

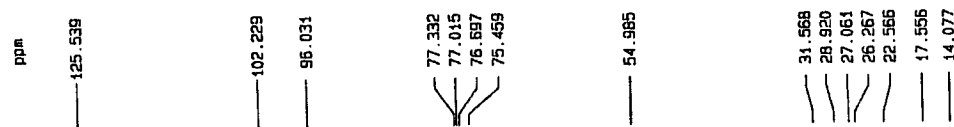
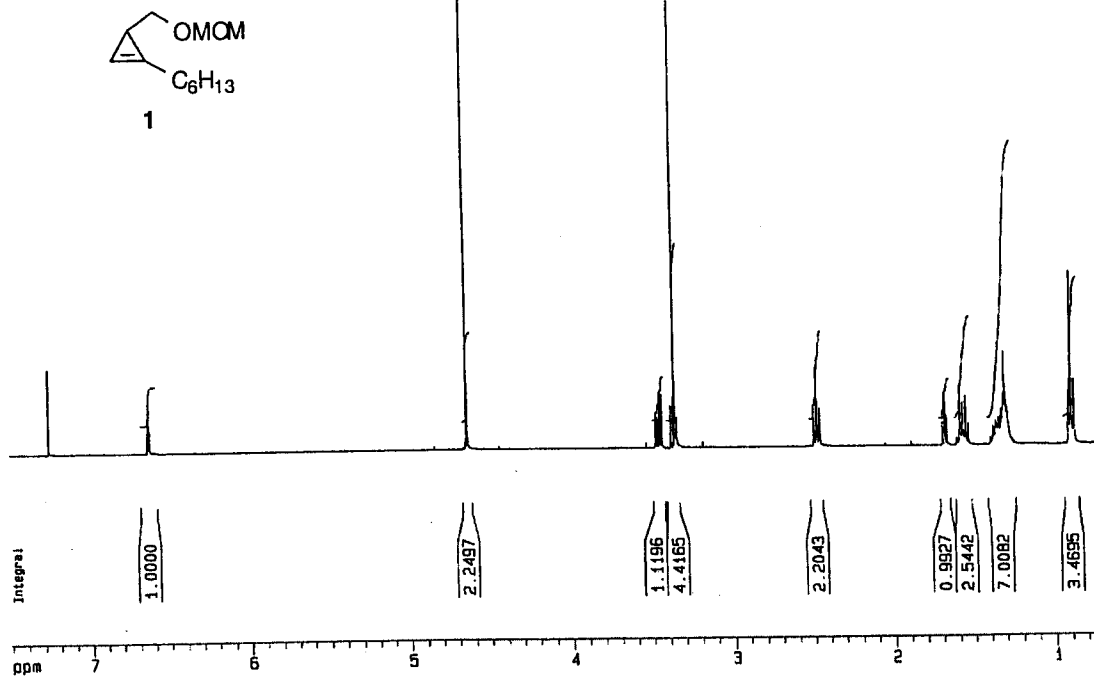
Supporting Information (Spectral data)

**A Copper Catalyzed Method for the Facially Selective Addition of
Grignard Reagents to Cyclopropenes**

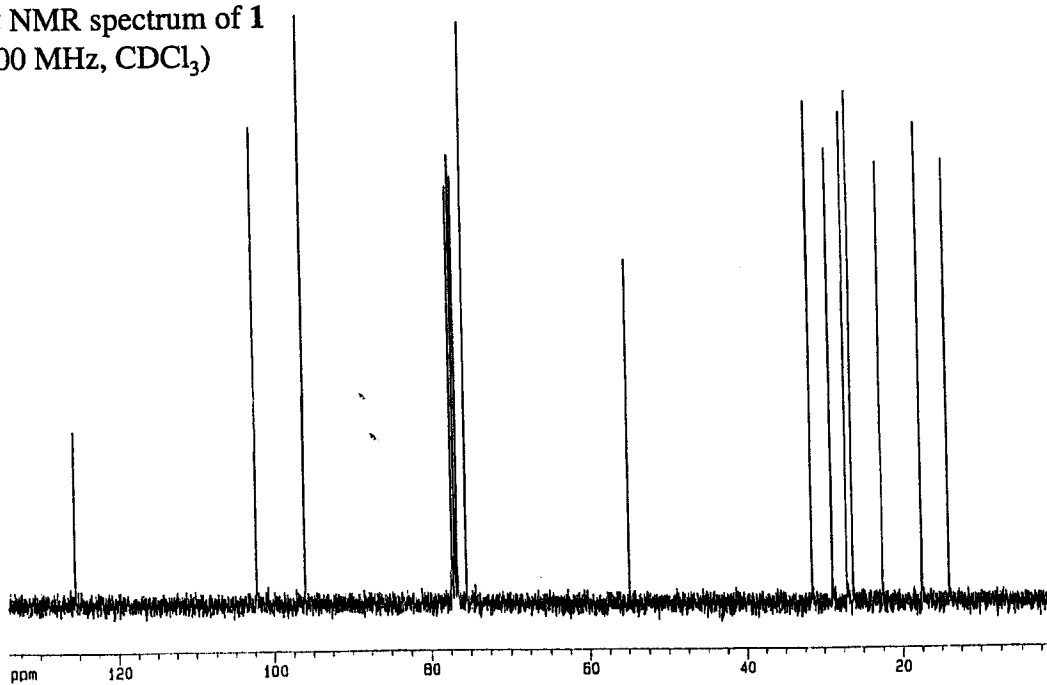
Lian-an Liao and Joseph M. Fox*

Brown Laboratories, Department of Chemistry and Biochemistry, University of
Delaware, Newark, DE 19716

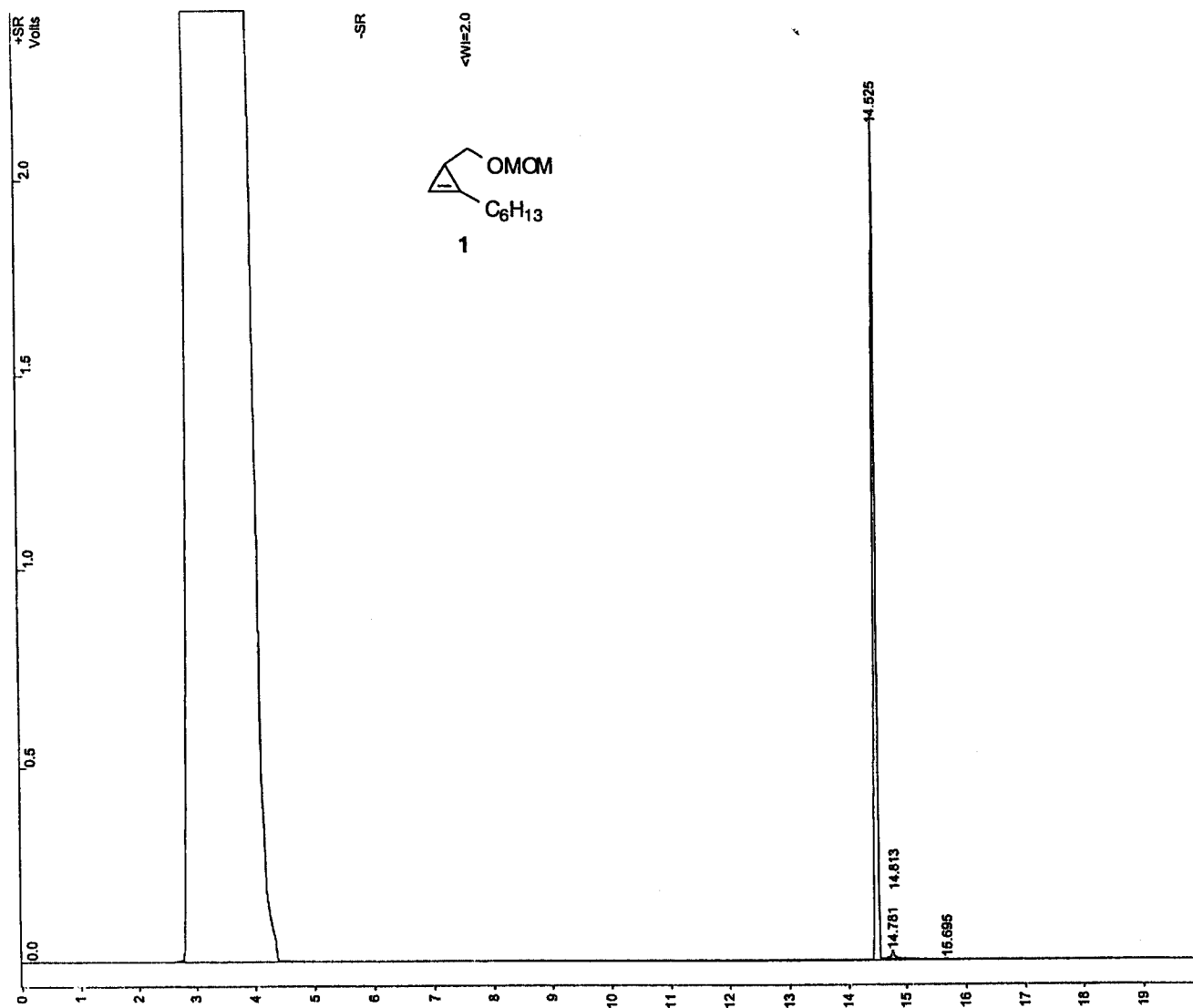
^1H NMR spectrum of **1** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **1**
(100 MHz, CDCl_3)

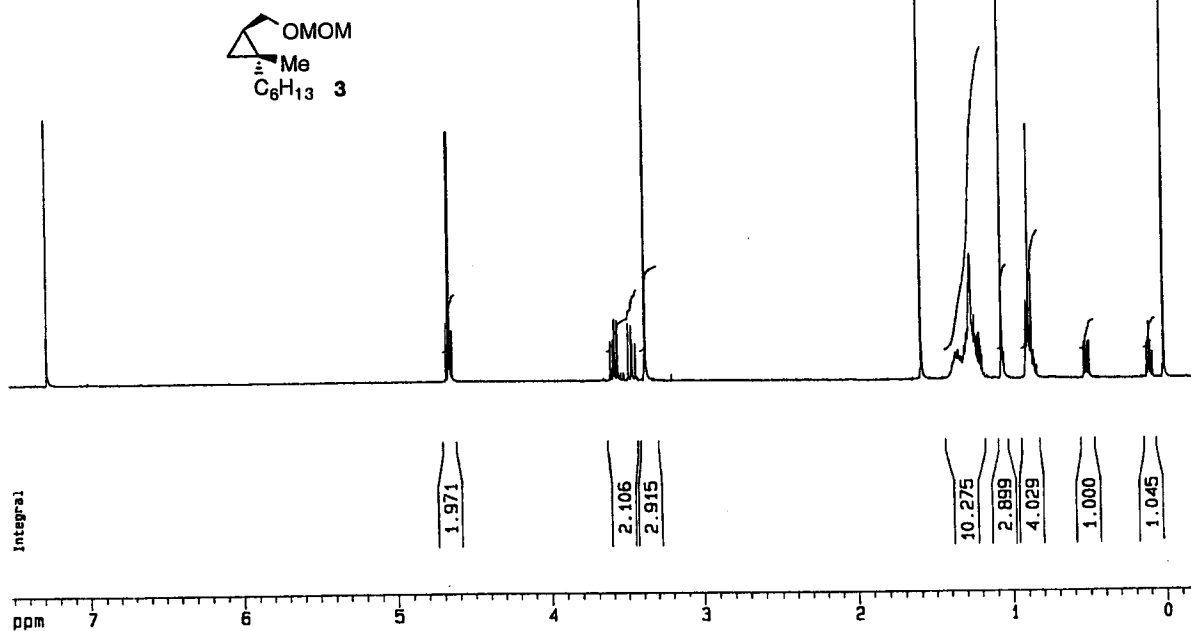


GC trace of 1 (HP5 column)

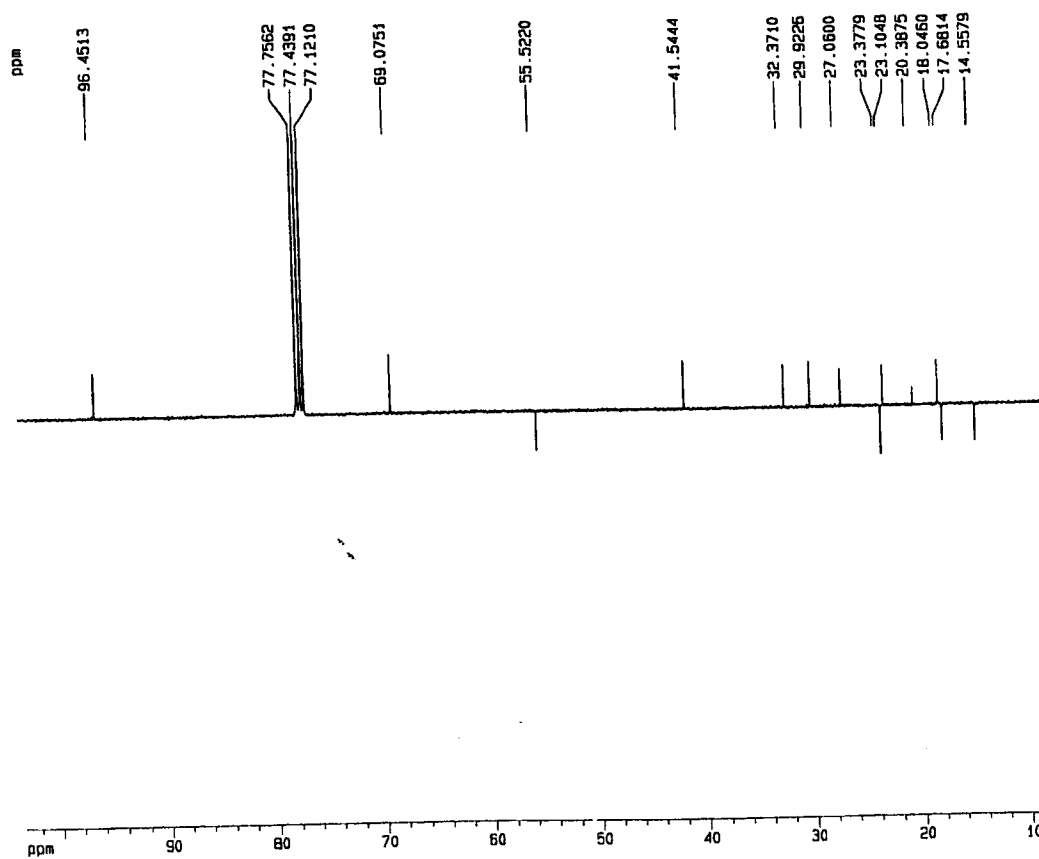


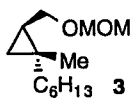
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.9290	14.525	0.000	6716273	VP	2.9	
2		0.8325	14.781	0.000	56518	TF	0.0	
3		0.1589	14.813	0.000	10788	TF	0.0	
4		0.0795	15.695	0.000	5400	TF	0.0	
Totals:		99.9999		0.000	6788979			

^1H NMR spectrum of **3** (400 MHz, CDCl_3)



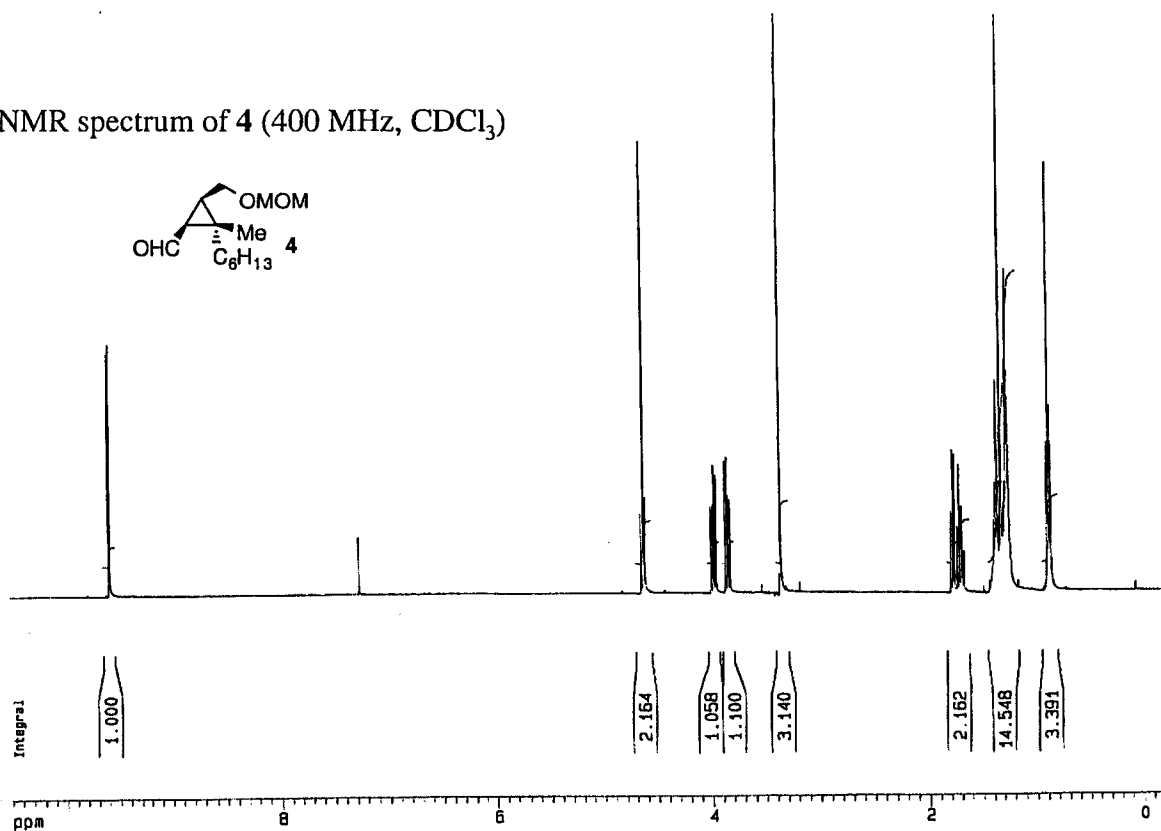
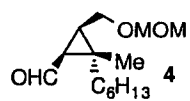
^{13}C NMR spectrum of **3** (100 MHz, CDCl_3)



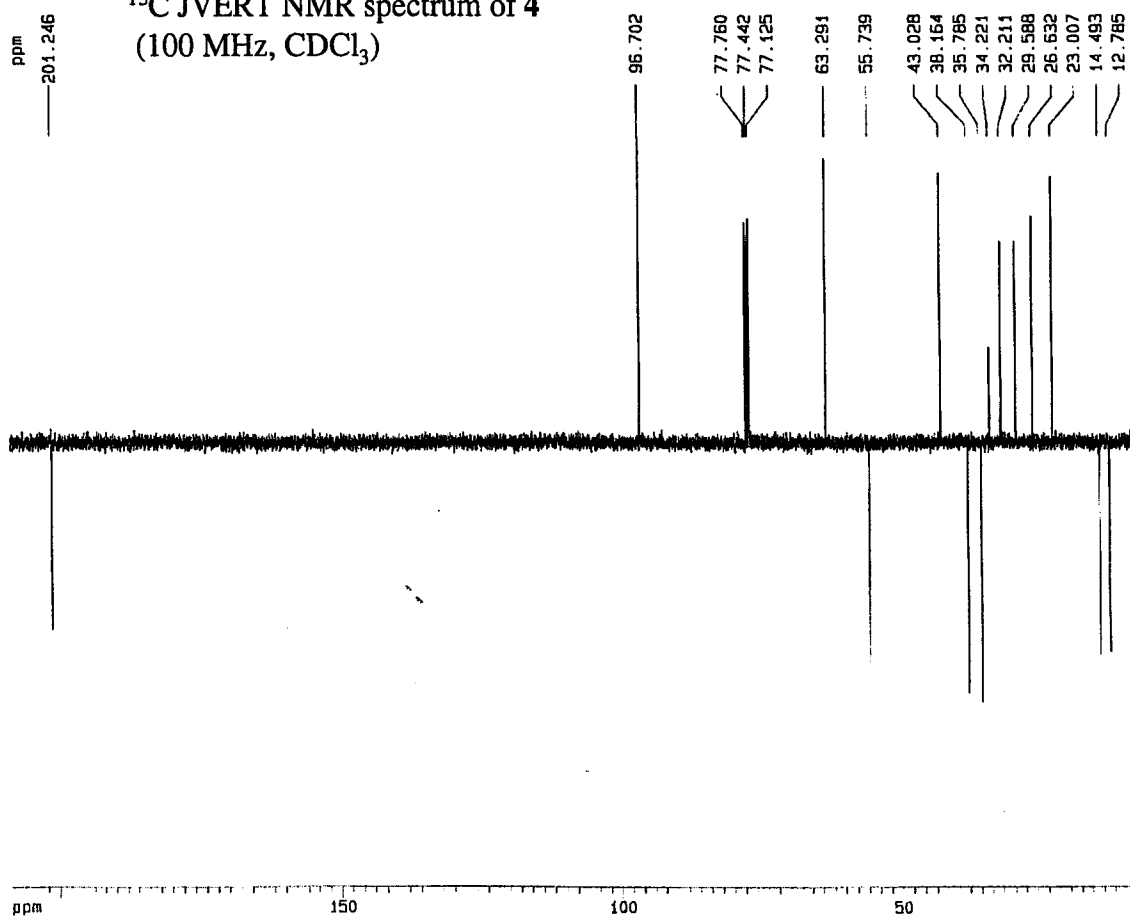
GC trace of **3** (HP5 column)

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		2.4907	10.415	0.000	86249	BB	2.6	
2		1.6339	10.630	0.000	56581	BB	2.8	
3		95.8753	10.902	0.000	3319979	BB	2.7	
Totals:		99.9999		0.000	3462809			

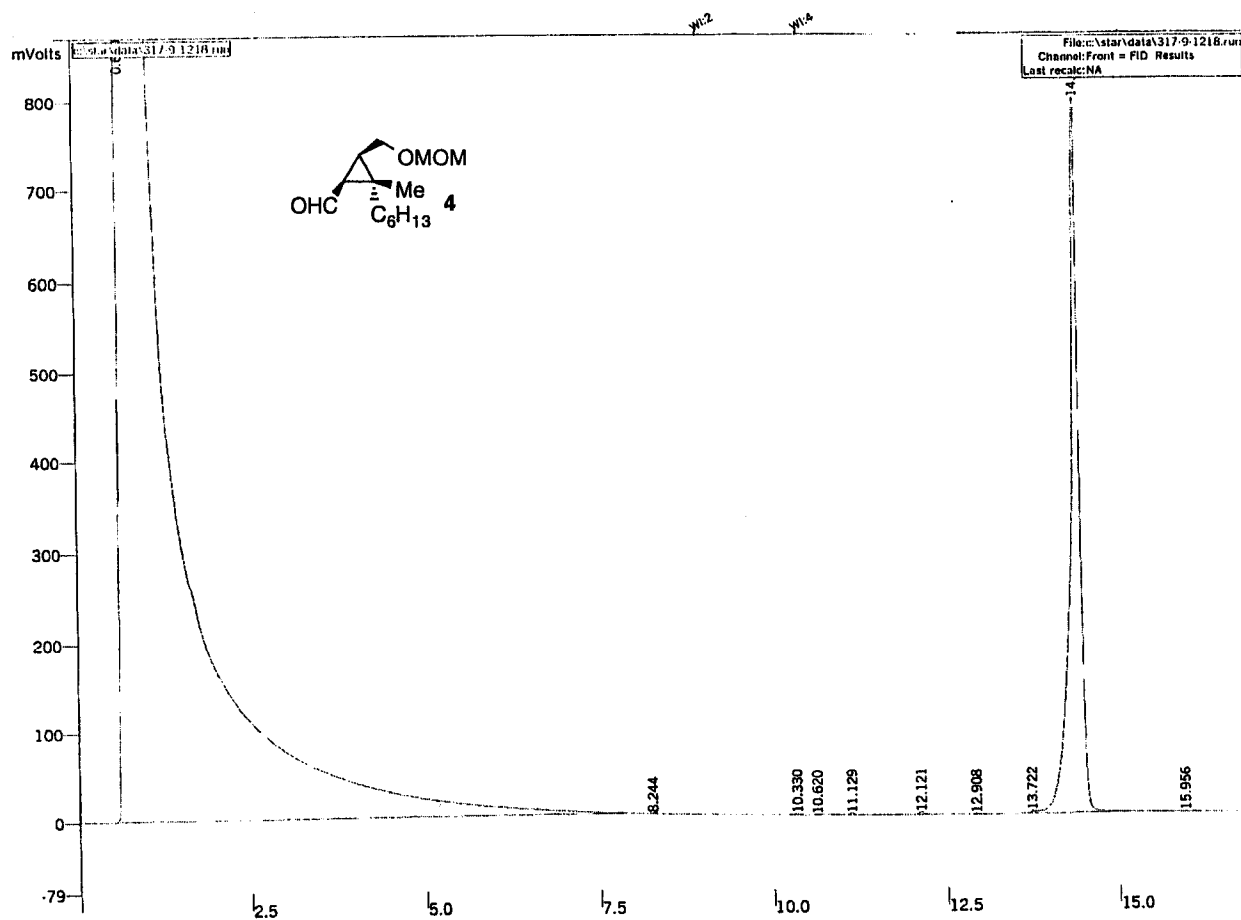
^1H NMR spectrum of **4** (400 MHz, CDCl_3)



^{13}C JVERT NMR spectrum of **4**
(100 MHz, CDCl_3)

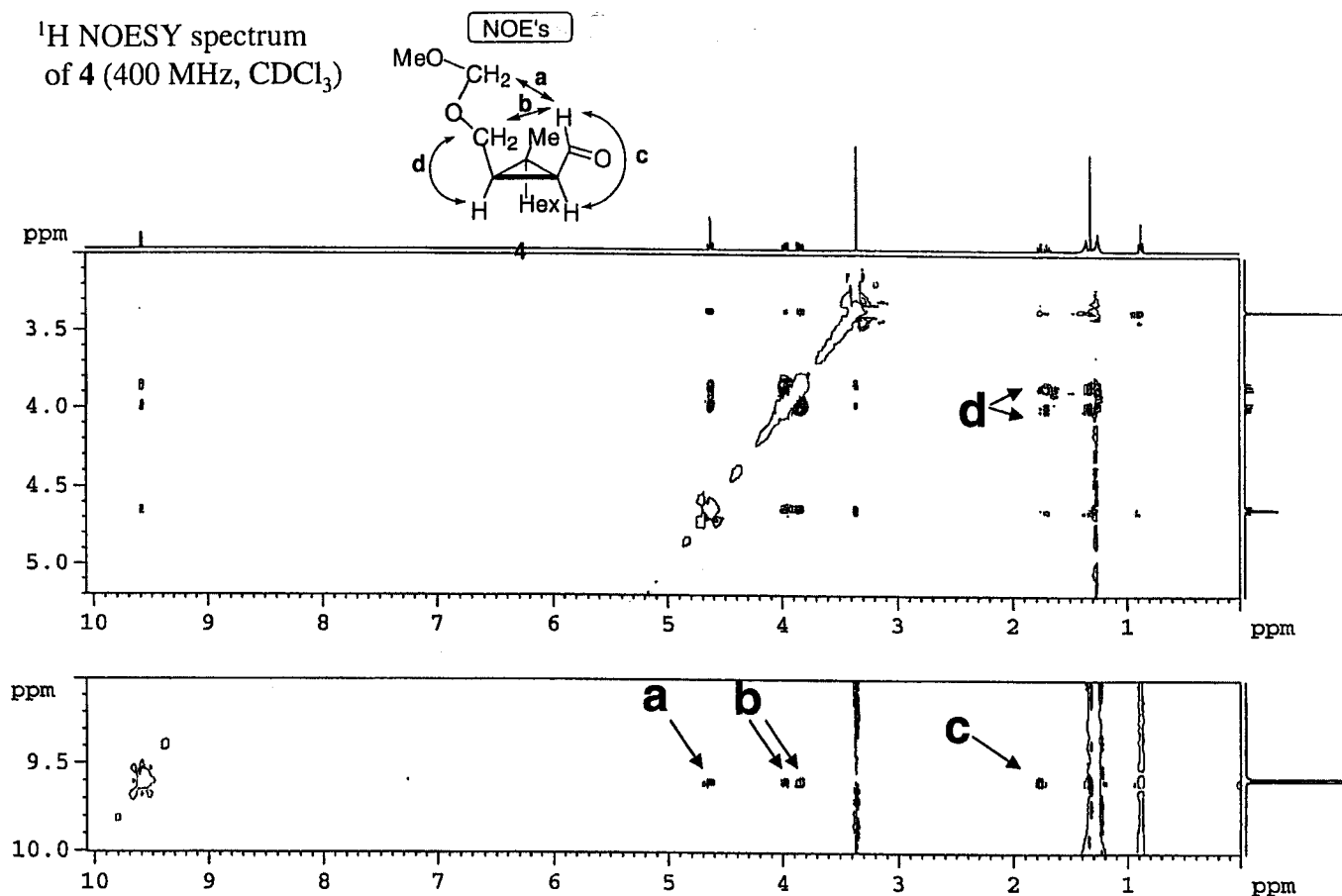


GC trace of 4 (HP1 column)

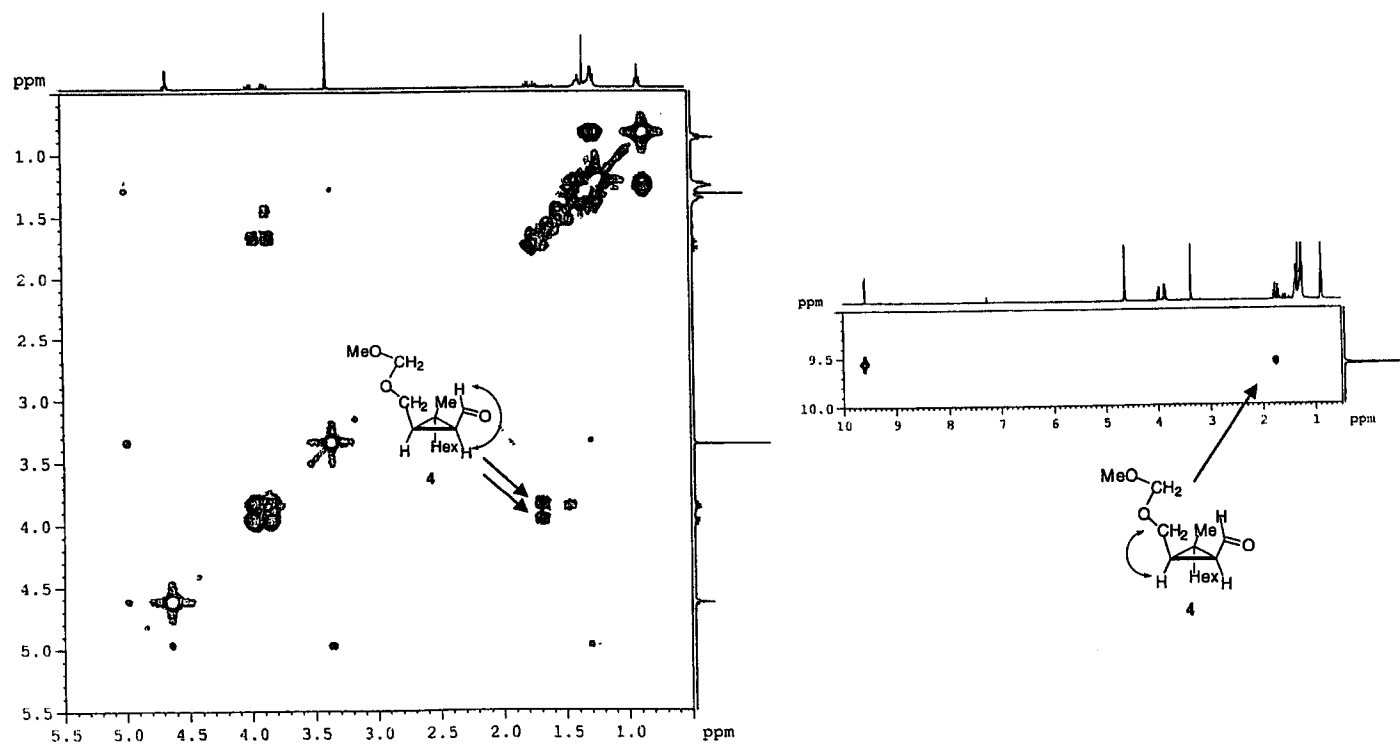


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.0750	0.680	0.000	804830528	BB	6.9	
2		0.0003	8.244	0.000	2290	BB	3.4	
3		0.0007	10.330	0.000	6002	VB	3.3	
4		0.0002	10.620	0.000	1574	BP	3.2	
5		0.0008	11.129	0.000	6624	BB	3.5	
6		0.0015	12.121	0.000	11945	BB	4.1	
7		0.0003	12.908	0.000	2215	BV	3.2	
8		0.0017	13.722	0.000	13761	BV	3.5	
9		0.9194	14.413	0.000	7468820	VB	6.4	
10		0.0001	15.956	0.000	1204	BB	4.4	
Totals:		100.0000		0.000	812344963			

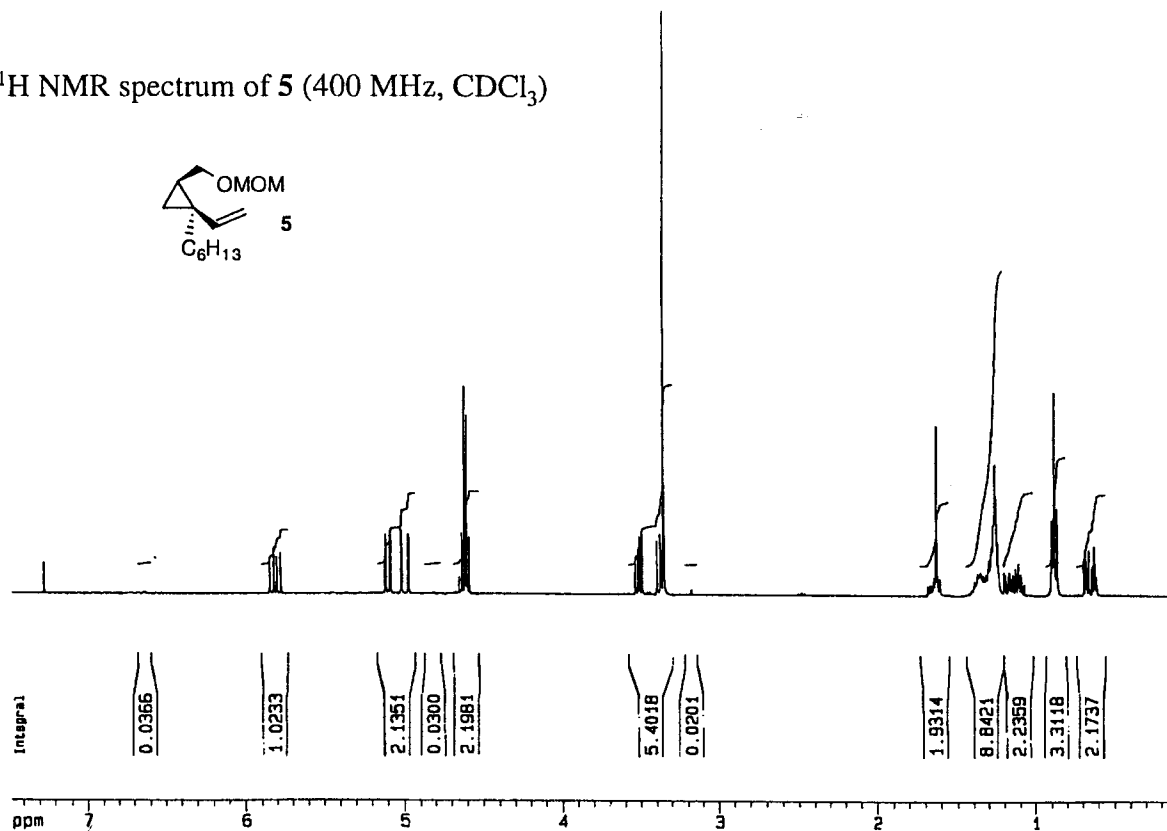
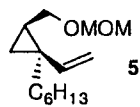
^1H NOESY spectrum of **4** (400 MHz, CDCl_3)



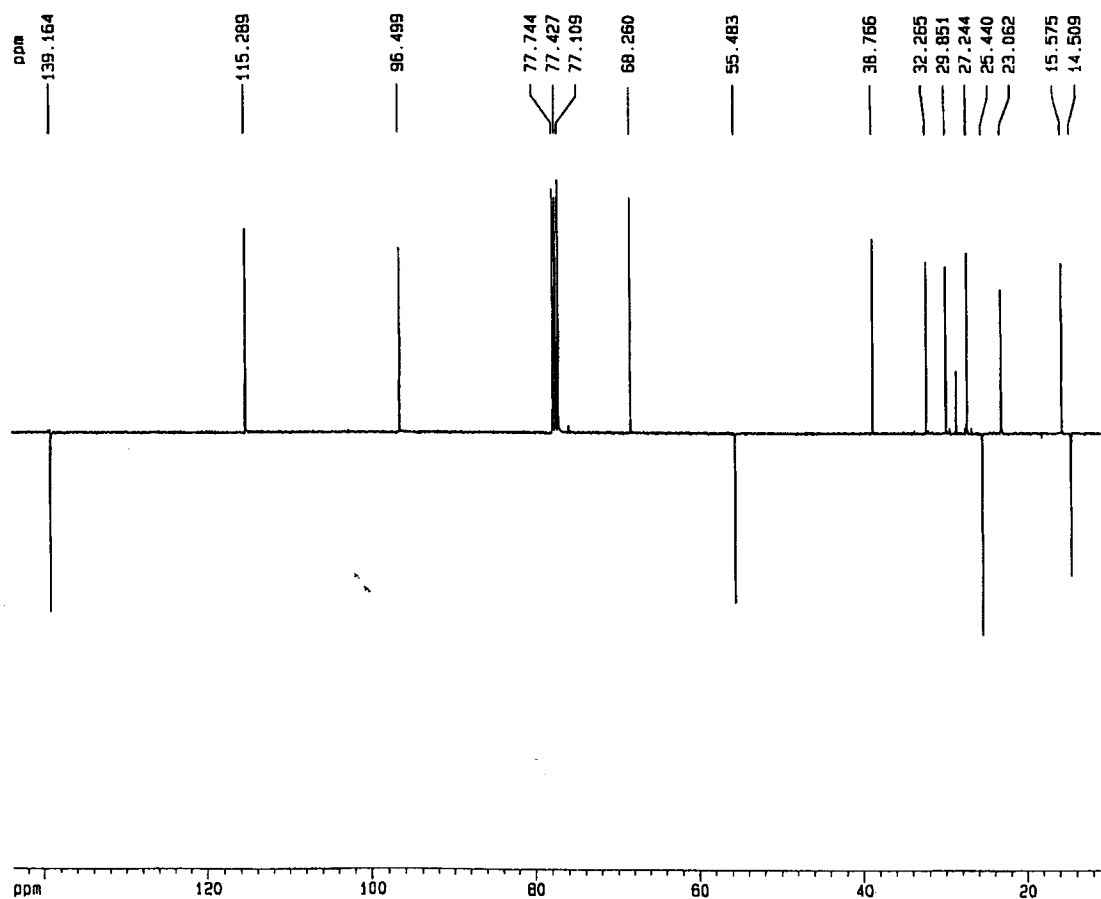
^1H COSY spectrum of **4** (400 MHz, CDCl_3)



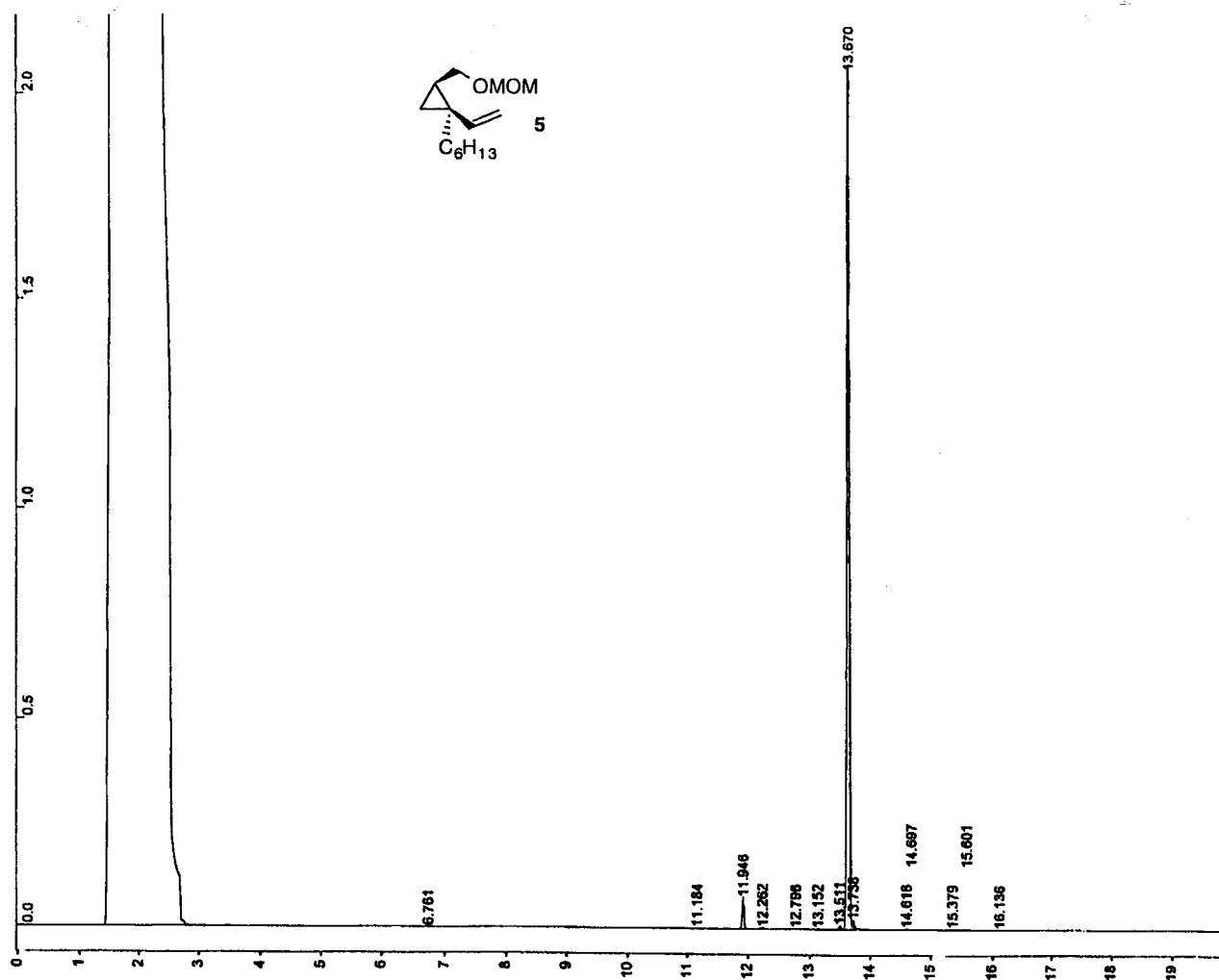
^1H NMR spectrum of **5** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **5** (100 MHz, CDCl_3)

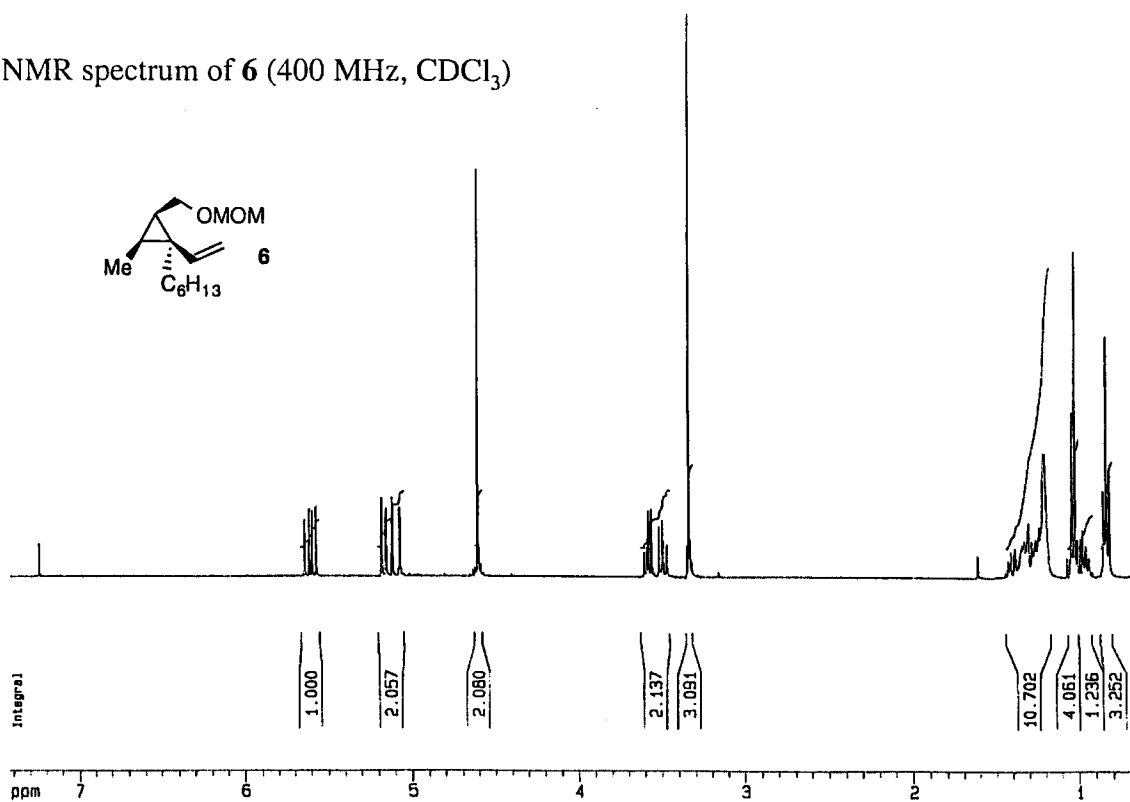


GC trace of 5 (HP5 column)

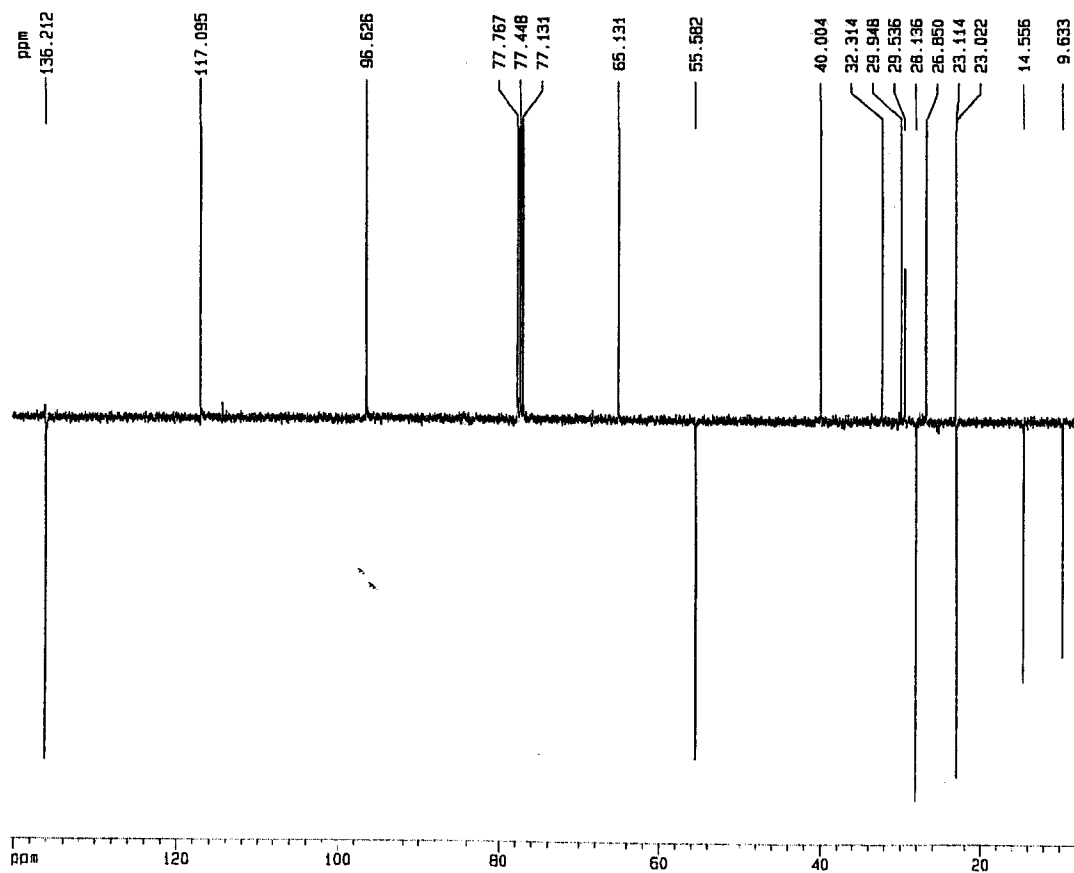


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.0060	6.761	0.000	342	BB	1.9	
2		0.0176	11.184	0.000	1000	BB	1.9	
3		2.8414	11.946	0.000	161739	BB	2.0	
4		0.1275	12.262	0.000	7256	BB	2.7	
5		0.0176	12.798	0.000	1004	BB	1.8	
6		0.0503	13.152	0.000	2866	BB	1.6	
7		0.3579	13.511	0.000	20371	BP	2.3	
8		95.8718	13.670	0.000	5457301	PB	2.5	
9		0.4741	13.738	0.000	26986	TS	0.0	
10		0.0850	14.618	0.000	4839	BV	1.9	
11		0.0202	14.697	0.000	1151	VB	1.8	
12		0.0422	15.379	0.000	2401	BB	2.0	
13		0.0828	15.601	0.000	4715	BB	2.1	
14		0.0056	16.136	0.000	320	BB	0.0	
Totals:		100.0000		0.000	5692291			

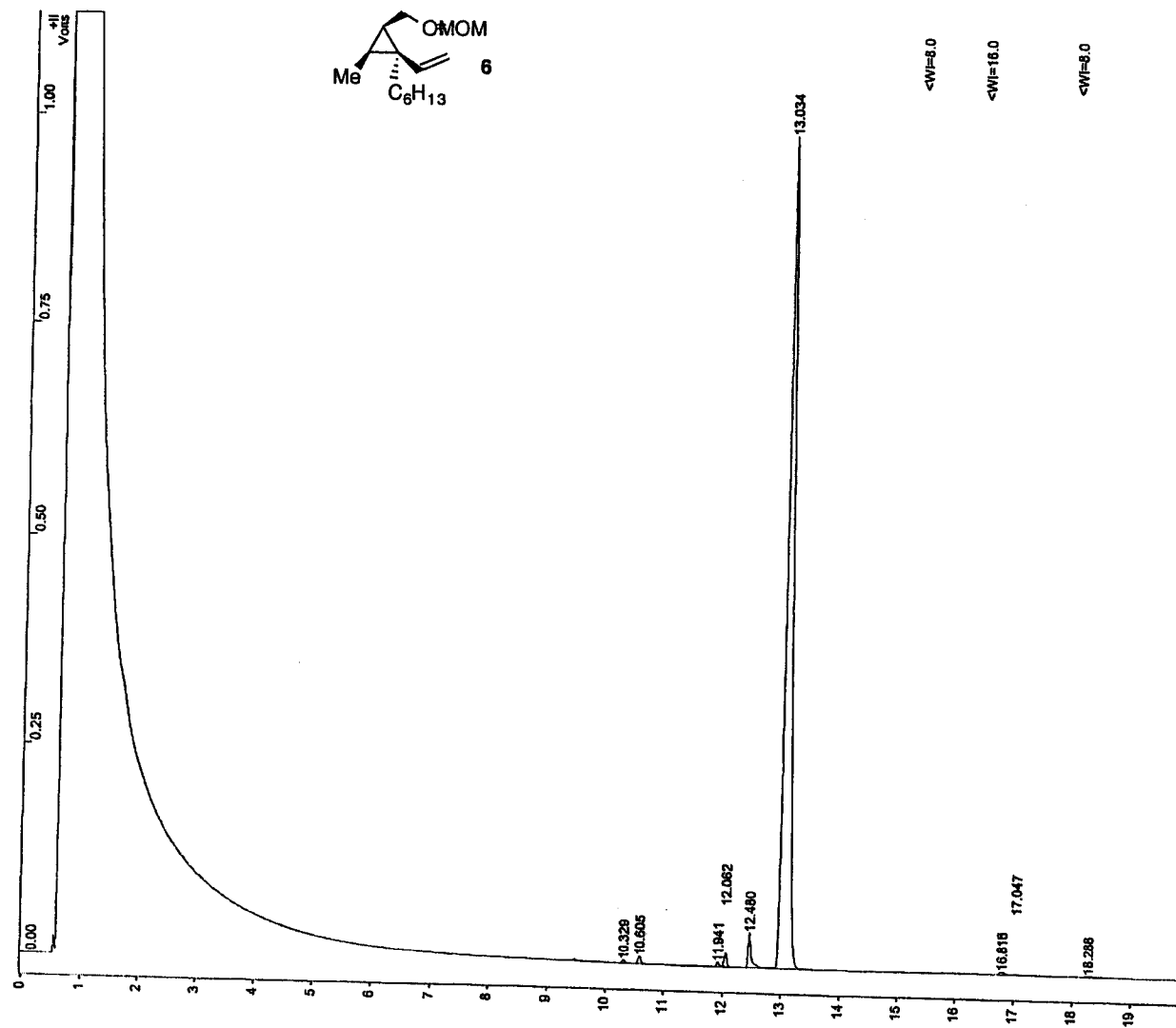
^1H NMR spectrum of **6** (400 MHz, CDCl_3)



^{13}C JVERT NMR spectrum of **6** (100 MHz, CDCl_3)

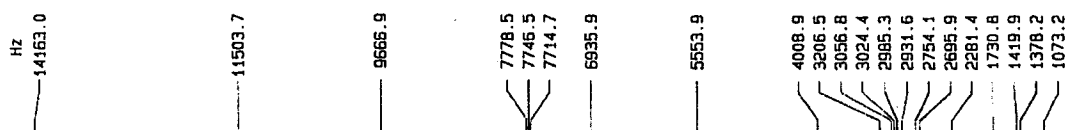
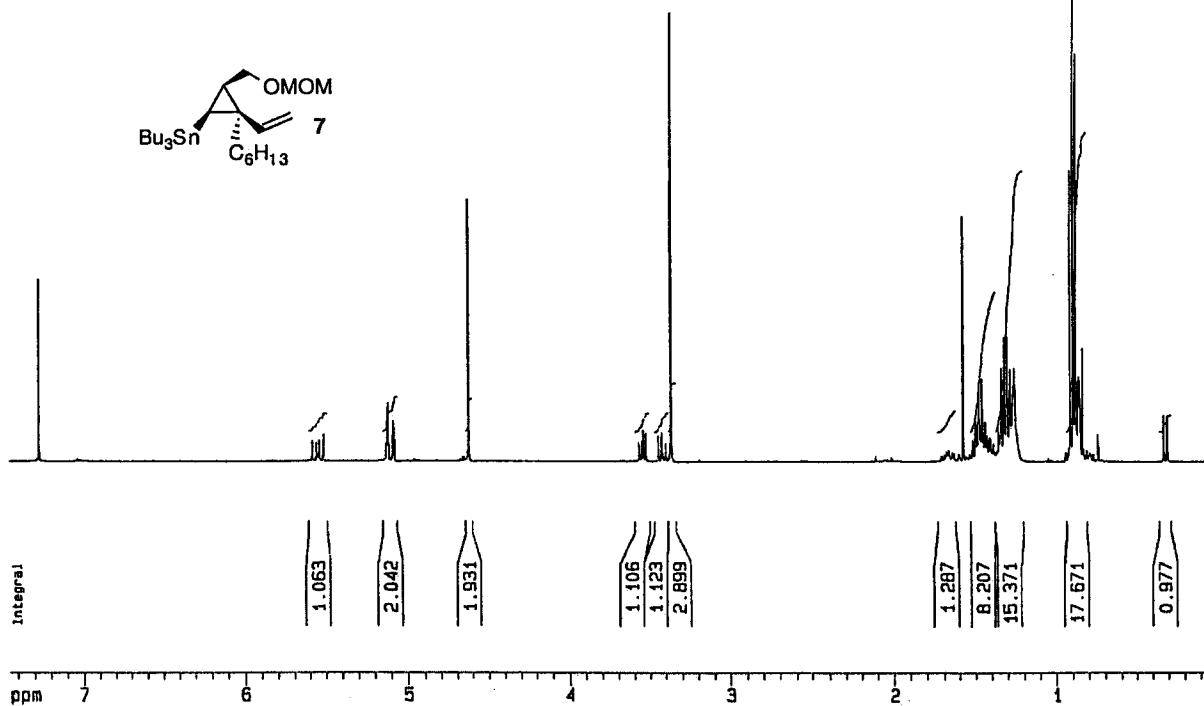


GC trace of **6** (HP1 column)

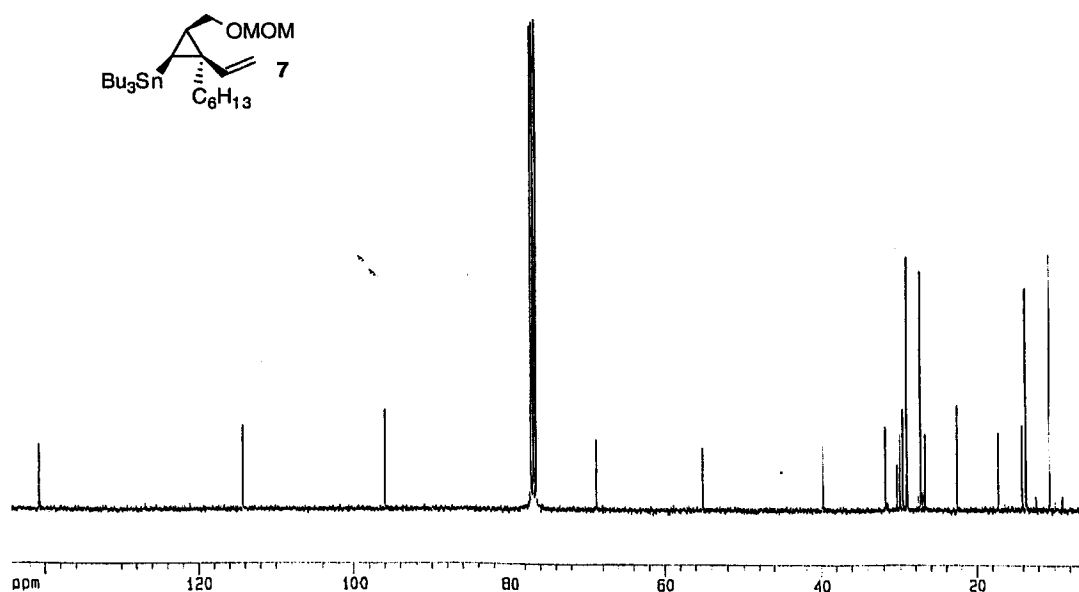


Peak No.	Peak Name	Result (%)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.2237	10.329	0.000	15430	PP	3.2	
2		0.5647	10.605	0.000	38952	PP	3.3	
3		0.2621	11.941	0.000	18083	BV	3.0	
4		0.8937	12.062	0.000	61651	VB	3.0	
5		2.6522	12.480	0.000	182956	BV	0.0	
6		94.6026	13.034	0.000	6525926	VB	5.9	
7		0.3584	16.816	0.000	24721	PV	6.0	
8		0.1943	17.047	0.000	13400	VB	6.1	
9		0.2483	18.288	0.000	17131	VB	11.0	
Totals:		100.0000		0.000	6898250			

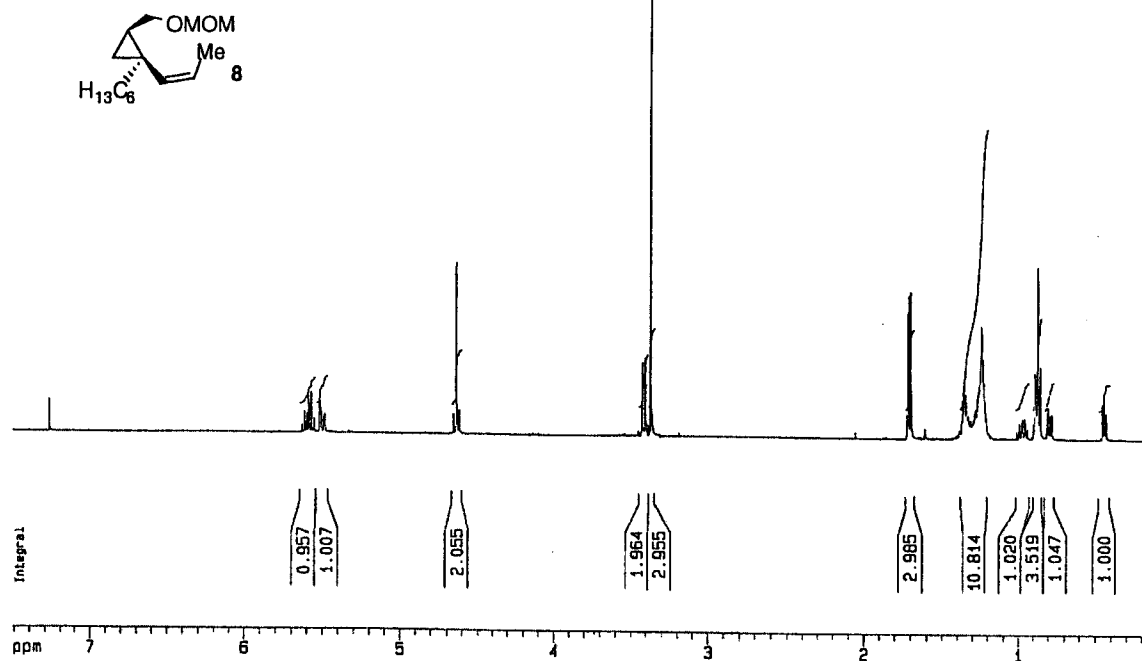
^1H NMR spectrum of **7** (400 MHz, CDCl_3)



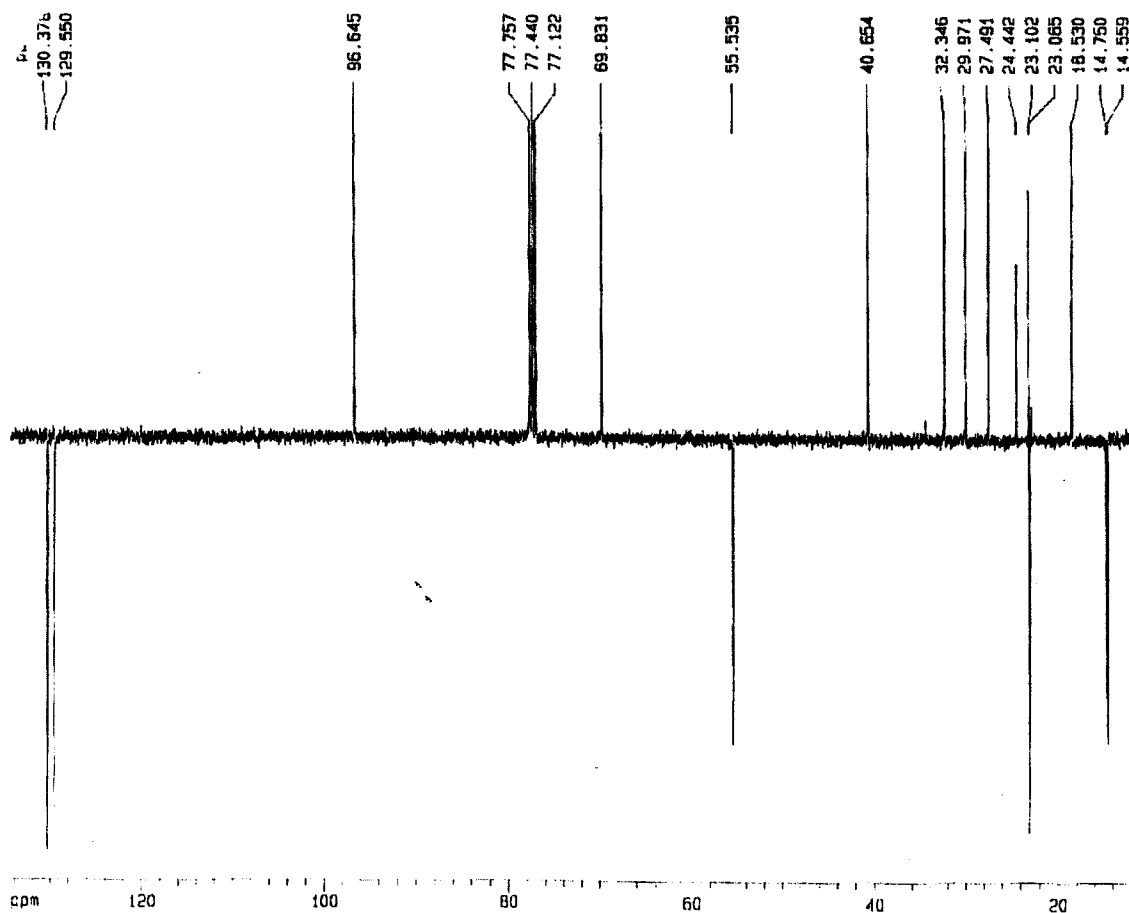
^{13}C NMR spectrum of **7** (100 MHz, CDCl_3)



^1H NMR spectrum of **8** (400 MHz, CDCl_3)



^{13}C JVERT NMR spectrum of **8** (100 MHz, CDCl_3)



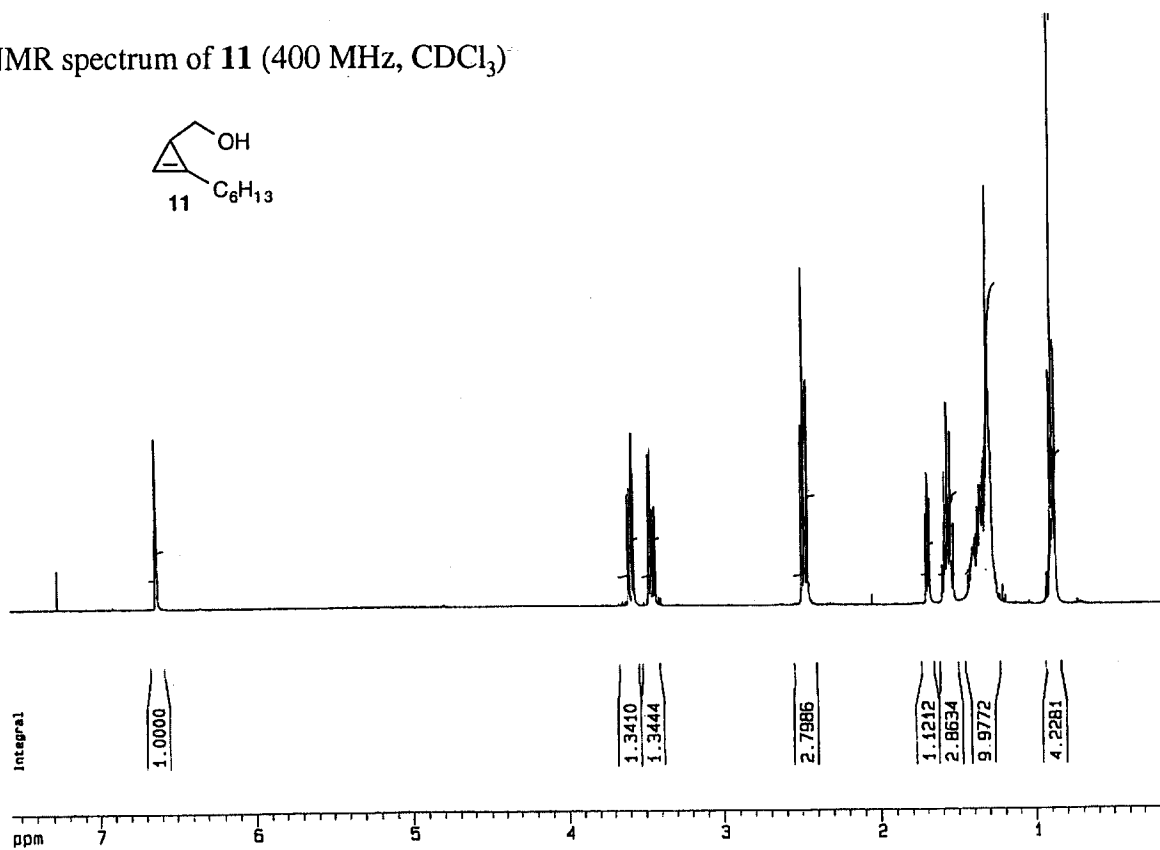
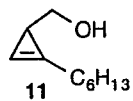
CC1=CC2(C1)C3(C2)C(C3)OC(=O)C

^1H NMR spectrum (CDCl₃) of compound **8**. The x-axis represents chemical shift (ppm) from 0 to 19. The y-axis represents intensity. A large peak is observed at 12.948 ppm, labeled with an integration value of 98.97. A smaller peak is observed at 12.114 ppm. The spectrum shows characteristic signals for the compound, including a broad peak around 12.9 ppm and a sharp peak around 12.1 ppm.

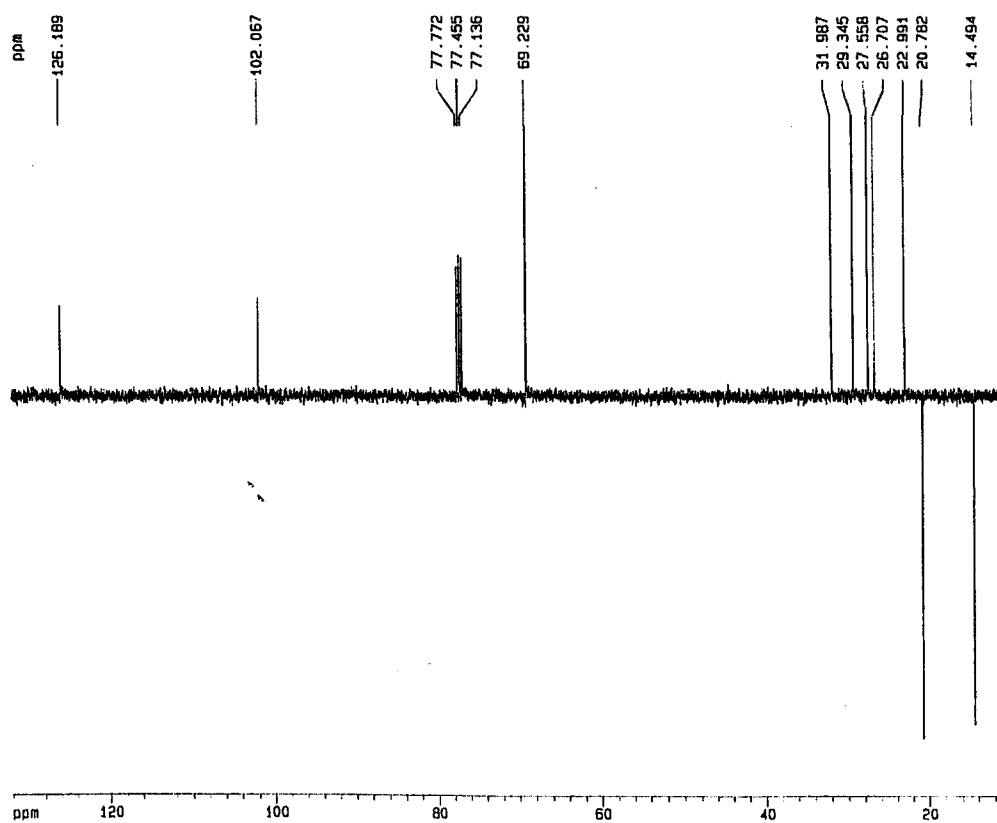
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		1.0607	12.114	0.000	8771	BB	2.2	
2		98.9393	12.948	0.000	818163	BB	2.4	
Totals:		100.0000		0.000	826934			

514

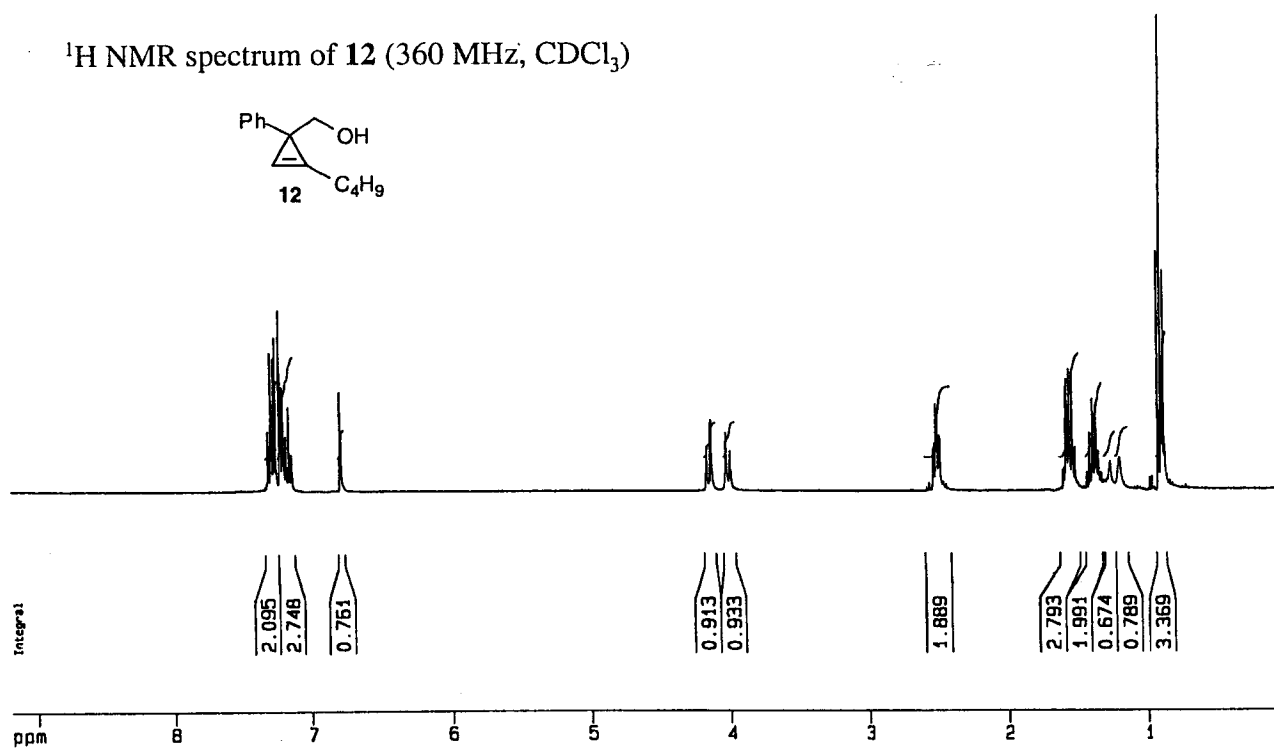
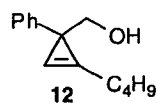
^1H NMR spectrum of **11** (400 MHz, CDCl_3)



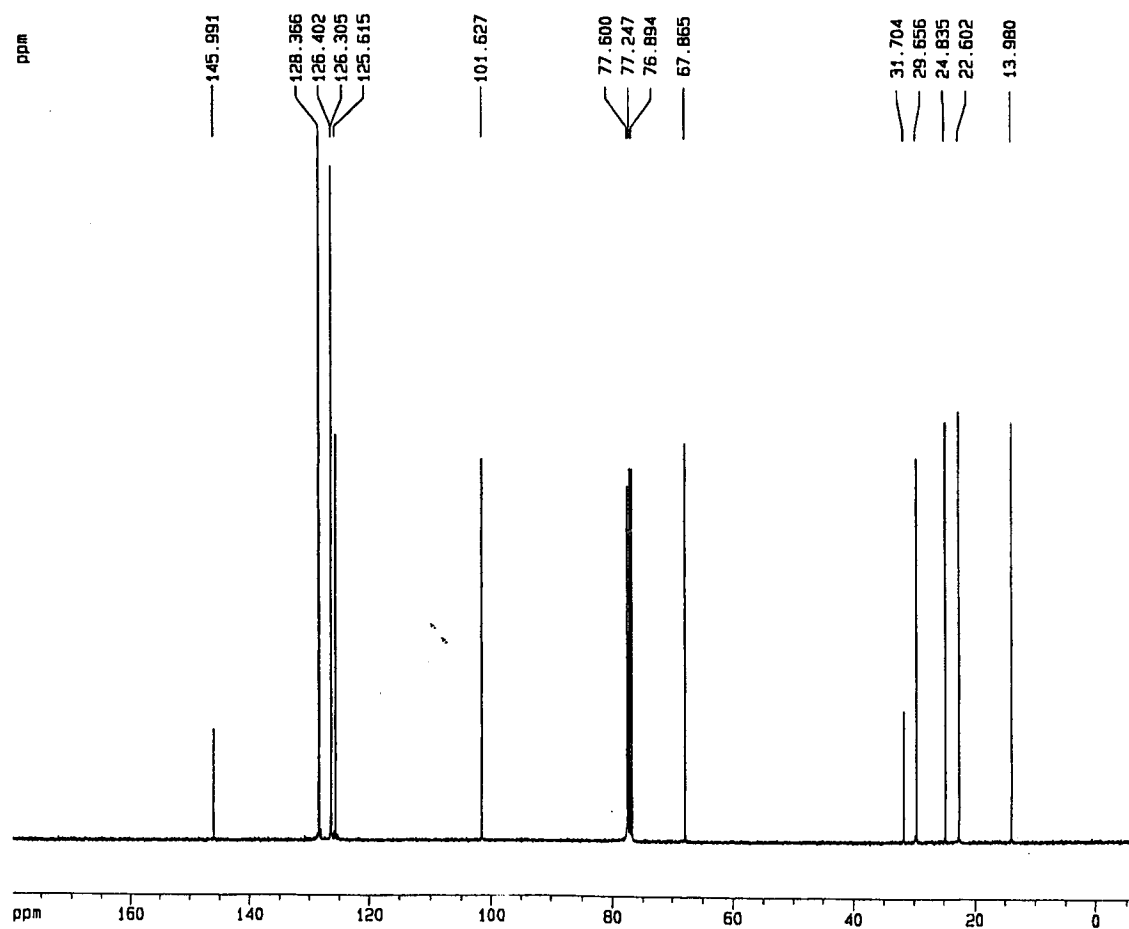
^{13}C JVERT NMR spectrum of **11** (100 MHz, CDCl_3)



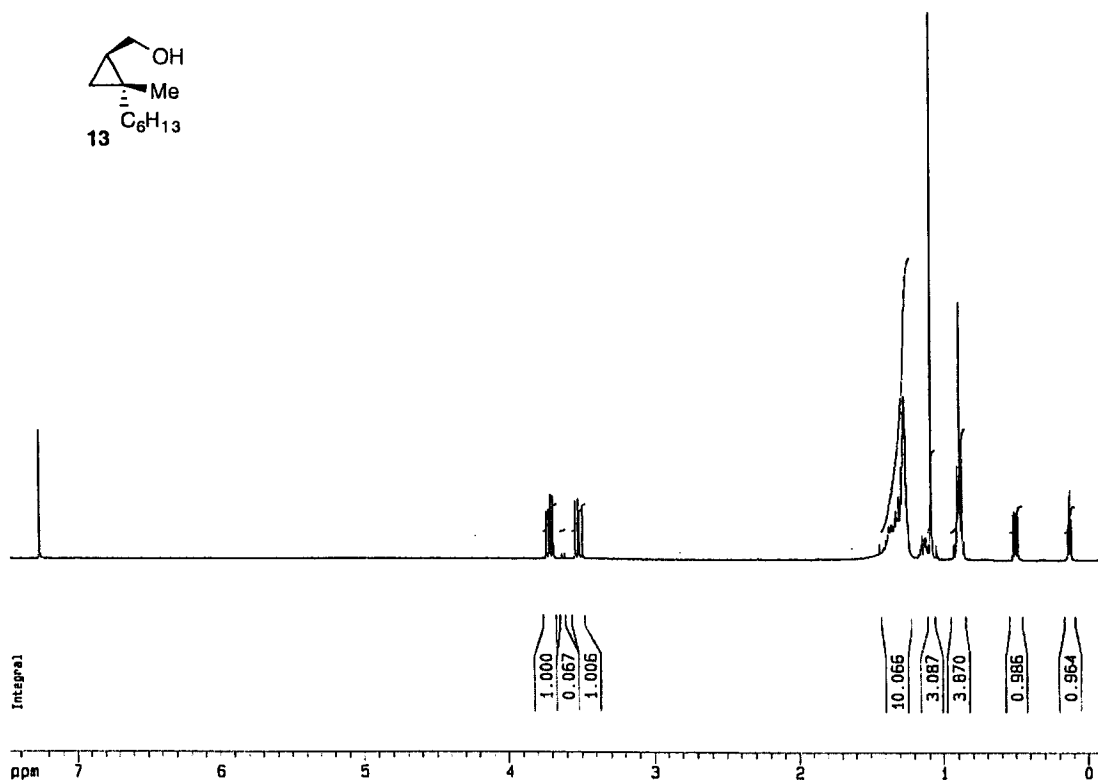
^1H NMR spectrum of **12** (360 MHz, CDCl_3)



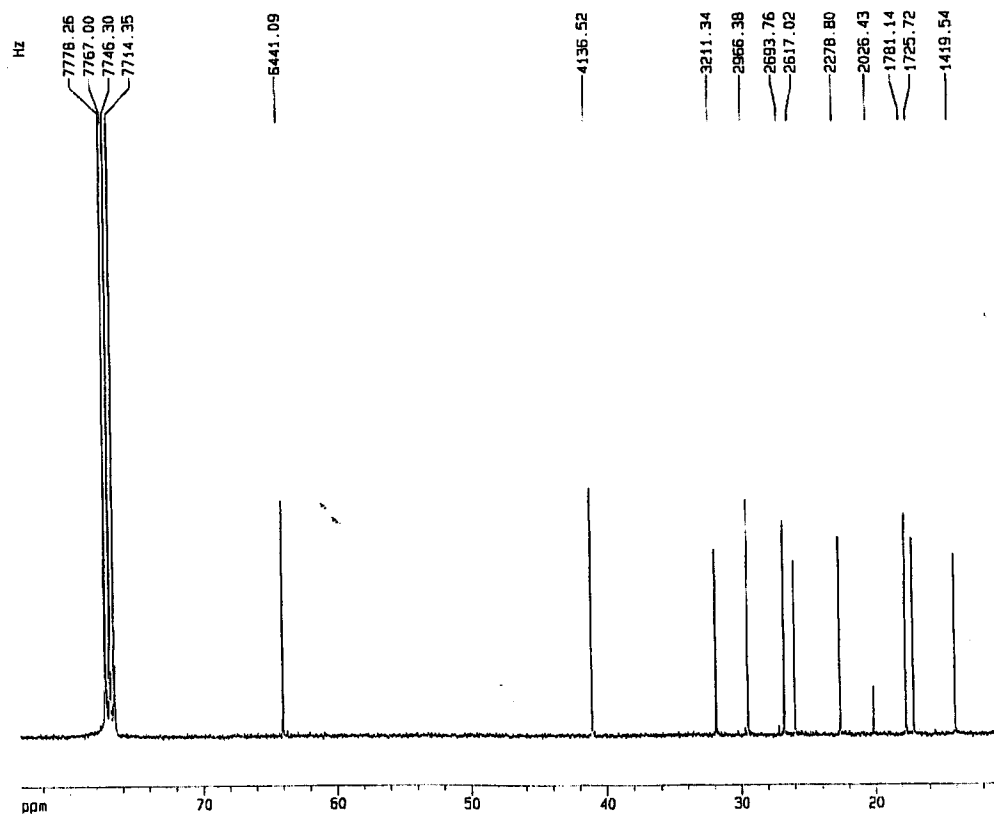
^{13}C NMR spectrum of **12** (90 MHz, CDCl_3)



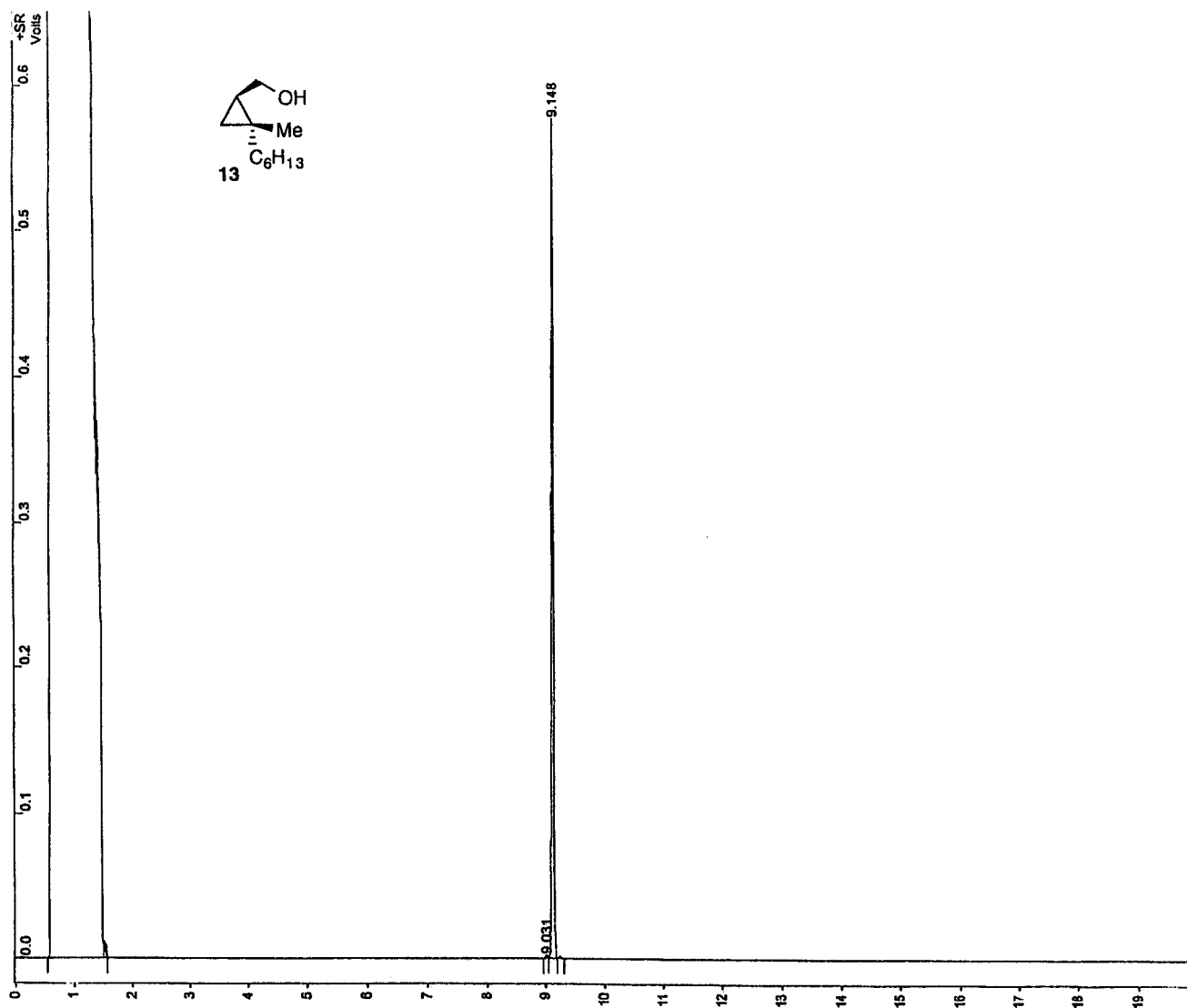
^1H NMR spectrum of **13** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **13** (100 MHz, CDCl_3)

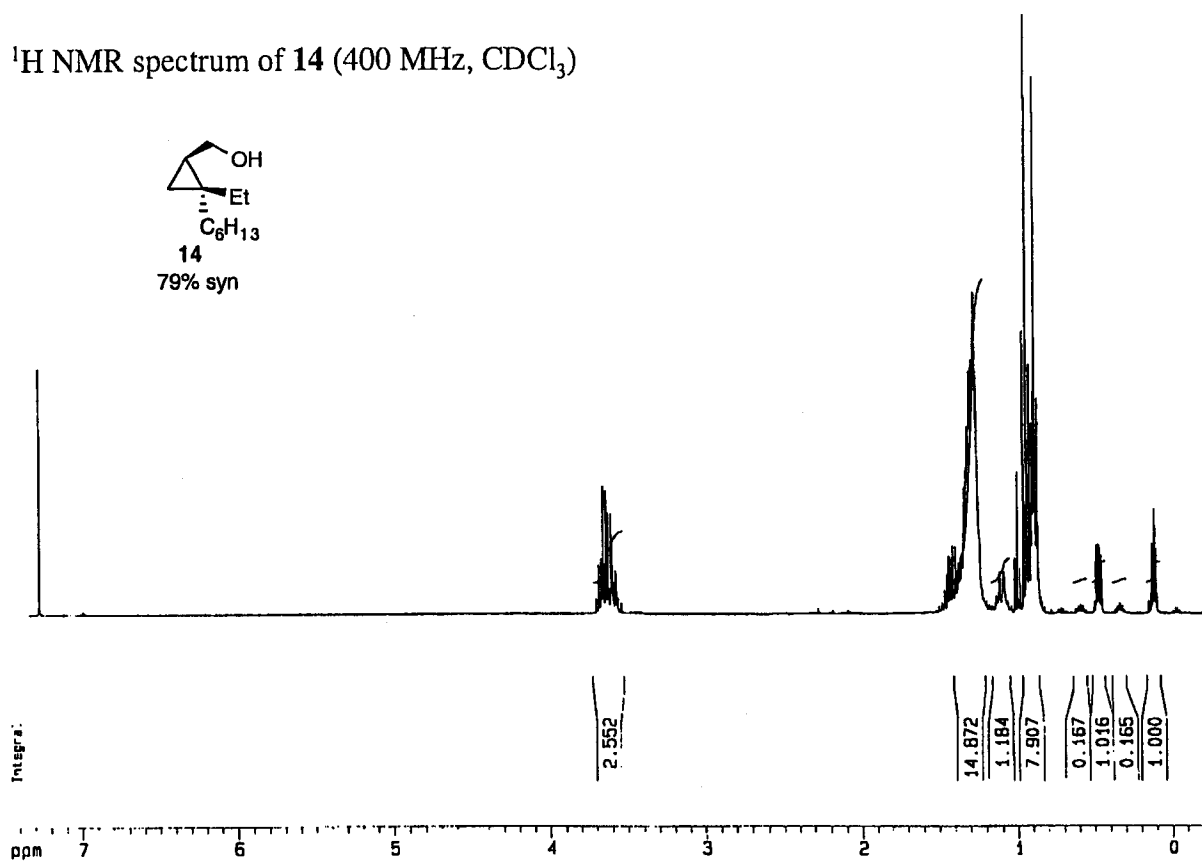
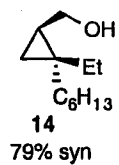


GC trace of 13 (HP5 column)

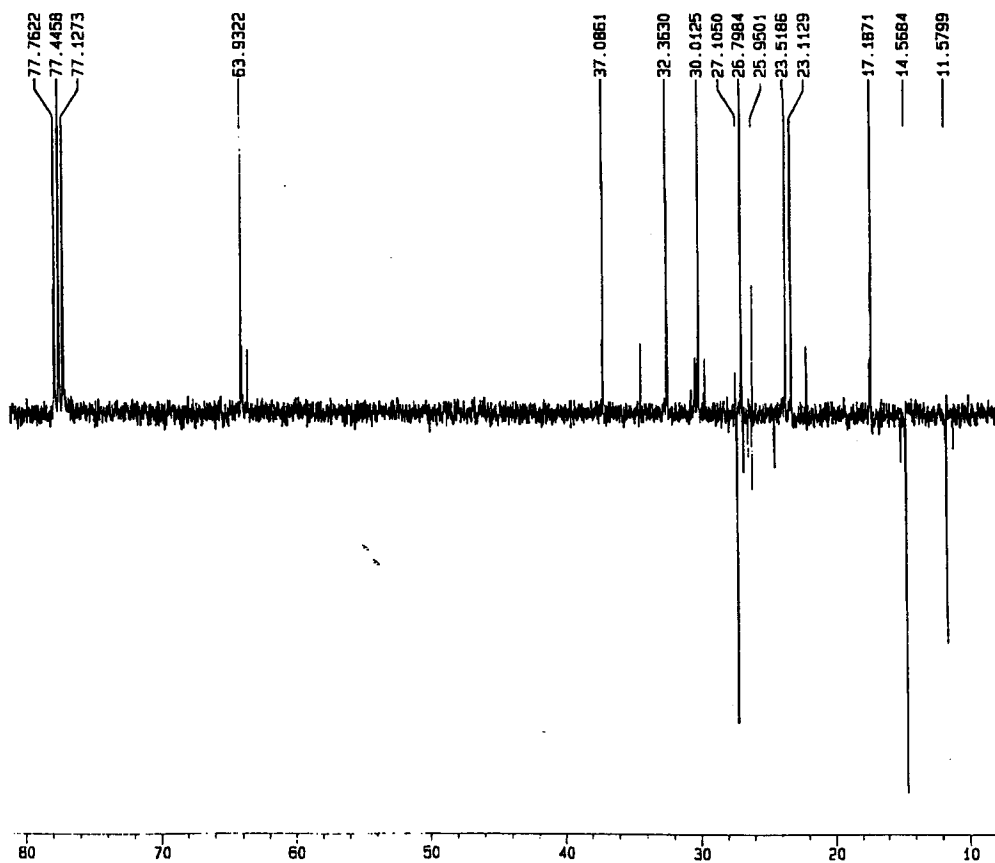


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.4156	9.031	0.000	5659	BV	2.4	
2		99.5844	9.148	0.000	1355951	VB	2.2	
Totals:		100.0000		0.000	1361610			

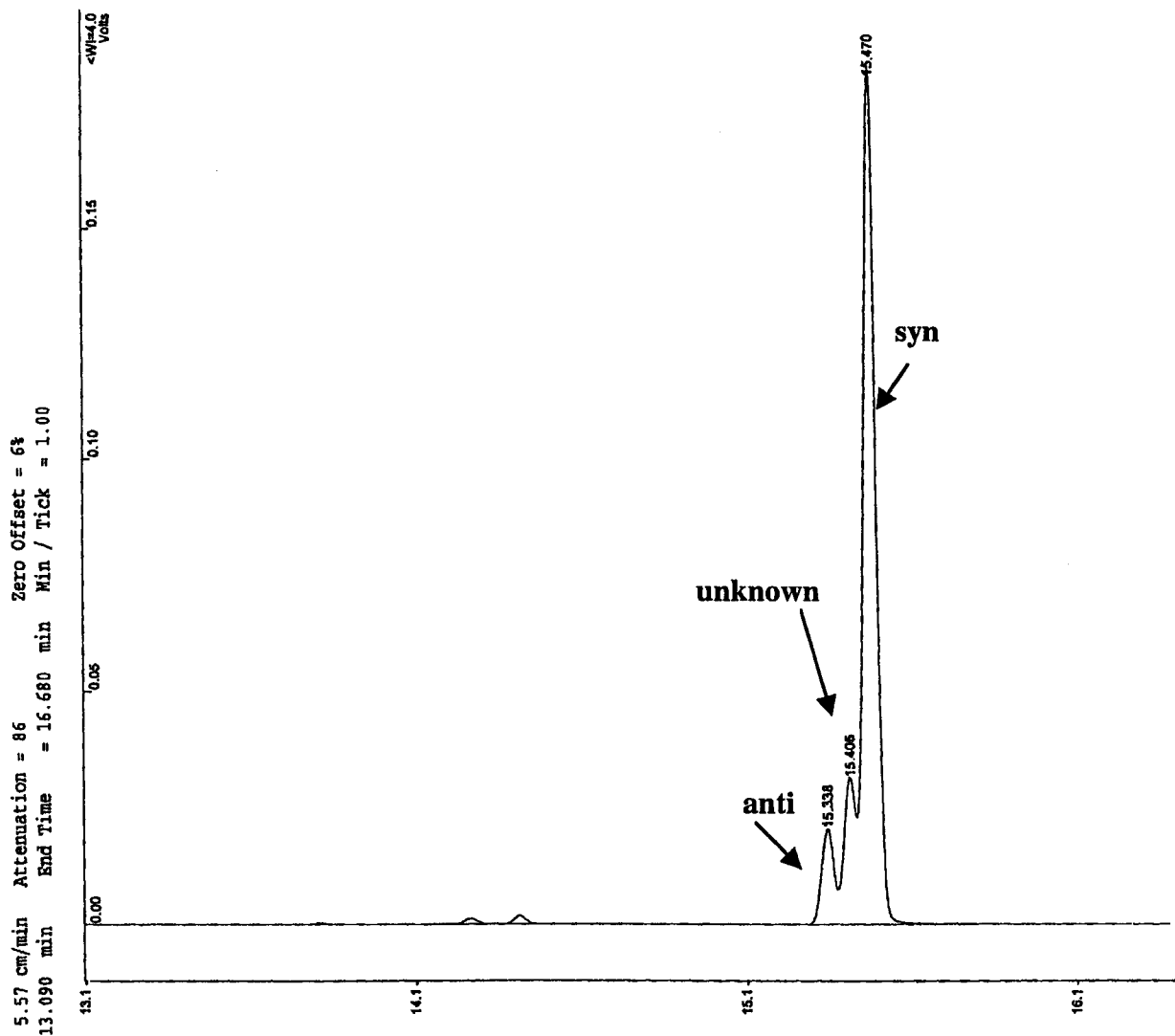
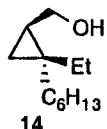
^1H NMR spectrum of **14** (400 MHz, CDCl_3)



^{13}C NMR (JVERT) spectrum of **14** (100 MHz, CDCl_3)

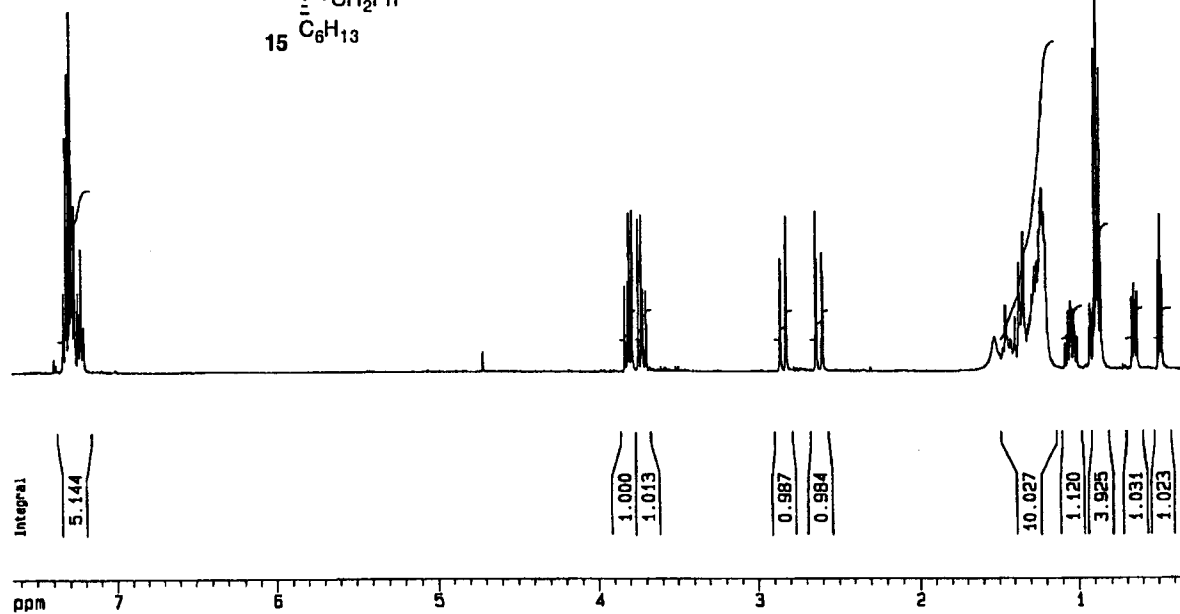
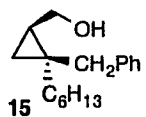


GC trace of **14** (HP5 column)

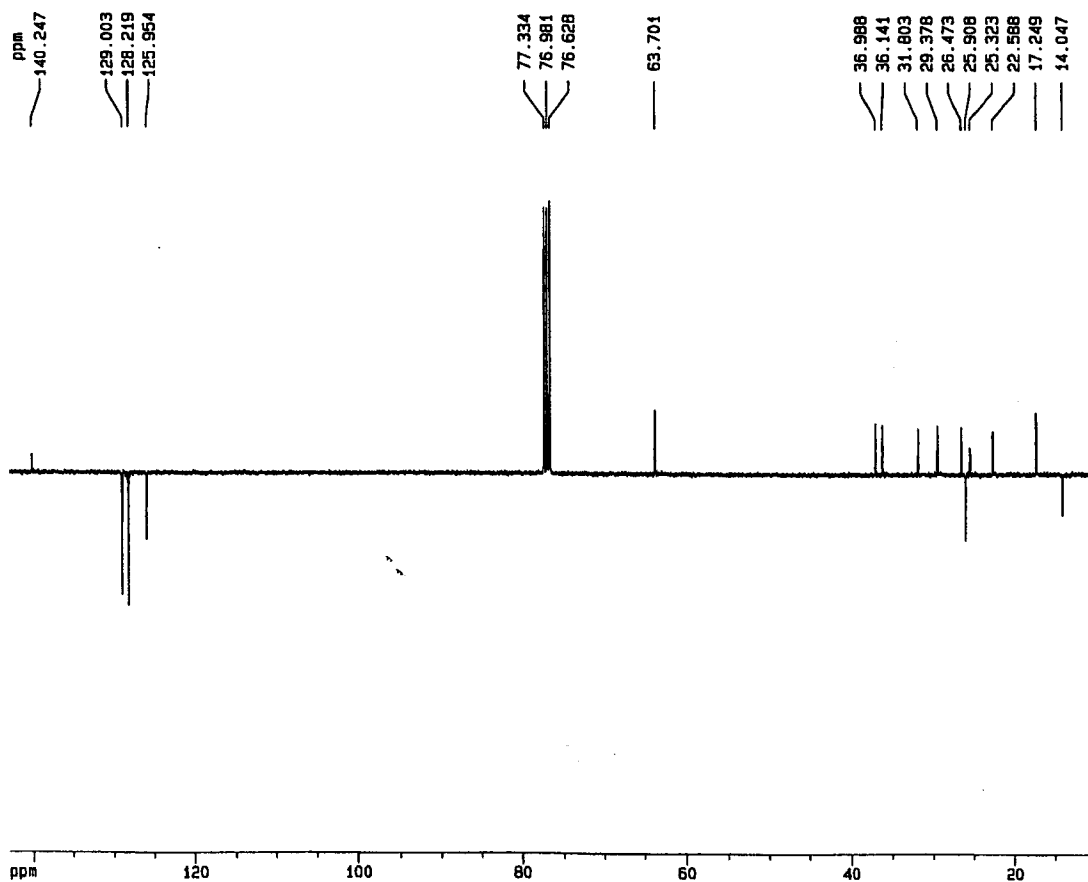


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		8.6596	15.338	0.000	52443	PV	2.5	
2		12.1107	15.406	0.000	73343	VV	2.6	
3		79.2297	15.470	0.000	479817	VB	2.4	
Totals:		100.0000		0.000	605603			

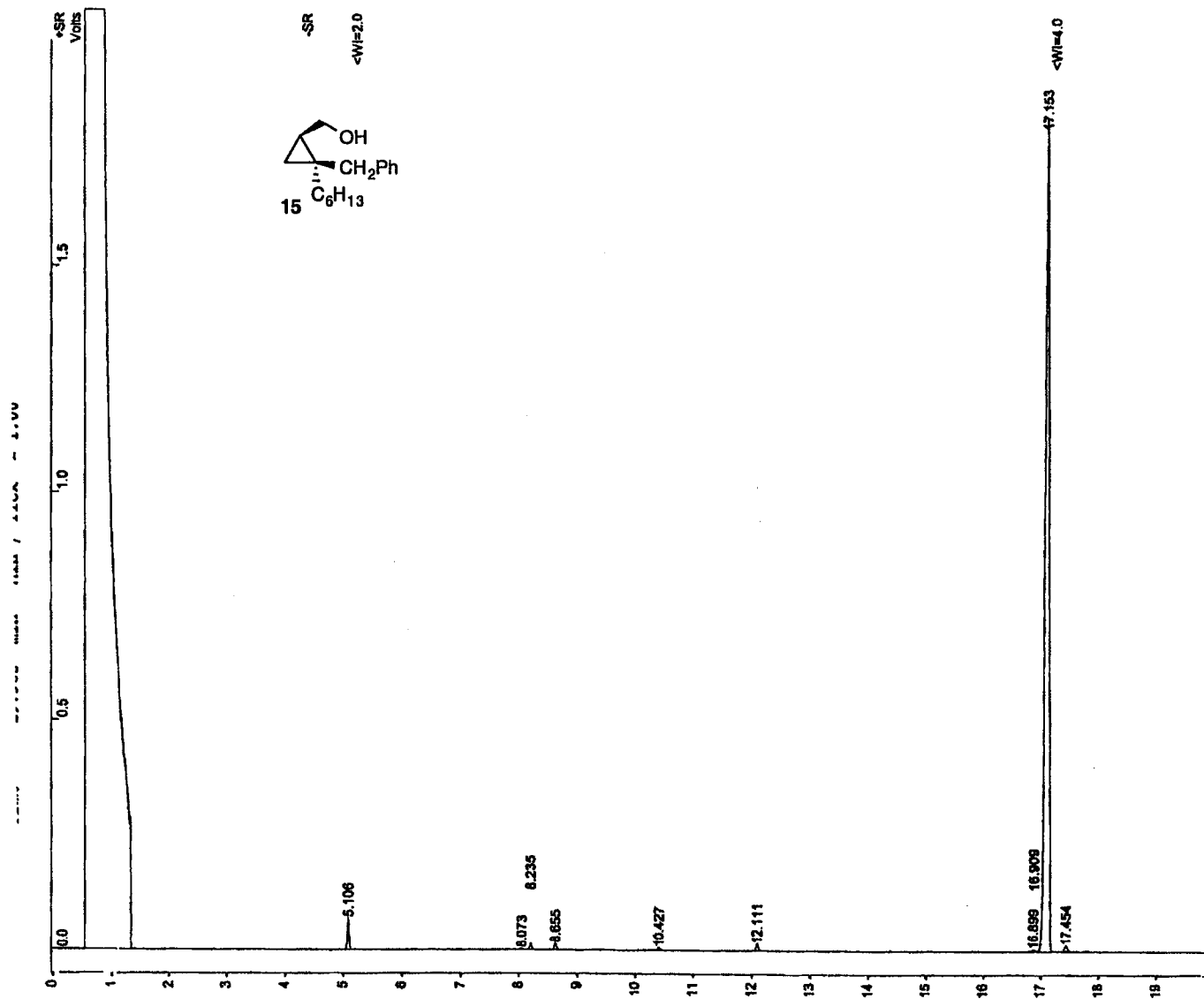
^1H NMR spectrum of **15** (400 MHz, CDCl_3)



^{13}C NMR (JVERT) spectrum of **15** (100 MHz, CDCl_3)

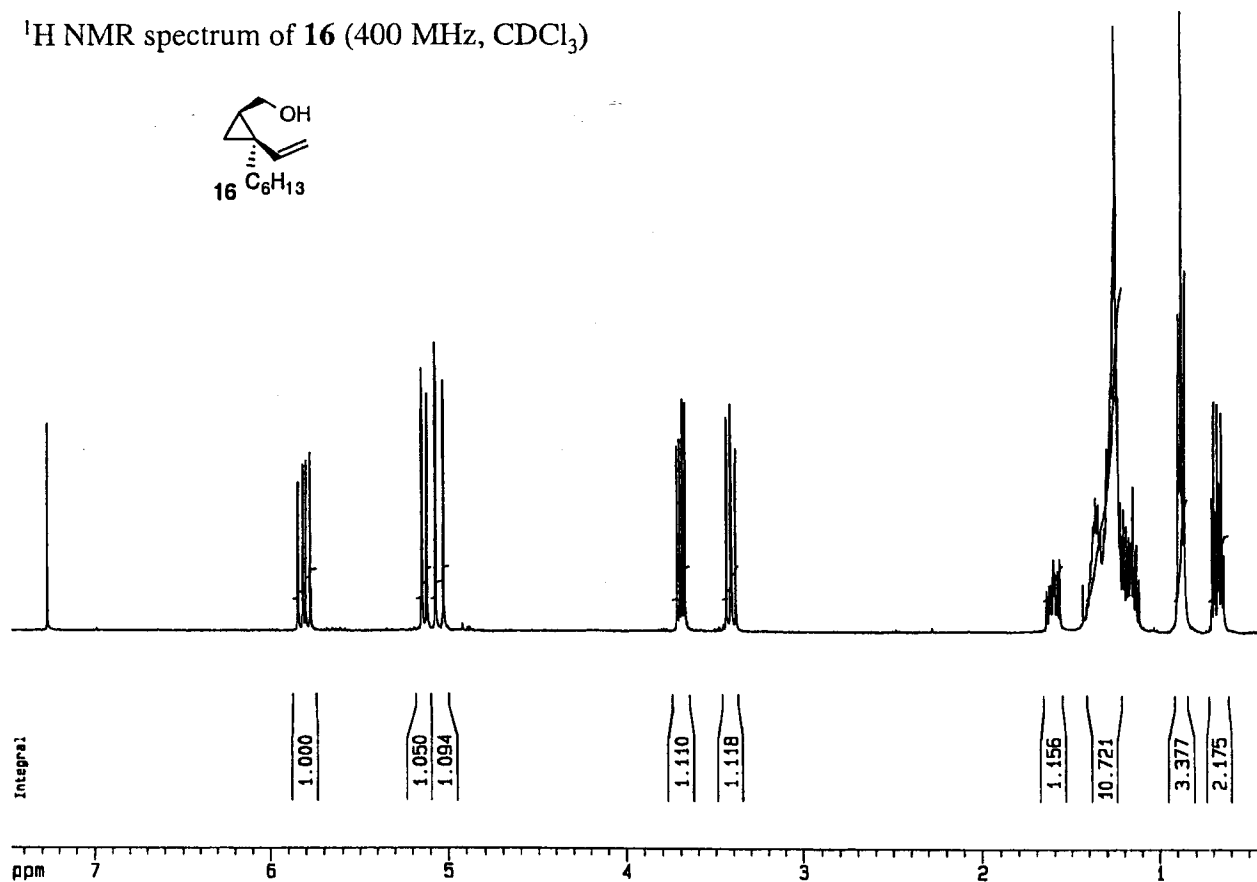
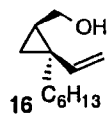


GC trace of 15 (HP5)

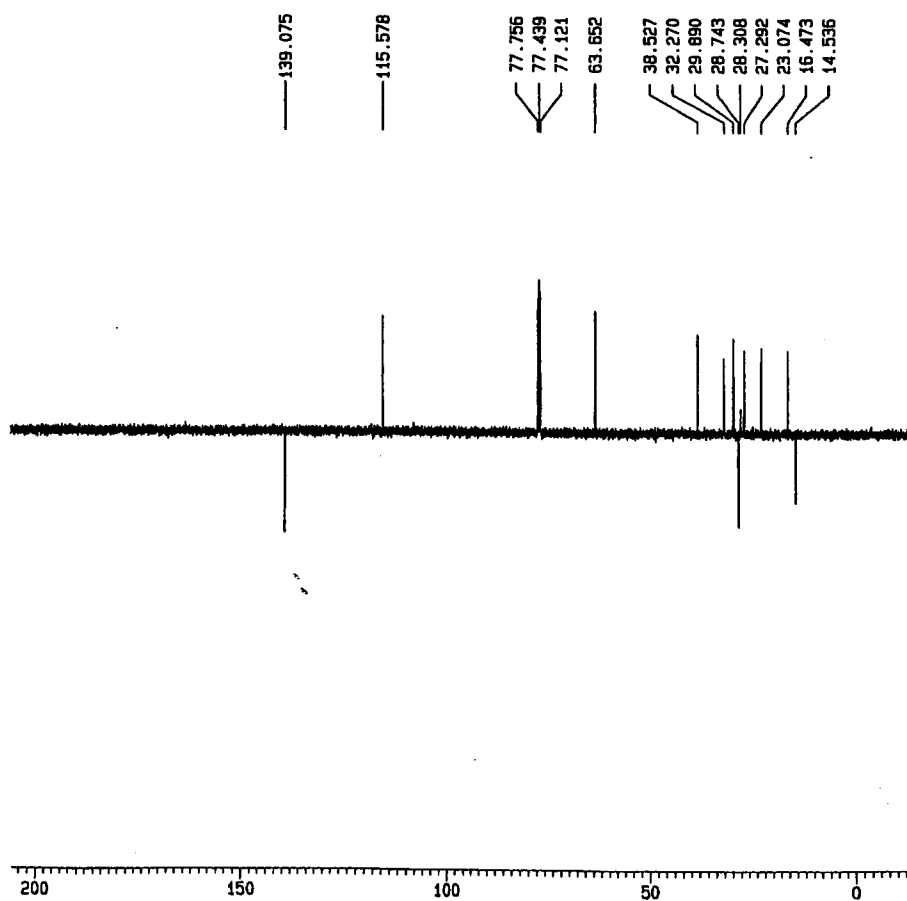


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		1.6960	5.106	0.000	151497	BB	2.0	
2		0.0605	8.073	0.000	5407	BB	1.8	
3		0.4087	8.235	0.000	36508	BB	2.4	
4		0.4536	8.655	0.000	40520	BB	2.3	
5		0.1780	10.427	0.000	15897	BB	2.4	
6		0.4836	12.111	0.000	43201	BB	2.6	
7		0.1015	16.899	0.000	9071	BV	2.9	
8		0.1189	16.909	0.000	10621	VV	4.4	
9		95.9152	17.153	0.000	8567851	VB	4.6	
10		0.5839	17.454	0.000	52160	BB	3.6	
Totals:		99.9999		0.000	8932733			

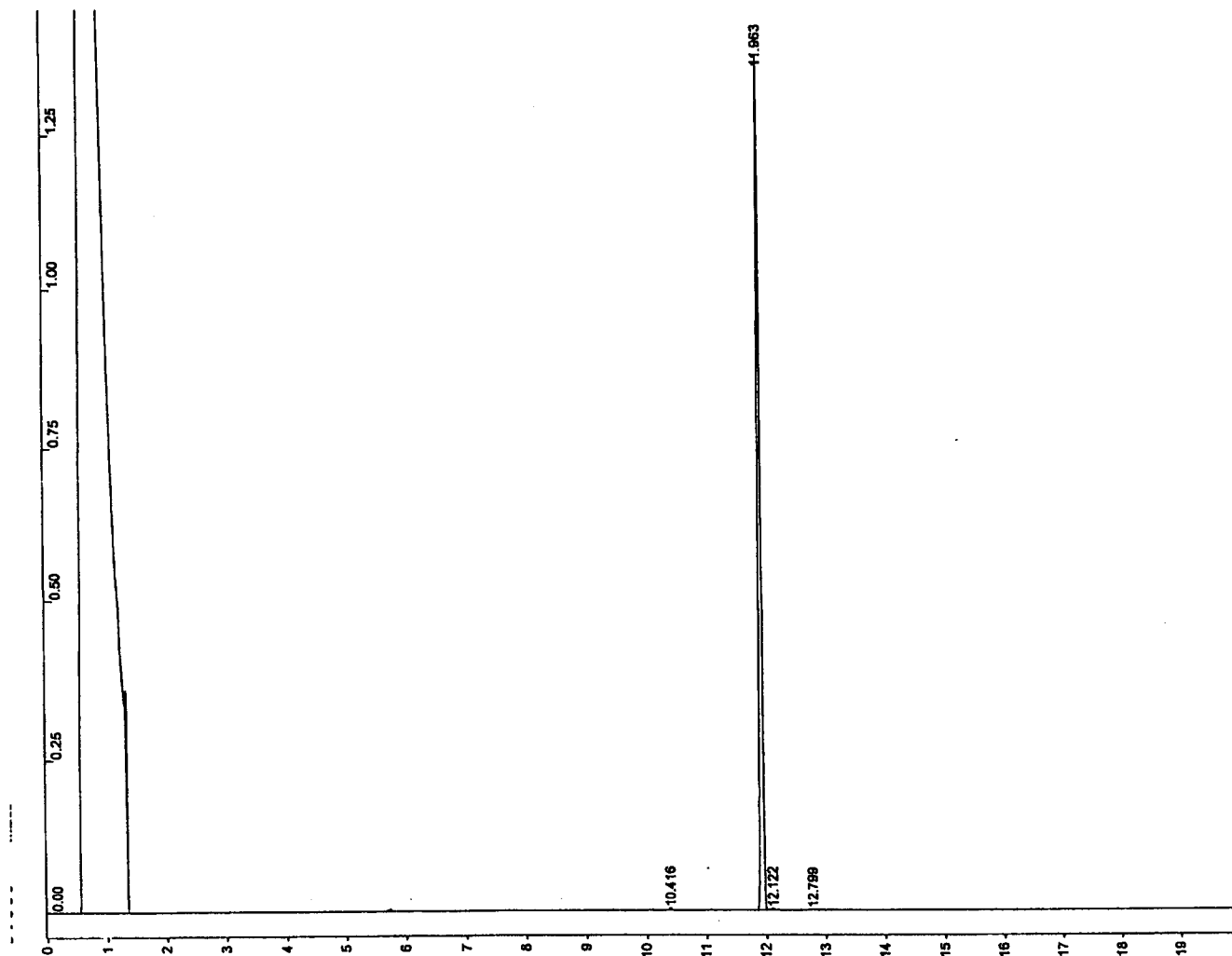
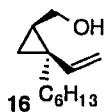
^1H NMR spectrum of **16** (400 MHz, CDCl_3)



^{13}C NMR (JVERT) spectrum of **16** (100 MHz, CDCl_3)

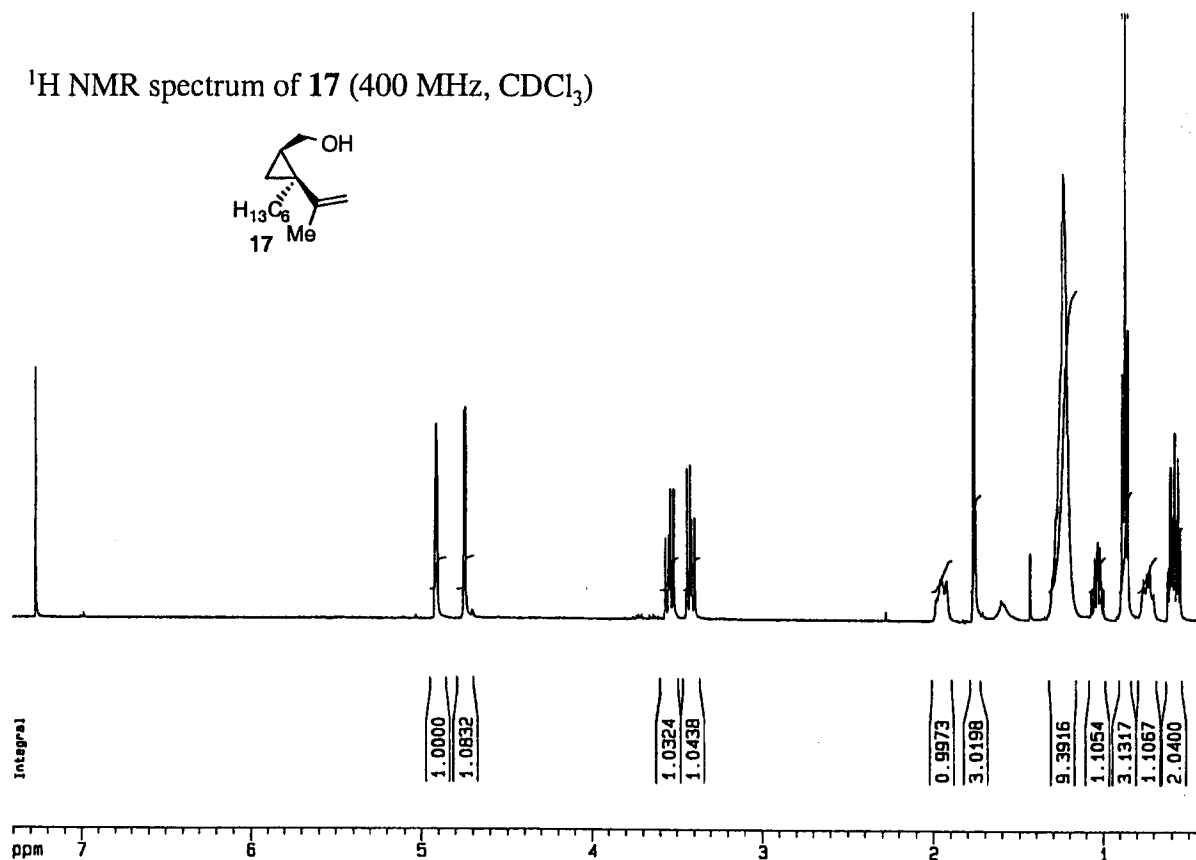
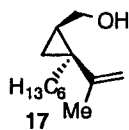


GC trace of 16 (HP5)

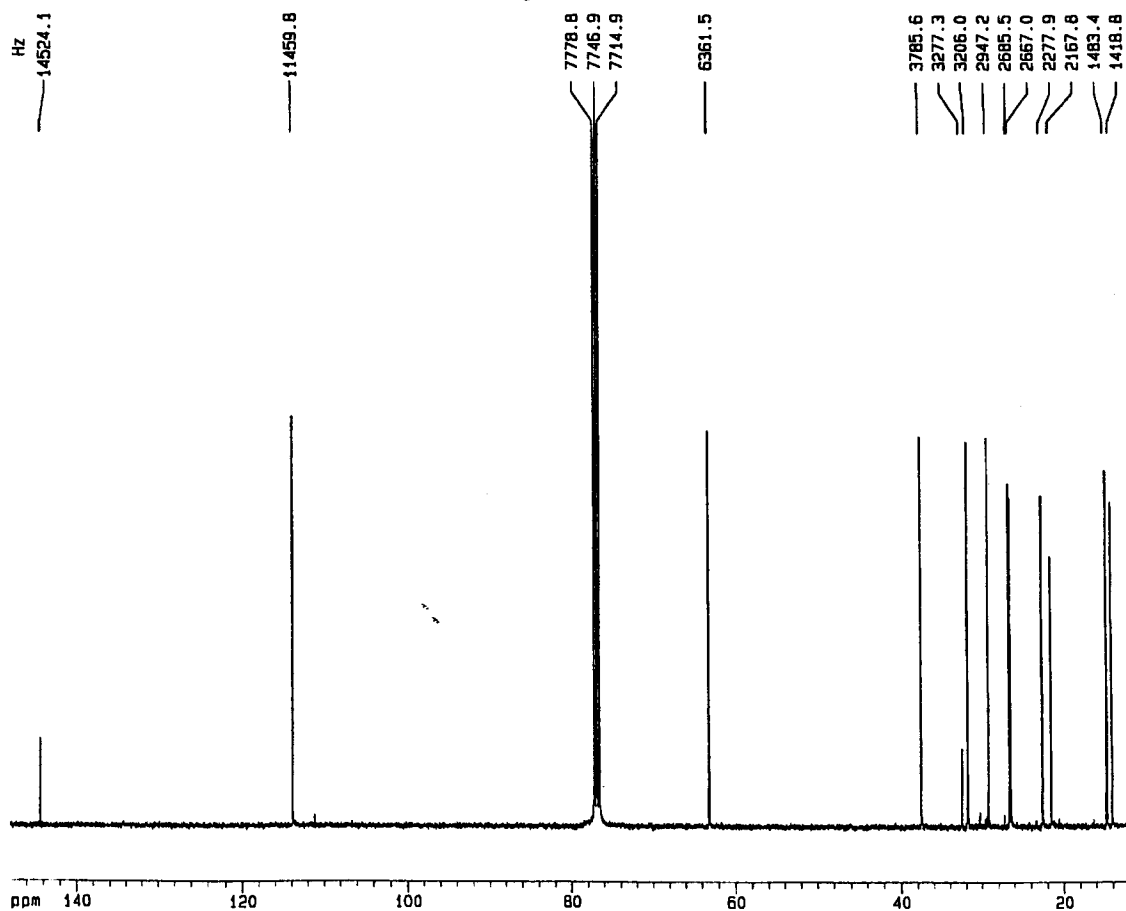


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.3077	10.416	0.000	12342	VB	2.6	
2		99.3658	11.963	0.000	3985142	BB	2.8	
3		0.1955	12.122	0.000	7843	TF	0.0	
4		0.1309	12.799	0.000	5251	BB	2.2	
Totals:		99.9999		0.000	4010578			

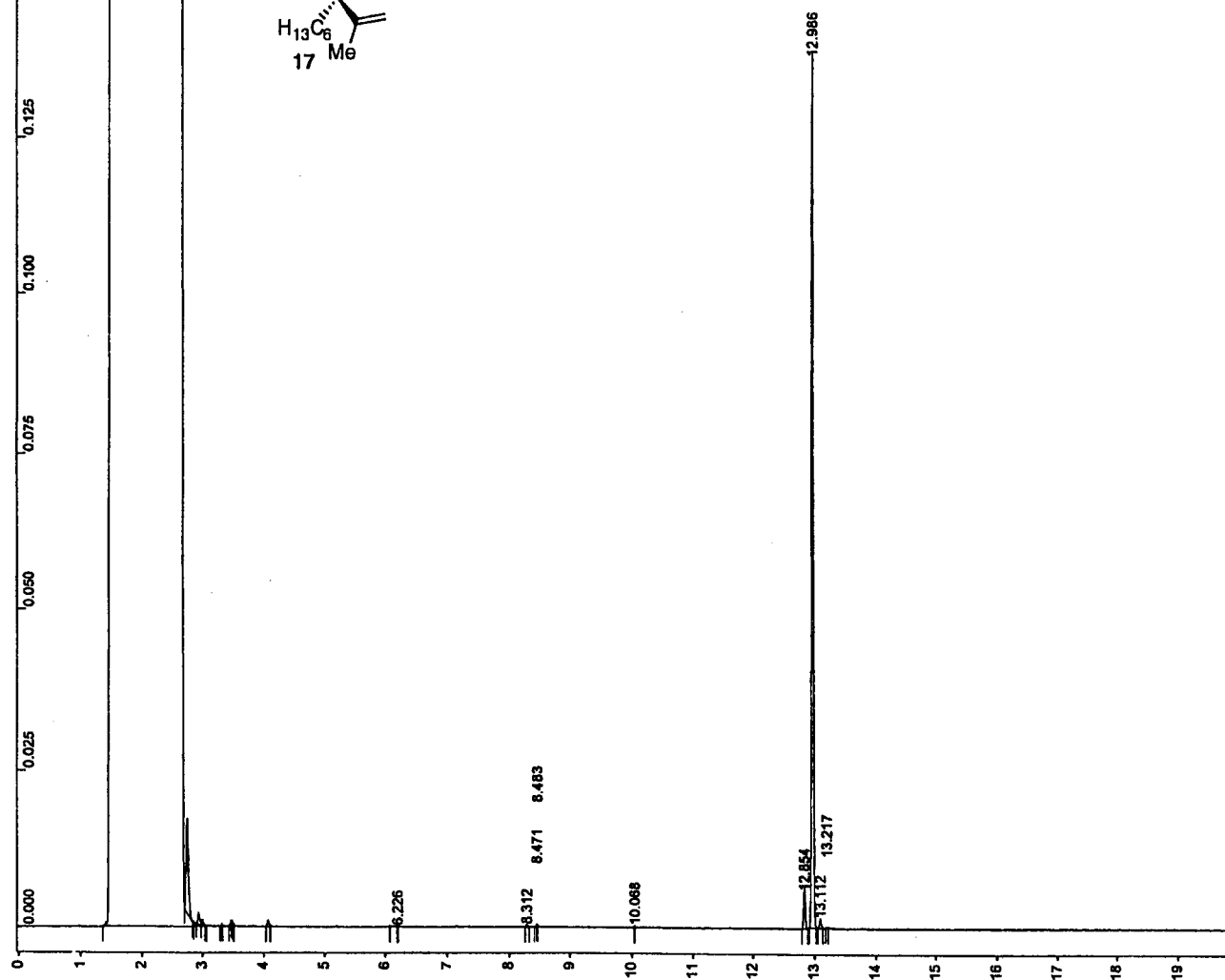
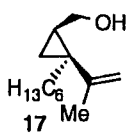
^1H NMR spectrum of **17** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **17** (100 MHz, CDCl_3)

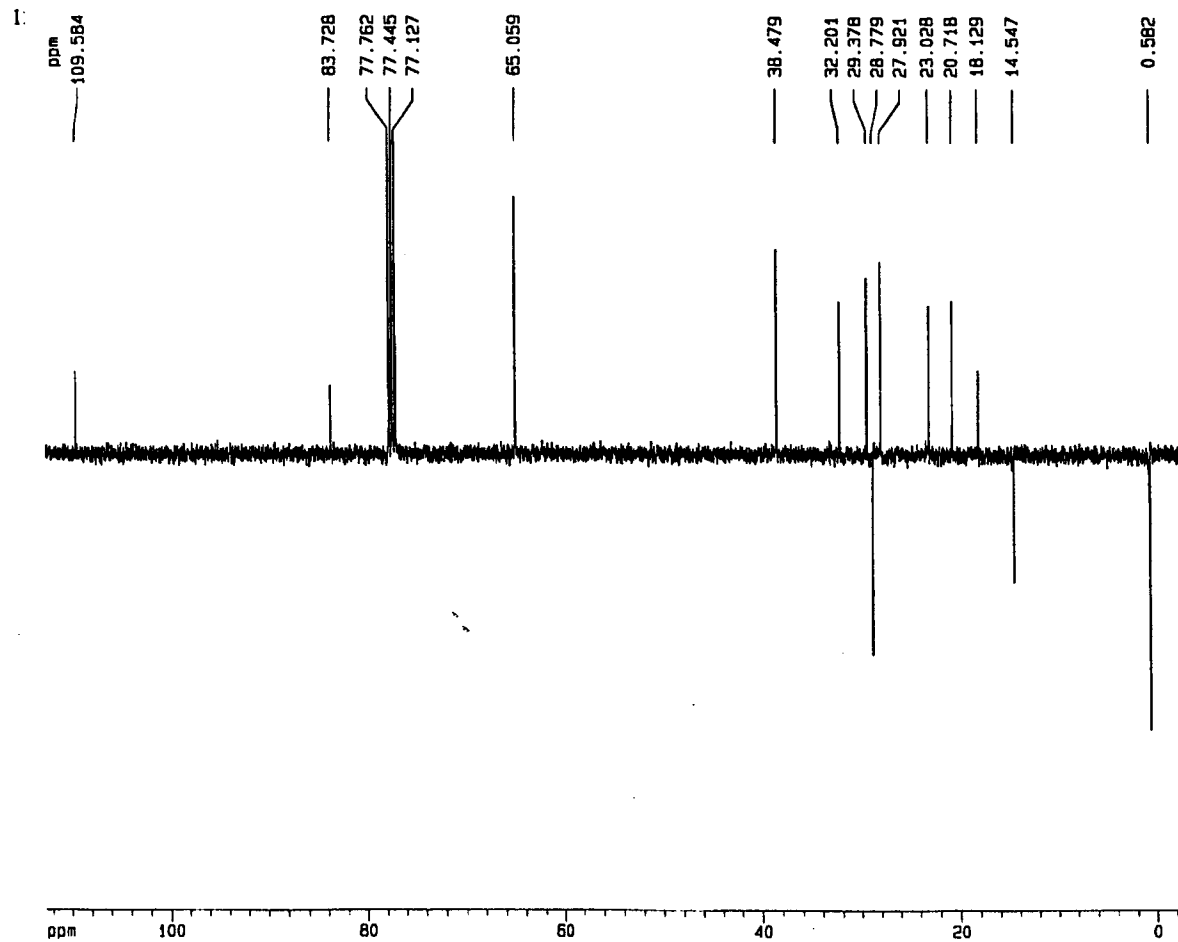
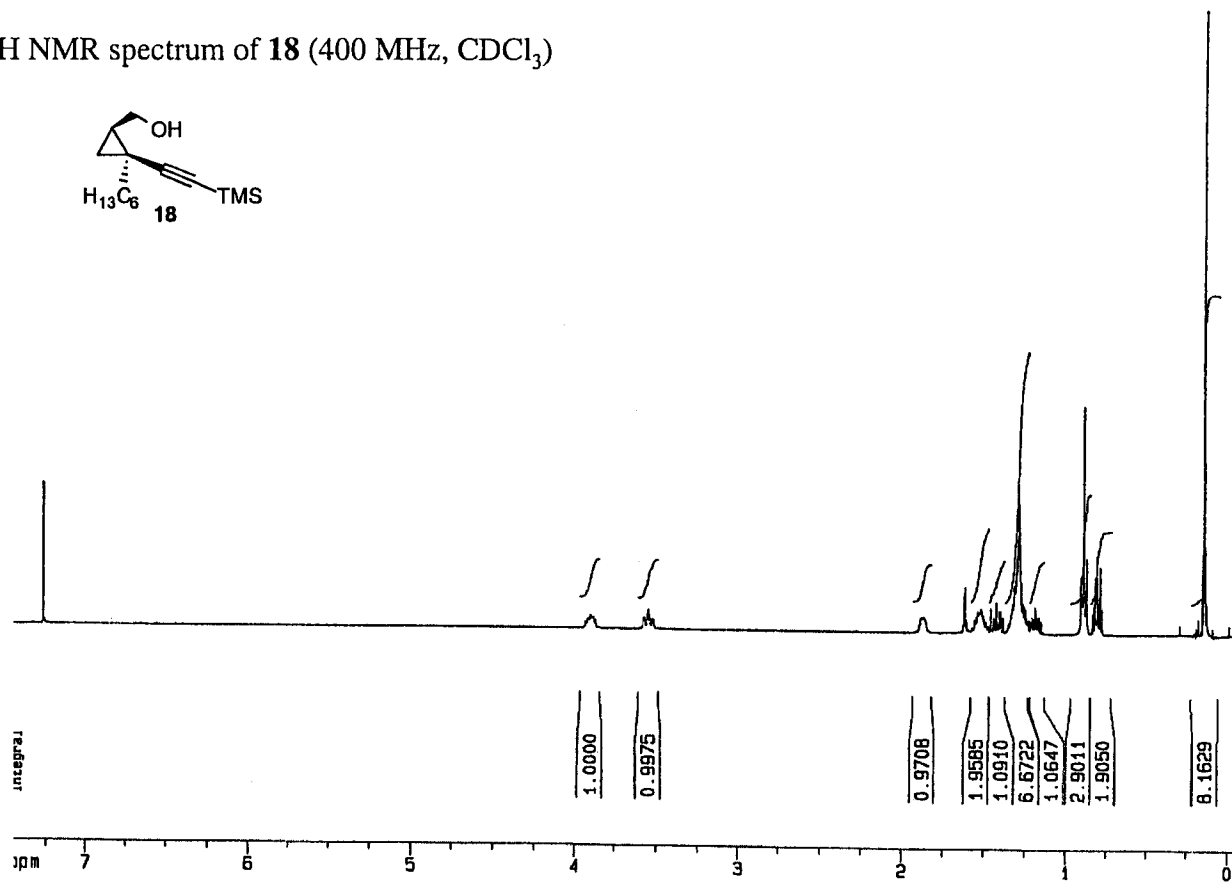
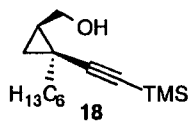


GC trace of 17 (HP5)

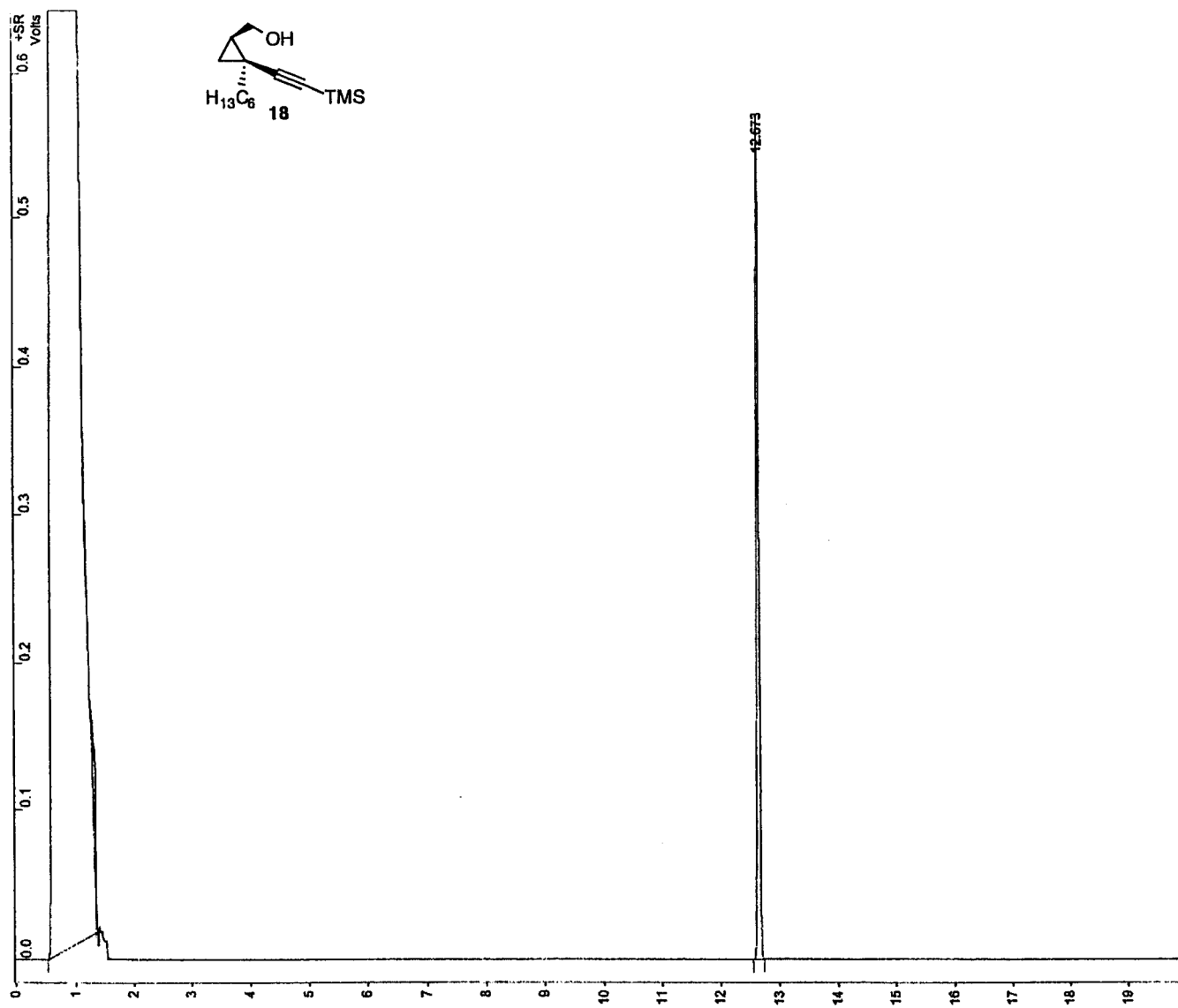


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.0482	6.226	0.000	135	BB	0.0	
2		0.2450	8.312	0.000	686	BB	0.0	
3		0.1409	8.471	0.000	394	BV	0.5	
4		0.0644	8.483	0.000	180	VB	1.2	
5		0.0447	10.068	0.000	125	BB	0.4	
6		4.0751	12.854	0.000	11405	BB	1.5	
7		94.2563	12.986	0.000	263782	BB	1.7	
8		1.0553	13.112	0.000	2953	BB	1.6	
9		0.0701	13.217	0.000	196	BB	0.0	
Totals:		100.0000		0.000	279856			

^1H NMR spectrum of **18** (400 MHz, CDCl_3)

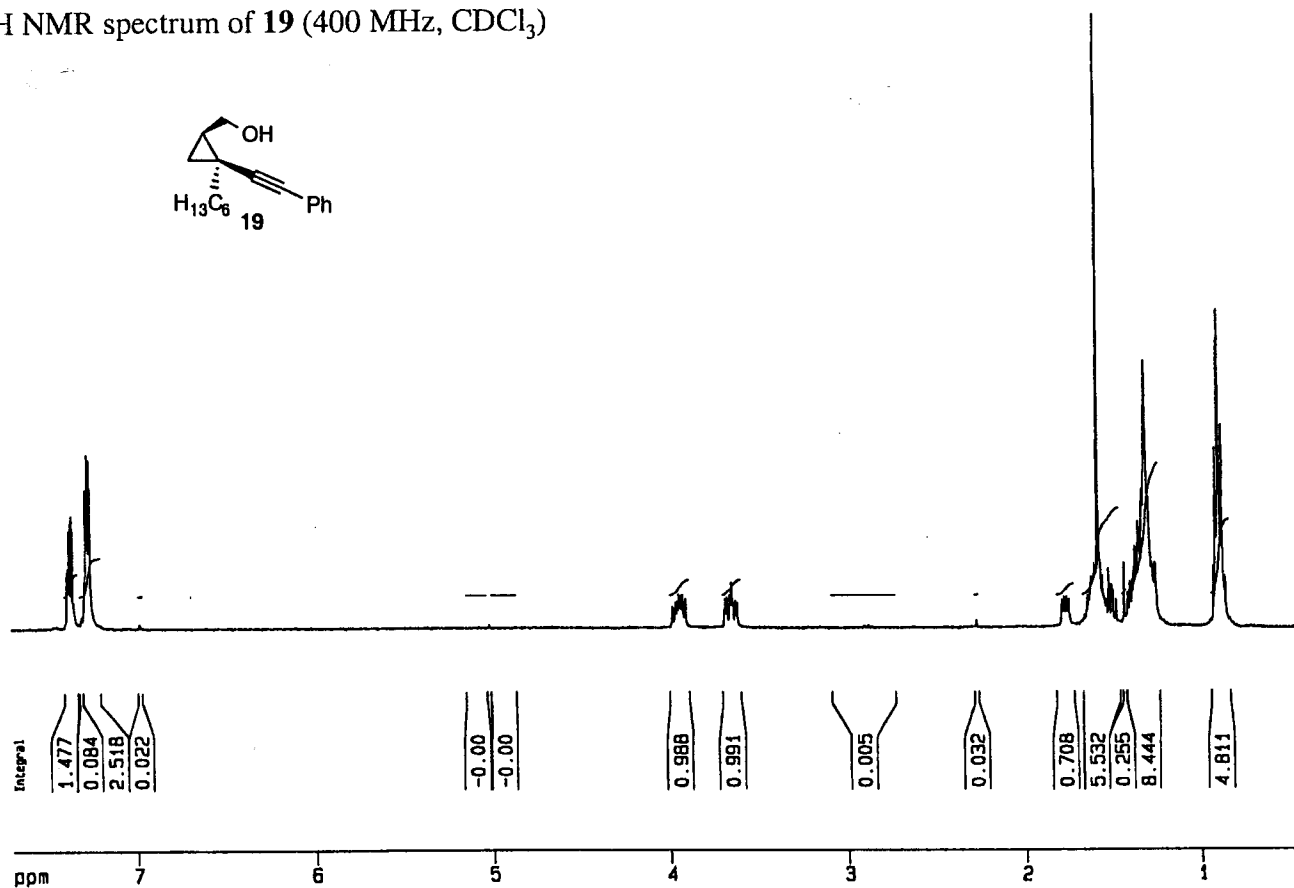


GC trace of 18 (HP5 column)

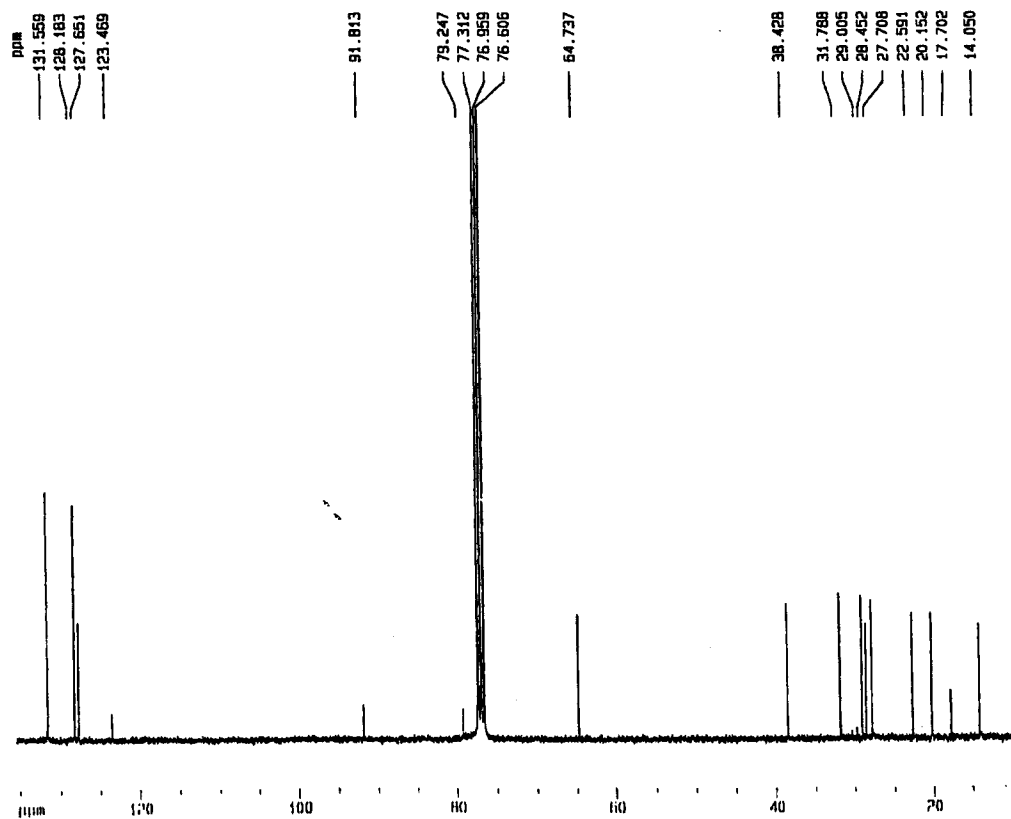


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	12.673	0.000	1540782	BB	2.6	
Totals:		100.0000		0.000	1540782			

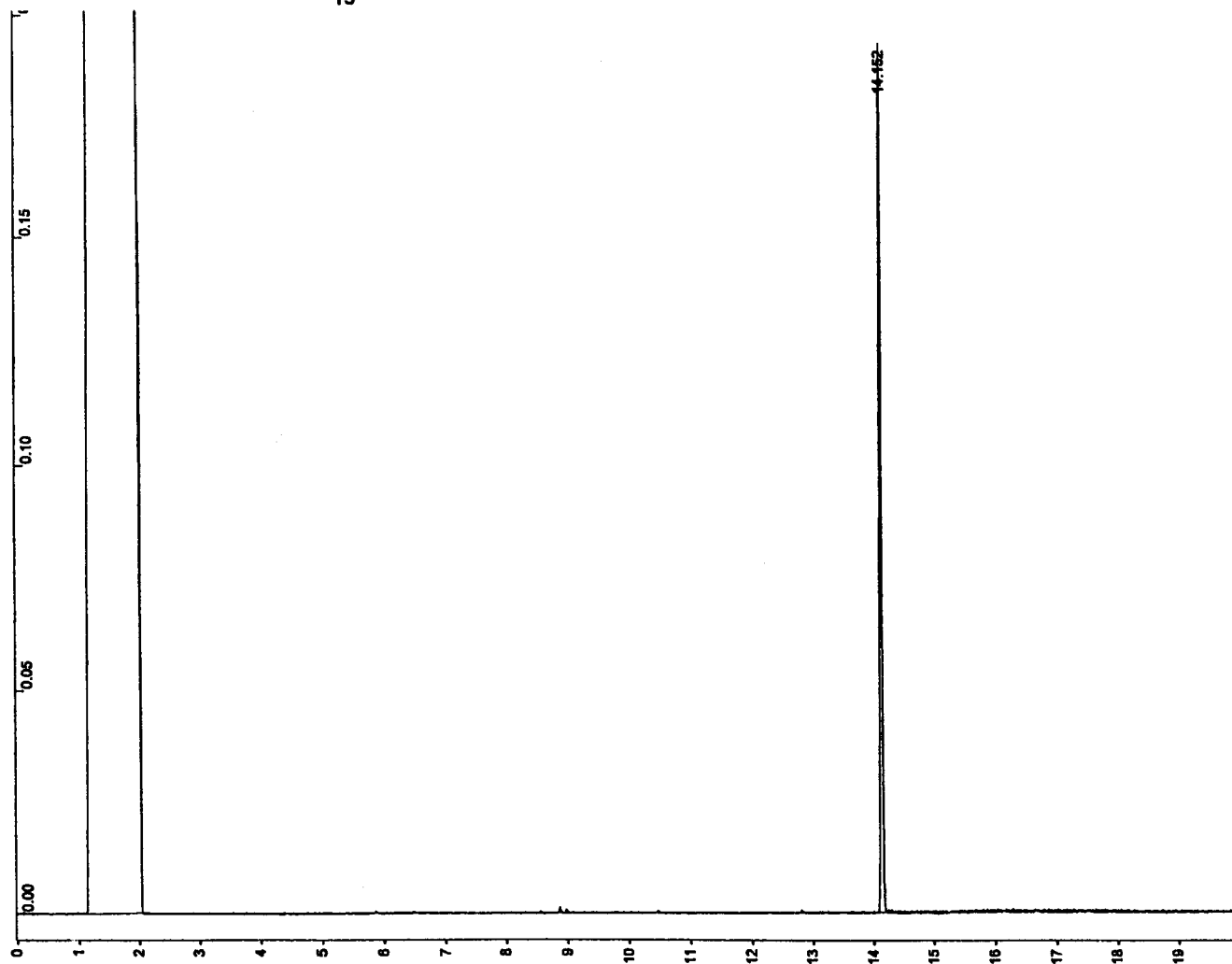
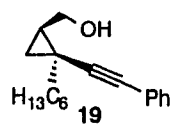
^1H NMR spectrum of **19** (400 MHz, CDCl_3)



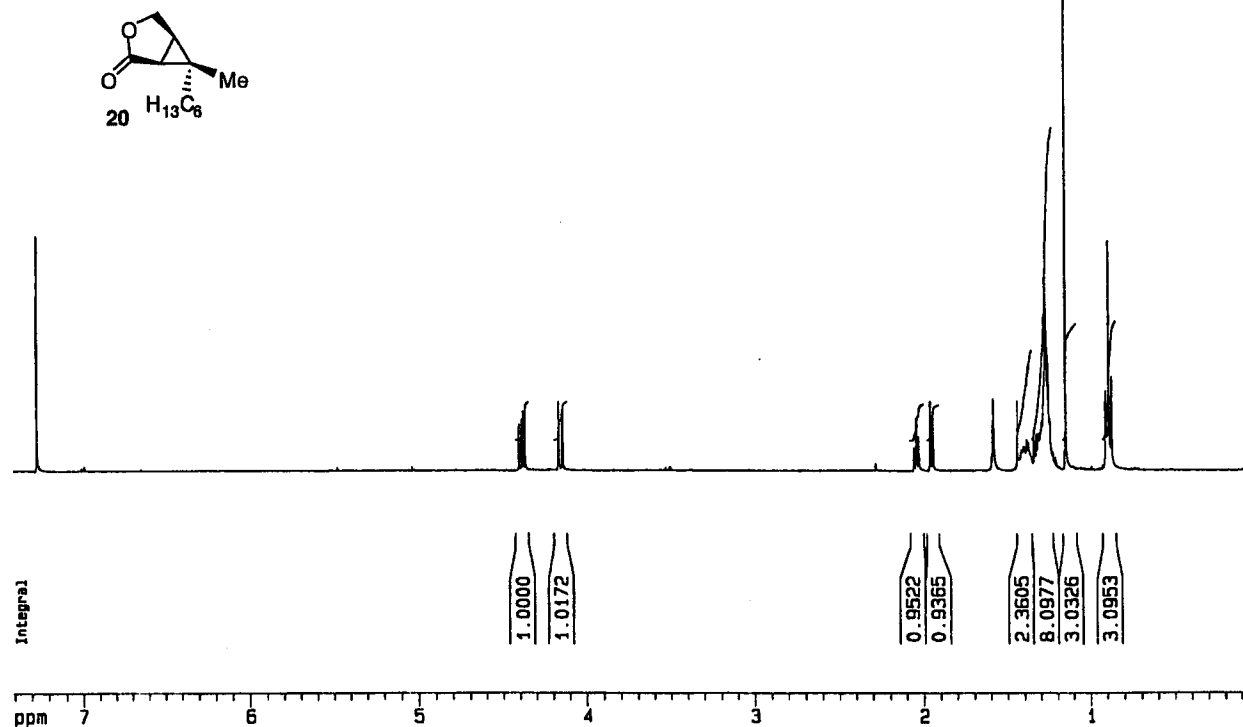
^{13}C NMR spectrum of **19** (100 MHz, CDCl_3)



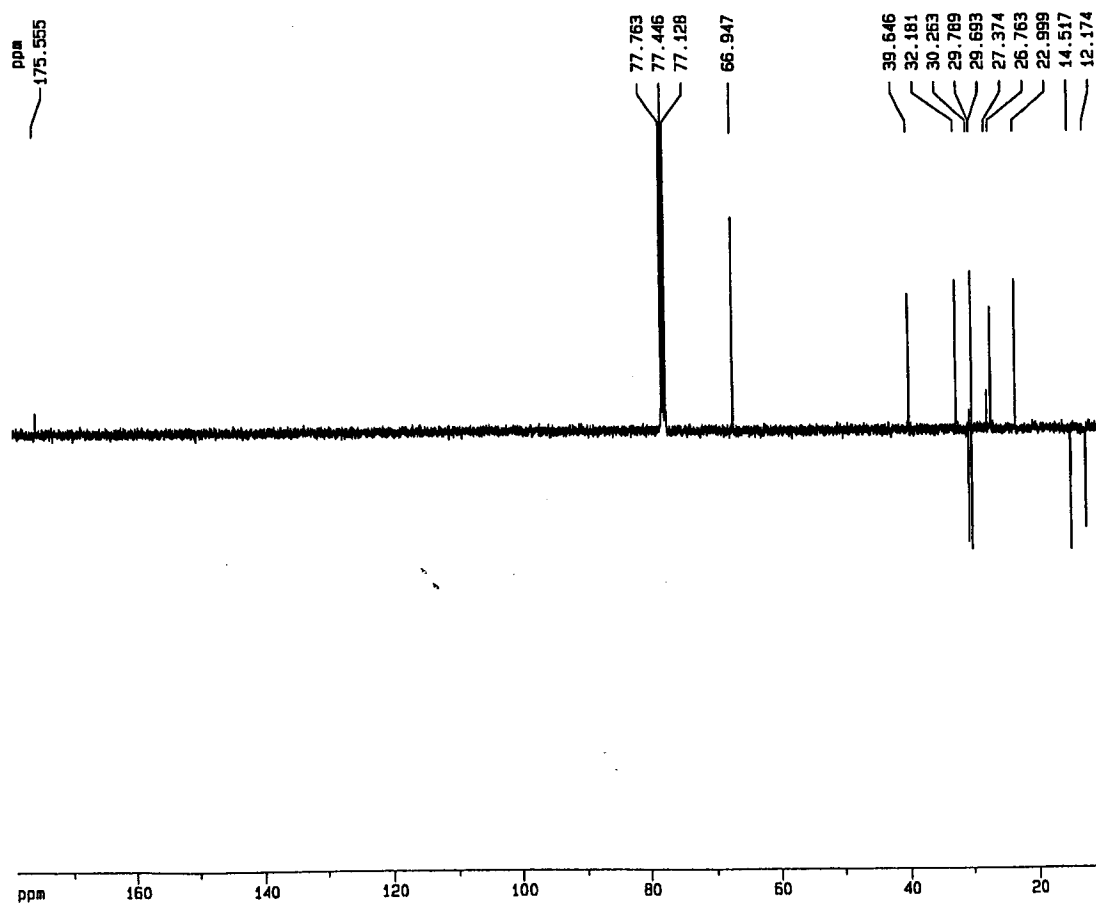
GC trace of **19** (HP5 column)



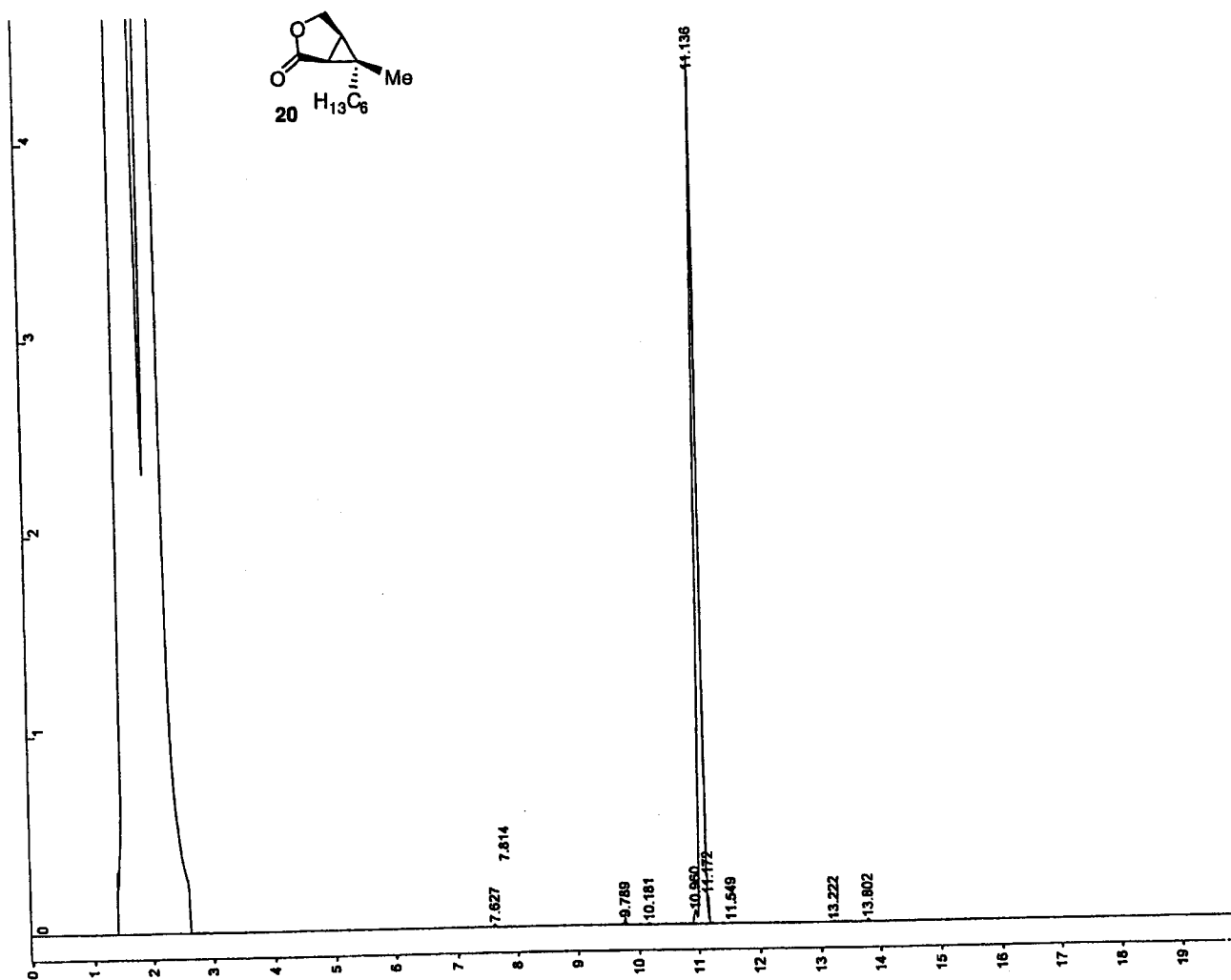
^1H NMR spectrum of **20** (400 MHz, CDCl_3)



^{13}C (JVERT) NMR spectrum of **20** (100 MHz, CDCl_3)

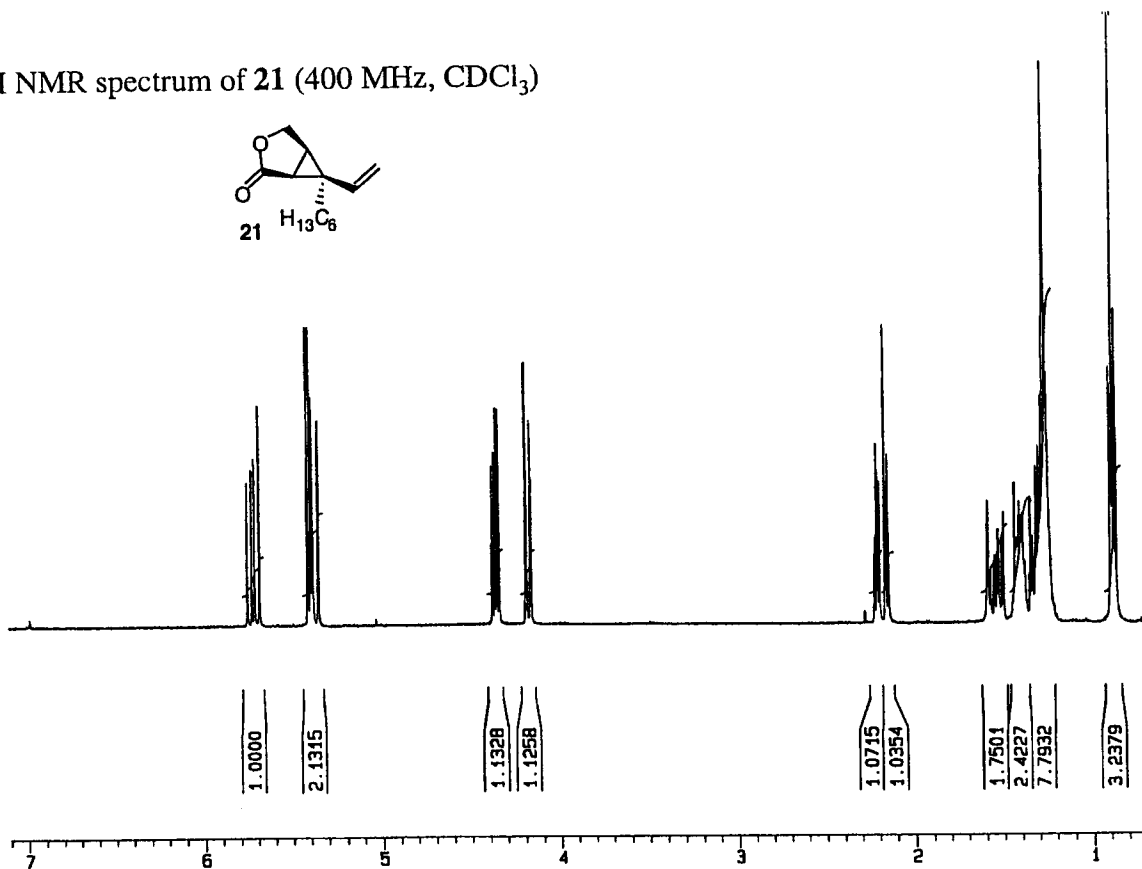
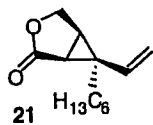


GC trace of **20** (HP5 column)

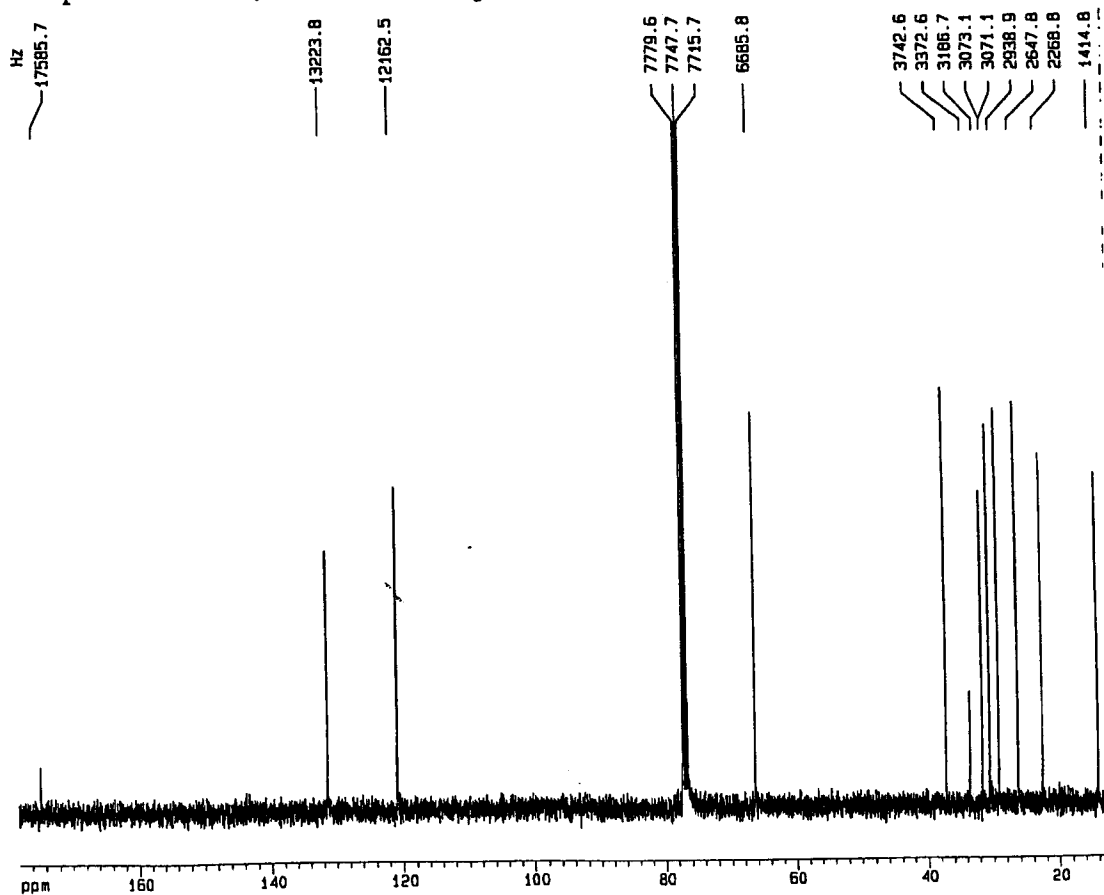


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.1718	7.627	0.000	31989	BB	1.9	
2		0.0288	7.814	0.000	5370	BB	2.0	
3		0.3494	9.789	0.000	65064	VB	1.9	
4		0.0859	10.181	0.000	15998	VB	1.9	
5		1.2375	10.960	0.000	230434	VV	4.0	
6		97.4375	11.136	0.000	18144260	VP	4.0	
7		0.4129	11.172	0.000	76896	TS	0.0	
8		0.0608	11.549	0.000	11316	TF	0.0	
9		0.0596	13.222	0.000	11092	TF	0.0	
10		0.1558	13.802	0.000	29019	TF	0.0	
Totals:		100.0000		0.000	18621438			

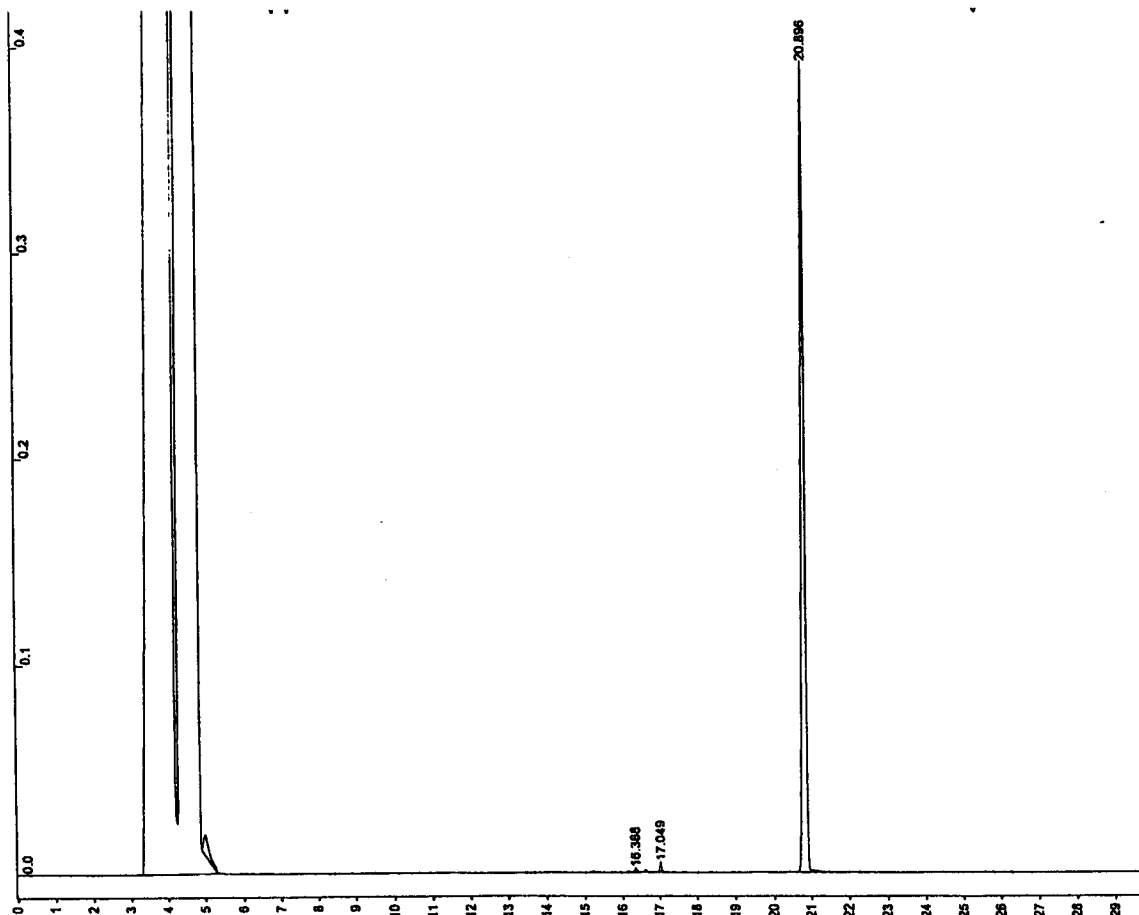
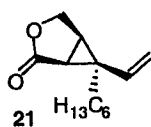
^1H NMR spectrum of **21** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **21** (100 MHz, CDCl_3)

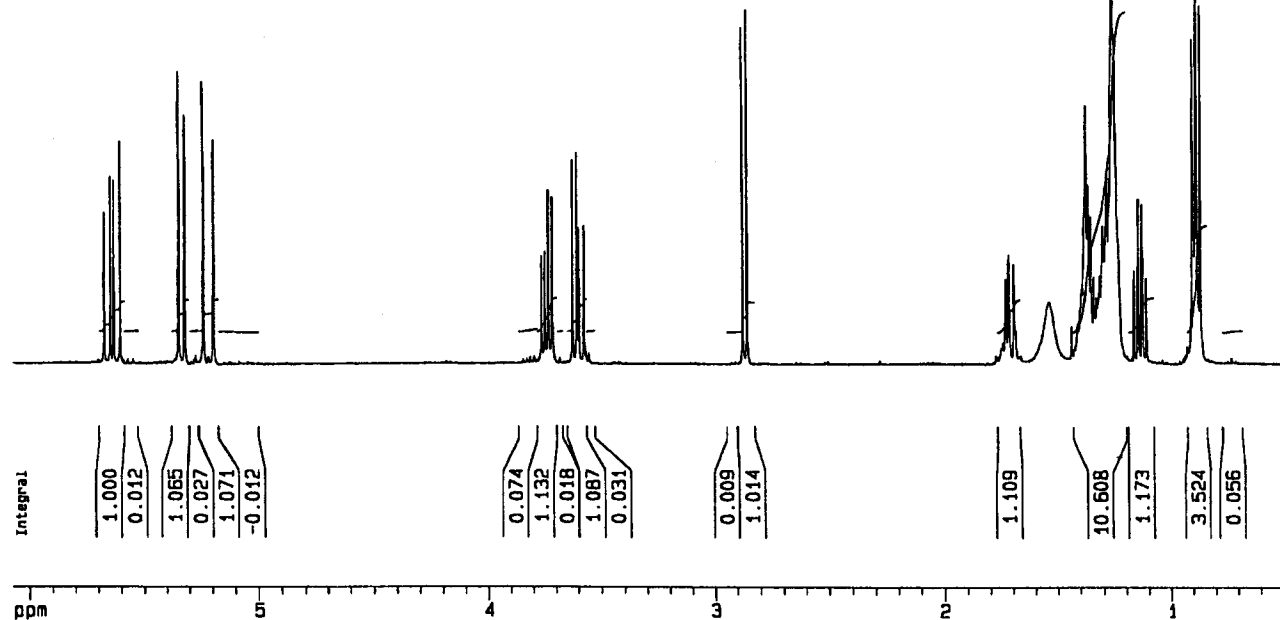
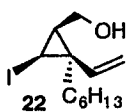


GC trace of **21** (HP5 column)

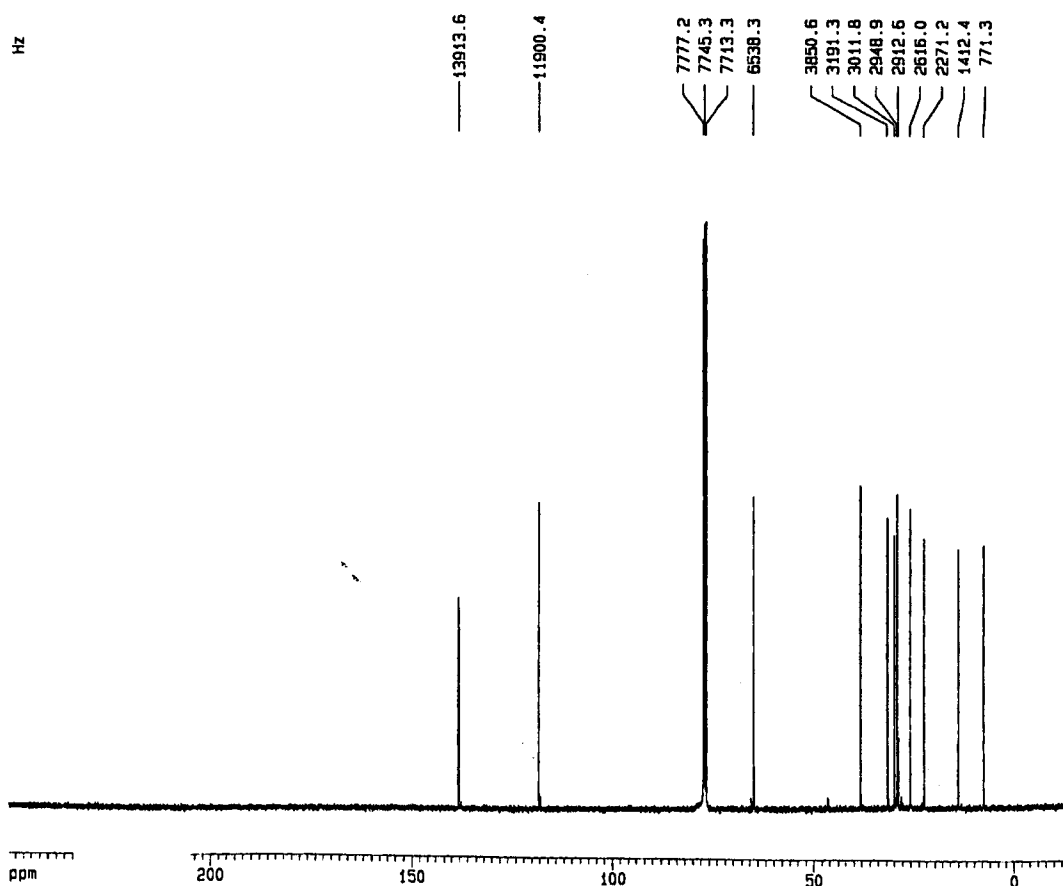


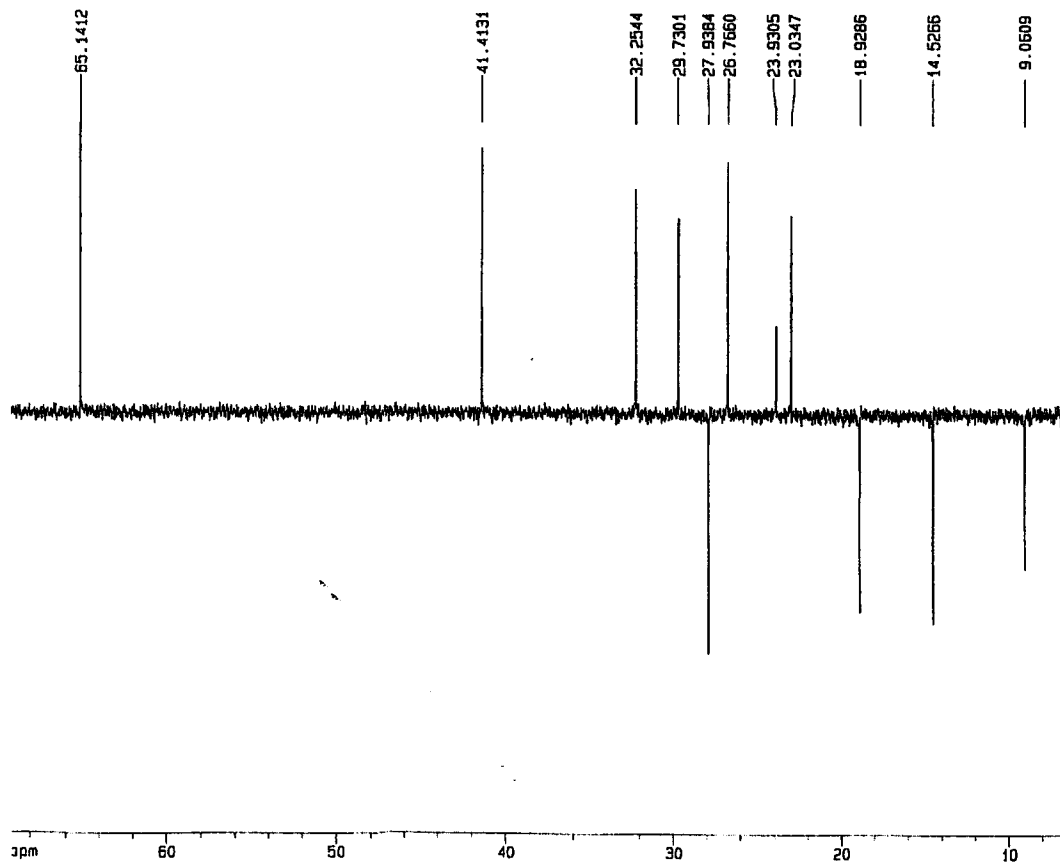
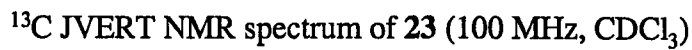
Peak No.	Peak Name	Result (°)	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.3880	16.368	0.000	9467	VV	3.2	
2		0.6964	17.049	0.000	16993	VB	2.9	
3		98.9155	20.896	0.000	2413431	BB	5.8	
Totals:		99.9999		0.000	2439891			

^1H NMR spectrum of **22** (400 MHz, CDCl_3)

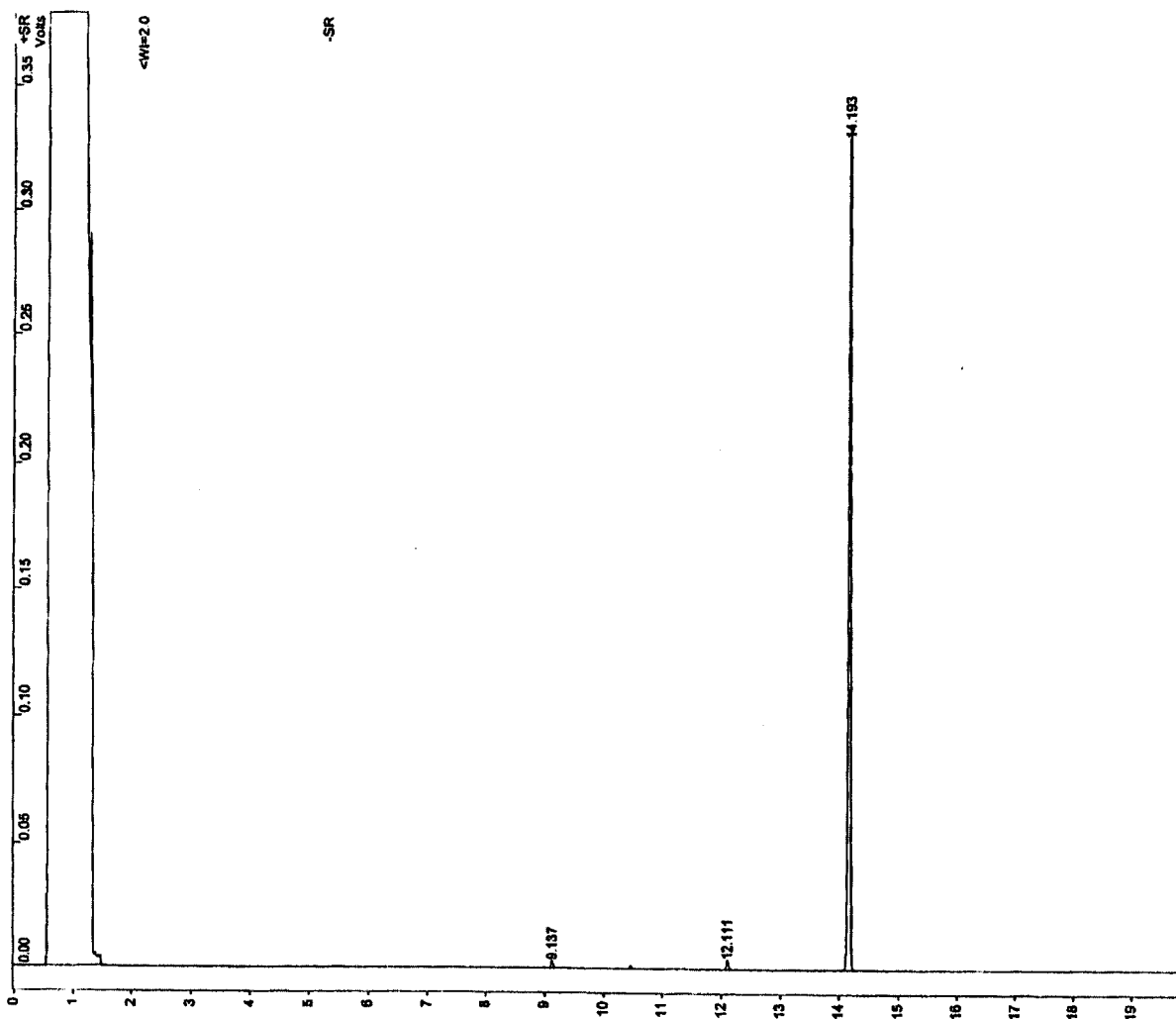
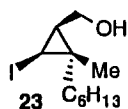


^{13}C NMR spectrum of **22** (100 MHz, CDCl_3)



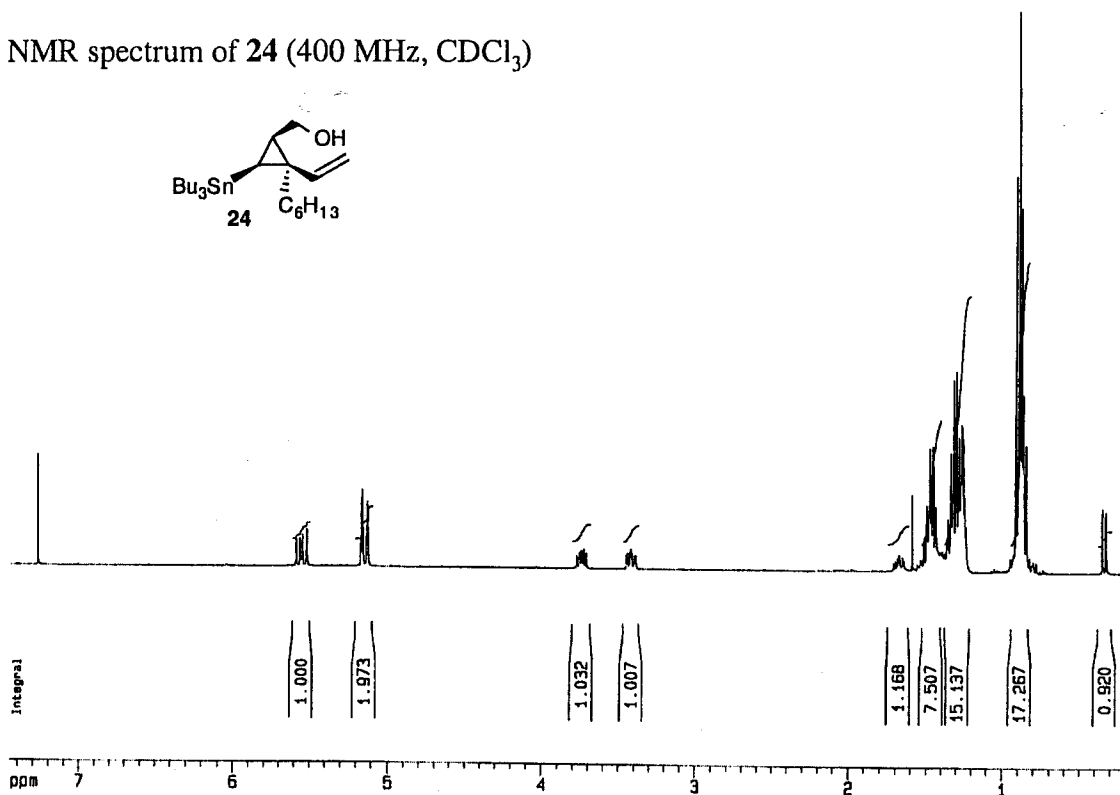


GC trace of 23 (HP5 column)

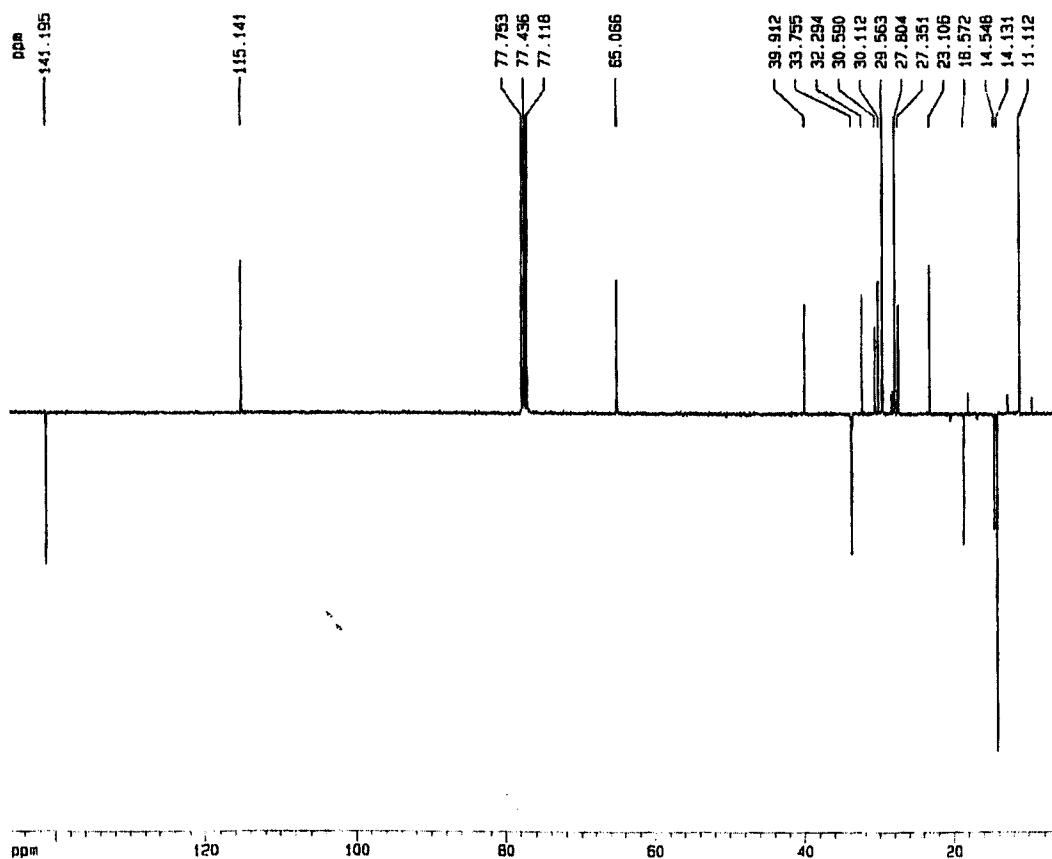


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.8083	9.137	0.000	6860	BB	2.2	
2		1.0943	12.111	0.000	9288	BB	2.3	
3		98.0974	14.193	0.000	832553	VP	2.4	
Totals:		100.0000		0.000	848701			

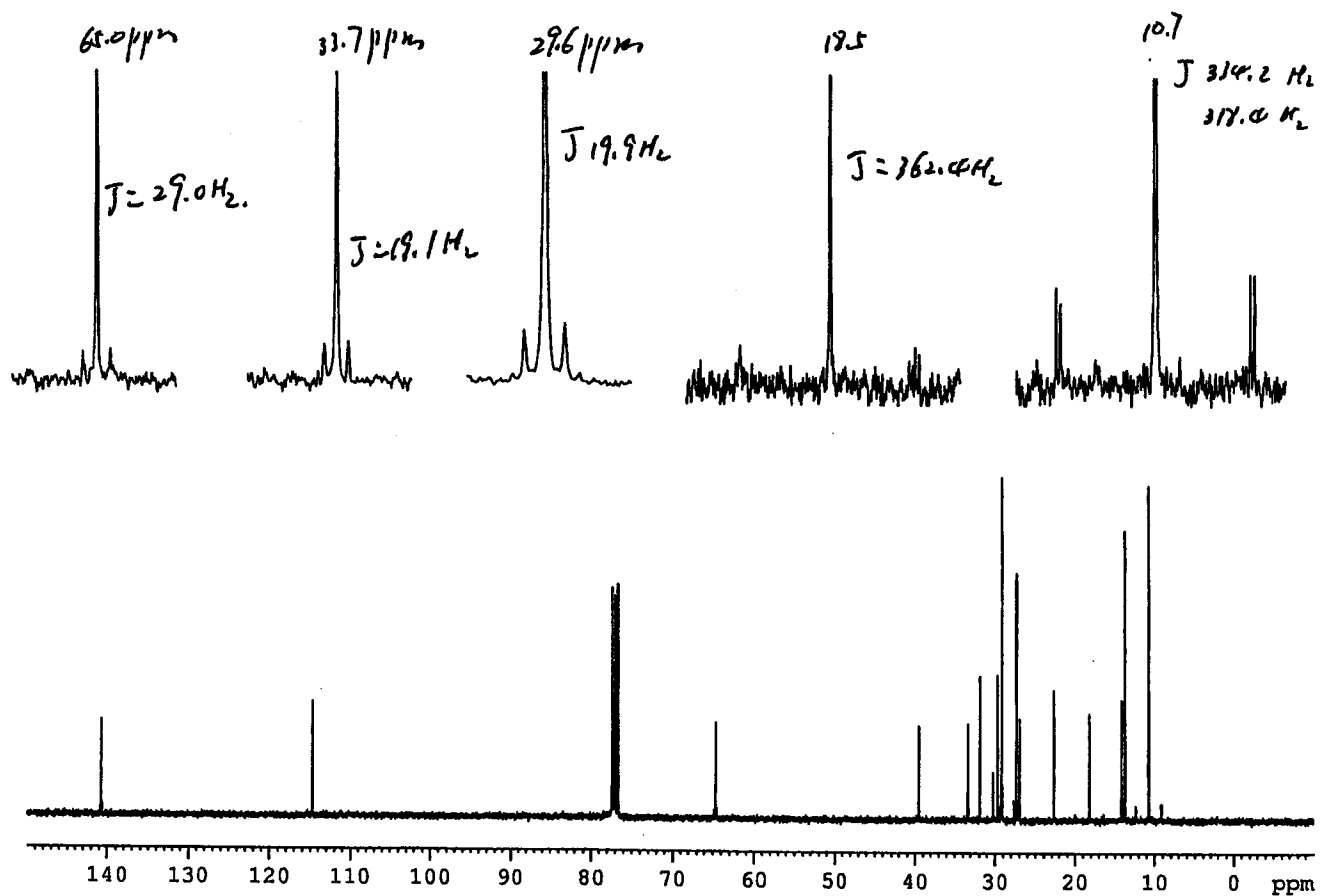
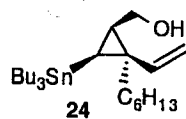
^1H NMR spectrum of **24** (400 MHz, CDCl_3)



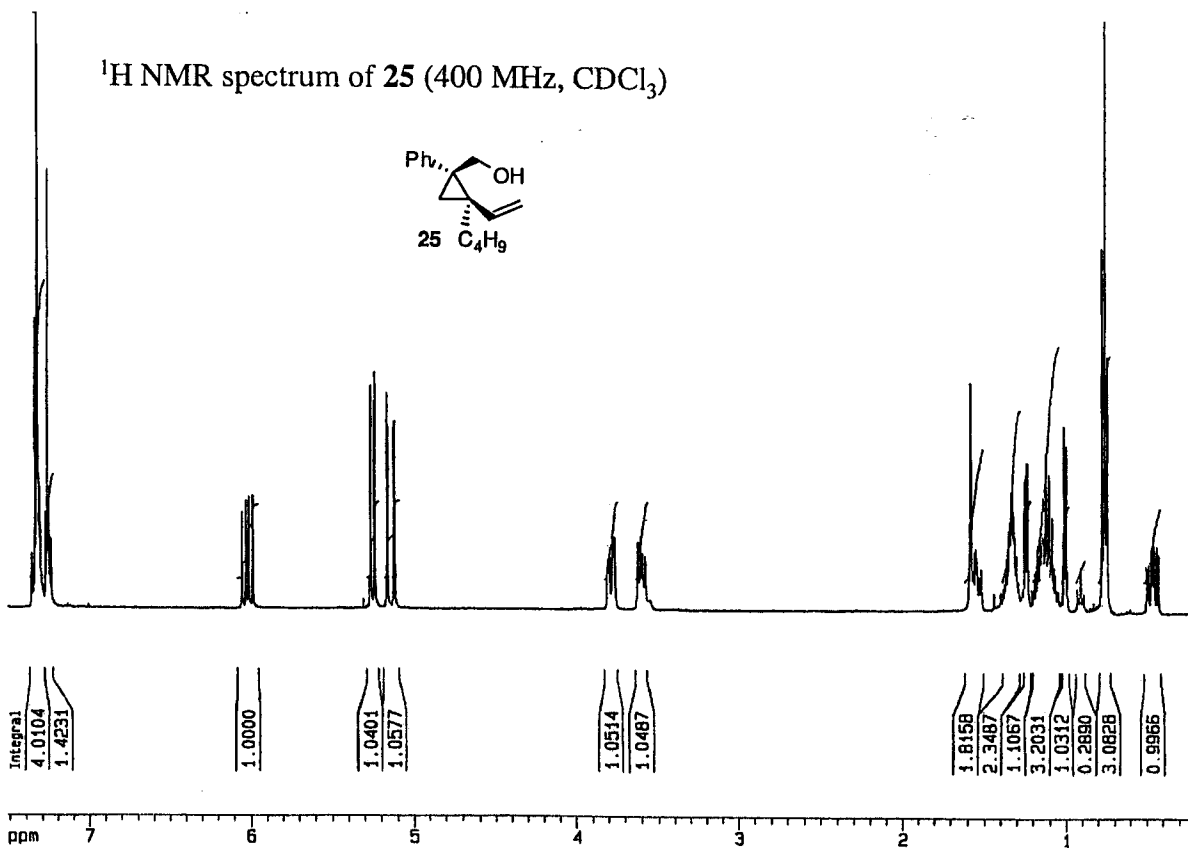
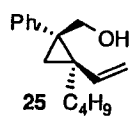
^{13}C JVERT NMR spectrum of **24** (100 MHz, CDCl_3)



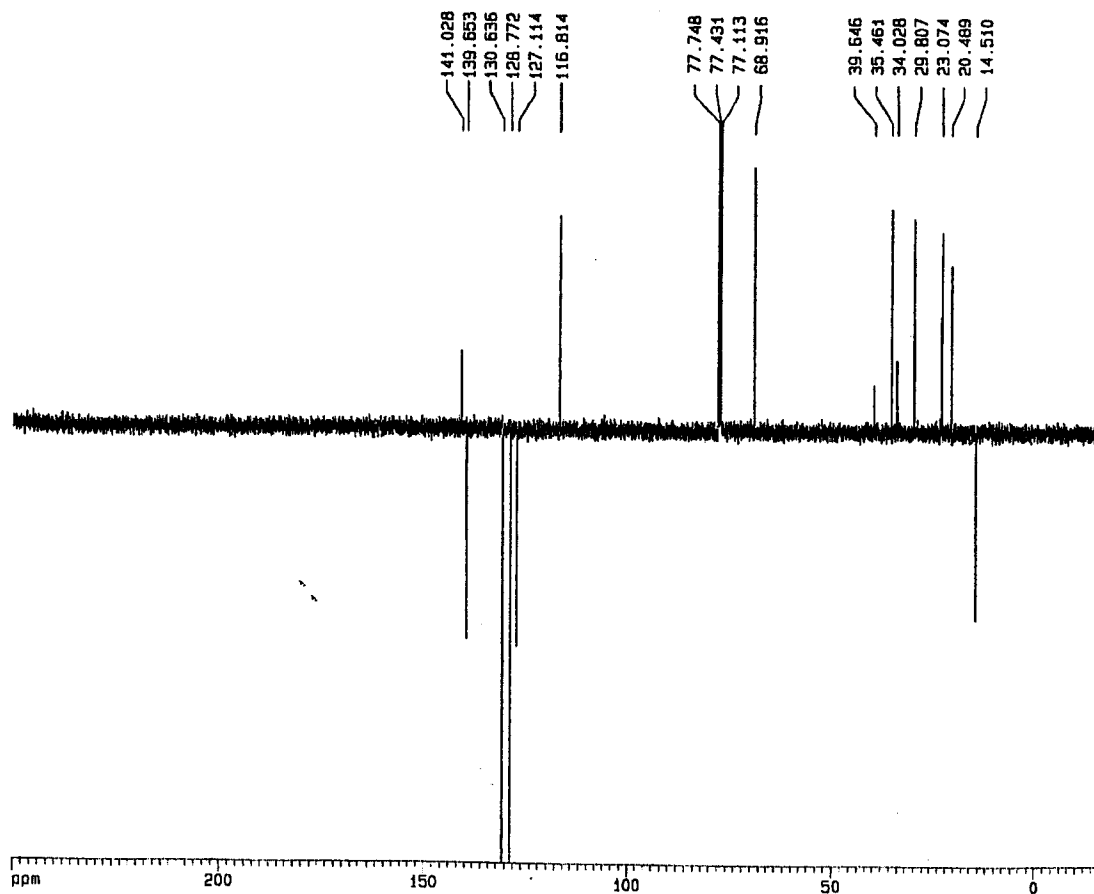
^{13}C NMR spectrum of **24** (100 MHz, CDCl_3)



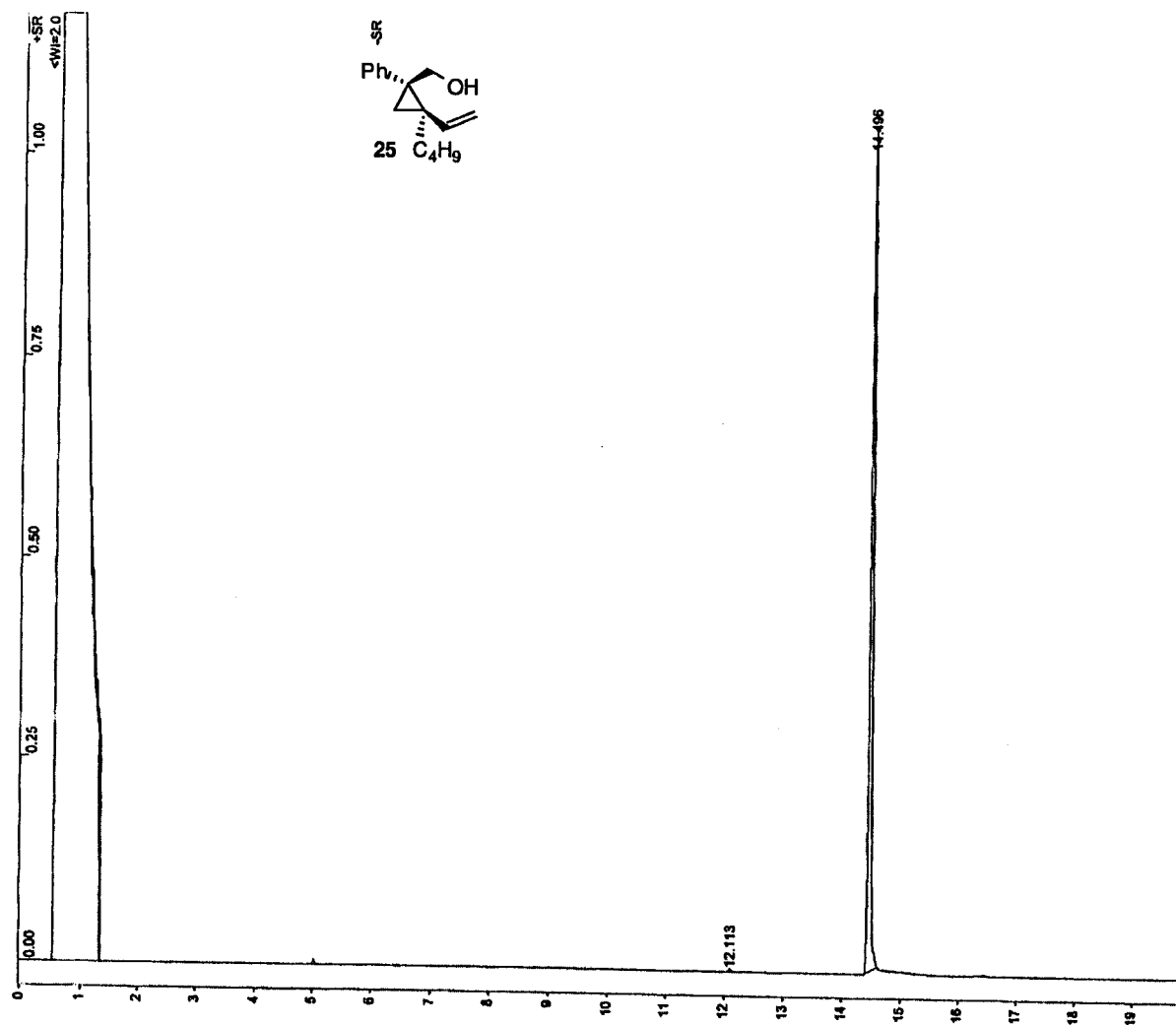
^1H NMR spectrum of **25** (400 MHz, CDCl_3)



^{13}C JVERT NMR spectrum of **25** (100 MHz, CDCl_3)

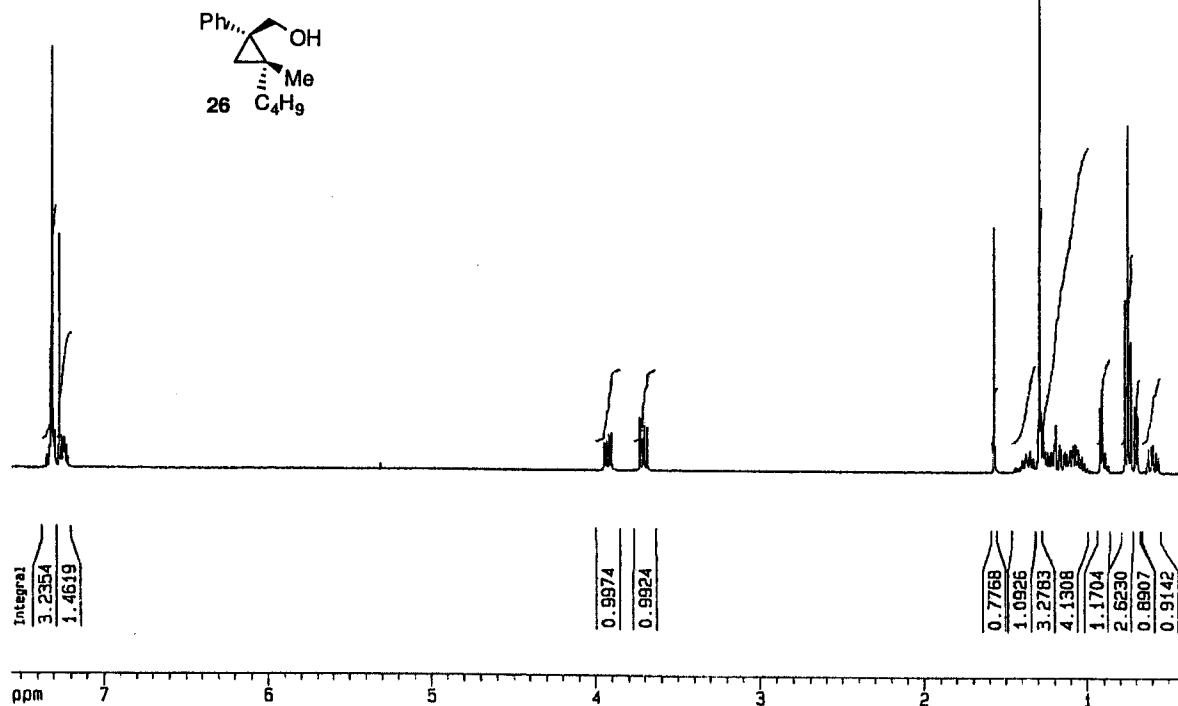


GC trace of **25** (HP5 column)

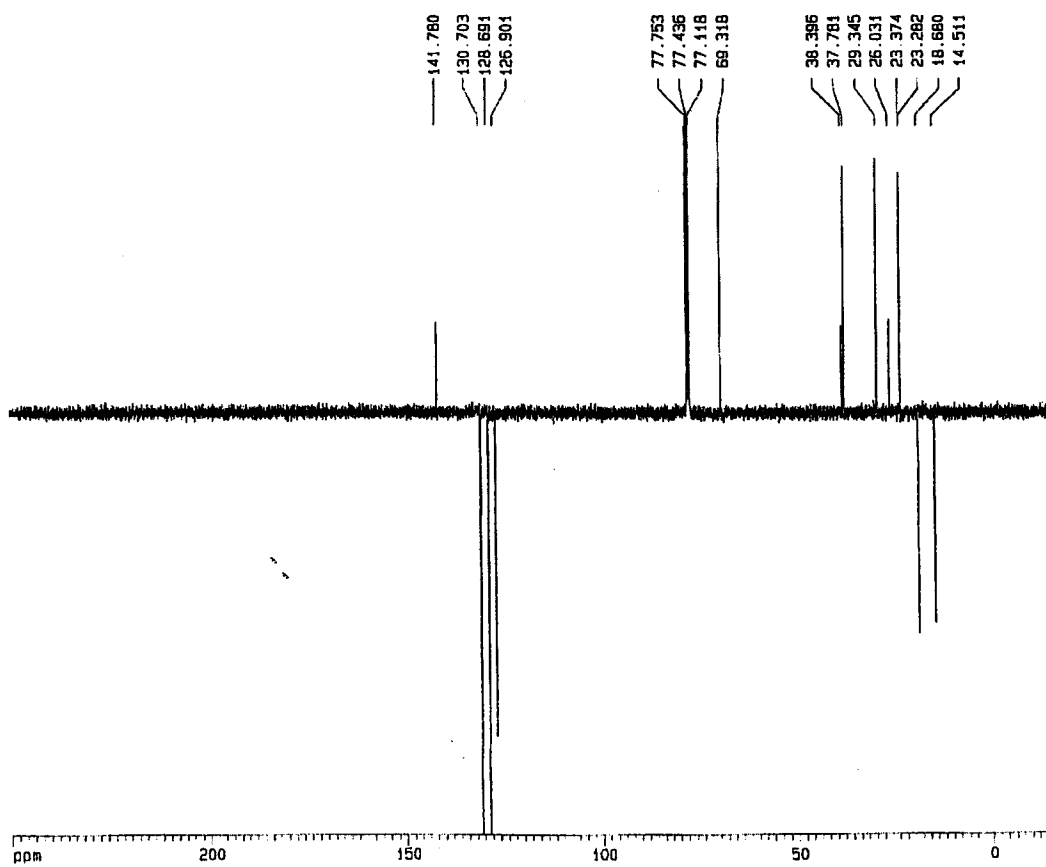


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.1984	12.113	0.000	6086	BV	2.0	
2		99.8016	14.496	0.000	3061122	BB	2.7	
Totals:		100.0000		0.000	3067208			

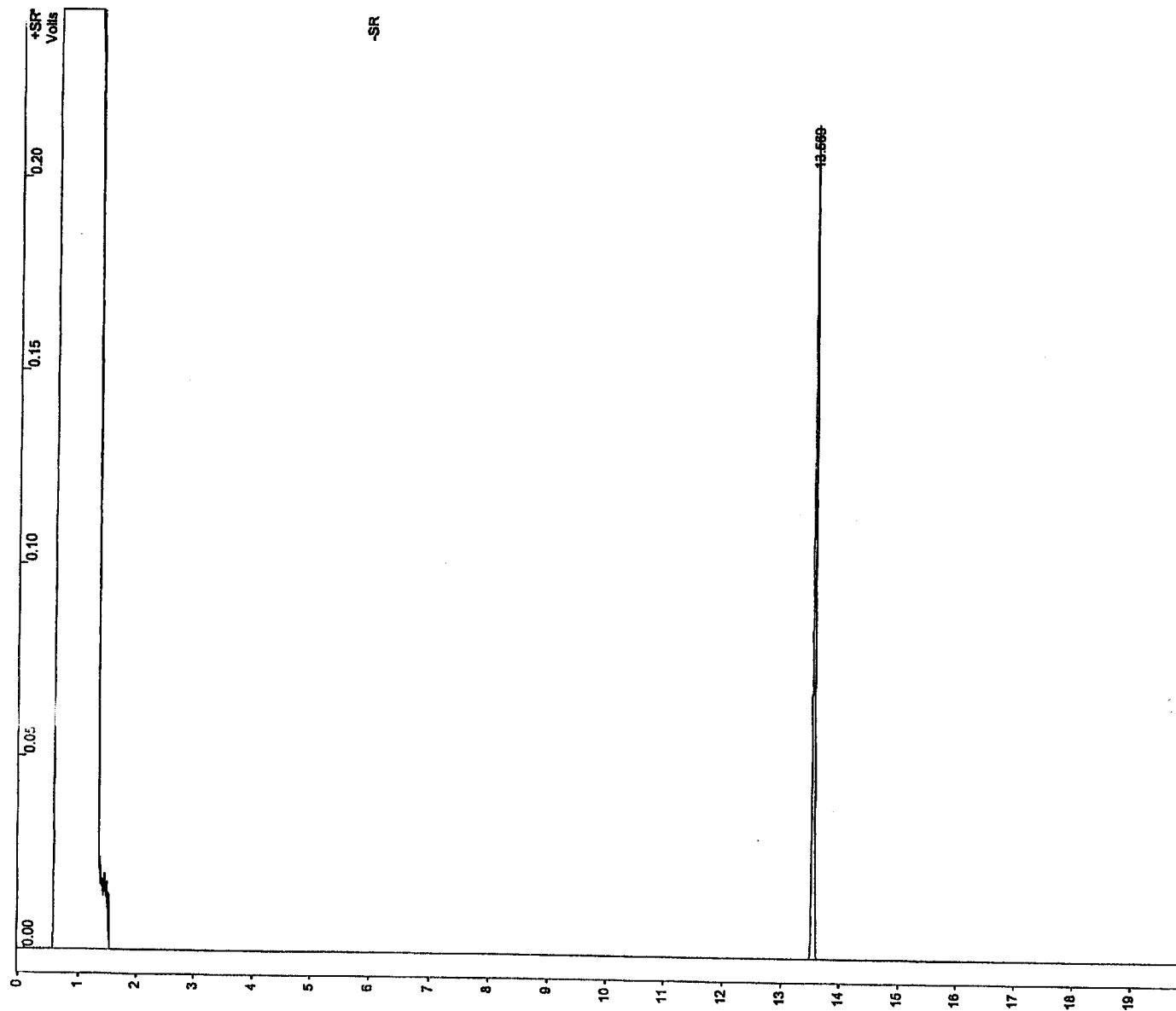
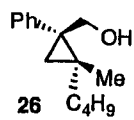
^1H NMR spectrum of **26** (400 MHz, CDCl_3)



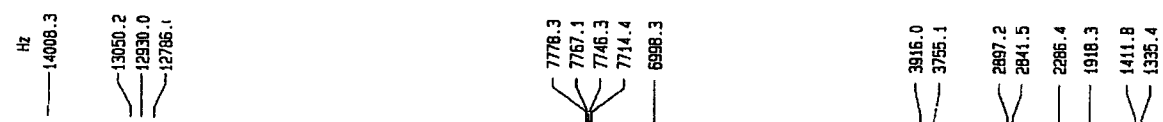
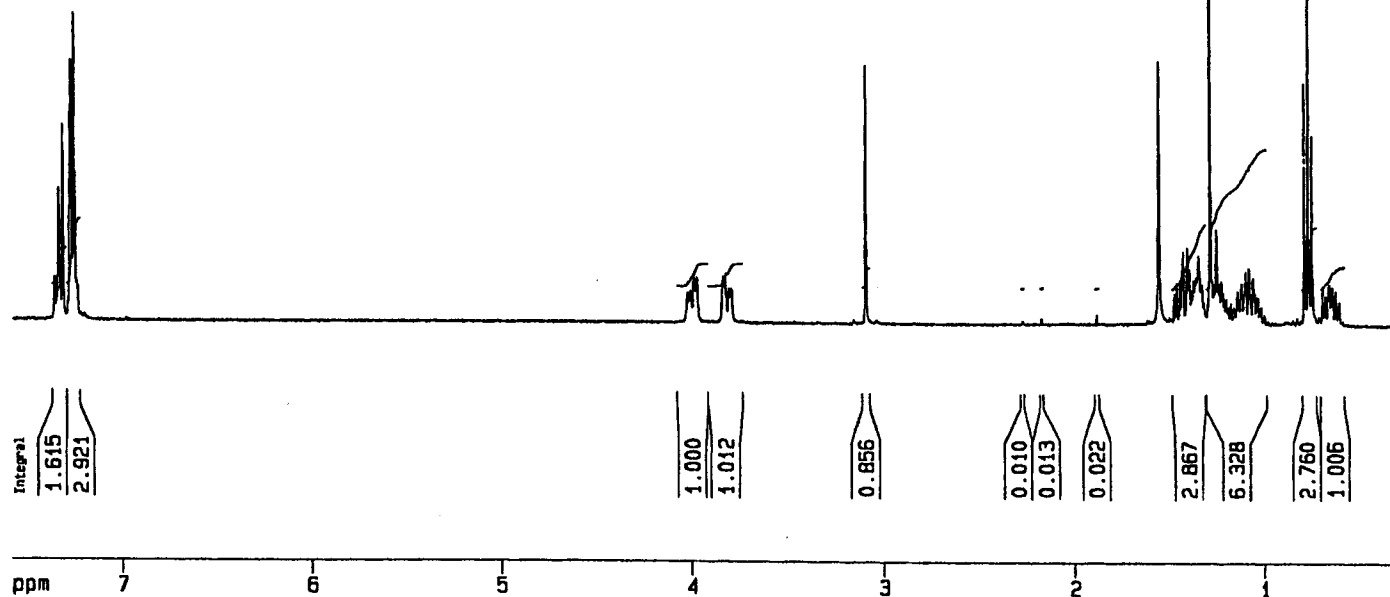
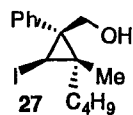
^{13}C JVERT NMR spectrum of **27** (100 MHz, CDCl_3)



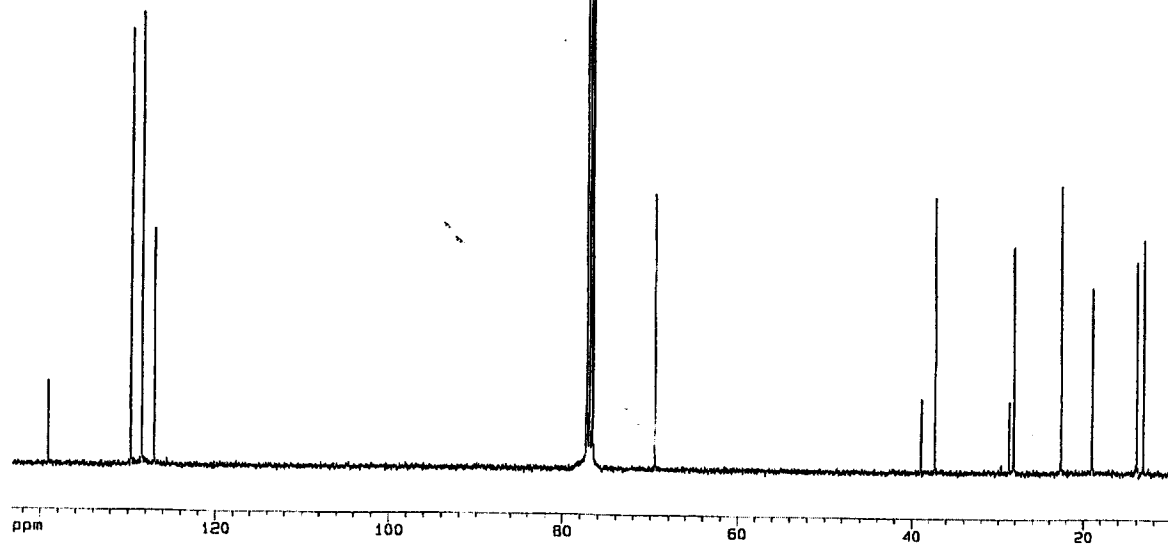
GC trace of **26** (HP5 column)



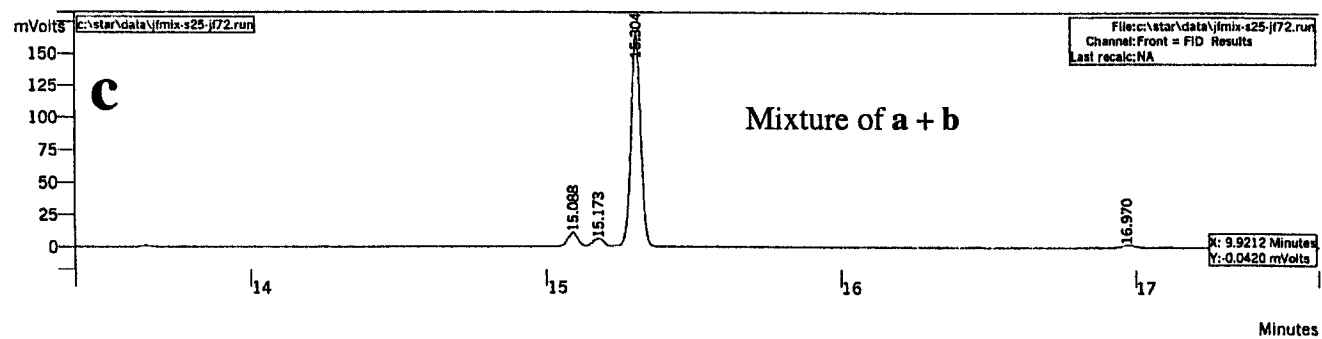
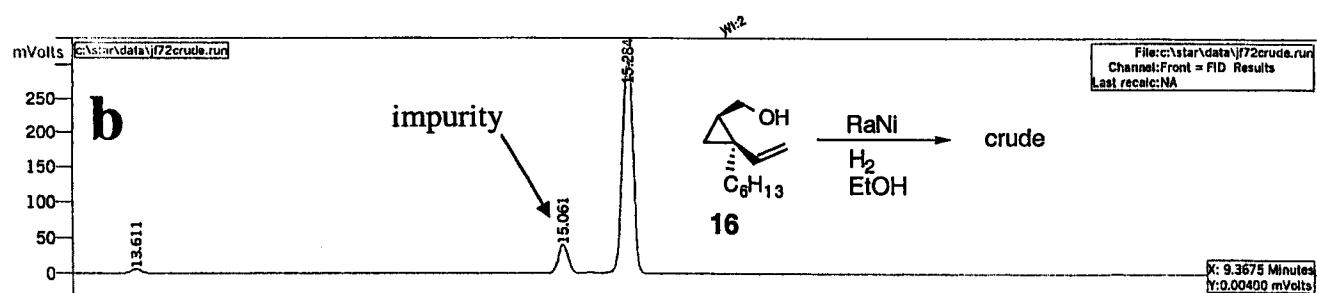
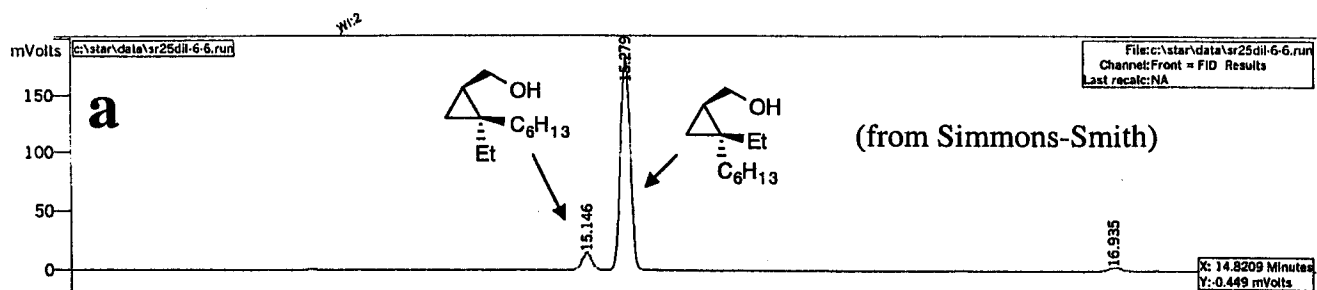
^1H NMR spectrum of **27** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **27**
(100 MHz, CDCl_3)

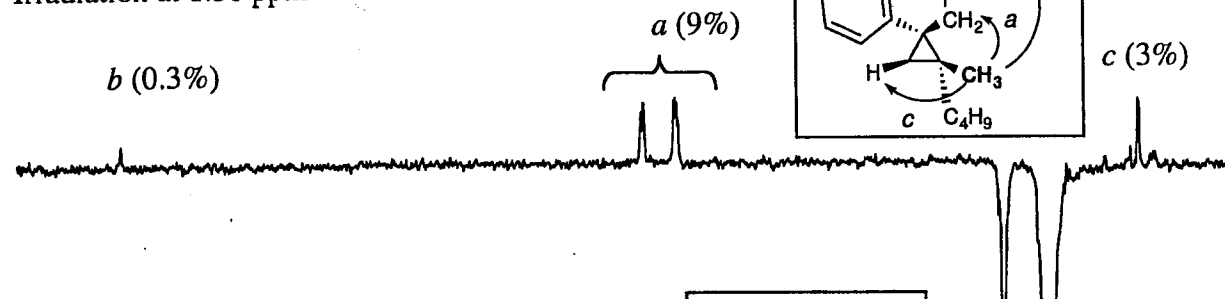


Assignment of relative stereochemistry for 16

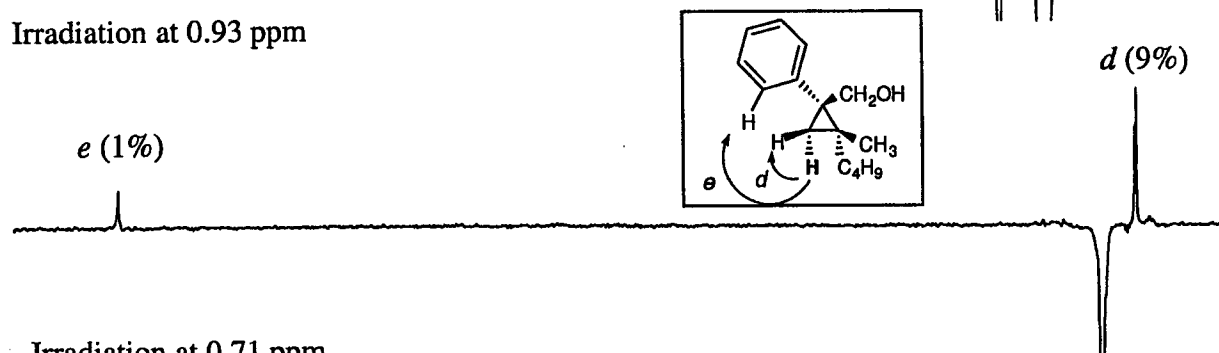


• ^1H NMR selective 1-D NOE spectra of **26**

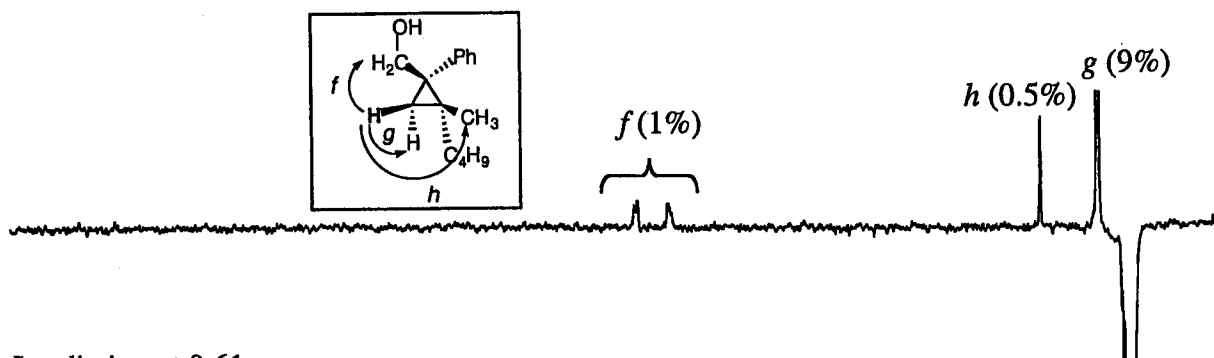
Irradiation at 1.30 ppm



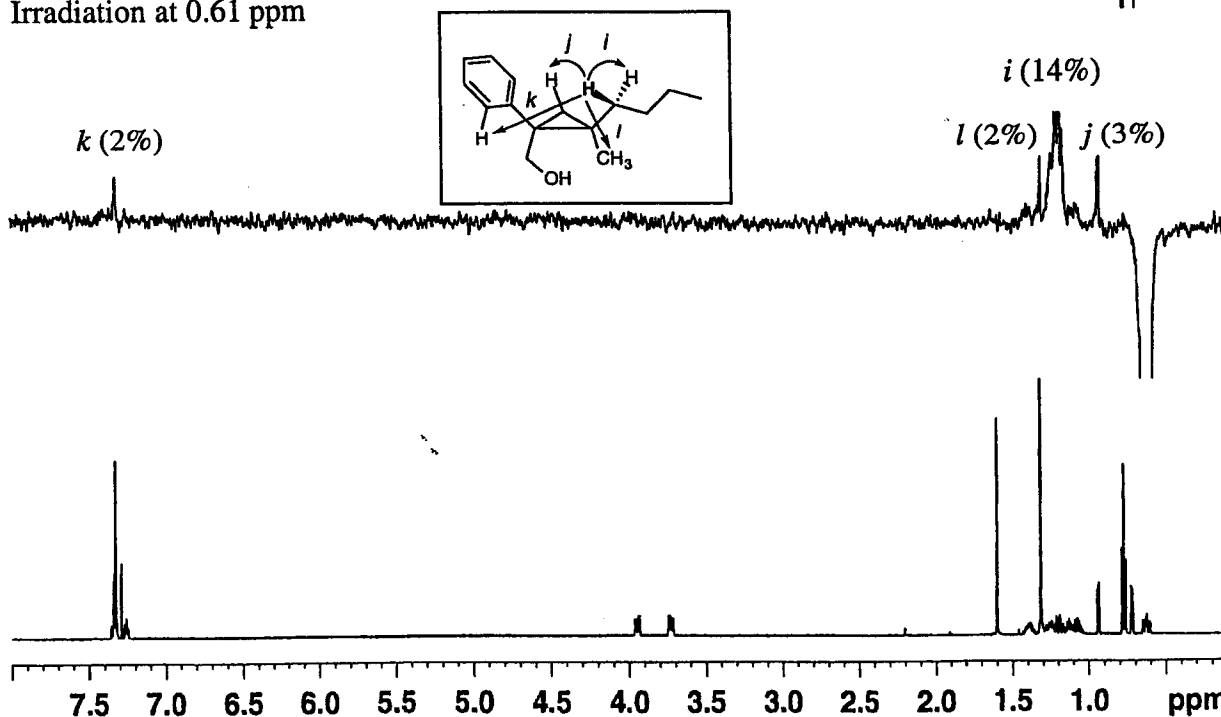
Irradiation at 0.93 ppm



Irradiation at 0.71 ppm

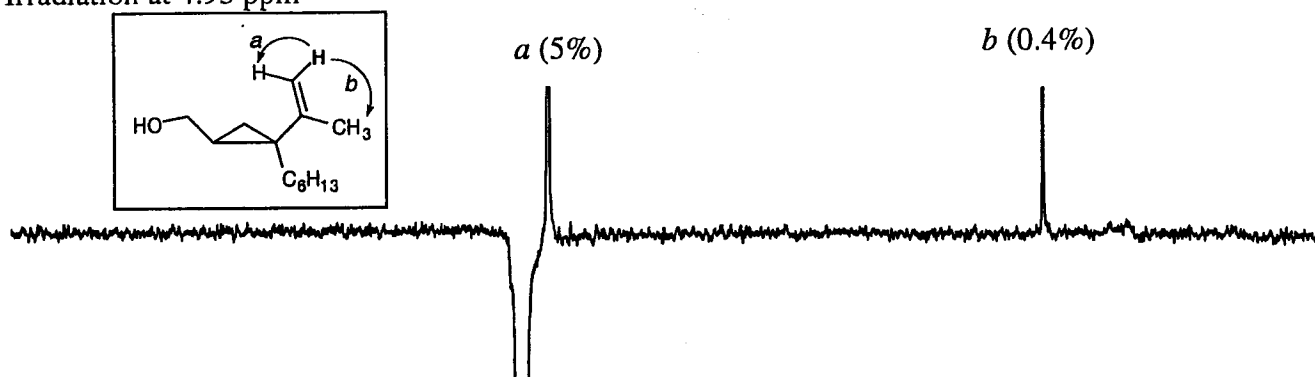


Irradiation at 0.61 ppm

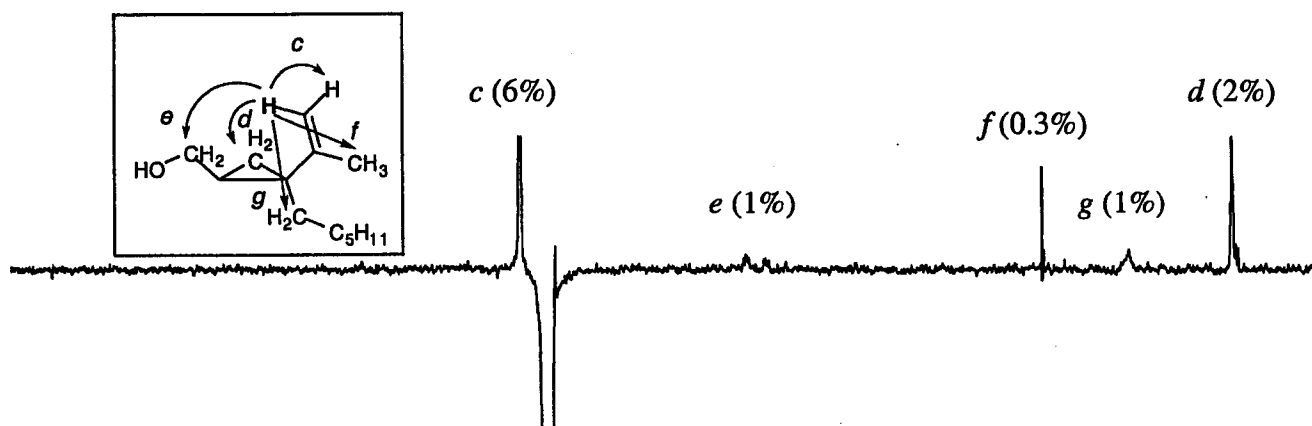


• ^1H NMR selective 1-D NOE spectra of 17

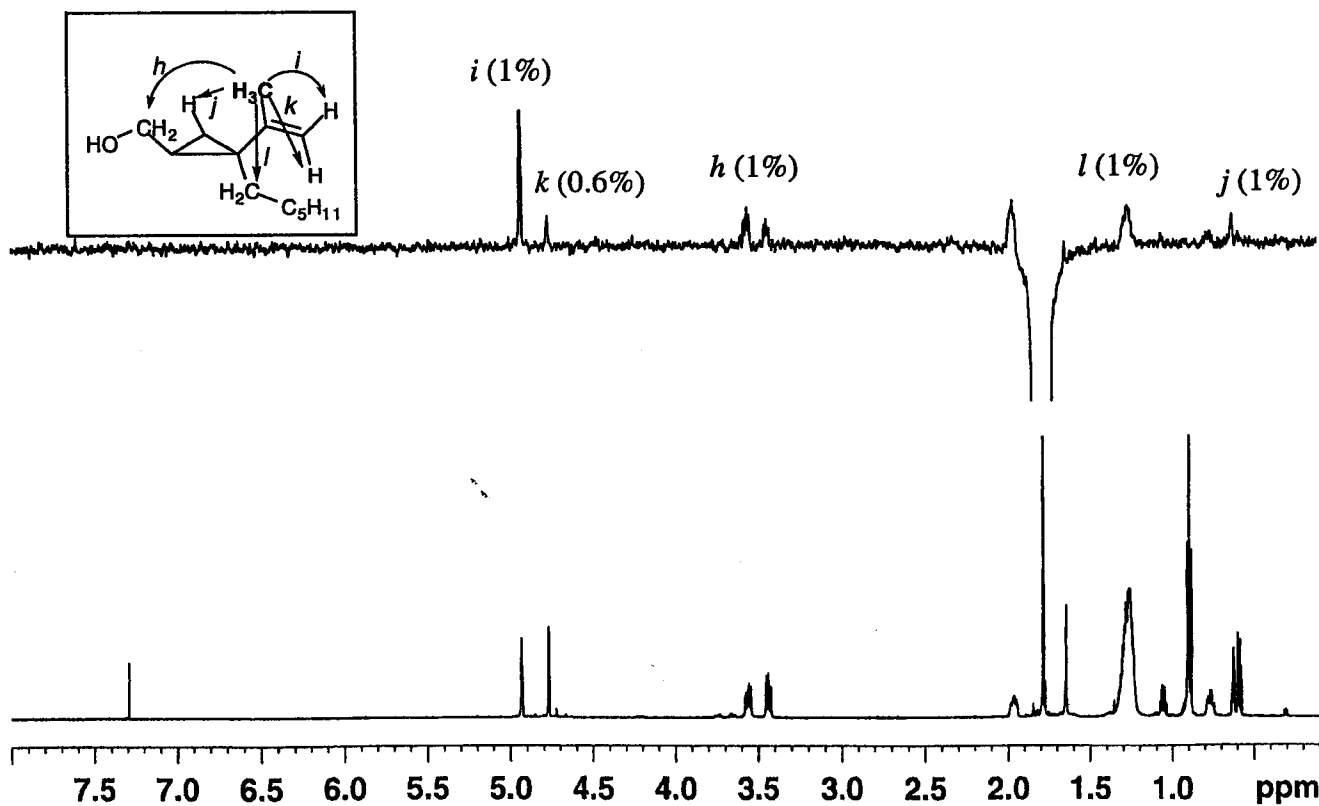
Irradiation at 4.93 ppm



Irradiation at 4.77 ppm

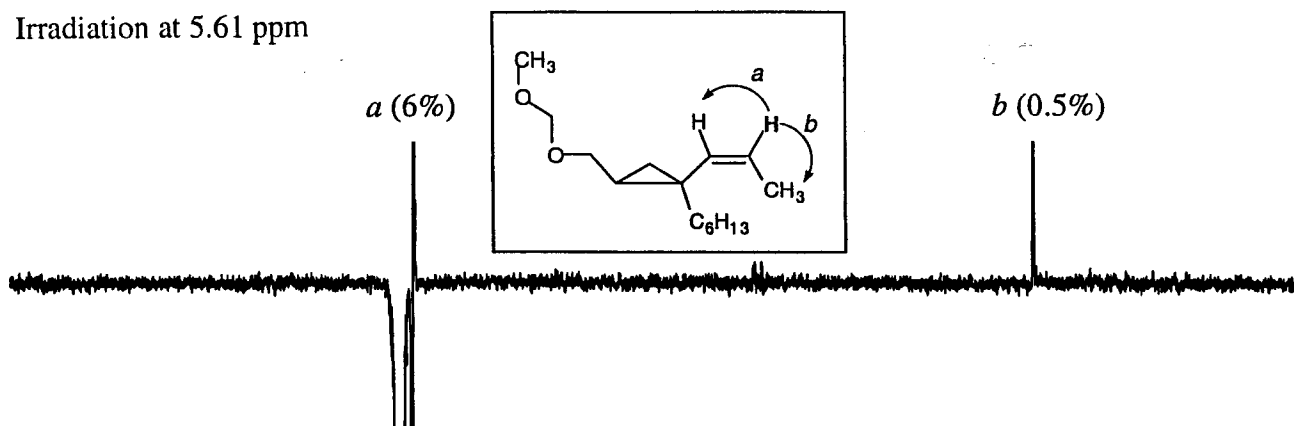


Irradiation at 1.78 ppm

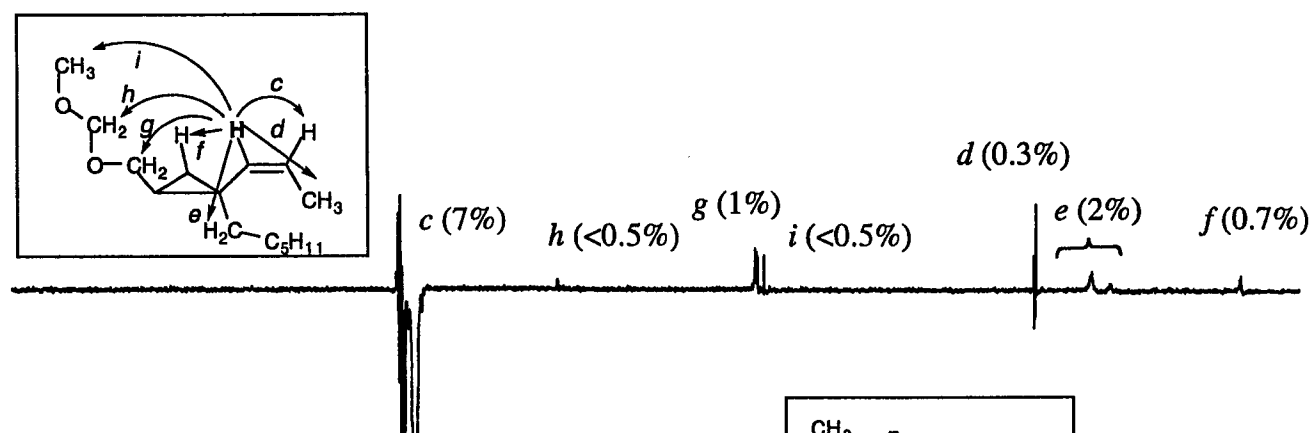


- ^1H NMR selective 1-D NOE spectra of **8**

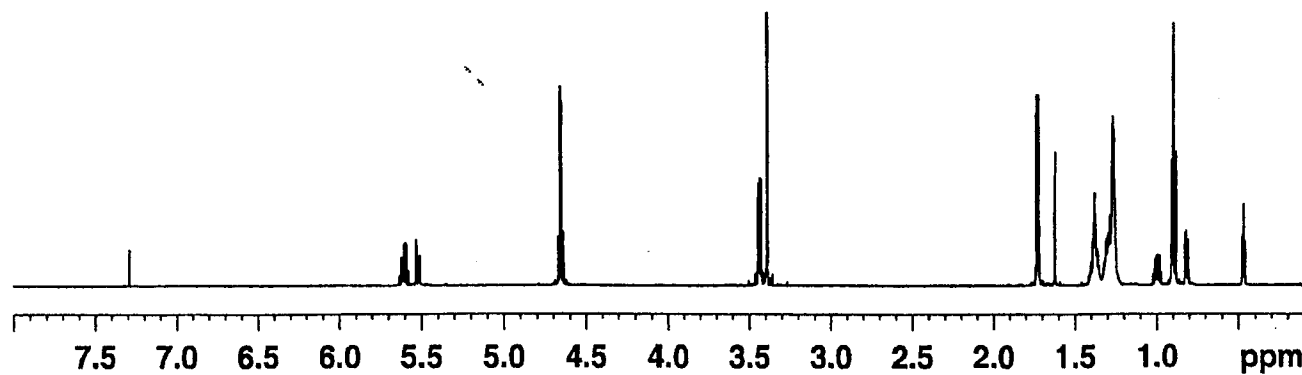
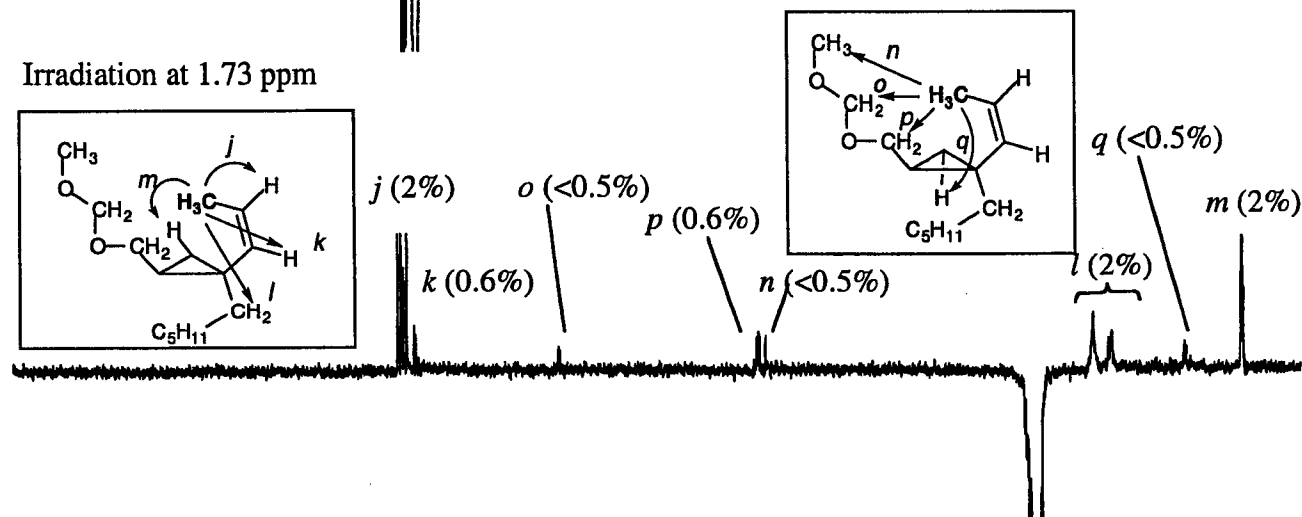
Irradiation at 5.61 ppm



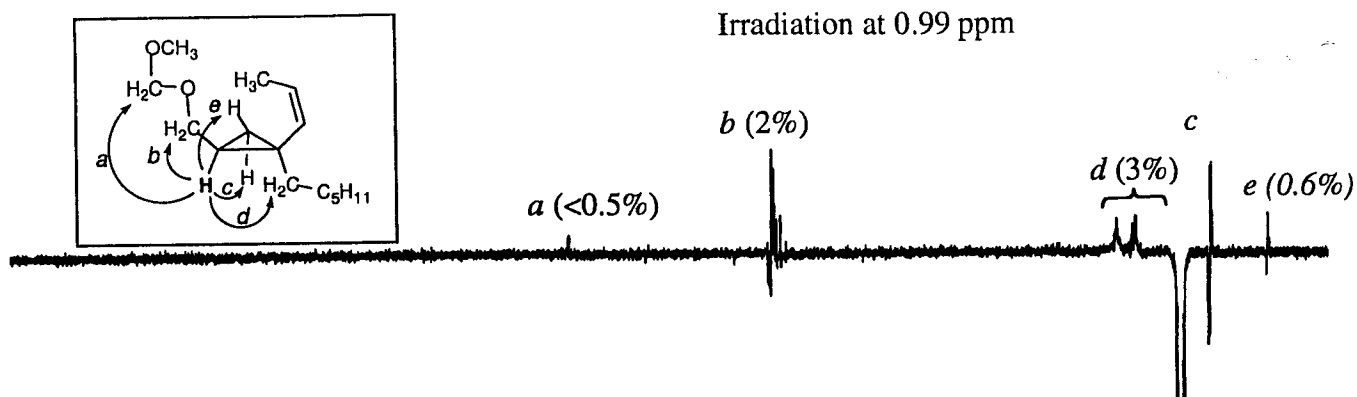
Irradiation at 5.52 ppm



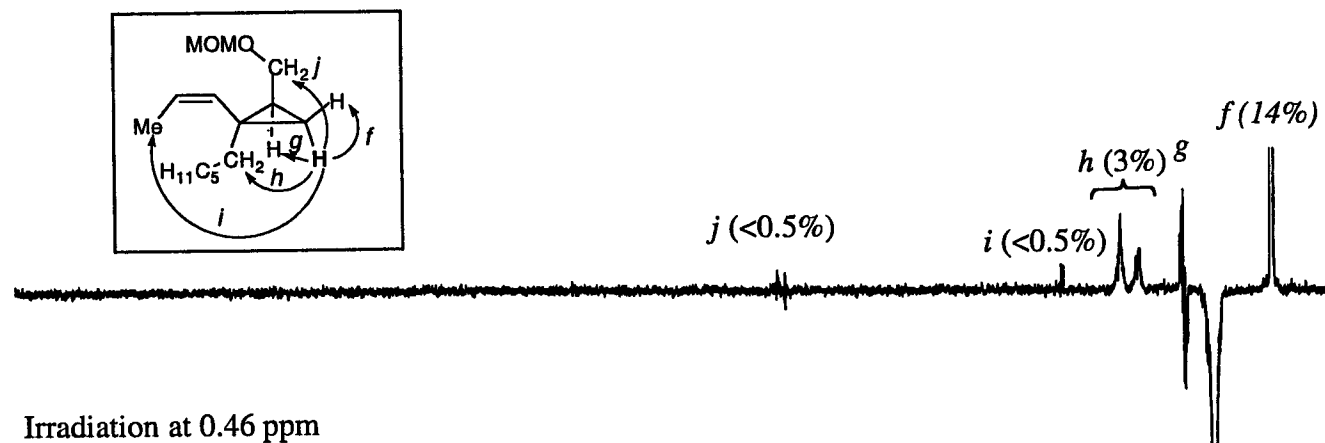
Irradiation at 1.73 ppm



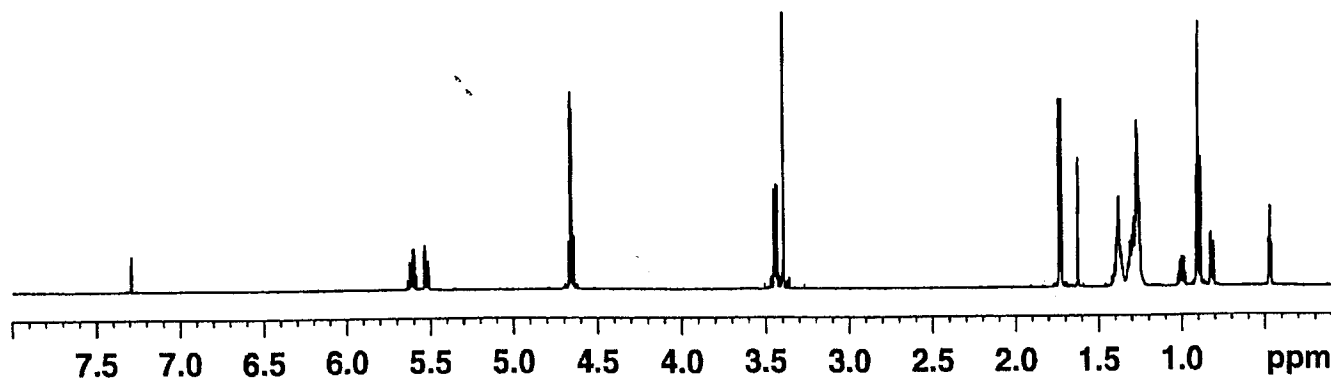
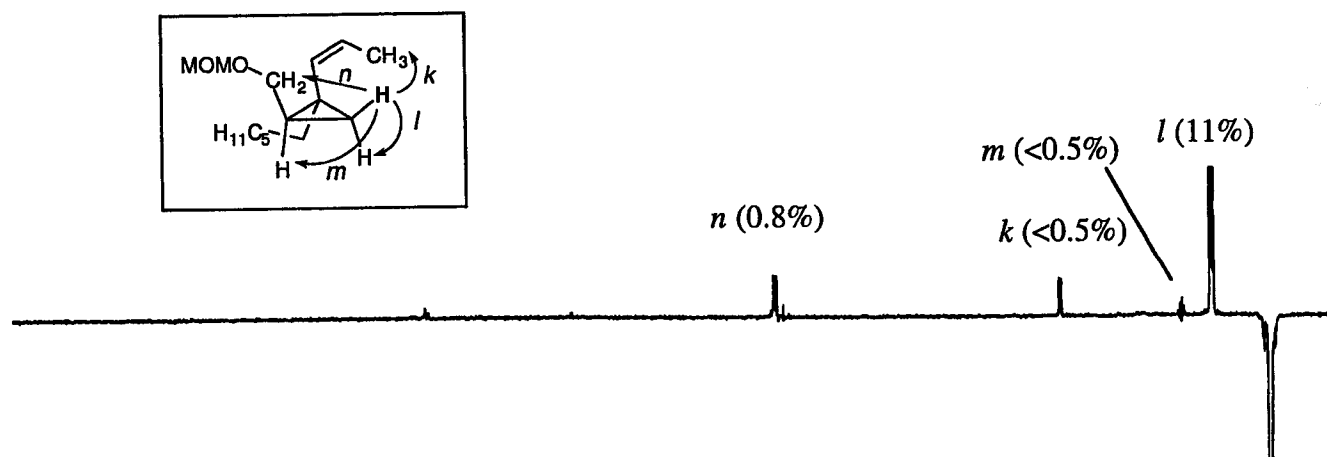
• ^1H NMR selective 1-D NOE spectra of **8** (cont')



Irradiation at 0.82 ppm

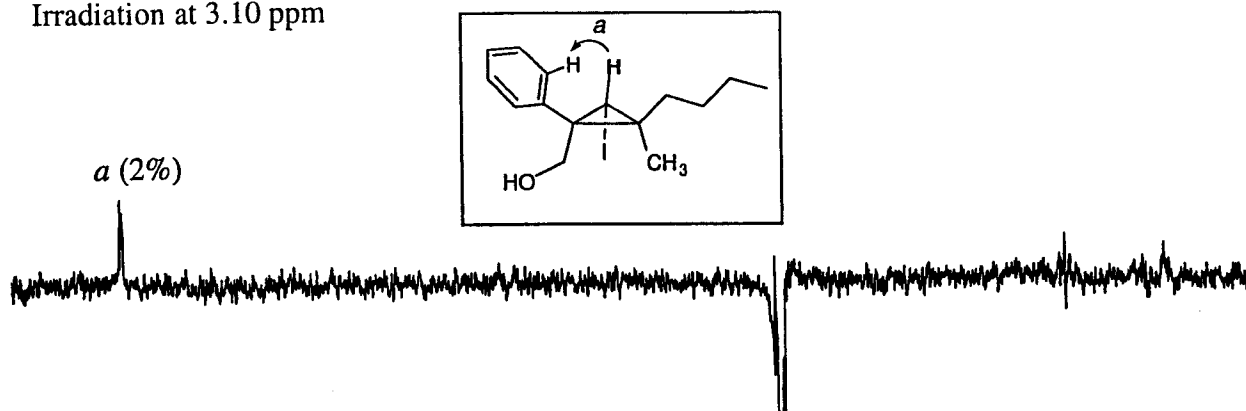


Irradiation at 0.46 ppm

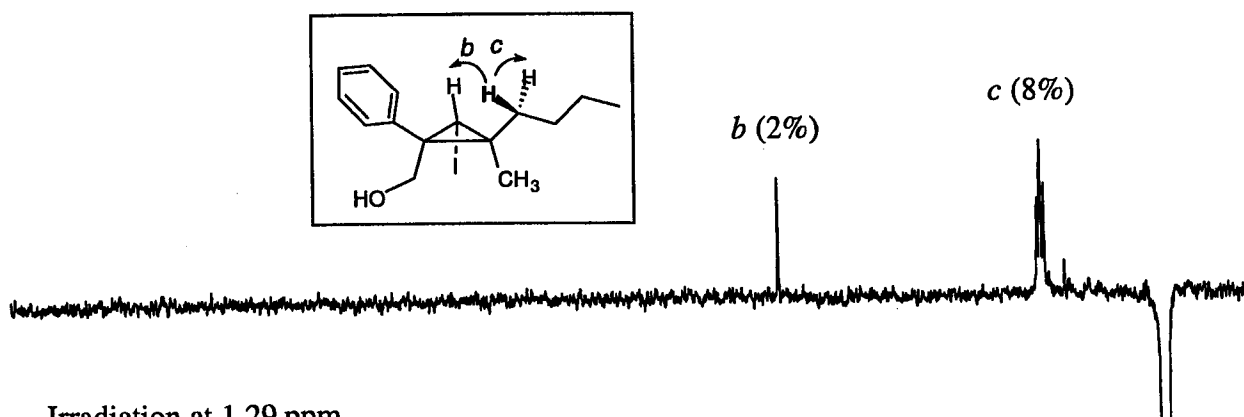


• ^1H NMR selective 1-D NOE spectra of **27**

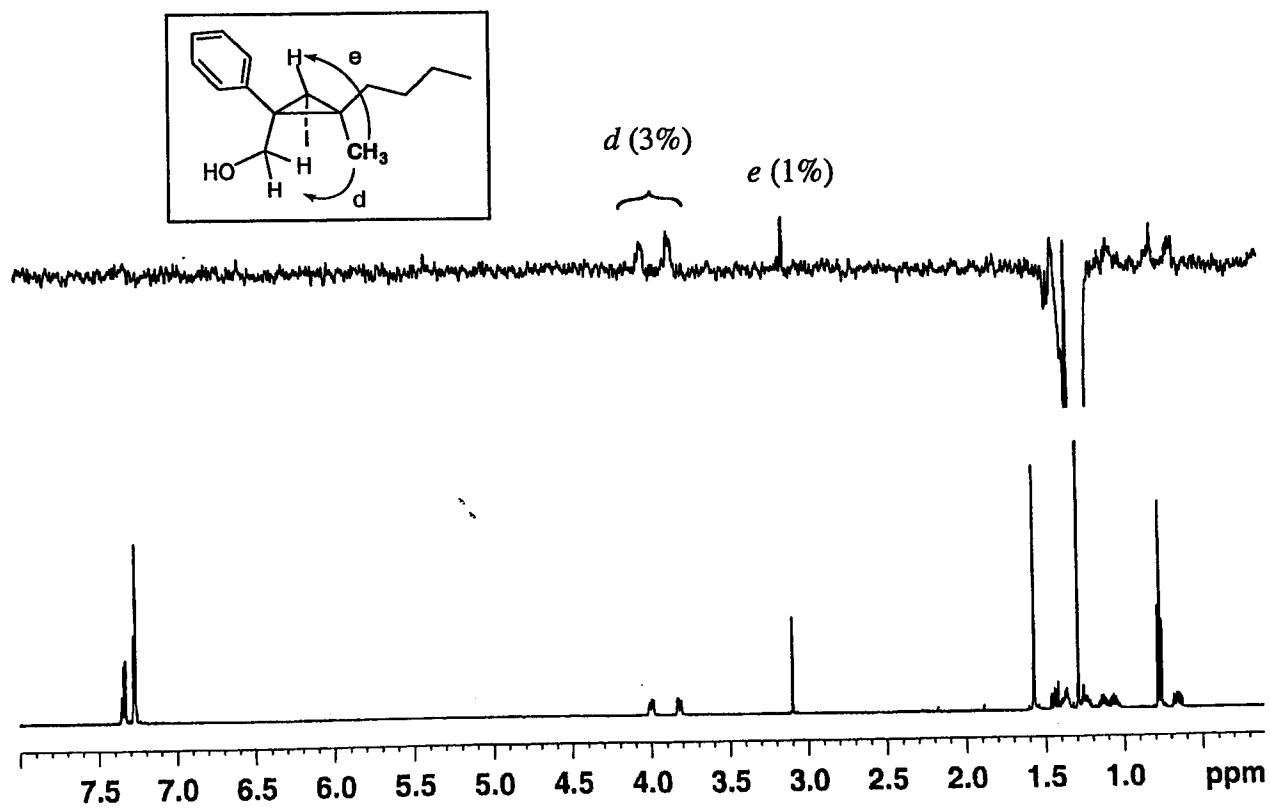
Irradiation at 3.10 ppm



Irradiation at 0.66 ppm

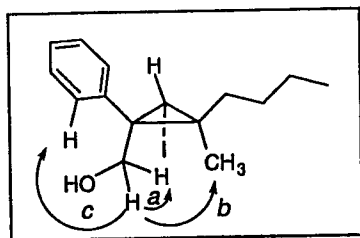


Irradiation at 1.29 ppm



- ^1H NMR selective 1-D NOE spectra of **27** (cont')

Irradiation at 3.99 ppm



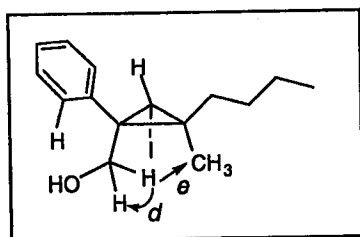
c (1%)

a (8%)

b (0.8%)

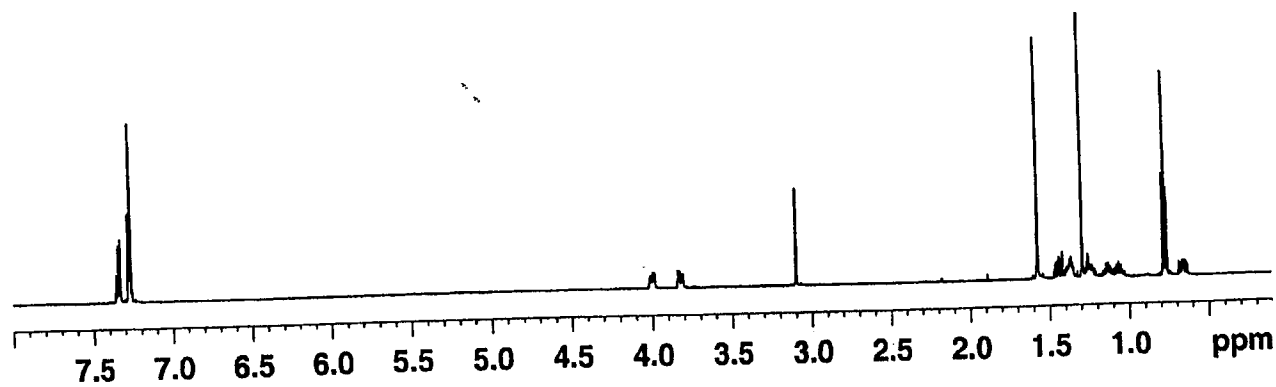


Irradiation at 3.82 ppm



d (26%)

e (<0.5%)



551