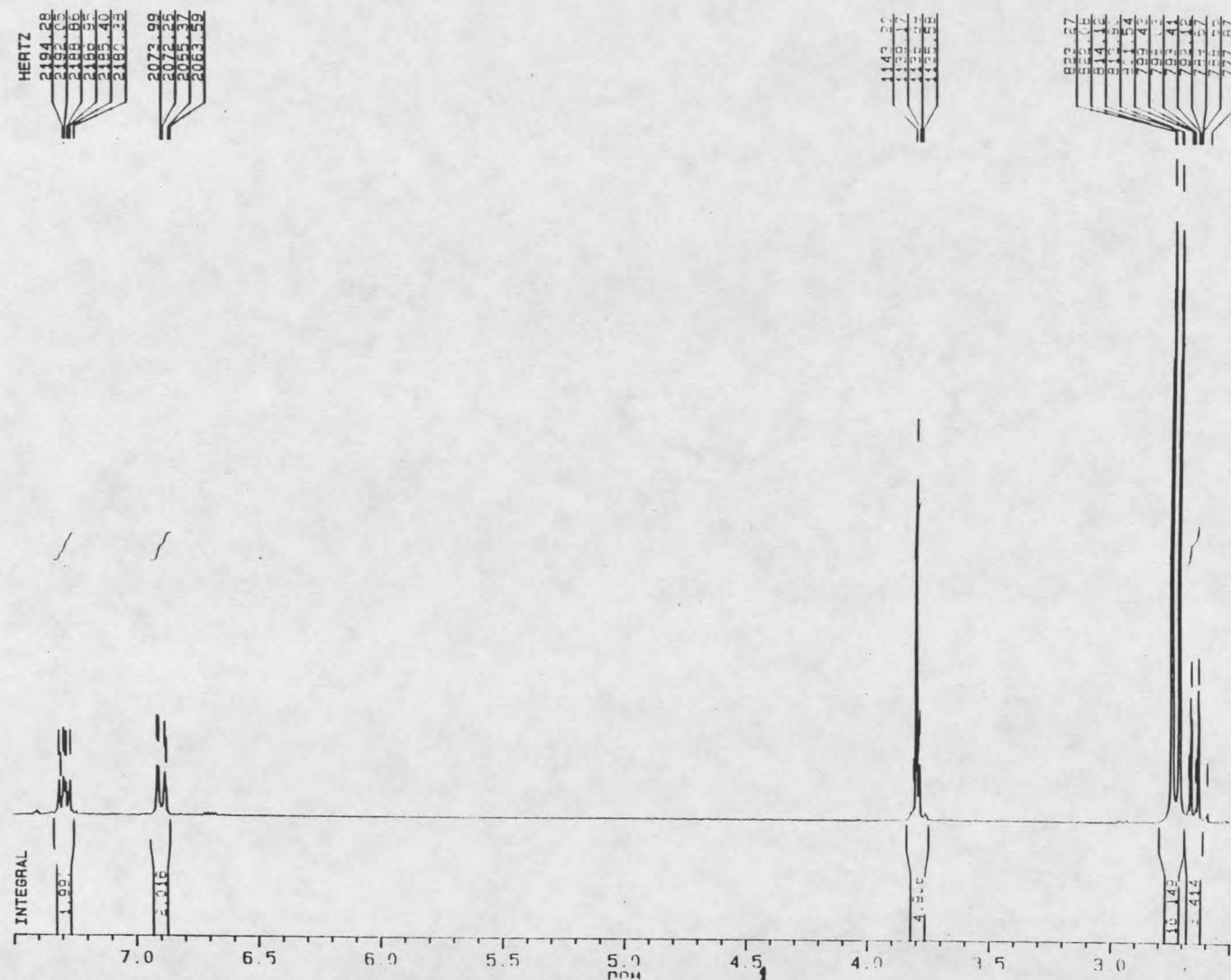


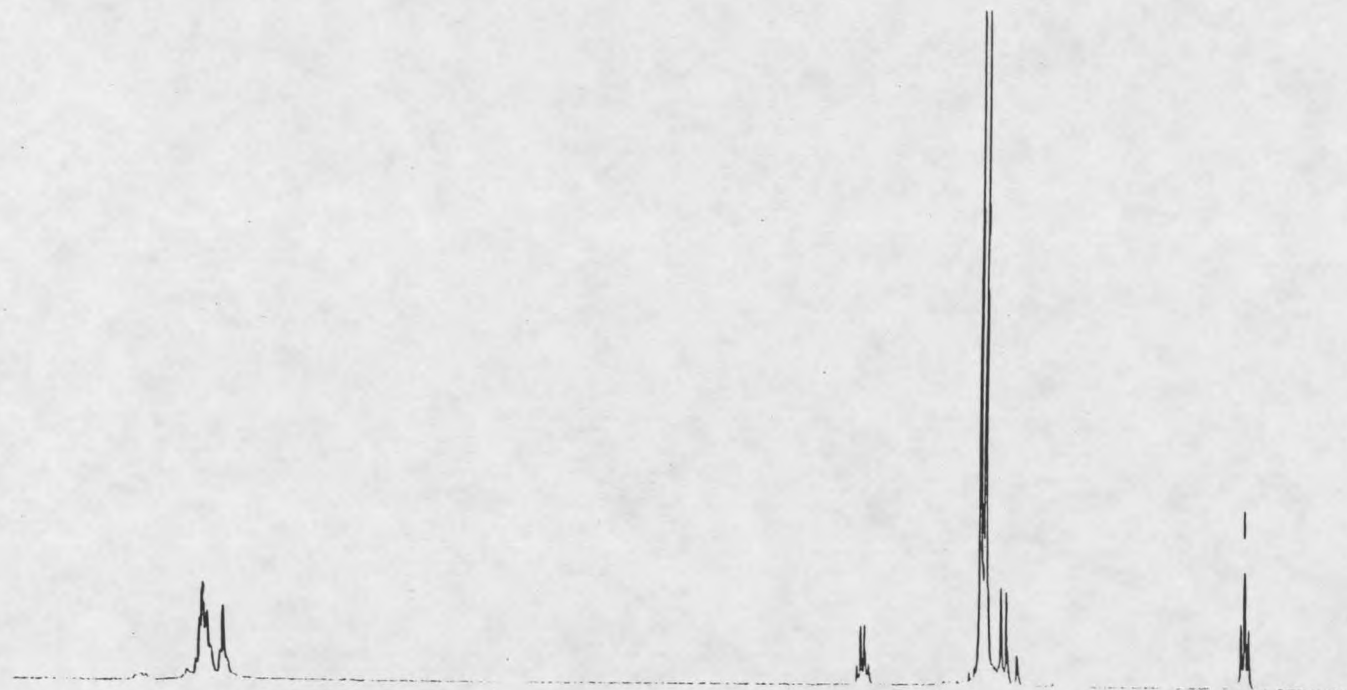
Figure 185. ^1H NMR Spectrum of MTPA Derivatives (R) and (S) of 14 (Ligand 3g)



HERTZ

47.2
47.1
47.0
46.9
46.8
46.7
46.6
46.5
46.4
46.3
46.2
46.1
46.0

150.952



315

Figure 188. ^1H NMR Spectrum of Bis(dimethylamino)phenyl phosphine (39c)

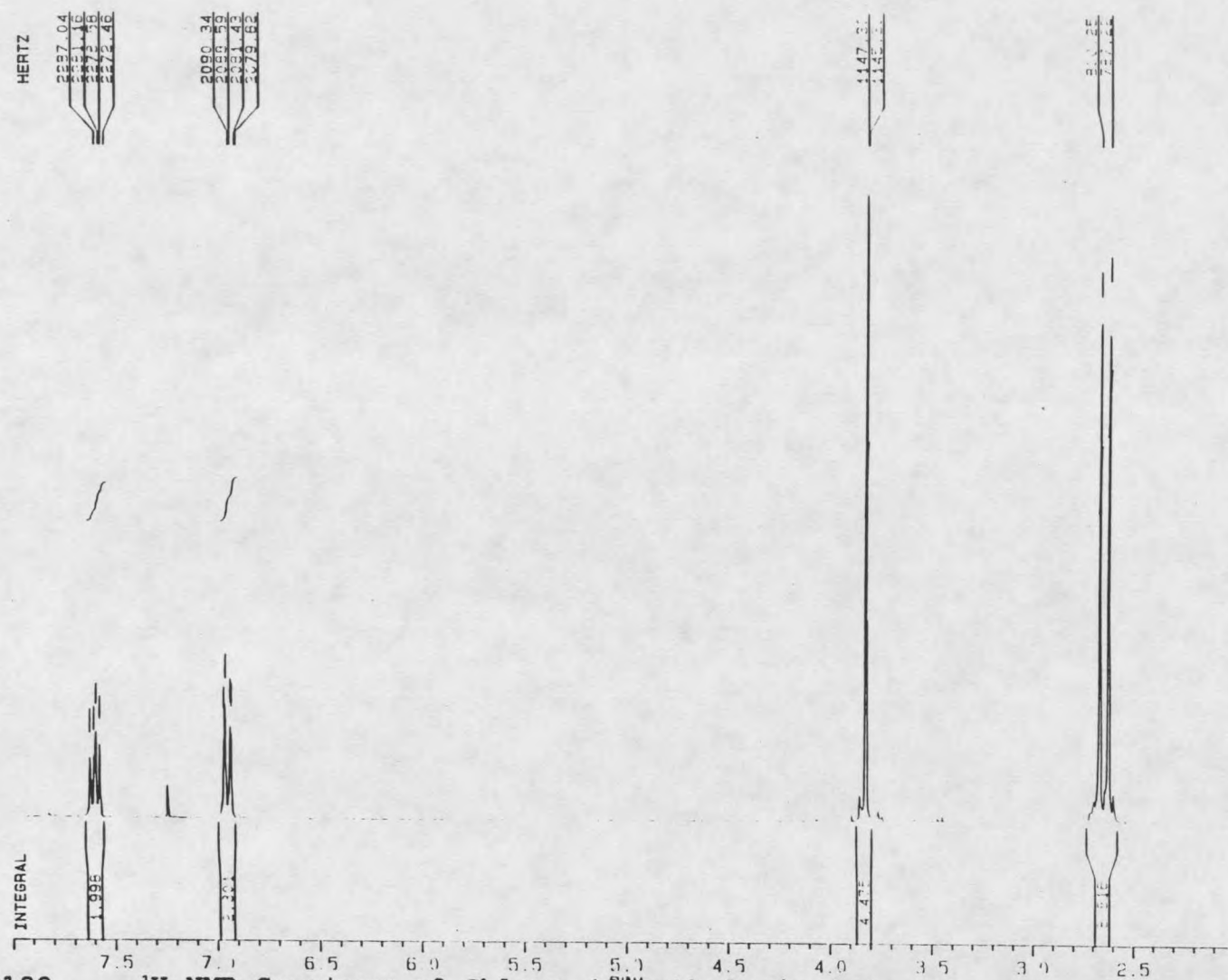


Figure 189. ^1H NMR Spectrum of Chloro-(dimethylamino)-4-methoxyphenyl phosphine (40a)

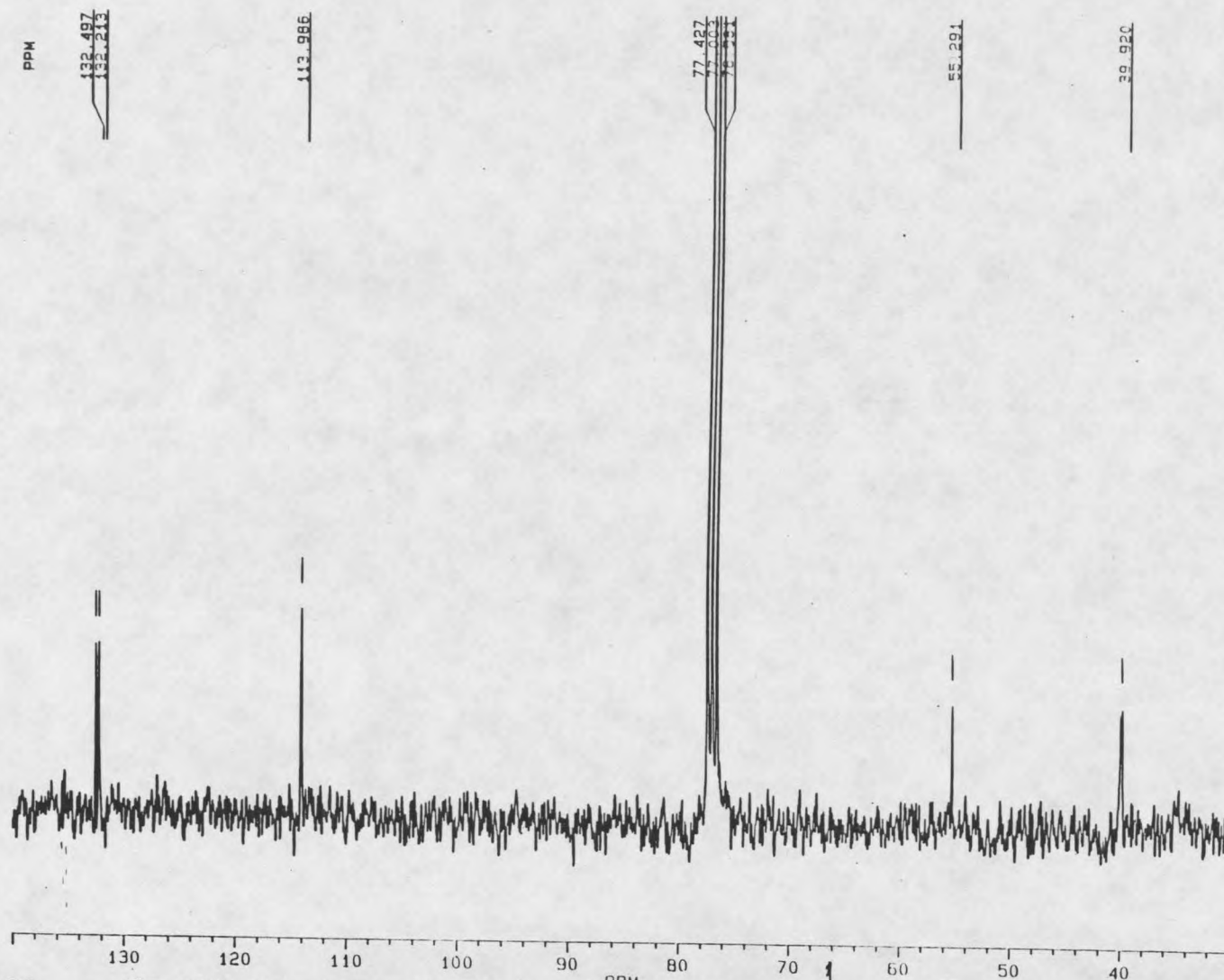


Figure 190. ^{13}C NMR Spectrum of Chloro-(dimethylamino)-4-methoxyphenyl phosphine (40a)

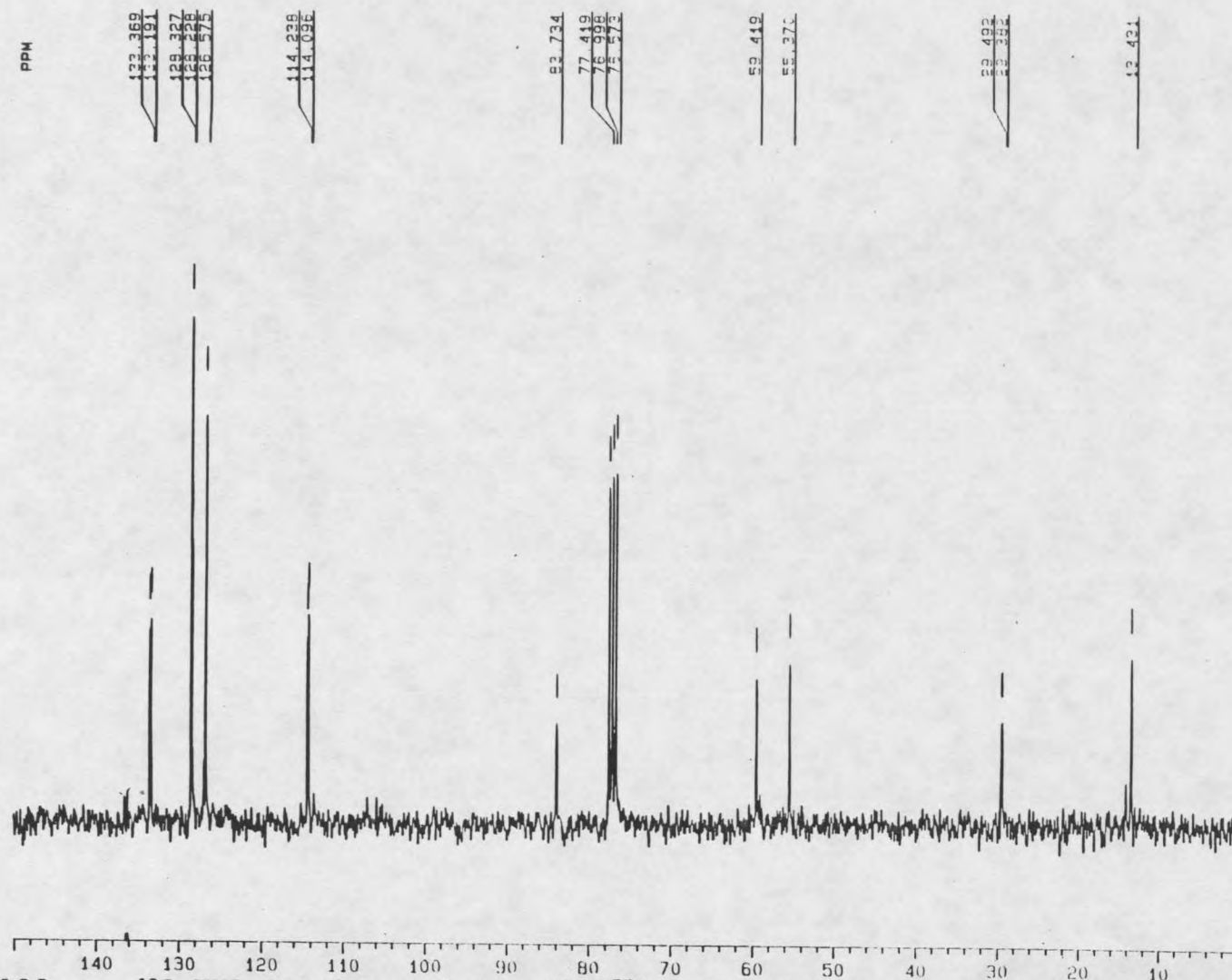


Figure 192. ^{13}C NMR Spectrum of $(2R,4S,5R)$ -2-(4-methoxyphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38a)

HERTZ

132.382
132.382
132.382
132.382

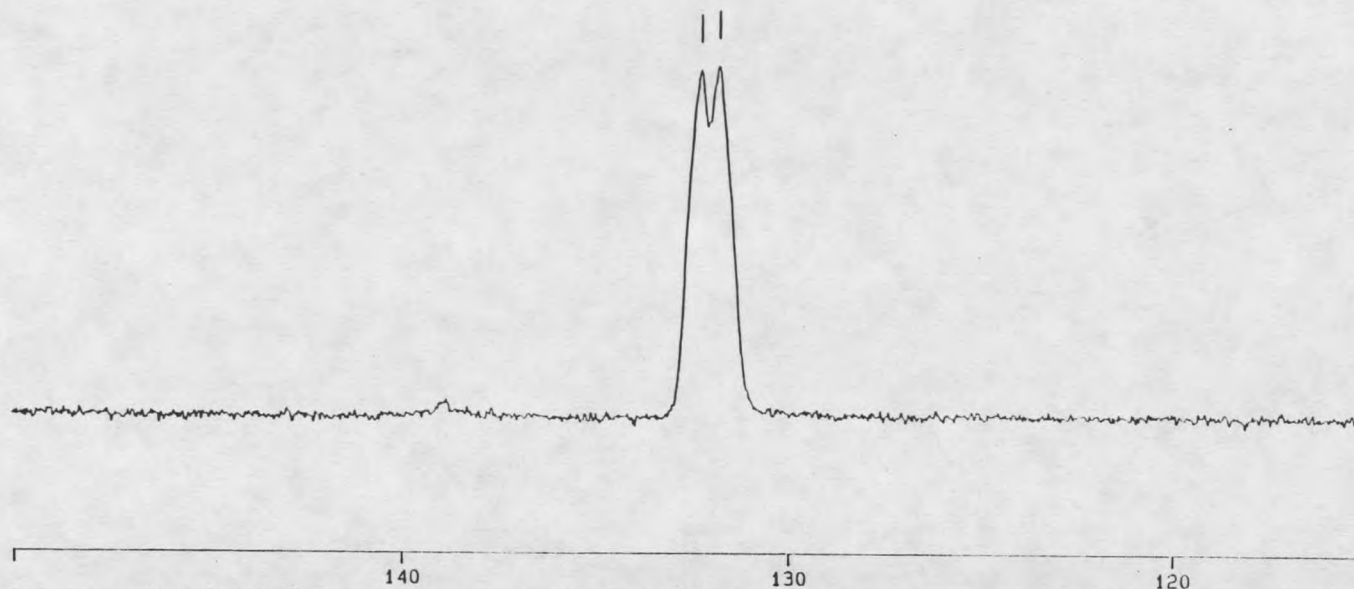


Figure 193.

^{31}P NMR Spectrum of (2R,4S,5R)-2-(4-methoxyphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38a)

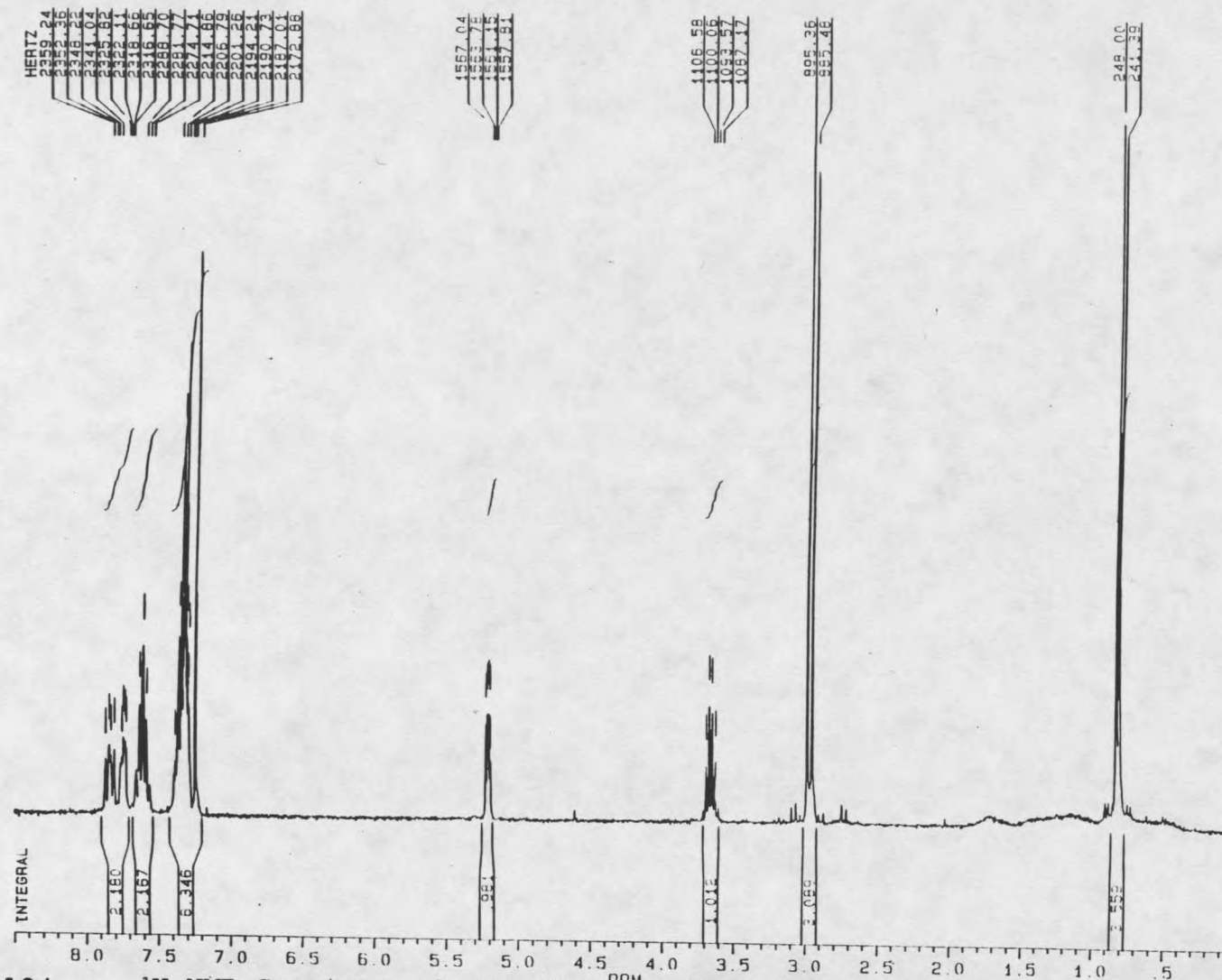


Figure 194. ^1H NMR Spectrum of (2R,4S,5R)-2-(2-Trifluoromethylphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38b)

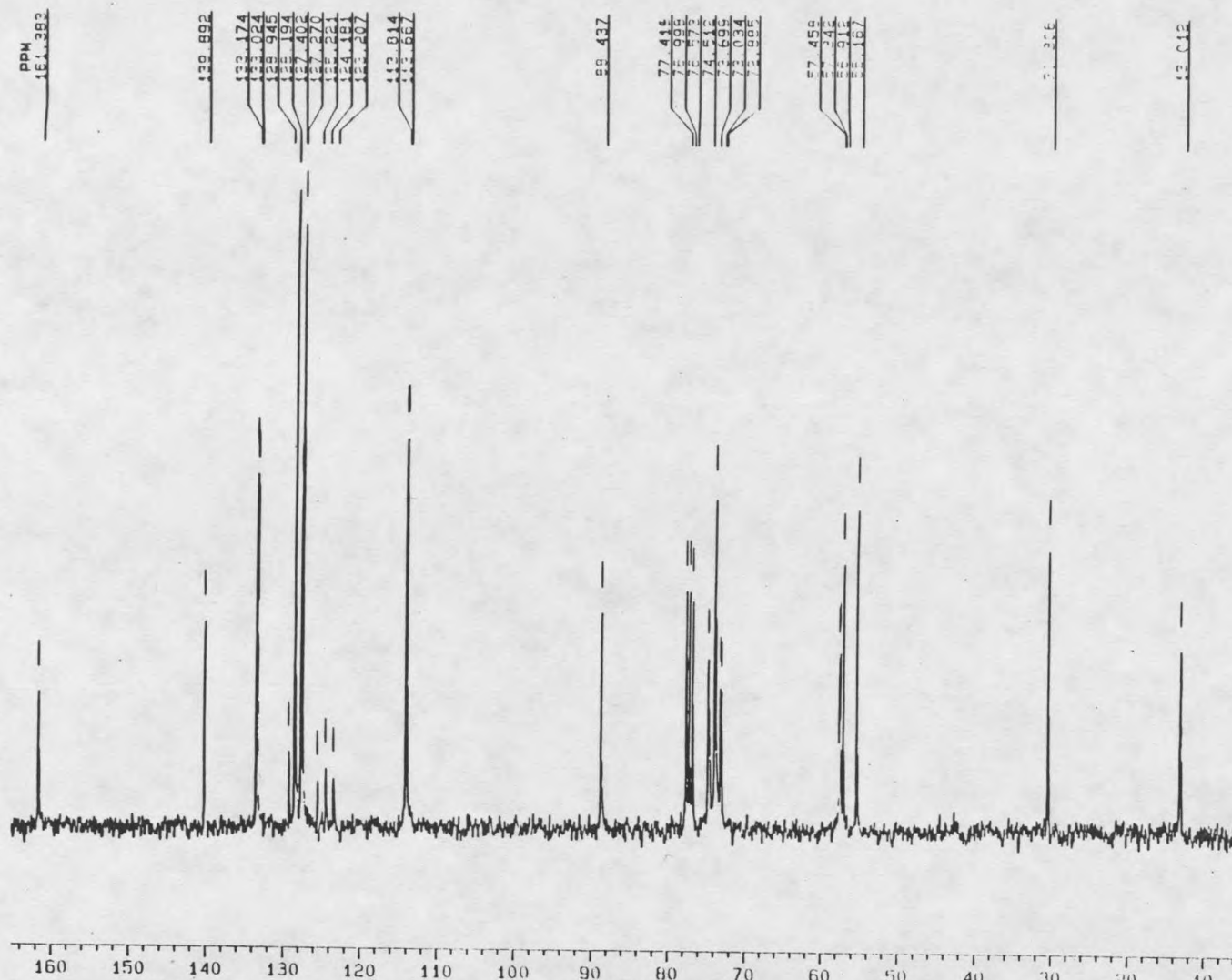


Figure 195. ^{13}C NMR Spectrum of (2R,4S,5R)-2-(2-Trifluoromethylphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38b)

HERTZ

1
2
3
4
5
6
7
8
9
10
11
12

323

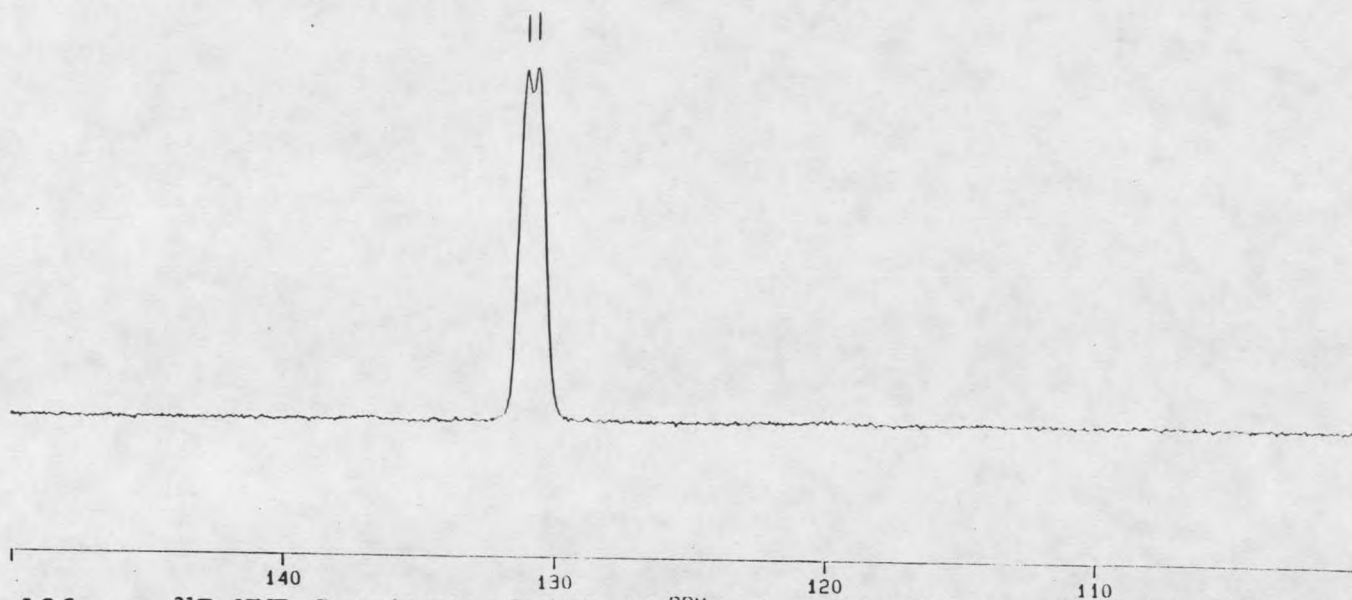


Figure 196. ^{31}P NMR Spectrum of (2R,4S,5R)-2-(2-Trifluoromethylphenyl)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (38b)

ppm

67.595

325



Figure 198.

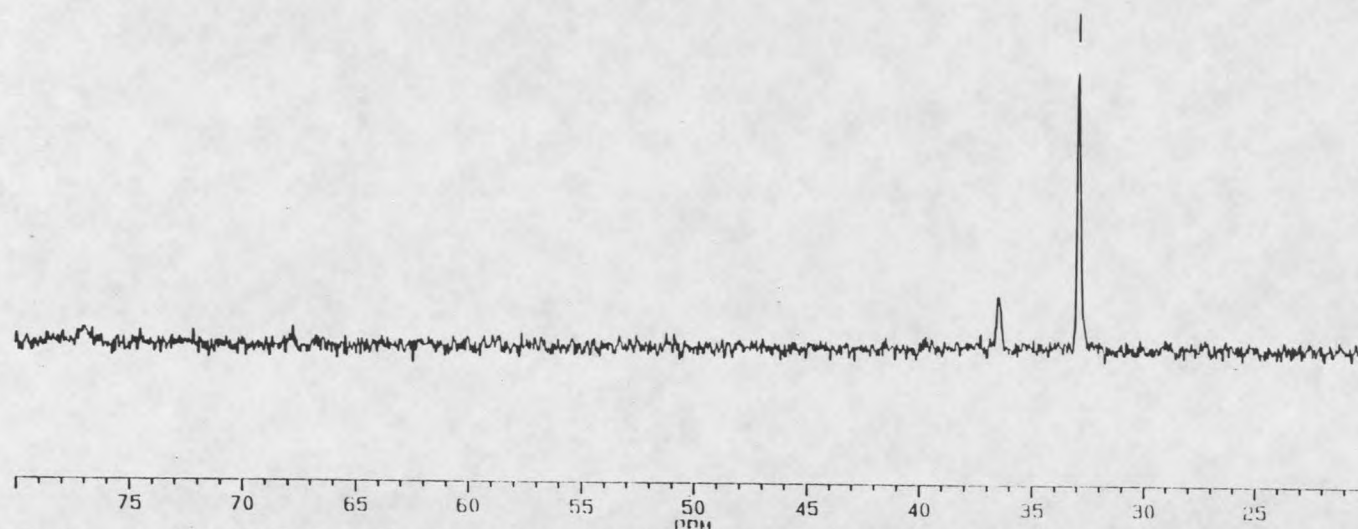
³¹P NMR Spectrum of 1-(Tri-*n*-butylstannyl)-1'-[(*Rp*)-N-methyl,N-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxyphenyl)phosphino]ferrocene (42a)



Figure 199. ¹H NMR Spectrum of 1-(Tri-n-butylstannyl)-1'-[(Rp(-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-trifluoromethylphenyl)phosphino)]ferrocene (42b)

ppm

152.823



327

Figure 200. ^{31}P NMR Spectrum of 1-(Tri-n-butylstannyl)-1'-[(Rp(-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-trifluoromethylphenyl)phosphino]ferrocene (42b)

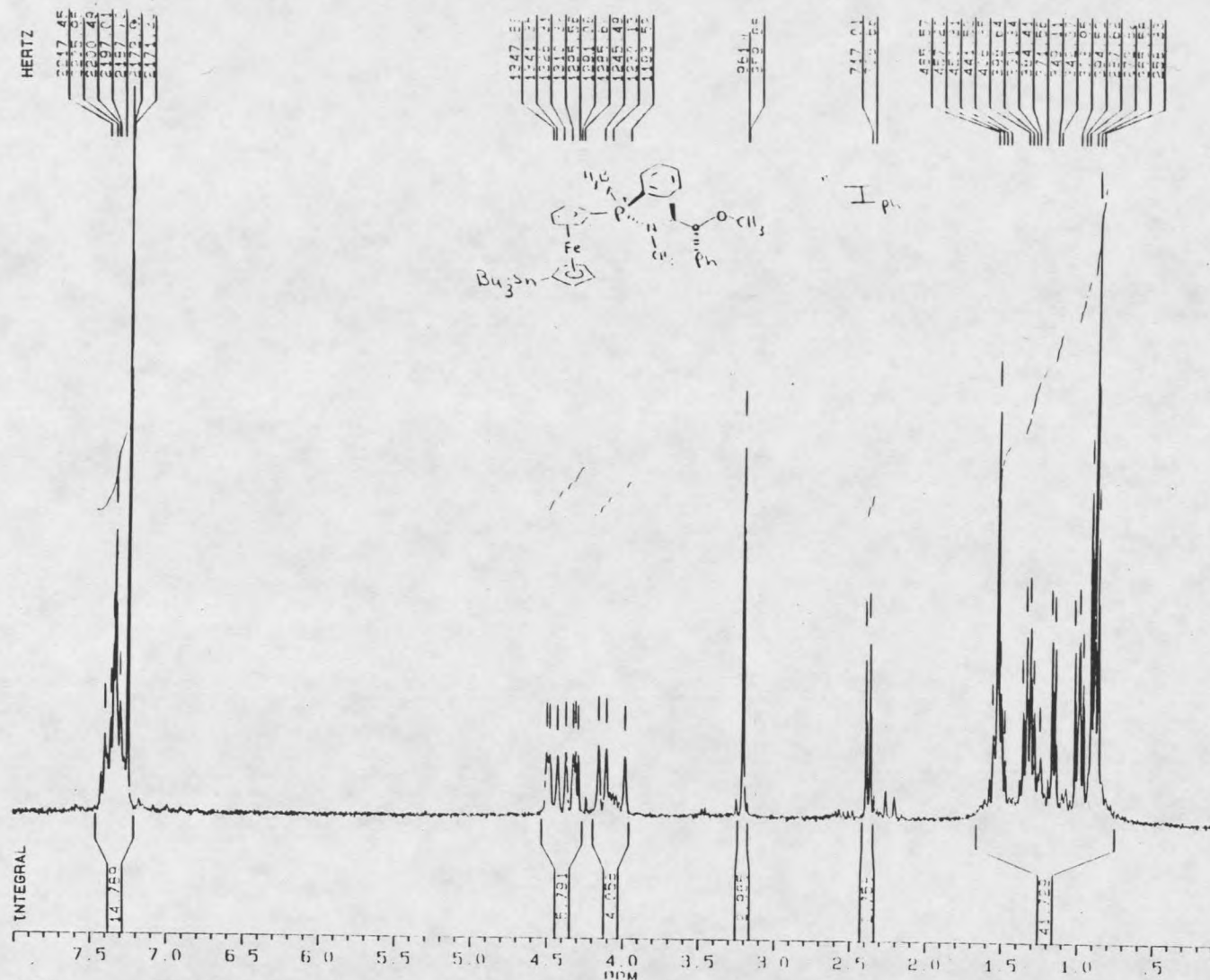


Figure 201. ^1H NMR Spectrum of 1-(Tri-*n*-butylstannyl)-1'-[(*Rp*)-N-Methyl, N-((1*R*, 2*S*)-(1-methoxy-1-phenyl-2-propyl)amino-boronatophenylphosphino]ferrocene (42c)

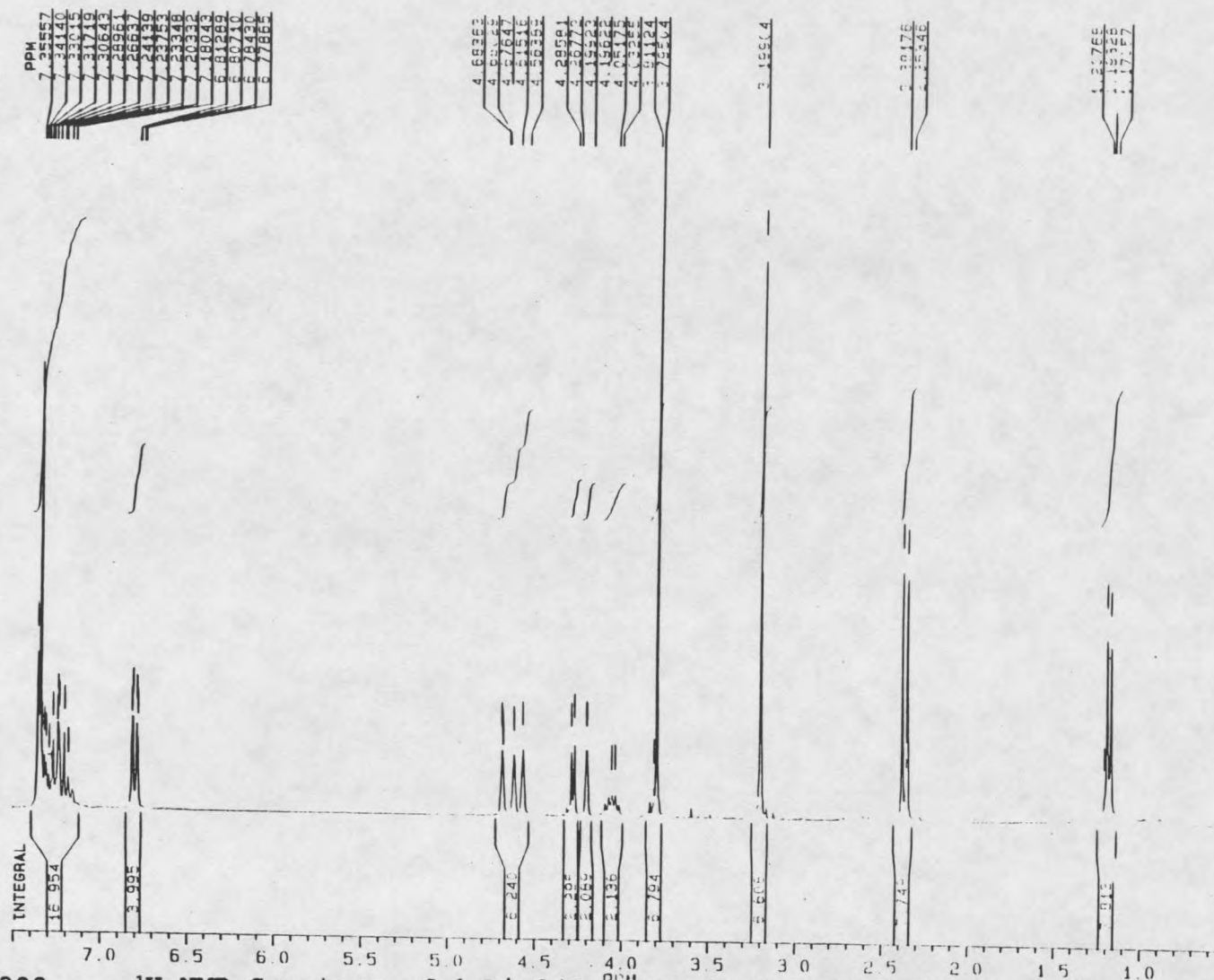
PPM

76.8097

329



Figure 202. ^{31}P NMR Spectrum of *n*-butylstannyl-1'-[(*R_p*)-*N*-Methyl,*N*-((1*R*,2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphino]ferrocene (42c)



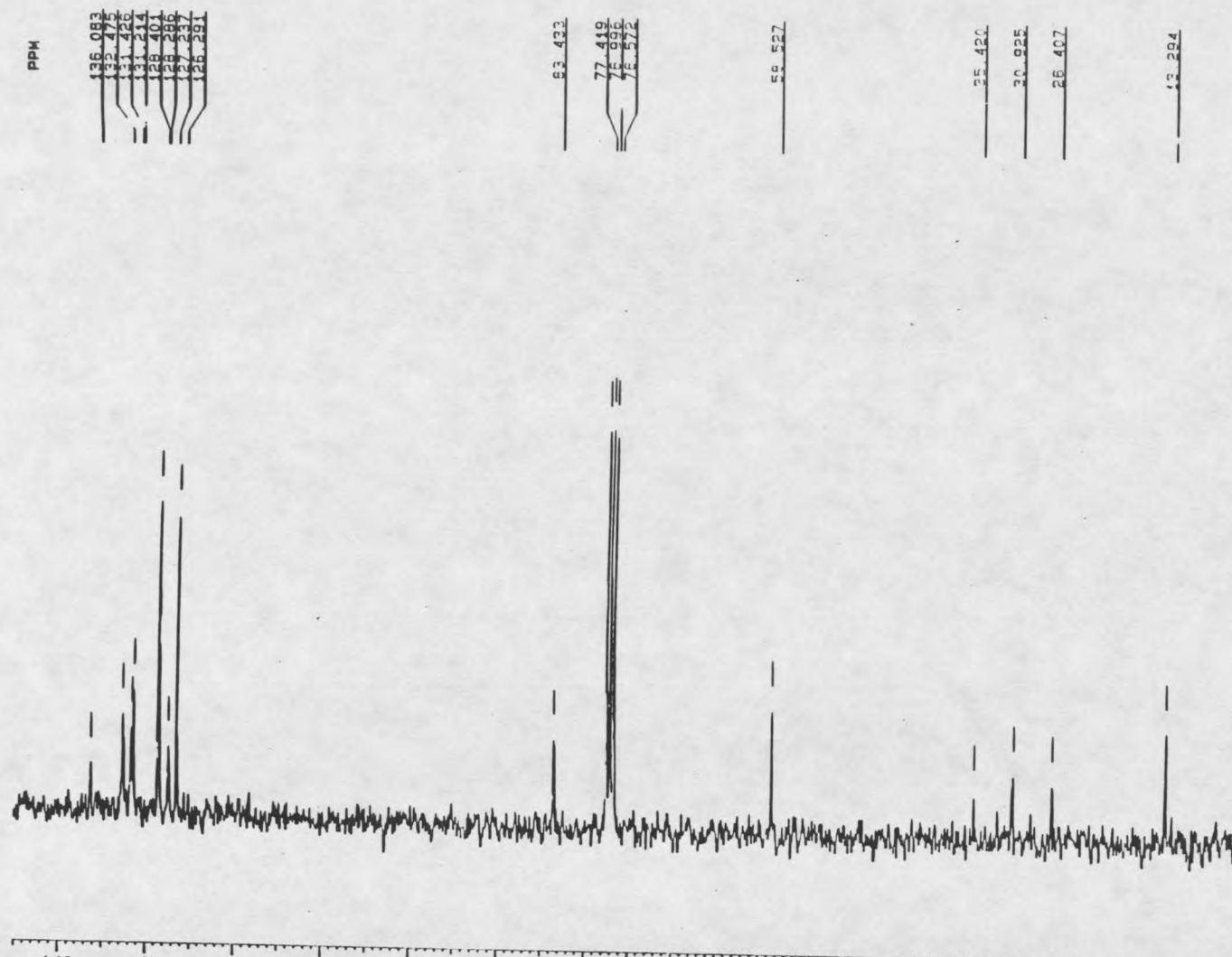


Figure 204. ^{13}C NMR Spectrum of $^1\text{-Bis}[(\text{R}_p)\text{-N-Methyl}, \text{N}^0((1\text{R}^0, 2\text{S})\text{-}(1\text{-methoxy-1-phenyl-2-propyl)})\text{amino-boronato-(4-methoxyphenyl)phosphino}]$ ferrocene (37a)

HERTZ

27993.1

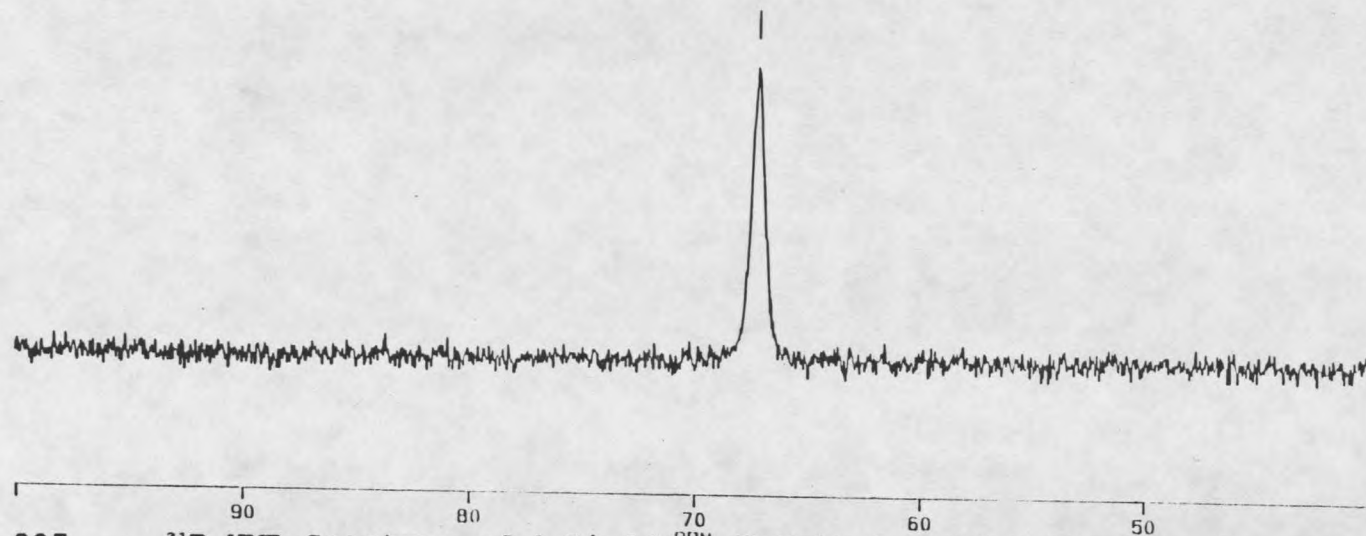


Figure 205. ^{31}P NMR Spectrum of 1-Bis[(R_P)-N-Methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(4-methoxyphenyl)phosphino]ferrocene (37a)

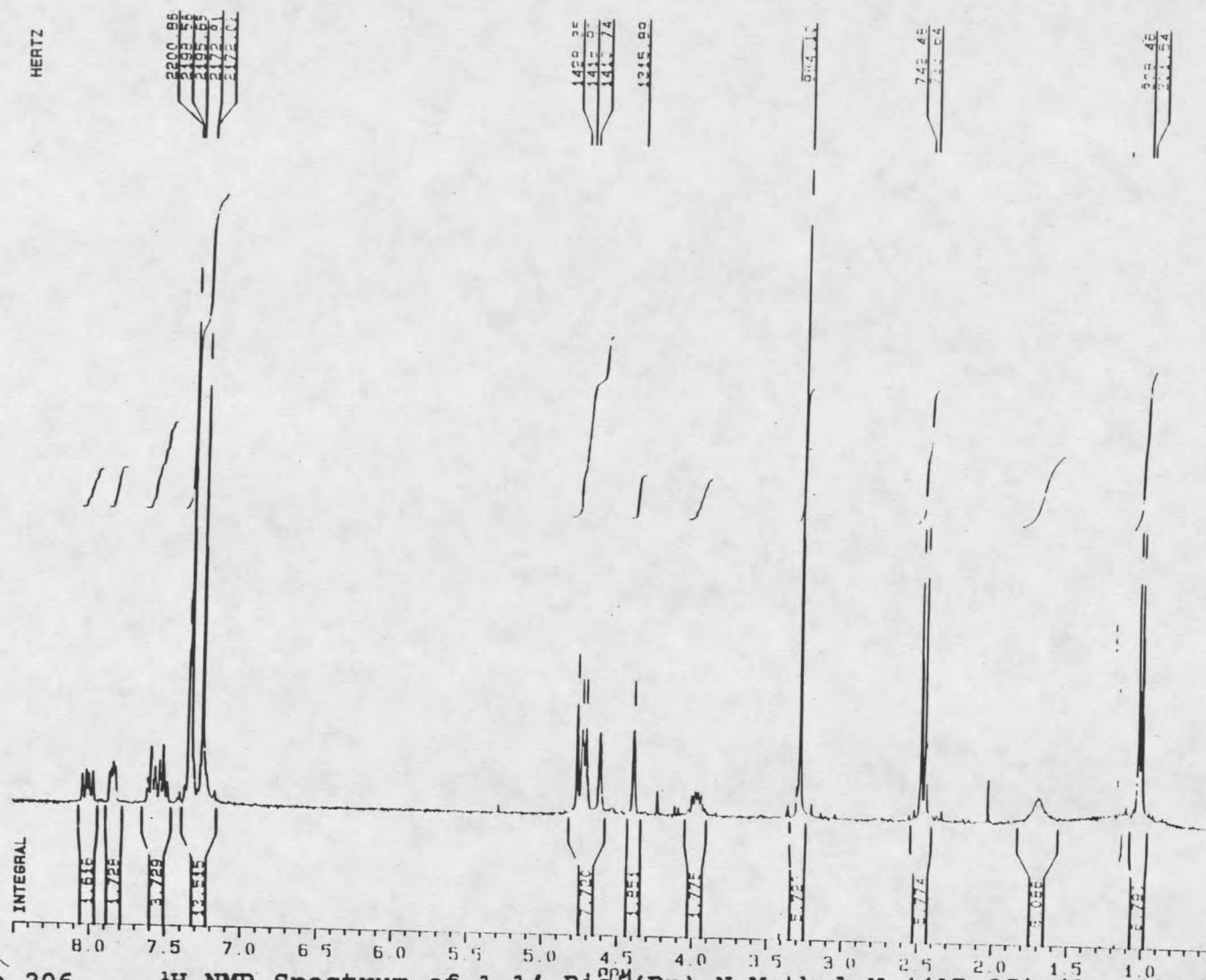


Figure 206. ^1H NMR Spectrum of 1,1'-Bis[(*Rp*)-N-Methyl, N-((1*R*, 2*S*)-(1-methoxy-1-phenyl-2-propyl))amino-boronato-(2-tri-fluoromethylphenyl)phosphino]ferrocene (37b)

PPM

76.2352

334

Figure 207. ^{31}P NMR Spectrum of 1,1'-Bis[(*Rp*)-N-methyl,N-(1-methoxy-1-phenyl-2-propyl)amino-boronato-(2-tri-fluoromethylphenyl)phosphino]ferrocene (37b)

PPM

52.1607

335



Figure 208. ^{31}P NMR Spectrum of 1,1'-Bis((Rp)-N-methyl,N-((1R,2S)-(1-methoxy-1-phenyl-2-propyl))amino-boronatophenylphosphine]ferrocene (37c)

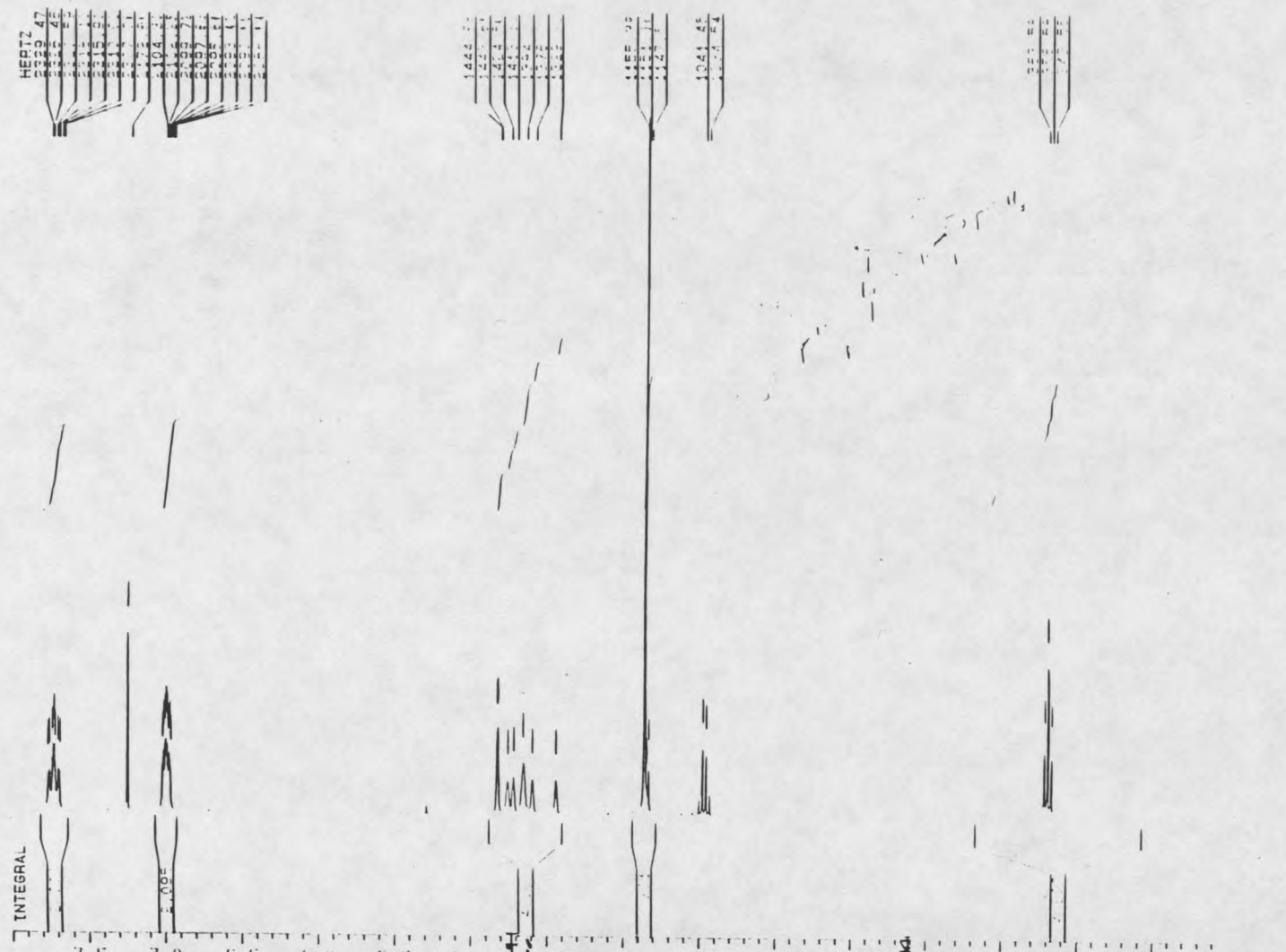


Figure 209. ^1H NMR Spectrum of 1,1'-Bis[boronatofluoro-(4-methoxyphenyl)]phino]ferrocene (36a)

ppm

147.754
143.500



Figure 210. ^{31}P NMR Spectrum of 1,1'-bis[boronatefluoro-(4-methoxyphenyl)]phosphinoferrocene (36a)

HERTZ

24252.6

20402.2



Figure 212.

^{31}P NMR Spectrum of 1,1'-Bis[boronatofluoro-(2-trifluoromethylphenyl)phosphino]ferrocene (36b)

ppm

14.1725

341

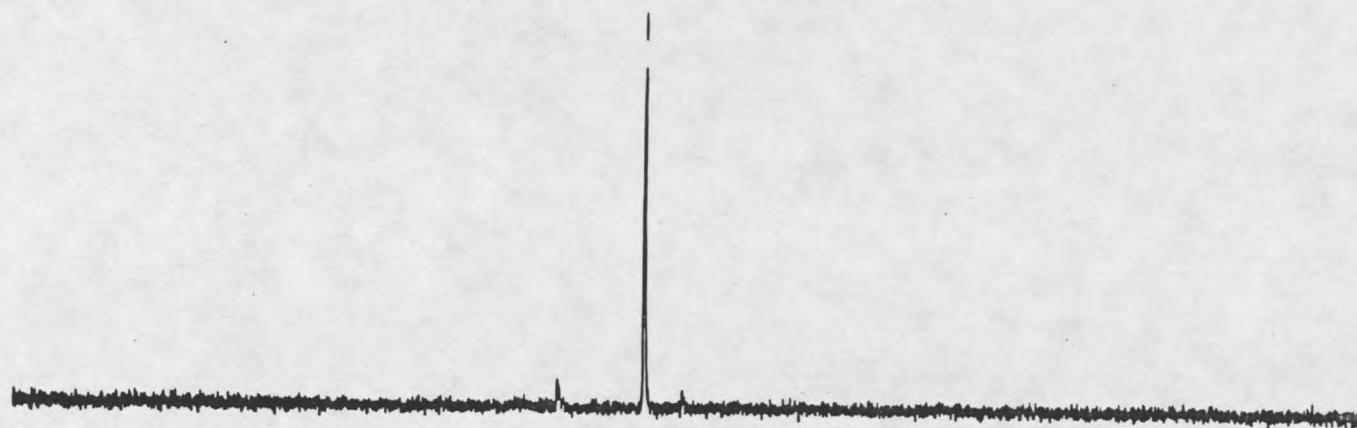


Figure 214.

³¹P NMR Spectrum of 1,1'-Bis[boronatomethyl-(2-trifluoromethylphenyl)phosphino]ferrocene (35b)

REFERENCES

1. Osborn, J.A.; Jardine, F.H.; Young, F.H.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 171.
2. a) For a review: Jardine, F.H. *Prog. Inorg. Chem.* **1981**, 28, 63. b) Mannig, D.; Nöth, H. *Angew. Chem. Int. Ed. Eng.* **1985**, 24, 878. c) Lane, C.F.; Kabalka, G.W. *Tetrahedron* **1976**, 32, 981.
3. For reviews of asymmetric hydrogenation with Rh(I)-phosphine catalysts see a) Halpern, J. *Science* **1982**, 217, 401. b) Halpern, J. *Asymmetric Synthesis* **1985**, 5, 41. c) Knowles, W.S.; Sabacky, M.J.; Vineyard, B.D. *J. Chem. Soc. Chem. Comm.* **1972**, 10, and references cited therein. d) Kagan, H.B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, 94, 6429, and references cited therein.
4. Jolly, R.S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, 112, 4965.
5. a) See Ref. 2b,c. b) Westcott, S.A.; Blom, H.P.; Marder, T.B.; Baker, R.T. *J. Am. Chem. Soc.* **1992**, 114, 8863 and references cited therein.
6. For a review: Otsuka, S.; Tani, K. *Asymmetric Synthesis*, **1985**, 5, 171.
7. For a review: Ojima, I.; Hirai, K. *Asymmetric Synthesis* **1985**, 5, 103.
8. a) Nugent, W.A.; Rajan Babu, T.V.; Burk, M.J. *Science* **1993**, 259, 479. b) Rajan Babu, T.V.; Casalnuovo, A.L. *J. Am. Chem. Soc.* **1992**, 114, 6265. c) Elmes, P.S.; Jackson, W.R. *J. Am. Chem. Soc.* **1979**, 101, 6129.
9. For a review: a) Bogdanovic', B. *Angew. Chem. Int. Ed. Eng.* **1973**, 12, 954. b) Bogdanovic', B. *Adv. Organomet. Chem.* **1979**, 17, 105.
10. For a review: Hayashi, T.; Kumada, M. *Asymmetric Synthesis* **1985**, 5, 147.
11. For a review: Bosnich, B.; Fryzuk, M.D. *Top. in Stereochem.* **1981**, 12, 126.

12. Rossiter, B.E. *Asymmetric Synthesis* 1985, 5, Ch. 7.
b) Finn, M.G.; Sharpless, K.B. *Asymmetric Synthesis* 1985, 5, Ch. 8. Hanson, R.M.; Sharpless, K.B. *J. Org. Chem.* 1986, 51, 1922.
13. For a review of ligand types: Kagan, H.B. *Asymmetric Synthesis* 1985, 5, 1.
14. a) Meisenheimer, J.; Lichtenstadt, L. *Chem. Ber.* 1911, 44, 356. b) Meisenheimer, J.; Casper, J.; Höring, M.; Lauter, W.; Lichtenstadt, L.; Samuel, W. *Justus Liebigs Ann. Chem.* 1926, 449, 213.
15. a) Horner, L. *Pure Appl. Chem.* 1964, 9, 255.
b) Horner, L.; Winkler, H.; Rapp, A.; Mentrup, A.; Hoffman, H.; Beck, P. *Tetrahedron Lett.* 1961, 161.
16. Kyba, E.P.; Clubb, C.N.; Larson, S.B.; Schneler, V.J.; Davis, R.E. *J. Am. Chem. Soc.* 1985, 107, 2141.
17. Morrison, J.D.; Masler, W.F. *J. Org. Chem.* 1974, 39, 270.
18. a) See ref. 3c. b) Dumont, W.; Poulin, J.C.; Dang, T.-P.; Kagan, H.B. *J. Am. Chem. Soc.* 1973, 95, 8295.
c) Masuda, T.; Stille, J.K. *J. Am. Chem. Soc.* 1978, 100, 268.
19. Lazzaroni, R.; Barsanti, S.; Salvadori, P. *Chim. Ind. (Milan)* 1977, 59, 456.
20. Kinoshita, I.; Kashiwahara, K.; Fujita, J. *Chem. Lett.* 1977, 831.
21. a) Hayashi, T.; Fukushima, M.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* 1980, 21, 79. b) Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* 1983, 48, 2195.
22. Cullen, W.R.; Einstein, F.W.B.; Huang, C.-H.; Willis, A.C.; Yeh, E.-S. *J. Am. Chem. Soc.* 1980, 102, 988.
23. Hayashi, T.; Kumada, M. *Acc. Chem. Res.* 1982, 15, 395.
24. Korpium, O.; Lewis, R.A.; Chickosand, J.; Mislow, K. *J. Am. Chem. Soc.* 1968, 90, 4842.

25. Jugé confirmed that acyclic alkyl phosphinates can be stereoselectively converted to phosphine oxides upon treatment with alkyl and aryl Grignard reagents.
a) Jugé, S. Genet, J.P. *Tetrahedron Lett.* **1989**, 30, 2783. b) Jugé, S. *Société Nationale Elf-Aquitaine, Fr. Pat.* 3,123,153 (1981).
26. Horner, L.; Balzer, W.D. *Tetrahedron Lett.* **1965**, 1157.
27. Zon, G.; Mislow, K. *Stud. in Phosph. Stereochem.* (1971).
28. Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, 91, 7012.
29. Jugé, S.; Legras, Y. unpublished results.
30. a) Mikolajczyk, M. *Pure Appl. Chem.* **1980**, 52, 959. b) Omelanczuk, J.; Perlikowska, W.; Mikolajczyk, M. *Chem. Comm.* **1980**, 24. c) Chodkiewicz, W.; Jore, O.; Wodzki, W. *Tetrahedron Lett.* **1979**, 1069.
31. a) Cooper, D.B.; Inch, T.D.; Lewis, G.J. *J. Chem. Soc. Perkin I* **1974**, 1043. b) Chodkiewicz, W.; J. *Organometal. Chem.* **1984**, 273, C55.
32. a) Carey, J.V.; Barker, M.D.; Brown, J.M.; Russell, M.J.H. *J. Chem. Soc. Perkin Trans. I* **1993**, 831. b) Brown, J.M.; Carey, J.V.; Russell, M.J.H. *Tetrahedron* **1990**, 46, 4877.
33. Hall, C.R.; Inch, T.D. *Tetrahedron* **1980**, 36, 2059.
34. Jugé, S.; Stephan, M.; Laffitte, J.A.; Genet, J.P. *Tetrahedron Lett.* **1990**, 31, 6357.
35. a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, 107, 5301. b) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, 112, 5244.
36. Wärd, T.R.; Venanzi, L.M.; Albinati, A.; Lianza, F.; Gerfin, T.; Gramlich, V.; Tombo, G.M.R. *Helv. Chim. Acta.* **1991**, 74, 983.
37. Brisset, H.; Gourdel, Y.; Pellon, P.; LeCorre, M. *Tetrahedron Lett.* **1993**, 34, 4523.
38. Corey, E.J.; Chen, Z.; Tanoury, G.J. *J. Am. Chem. Soc.* **1993**, 115, 11000.

39. Zon, G.; DeBruin, K.E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023.
40. Horner, L.; Mentrup, A. *Justus Liebigs Ann. Chem.* **1961**, *646*, 65.
41. Burgess, K.; Ohlmeyer, M.; Whitmire, K.H. *Organometallics* **1992**, *11*, 3588.
42. a) Morimoto, T.; Chiba, M.; Achiwa, K. *Chem. Pharm. Bull.* **1992**, *40*, 2894. b) Morimoto, T.; Chiba, M.; Achiwa, K. *Tetrahedron Lett.* **1989**, *30*, 735. c) Tani, K.; Suwa, K.; Yamagata, T.; Otsuka, S. *Chem. Lett.* **1982**, 265. d) Tanaka, M.; Ikeda, Y.; Ogata, I. *Chem. Lett.* **1975**, 115. e) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. f) Refs. 42a and 42g. g) Chiba, M.; Takahashi, H.; Morimoto, T.; Achiwa, K. *Tetrahedron Lett.* **1987**, 3675. h) Yamagishi, T.; Yatagai, M.; Hatakeyama, H.; Hida, M. *Bull. Chem. Soc. Jpn.* **1986**, *56*, 1897.
43. Dang, T.P.; Poulin, J.C.; Kagan, H.B. *J. Organomet. Chem.* **1975**, *91*, 105.
44. Bakos, J.; Toth, I.; Heil, B.; Marko, L. *J. Organomet. Chem.* **1985**, *279*, 23.
45. Aviron-Violet, P.; Colleuille, Y.; Varagnat, J. *J. Mol. Catal.* **1979**, *5*, 41.
46. Brunner, H.; Pieronczyk, W.; Schönhammer, B.; Streng, K.; Bernal, I.; Korp, J. *Chem. Ber.* **1981**, *114*, 1137.
47. Samuel, O.; Couffignal, R.; Lauter, M.; Zhang, S.; Kagan, H.B. *Nouv. J. Chim.* **1981**, *5*, 15.
48. Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180, and references cited therein.
49. Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.
50. a) Hayashi, T. In *Organic Synthesis: An Interdisciplinary Challenge*; Streith, J.; Prinzbach, H.; Schill, G., Eds.; Blackwell: 1985, pp. 35-42. b) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7.

51. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.
52. a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. b) Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, *40*, 1245.
53. Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R. *J. Chem. Soc. Chem. Commun.* **1982**, 600.
54. a) Otsuka, S.; Nakamura, A.; Kano, G.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301. b) Tani, K.; Brown, L.D.; Ahmed, T.; Ibers, J.A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876.
55. Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629.
56. a) Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* **1988**, *71*, 897. b) Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370, and references cited therein.
57. Knowles, W.S.; Sabacky, M.J.; Vineyard, B.D.; Weinkauff, D.J. *J. Am. Chem. Soc.* **1975**, *97*, 2567.
58. The elimination of meso products was accomplished by fine-tuning the reaction conditions. See ref. 37.
59. a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Masatoshi, M.; Hikosaka, T.; Yanagawa, M. *Hetero-Atom Chemistry* **1992**, *3*, 563. b) Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655, and references cited therein.
60. Hengartner, J.; Valentine, D.; Johnson, K.K.; Larscheid, M.E.; Pigott, F.; Scheidl, F.; Scott, J.W.; Sun, R.C.; Townsend, J.M.; Williams, T.H. *J. Org. Chem.* **1979**, *44*, 3741.
61. Hobbs, C.F.; Knowles, W.S. *J. Org. Chem.* **1981**, *46*, 4422.
62. Vineyard, B.D.; Knowles, W.S.; Sabacky, M.J.; Backman, G.L.; Weinkauff, D.J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

63. a) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: New York, 1970; Ch. 1. b) Paulik, F.E. *Catal. Rev.* **1972**, *6*, 49. c) Pino, P.; Placenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*, Wender, I., Pino, P., Eds.; Wiley: New York, 1977; pp. 43-231. d) Pruett, R.L. *Adv. Organomet. Chem.* **1979**, *17*, 1.
64. Wilke, G.; Bogdanovik, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. *Angew. Chem. Int. Ed. Eng.* **1966**, *5*, 151.
65. van Leeuwen, P.W.N.M.; Roobeek, C.F. *Tetrahedron* **1981**, *37*, 1973 and references cited therein.
66. a) Kagan, H.B. *Pure Appl. Chem.* **1975**, *43*, 401. b) Kagan, H.B.; Fiaud, J.C. *Top. Stereochem.* **1978**, *10*, 175. c) Morrison, J.D.; Masler, W.F.; Neuberg, M.K. *Adv. Catal.* **1976**, *25*, 81. d) Valentine, D. Jr.; Scott, J.W. *Synthesis* **1978**, 329. e) James, B.R. *Adv. Organomet. Chem.* **1979**, *17*, 319.
67. Morrison, J.D.; Burnett, R.E.; Aguiar, A.M.; Morrow, C.J.; Phillips, C. *J. Am. Chem. Soc.* **1971**, *93*, 1301 and references cited therein. b) Valentine, D. Jr.; Blount, J.F.; Toth, K. *J. Org. Chem.* **1980**, *45*, 3691. c) Fisher, C.; Mosher, H.S. *Tetrahedron Lett.* **1977**, 2487.
68. a) Knowles, W.S.; Sabacky, M.J. *Chem. Commun.* **1969**, 1445.
69. Masuda, T.; Stille, J.K. *J. Am. Chem. Soc.* **1978**, *100*, 268.
70. Genet, J.P.; Pinel, C.; Mallart, S.; Juge, S.; Thorimbert, S.; Laffitte, J.A. *Tetrahedron Asymmetry*, **1991**, *2*(7), 555.
71. Cabri, W.; Candiani, T.; Bedeschi, A. *J. Org. Chem.* **1992**, *57*, 3558.
72. Spindler, F.; Pittlekow, U.; Blaser, H.U. *Chirality*, **1992**, *3*, 370.
73. Schrock, R.R.; Osborn, J.A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.
74. a) Corey, E.J.; Bailer, J.C. *J. Am. Chem. Soc.* **1959**, *81*, 2620. b) Beattie, J.K. *Acc. Chem. Res.* **1971**, *4*, 253.

75. Botteghi, C.; Giacomelli, G. *Gazz. Chim. Ital.* **1976**, *106*, 1131.
76. a) Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R. *ACS Symp. Ser.* **1982**, *185*, 187. b) Tani, K.; Yamagata, T.; Otsuka, S.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R. *J. Chem. Soc. Chem. Commun.* **1982**, 600. c) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.
77. Stille, J.K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139.
78. a) Cram, D.J. *J. Am. Chem. Soc.* **1952**, *74*, 2137. b) Skoriantz, W.; Giger, H.; Ohloff, G. *Helv. Chim. Acta.* **1971**, *54*, 1797.
79. Brunner, H. *Top. in Stereochem.* **1988**, *18*, 129.
80. a) Meriwether, L.S.; Cothup, E.C.; Kennerly, G.W.; Reusch, R.N. *J. Org. Chem.* **1961**, *26*, 5155. b) Reikhsfeld, V.O.; Makovetskii, K.L. *Russ. Chem. Reviews* **1966**, *35*, 510.
81. a) Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26. b) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc. Dalton.* **1978**, 1278. c) Bonnemann, H. *Angew. Chem. Int. Ed. Eng.* **1978**, *17*, 505.
82. a) Vollhardt, K.P.C. *Accts. Chem. Res.* **1977**, *10*, 1. b) Gesing, E.R.F.; Vollhardt, K.P.C. *J. Organomet. Chem.* **1981**, *217*, 105. c) Ville, G.; Vollhardt, K.P.C.; Winter, M.J. *J. Am. Chem. Soc.* **1981**, *103*, 5267. d) Gadek, T.R.; Vollhardt, K.P.C. *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 802.
83. Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691.
84. Lautens, M.; Lautens, J.C.; Smith, A.C. *J. Am. Chem. Soc.* **1990**, *112*, 5627.
85. For a review: Narasaka, K. *Synthesis* **1991**, 1.
86. a) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc. Chem. Commun.* **1979**, 437. b) Takemura, H.; Komeshima, N.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 5687.

87. a) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, 24, 3451. b) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, 105, 6968.
88. a) Reetz, M.T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind.* **1986**, 824. b) Seebach, D.; Beck, A.K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, 70, 954. c) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109. d) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967.
89. a) Kelly, T.R.; Whiting, A.; Chandrakumar, N.S. *J. Am. Chem. Soc.* **1986**, 108, 3510. b) Maruoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Tetrahedron Lett.* **1986**, 27, 4895.
90. Faller, J.W.; Smart, C.J. *Tetrahedron Lett.* **1989**, 30, 1189.
91. a) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1990**, 1295.
92. a) Corey, E.J.; Imwinkelried, R.; Pikul, S.; Xiang, Y.B. *J. Am. Chem. Soc.* **1989**, 111, 5493. b) Corey, E.J.; Imai, N.; Pikul, S. *Tetrahedron Lett.* **1991**, 32, 7517. c) Pikul, S.; Corey, E.J. *Org. Synth* **1992**, 71, 22, 30 and references cited therein. d) Corey, E.J. *Pure and Appl. Chem.* **1990**, 62, 1209 and references cited therein. e) Corey, E.J.; Sarshar, S. Bordner, J. *J. Am. Chem. Soc.* **1992**, 114, 7938.
93. a) Matsuda, I.; Shibata, M.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, 28, 3361. b) Tom Dieck, H.; Diercks, R. *Angew. Chem. Int. Ed. Eng.* **1983**, 22, 778 and references cited therein. c) Tom Dieck, H.; Diercks, R. *Angew. Chem. Suppl.* **1983**, 1138-1146. d) Mach, K.; Antropinsova, H.; Petrusova, L.; Tureck, F.; Hanus, V. *J. Organomet. Chem.* **1985**, 289, 331.
94. Wender, P.A.; Jenkins, T.E. *J. Am. Chem. Soc.* **1989**, 111, 6432.
95. Ligand sphere effects--reviews
96. Larock, R.C.; Oertle, K.; Potter, G.F. *J. Am. Chem. Soc.* **1980**, 102, 190.
97. van Leeuwen, P.W.N.M.; Roobeek, C.F. *J. Organomet. Chem.* **1983**, 258, 343.
98. Sheehan, D.J. personal communication.

99. a) Dawans, F.; Morel, D. *J. Mol. Catal.* **1977-78**, 3, 403. b) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, 2, 65.
100. a) Miller, E.F.; Shaw, B.L. *J. Chem. Soc. Dalton* **1974**, 480. b) Shaw, B.L.; Stainbank, R.E. *J. Chem. Soc. Dalton* **1972**, 223.
101. Achiwa, K. *J. Am. Chem. Soc.* **1976**, 98, 8265.
102. a) Dale, J.A.; Dull, D.L.; Mosher, H.S. *J. Org. Chem.* **1969**, 34, 2543. b) Dale, J.A.; Mosher, H.S. *J. Am. Chem. Soc.* **1973**, 95, 512.
103. Knowles, W.S. *Acc. Chem. Res.* **1983**, 16, 106.
104. a) Narasaka, K. *Synthesis* **1991**, 1. b) Narasaka, K.; Tanaka, H.; Kanai, F. *Bull. Chem. Soc. Jpn.* **1991**, 64 387. c) Iawasawa, N.; Sugimori, J.; Kawase, Y.; Narasaka, K. *Chem. Lett.* **1989**, 1947.
105. McKinstry, L.; Livinghouse, T. *Tetrahedron* **1994**, accepted for publication.
106. McKinstry, L.; Livinghouse, T. *Tetrahedron* **1994**, accepted for publication.
107. ^1H and ^{31}P NMR resonances were measured at 500 MHz and 202 MHz respectively, with a Bruker AM-500 spectrometer.
108. McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, submitted for publication.
109. Noth, H.; Vetter, H.-J. *Chem. Ber.* **1963**, 96, 1109.
110. Prepared by lithiation of 4-bromo-3-methylanisole.
111. Smoot, C.H. *Can J. Chem.*, **1956**, 34, 1464.
112. Sheehan, S.K.; Jiang, M.; McKinstry, L.; Livinghouse, T.; Garton, D. *Tetrahedron* **1994**, accepted for publication.
113. Sheehan, S.K.; Jiang, M.; McKinstry, L.; Livinghouse, T.; Garton, D. *Tetrahedron*, **1994**, 50, 6155.
114. a) M. Jiang Masters Thesis Dissertation. b) S. Sheehan Ph.D. Thesis Dissertation.

115. A Perkin-Elmer 237B grating IR spectrometer was generously provided (on loan) by the Department of Chemistry at Fort Lewis College, Durango, Colorado.
116. CHIRALPAK is a registered trademark of DAICEL CHEMICAL INDUSTRIES LTD.
117. Still, W.C.; Kahn, M; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
118. The procedure for preparation of phosphine oxides is a modification of an unpublished procedure provided by C.F. Hobbs of the Monsanto Corporation, through personal communication.
119. Prepared according to the procedure described in *Can J. Chem.* **1956** *34*, 1464.
120. Lieser, J.K. *Synth. Comm.* **1983**, *13*(9), 765.
121. Prepared and characterized by D.J. Sheehan.
122. Prepared from commercially available (2*S*,4*S*)-2,4-dihydroxypentane.
123. Prepared and characterized by Wender et al.⁹⁴ The physical data for these compounds was compared to that found in the supplementary material.
124. Meyers, A.I.; Collington, E.W. *J. Org. Chem.* **1971**, *36*, 3044.
125. Van Der Ent, A.; Onderdelinder, A.L. *Inorg. Synth.* **1973**, *14*, 92.
126. Denney, D.B.; Denney, D.Z.; Hammond, P.J.; Liu, L.T.; Wung, Y.P. *J. Org. Chem.* **1983**, *48*, 2159.
127. The Wilkinson's catalyst was utilized as an alternative to that described for 110 which resulted, in this case, in very low isolated yields.
128. a) The amine exchange rxn that results in cyclization is catalyzed by proton sources (in the form of ammonium salts).²⁰ In cases where cyclization is sluggish (as evidenced by the absence of copious Me₂NH evolution), a few μ L of Me₃SiCl may be added to provide the required catalysis. b) Nielsen, J.; Dahl, O. *J. Chem. Soc. Perkin Trans. II* **1984**, 553.
129. Wright, M.E. *Organometallics* **1990**, *9*, 853.

130. Umezawa, J.; Takahashi, O.; Furuhashi, K. *Tetrahedron: Asymm.* **1993**, *4*, 2053.

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10254040 6