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**Thermal Allylations of Aldehydes with a Fluorous
Allylstannane. Separation of Organic and Fluorous Products
by Solid Phase Extraction (SPE) with Fluorous Reverse Phase
(FRP) Silica Gel**

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Pittsburgh, Pennsylvania, 15260

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Supporting Information

Journal of Organic Chemistry

**Preparation of (1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)dimethylsilyl Bonded Silica
Gel:^{1,2}**

Flash chromatography silica gel (12 g) was dried in a vacuum oven (180°C, 0.05 mm of Hg) for 12 h and dispersed in a flask containing dry toluene (300 ml, dried over sodium), dry pyridine (7.5 ml, 92.73 mmol) and 1*H*,1*H*,2*H*,2*H*,-perfluorooctyldimethylchlorosilane (13.6 ml, 45.07 mmol). The mixture was heated for 120 h at 100-105 °C and gently shaken with care occasionally. The product was then filtered on a scintered glass filter, washed sequentially with toluene (200 ml), methanol (200 ml), methanol-water 1/1 (200 ml), water (200 ml), methanol (200 ml) and ether (300 ml) and dried in a vacuum oven (120-140 °C, 0.05 mm of Hg) for 12 h to yield 17.0 g of (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)dimethylsilyl bonded silica gel.

Elemental Analysis of a typical batch: carbon 9.73%; fluorine 14.90%; chlorine <0.5%; hydrogen 0.71%

**Representative Experimental Procedure for Thermal Allylation Reactions of
Aldehydes:**

A mixture of 1-naphtaldehyde (11.3 µl, 0.083 mmol) and tris (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)allyltin (300 mg, 0.25 mmol) was heated at 140°C in a sealed tube under Ar or N₂ for 72 h.

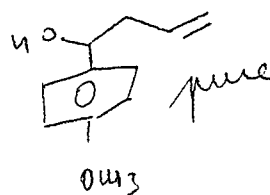
Liquid-Liquid Extraction: The residue obtained was partitioned between acetonitrile (10 ml) and FC-72 (10 ml). The layers were separated and the acetonitrile phase was extracted with FC-72 (2 x 10 ml). Evaporation of the organic phase yielded 1-(1-naphthyl)-3-buten-1-ol (15 mg, 92% yield, 85% GC purity).

Solid Phase Extraction: The residue obtained was dissolved in ether (10 mL). (1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)dimethylsilyl bonded silica gel (500 mg) was added to the mixture and the solvent was evaporated to dryness. The powder obtained was then loaded on a column of (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)dimethylsilyl bonded silica gel (10 g). Elution with acetonitrile (30 ml) yielded 1-(1-naphthyl)-3-buten-1-ol (15.6 mg, 95% yield, 84% purity). Elution with hexane (30 ml) yielded the tin fraction.

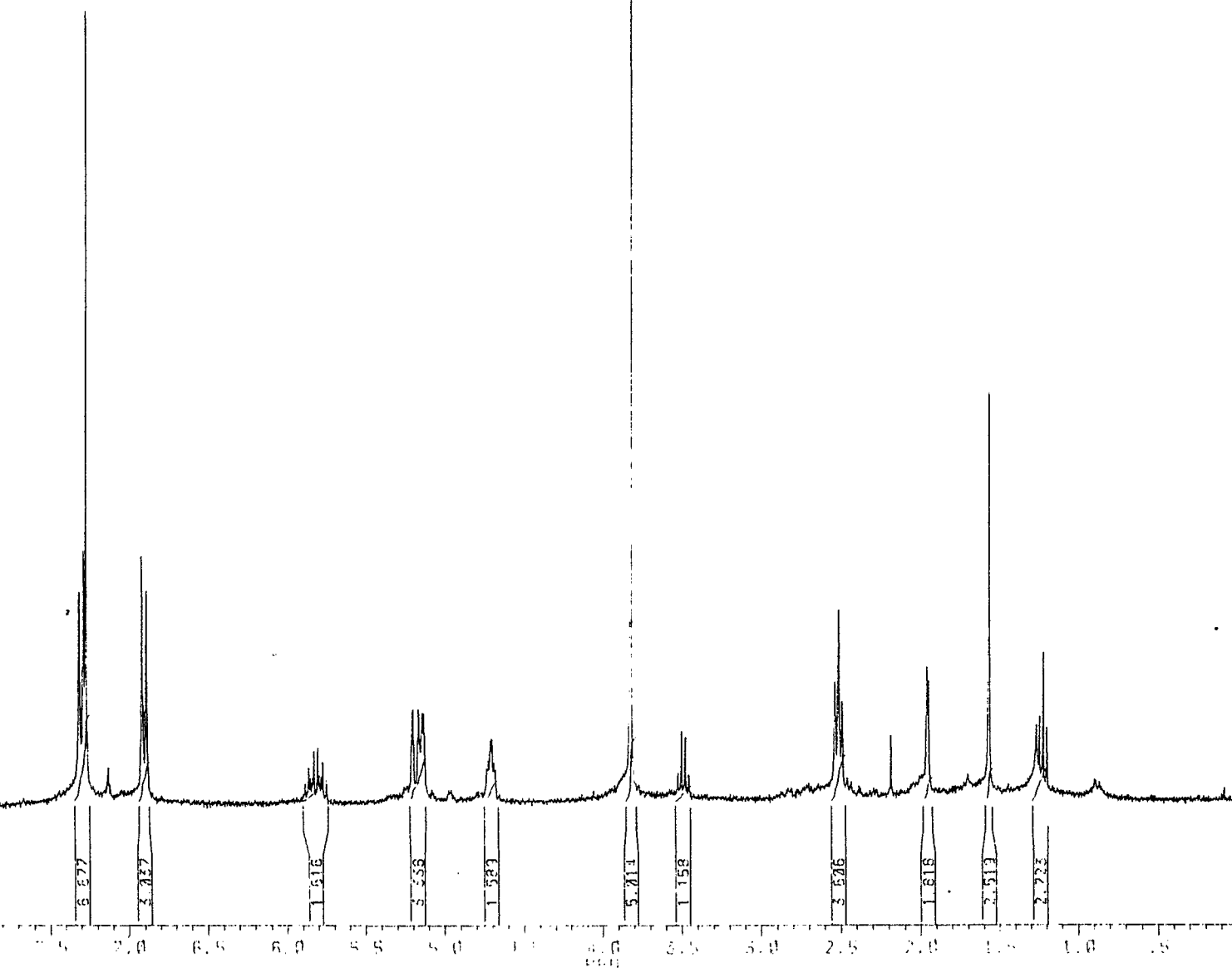
References:

1. G. E. Berendsen; Galan, L. D. *J. Liquid Chromatogr.*, **1978**, *1*, 561.
2. G. E. Berendsen; R., A., Pikaort, Galan, L. D., *J. Liquid Chromatogr.*, **1980**, *3*, 1437.

1H NMR spectrum of 1-(4-oxocyclopent-1-en-1-yl)but-3-en-2-ol



POOR QUALITY ORIGINAL

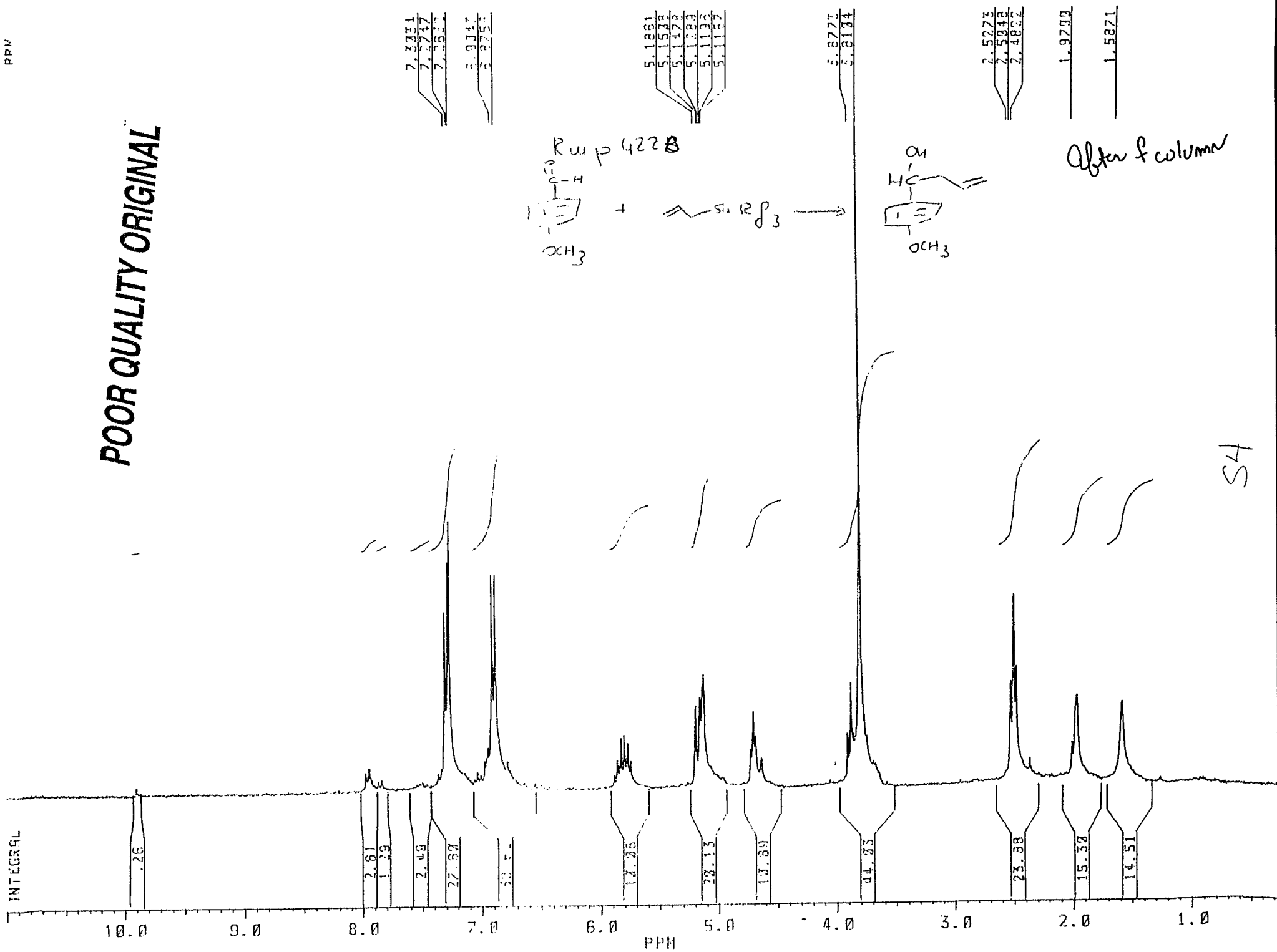


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INTEGRAL

PPM

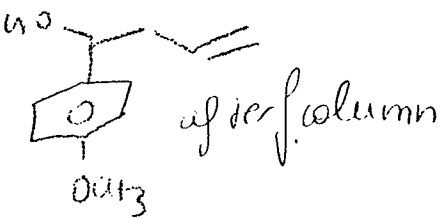
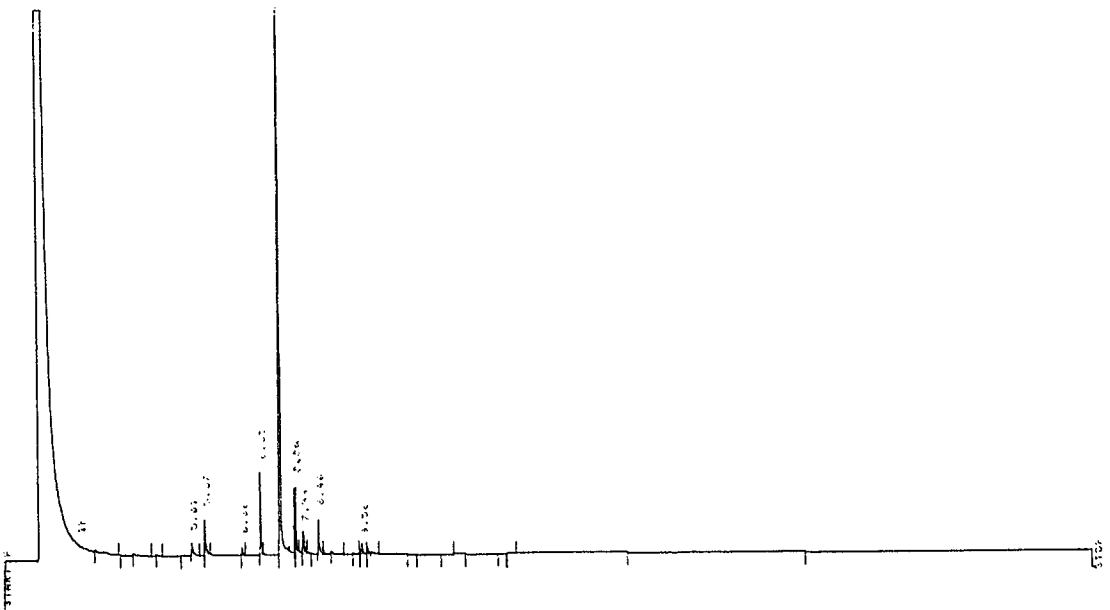
POOR QUALITY ORIGINAL



[illegible]

h

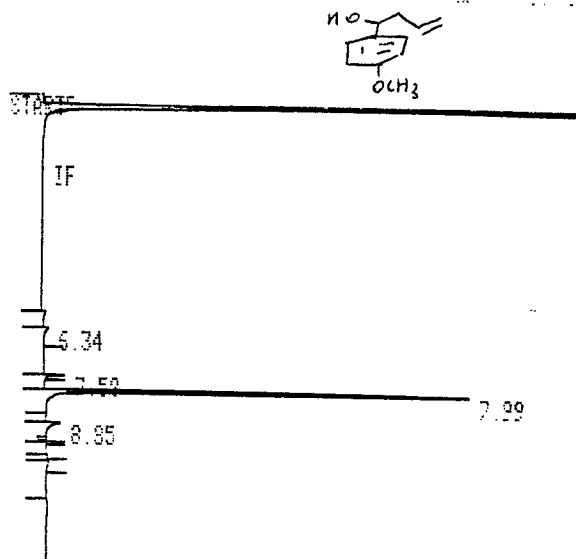
POOR QUALITY ORIGINAL

[illegible]

56

LS

after F. extraction



RUN # 141
WORKFILE ID: C5
WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
	6.34	370420	PB	0.123	4.517
	7.58	397640	PB	0.043	4.849
→	7.99	6784600	PB	0.036	82.727 ←
	8.85	648550	PV	0.093	7.908

TOTAL AREA= 8201200
MUL FACTOR= 1.0000E+00

POOR QUALITY ORIGINAL

801554 (RESIDUE AFTER DISTILLATION AT 100°C)

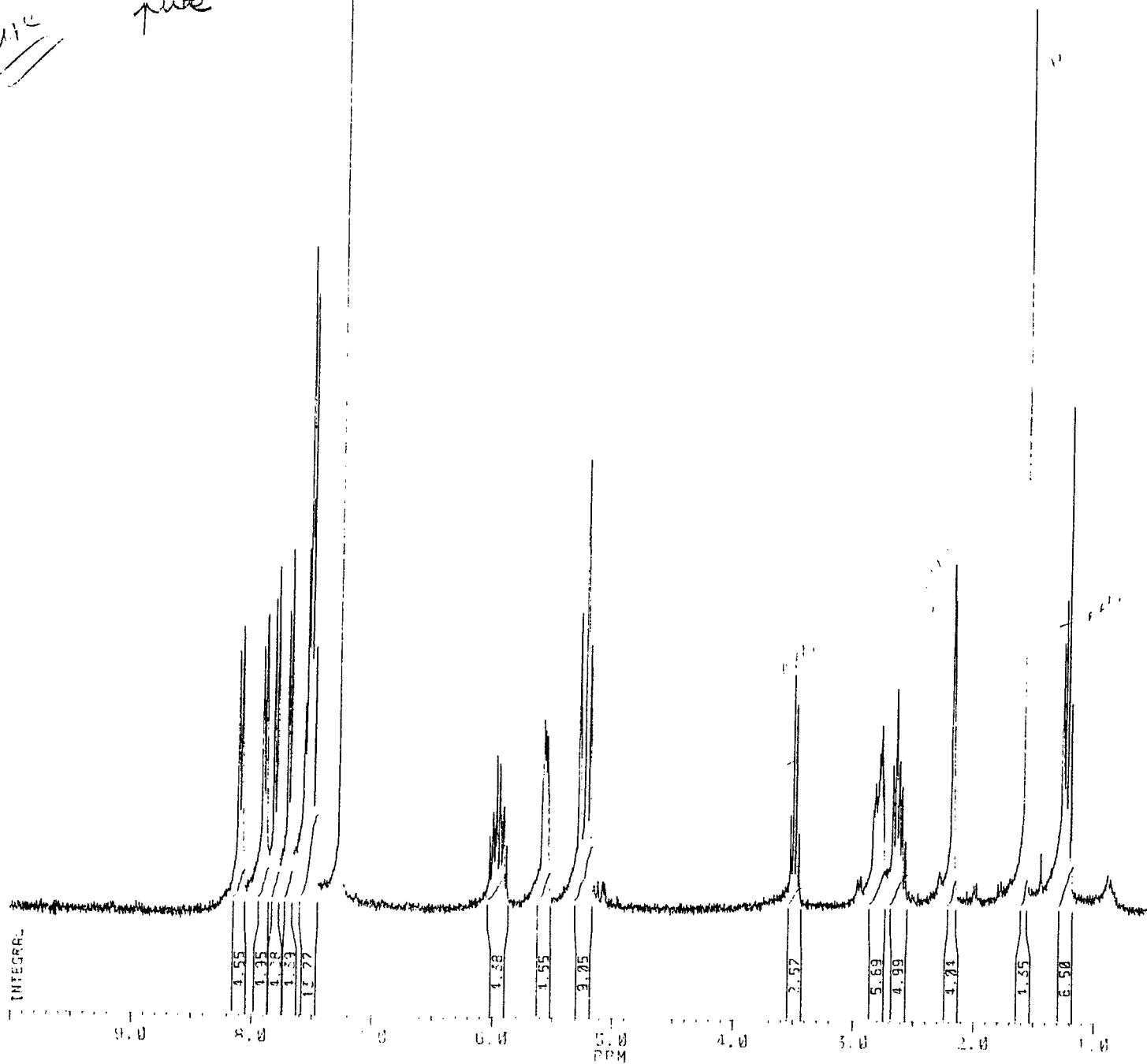
6. from chro.



pure

pure

POOR QUALITY ORIGINAL

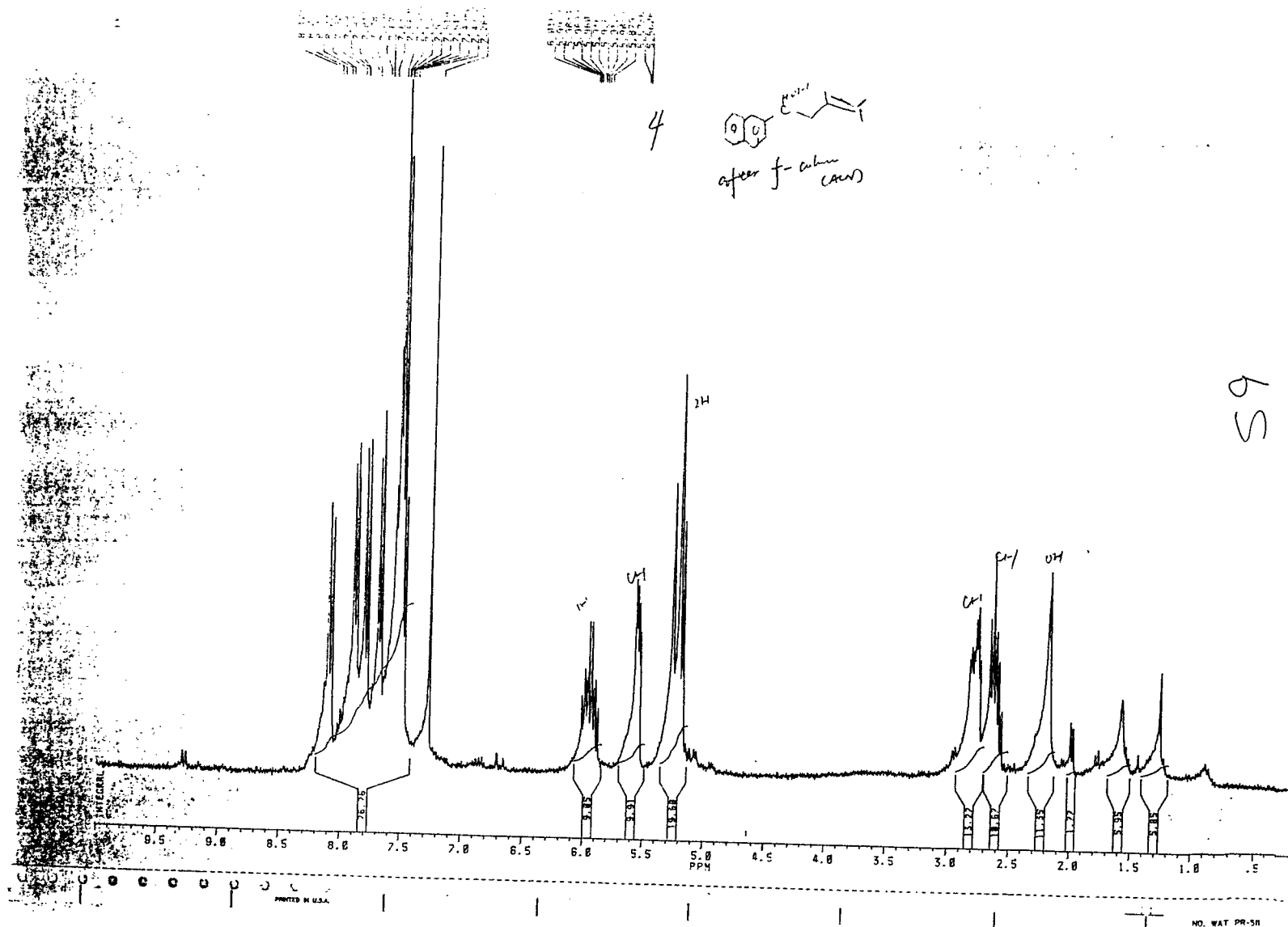


NO. WAT PR-511

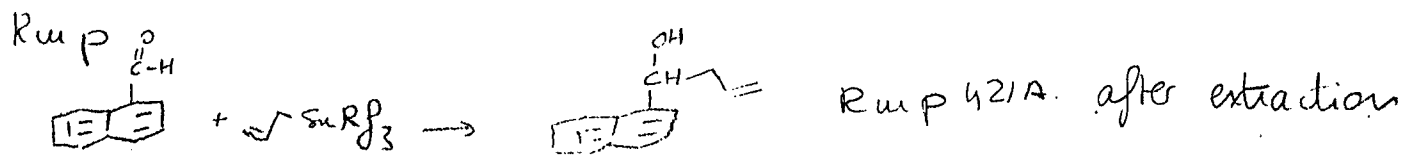
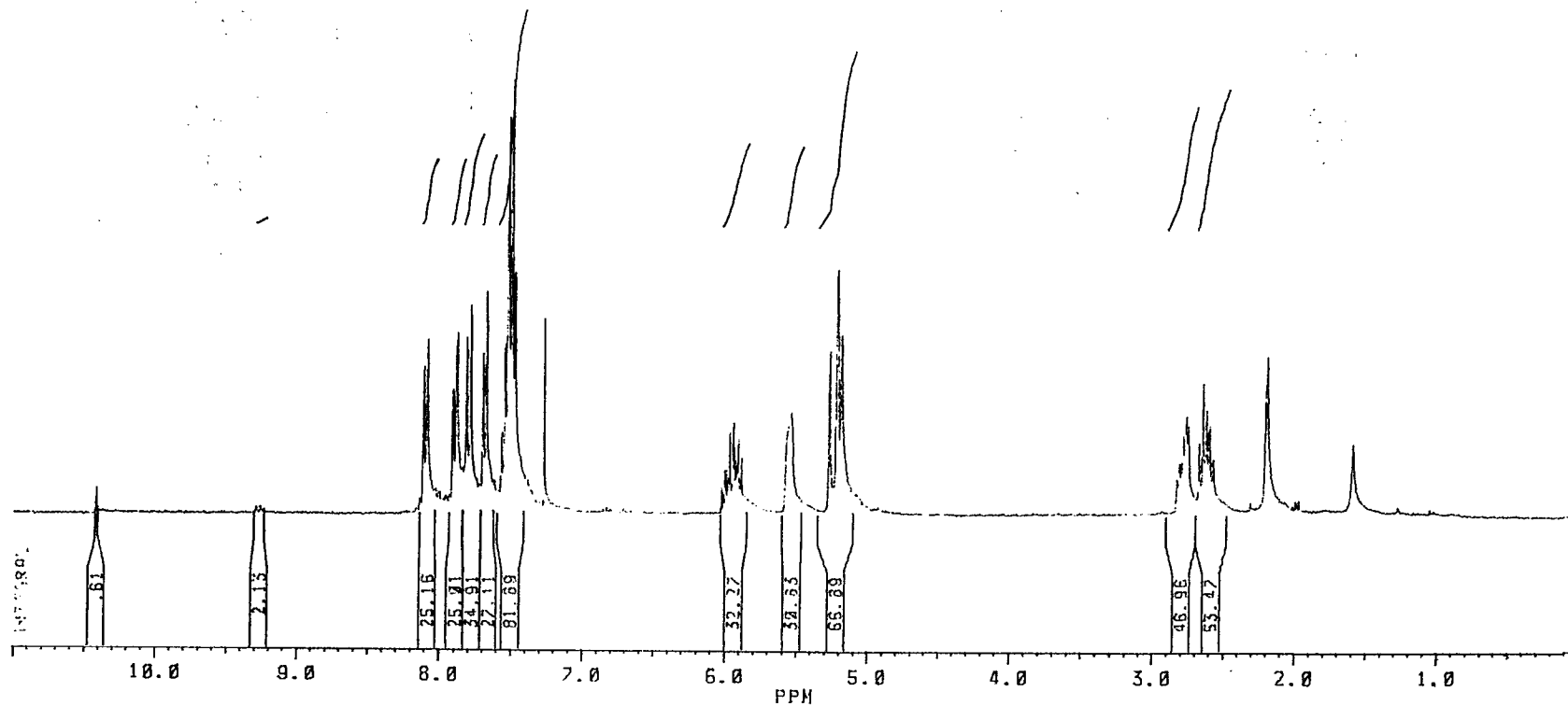
GRAPHIC CONTROLS CORPORATION

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S8



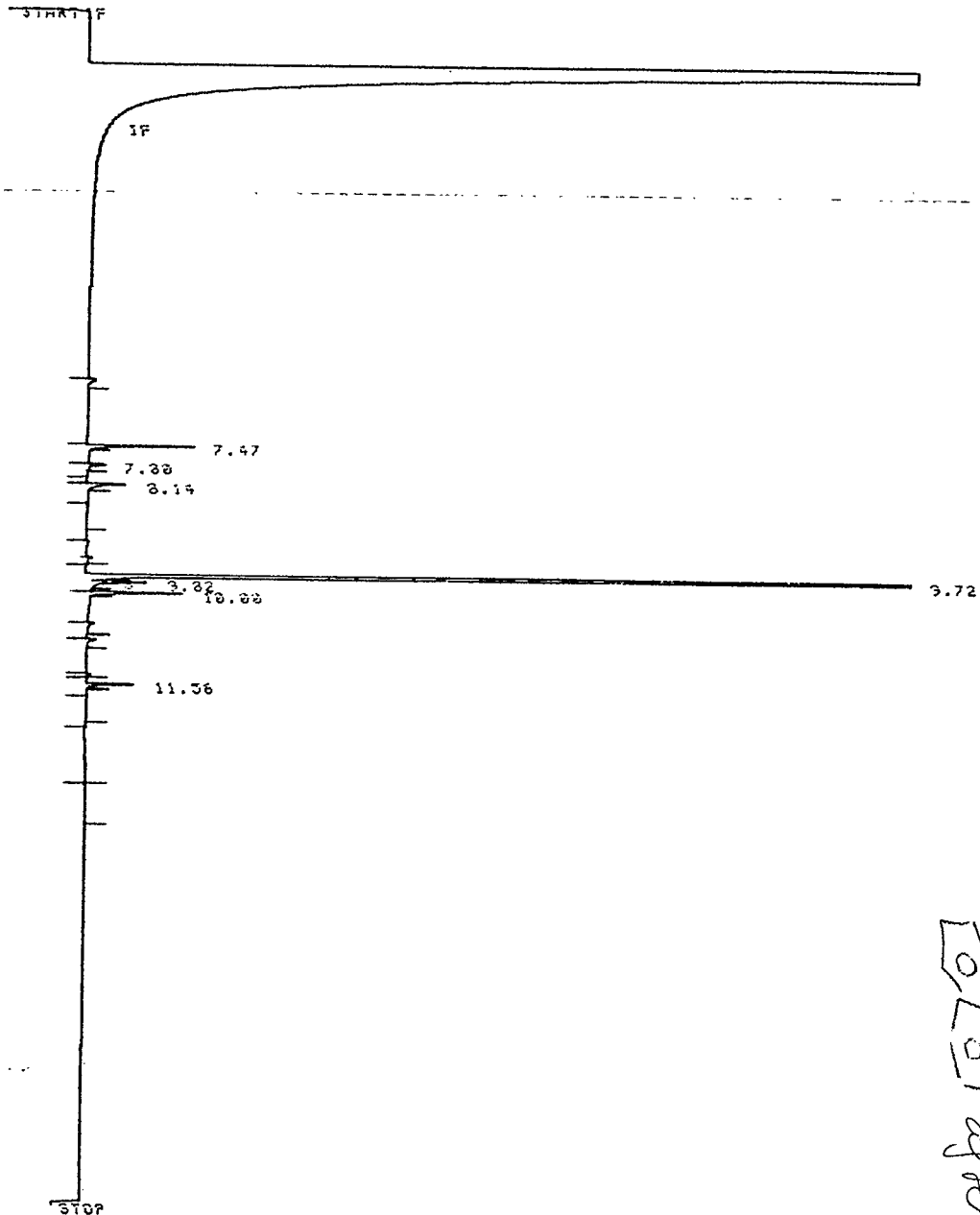
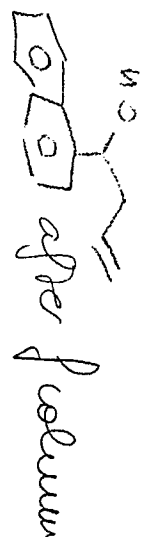
on



570

POOR QUALITY ORIGINAL

4



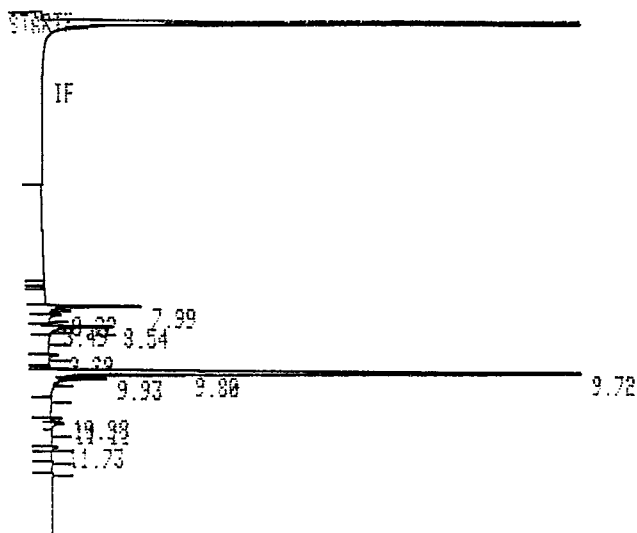
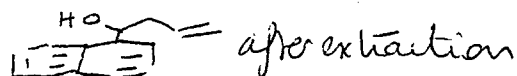
RUN # 323

AREA%

RT	AREA	TYPE	RR/HT	AREA%
7.47	102600	PB	0.027	4.523
7.38	20227	PB	0.042	1.243

S11

POOR QUALITY ORIGINAL



RUN # 135
 WORKFILE ID: C5
 WORKFILE NAME:

AREA%					
RT	AREA	TYPE	AR/HT	AREA%	
7.99	1802600	PB	0.043	4.265	
9.22	265520	BB	0.046	0.628	
9.49	52239	PV	0.028	0.124	
9.54	1449400	VB	0.050	3.429	
9.72	185510	BB	0.042	0.439	
→ 9.72	3.5988E+07	↑SPB	0.072	85.145	←
9.80	1130100	TBP	0.023	2.674	
9.93	757750	TVP	0.036	1.793	
10.98	192720	BP	0.038	0.456	
11.11	336090	PV	0.056	0.795	
11.73	106710	PB	0.039	0.253	

TOTAL AREA= 4.2266E+07
 MUL FACTOR= 1.0000E+00



after f-column

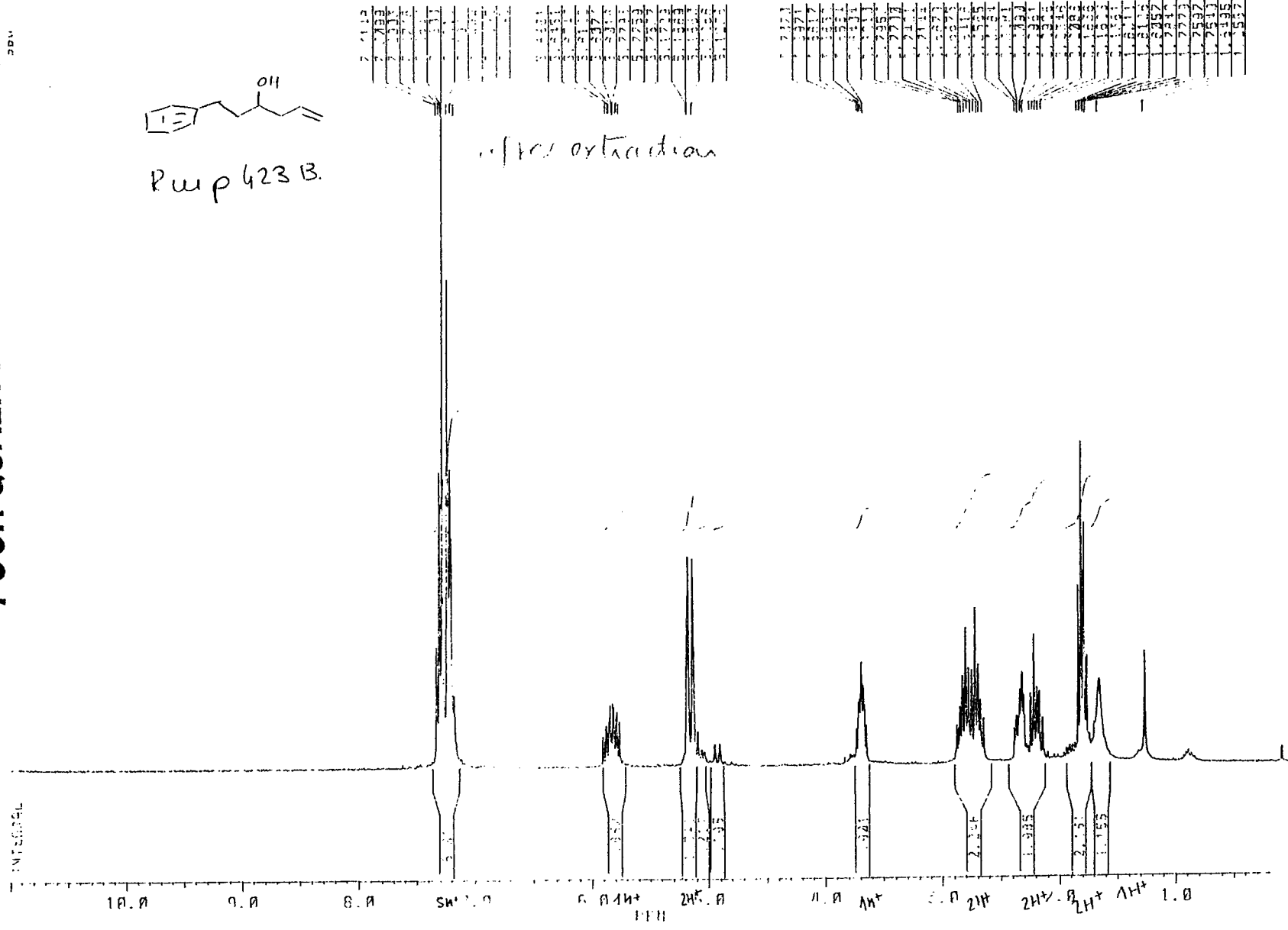
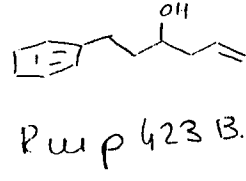
CCCCC(C)C=C
 after f-column

POOR QUALITY ORIGINAL

1H NMR spectrum (400 MHz, CDCl₃) of 4-phenyl-1-pentene. The spectrum shows peaks from 0 to 8 ppm. Aromatic protons are at ~7.2 ppm (integration 1.93, 3.9). The alkene proton is at ~6.7 ppm (integration 1.20, 2.4). The methylene protons adjacent to the alkene are at ~2.1 ppm (integration 2.27, 4.5). The methylene protons adjacent to the phenyl ring are at ~2.7 ppm (integration 1.81, 3.6). The terminal methyl protons are at ~1.0 ppm (integration 3.43, 6.9). The integration values are slightly off from the expected 1:2:2:2:3 ratio.

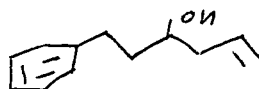
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S 14

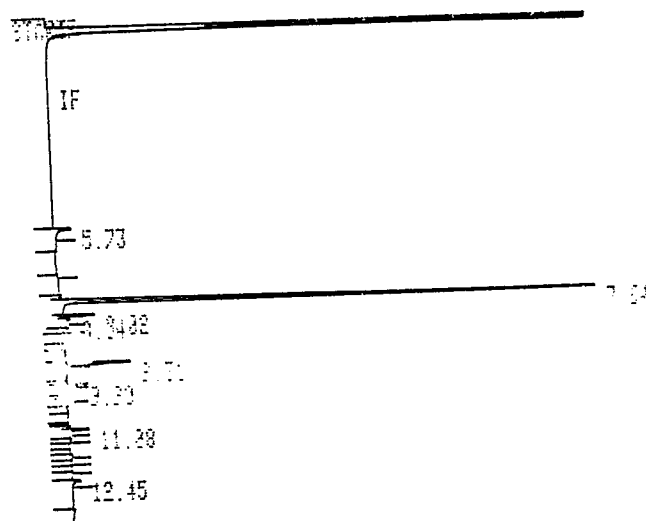


5/5

POOR QUALITY ORIGINAL



88% after extraction



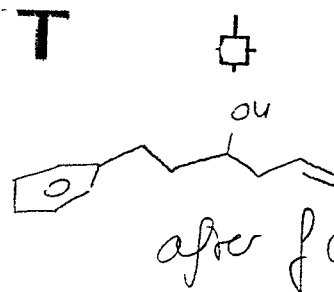
RUN # 137
WORKFILE ID: C5
WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
	5.73	611480	PB	0.081	2.061
	7.64	2.6141E+07	↑SPB	0.052	88.111 ←
	8.02	691570	BV	0.048	2.231
	8.14	137650	VB	0.043	0.464
	9.31	1237600	PB	0.043	4.171
	9.90	194380	BB	0.037	0.655
	11.08	451870	VB	0.048	1.523
	12.45	202640	PB	0.051	0.683

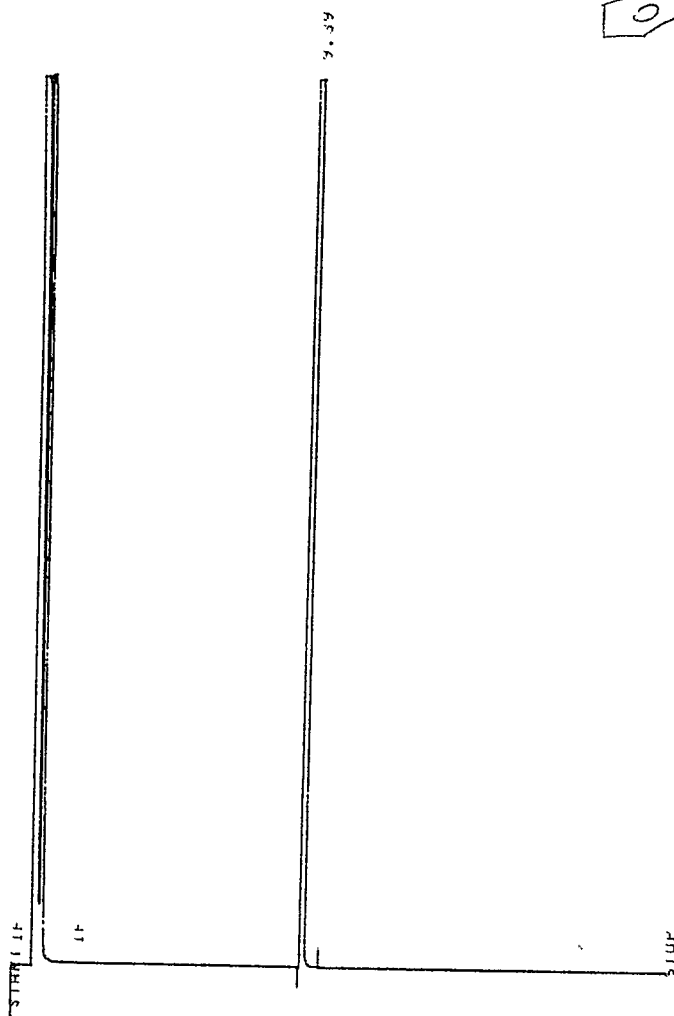
TOTAL AREA= 2.9669E+07
MUL FACTOR= 1.0000E+00

516

POOR QUALITY ORIGINAL



after column



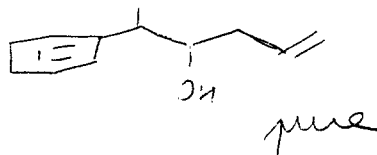
KUN #	00
AKKEN:	
KI	AKEN TYPE
9.39	405300 USDB
	HK HI
	0.000
	HKRX
	100.000
TOTAL AKEN=	405300
MUL FACIOK=	1.0000E+00

HEWLETT-PACKARD
PART NUMBER 518

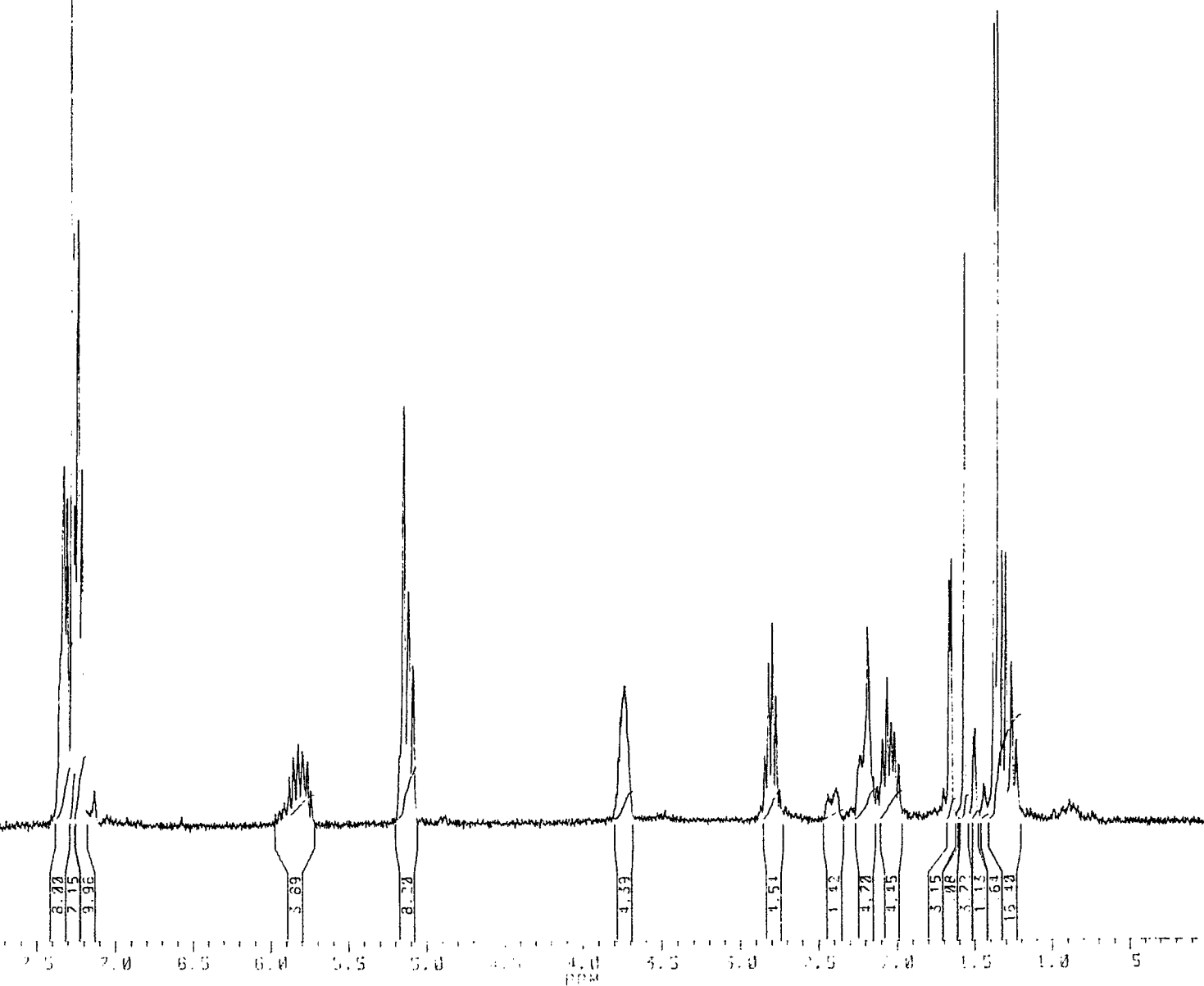
ENT THIS SIDE

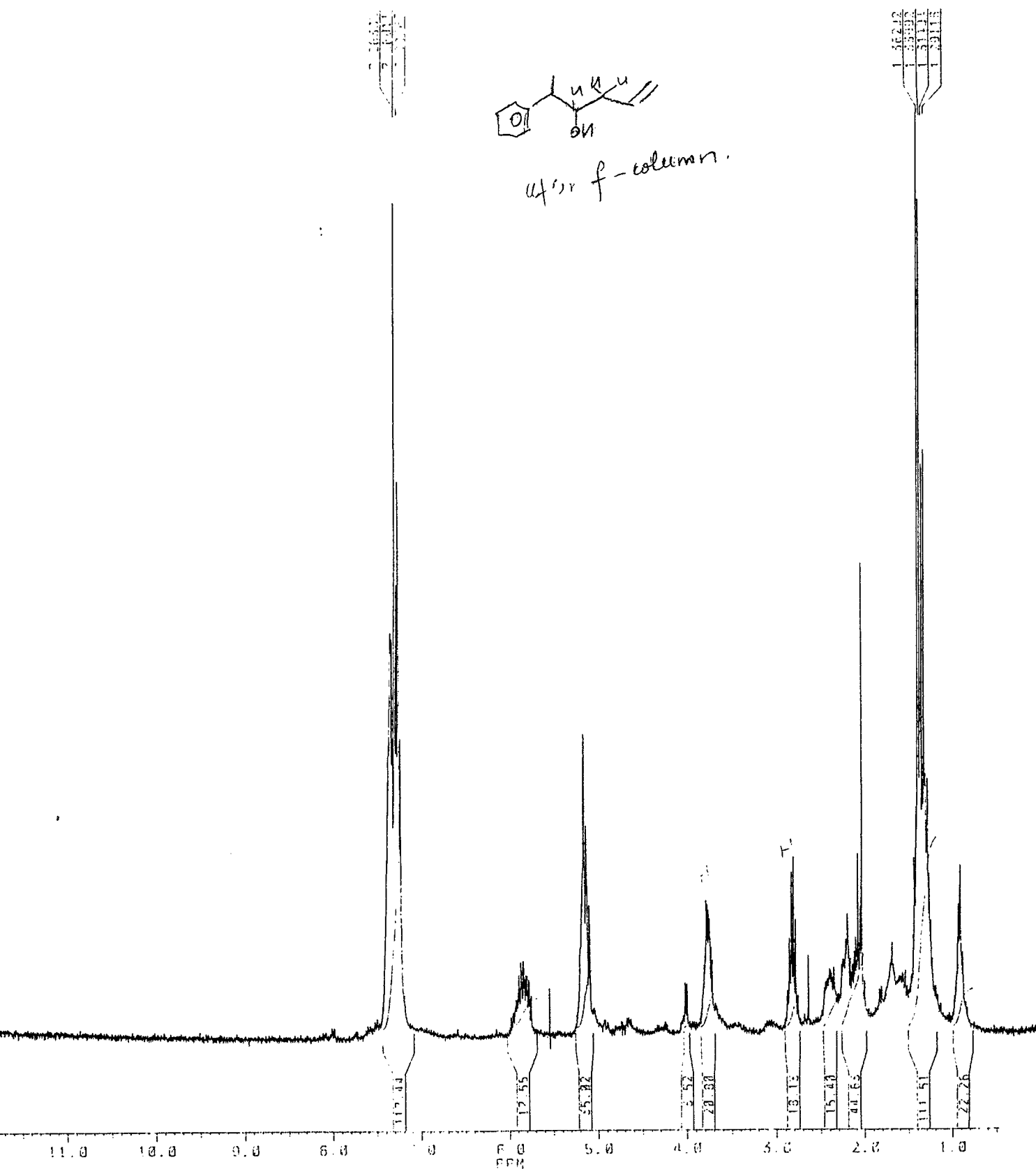
517

SOLVENT: CDCl₃ (TMS) (100 MHz, 25 °C)



POOR QUALITY ORIGINAL

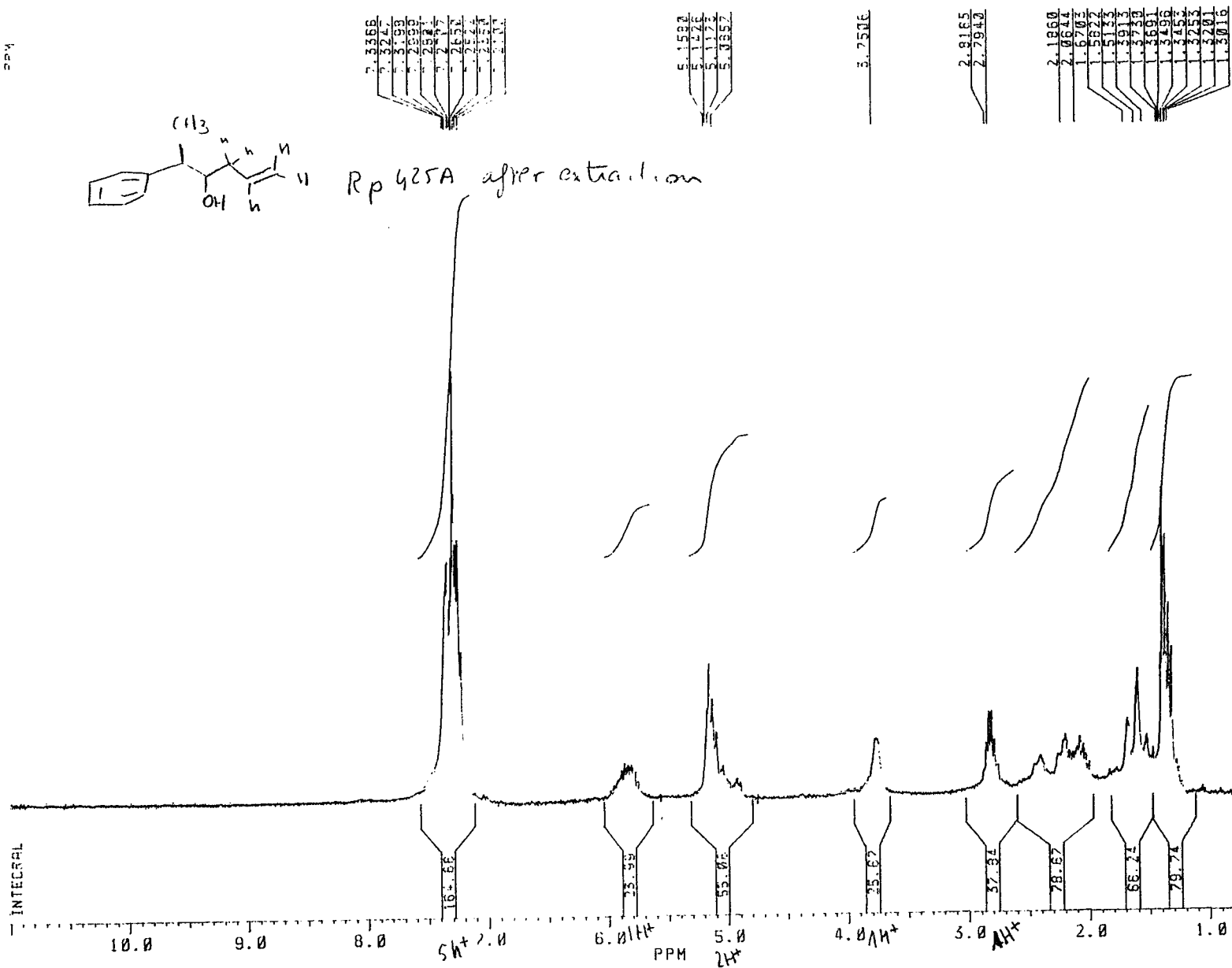




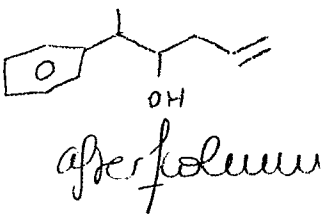
NO. WAT PR-511

519

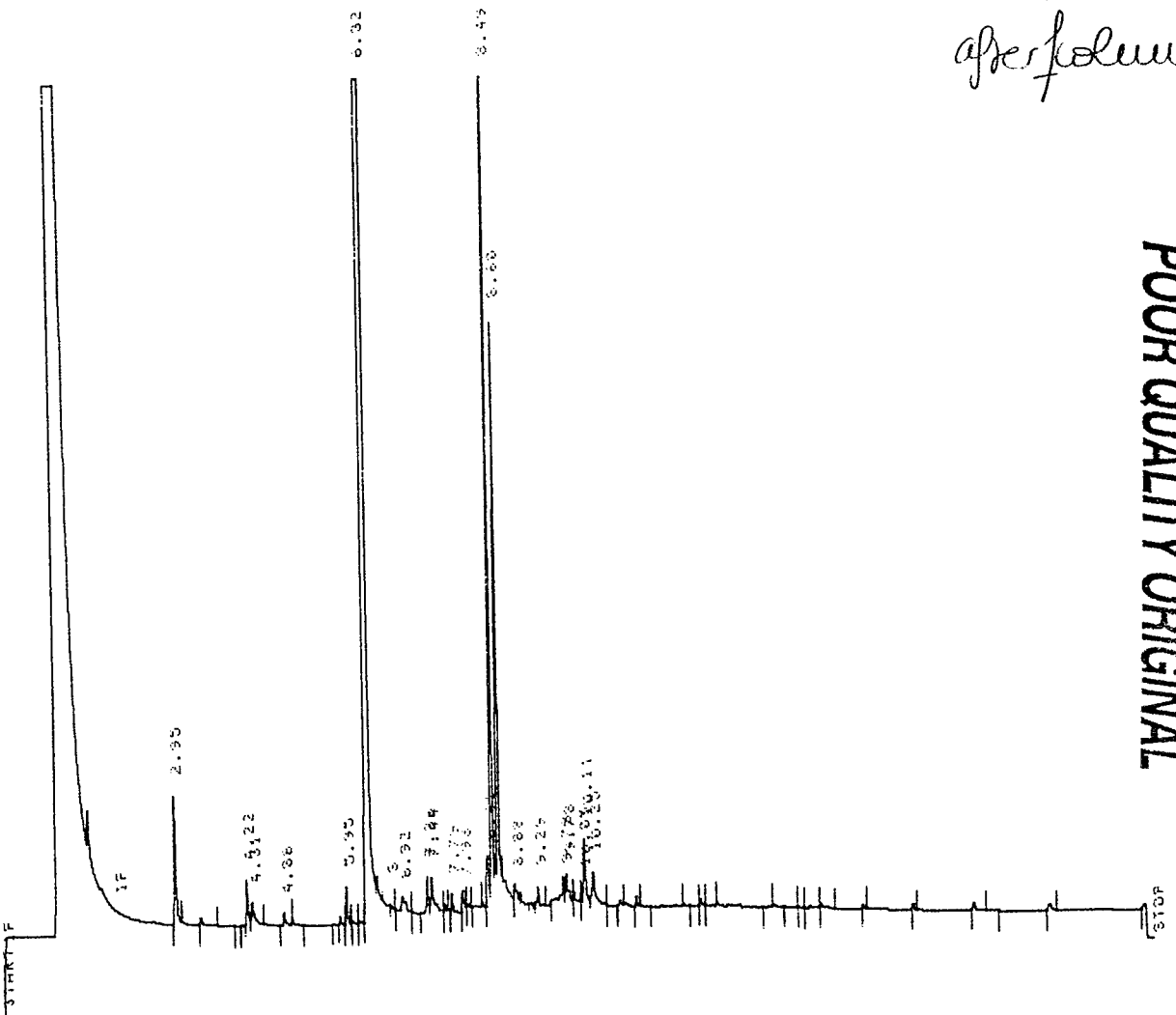
POOR QUALITY ORIGINAL



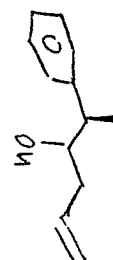
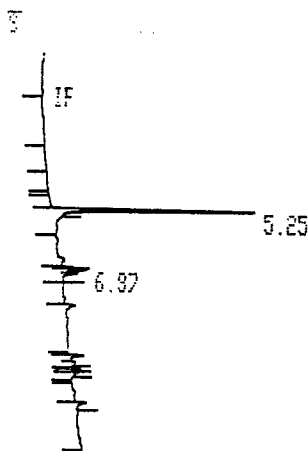
520



POOR QUALITY ORIGINAL



ees

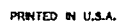


RUN # 15
WORKFILE ID: C5
WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
	5.25	1404600	PB	0.061	93.162
	6.87	103100	BP	0.046	6.838

TOTAL AREA= 1507700
MUL FACTOR= 1.0000E+00

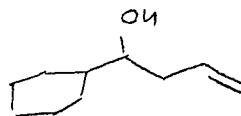
after extraction



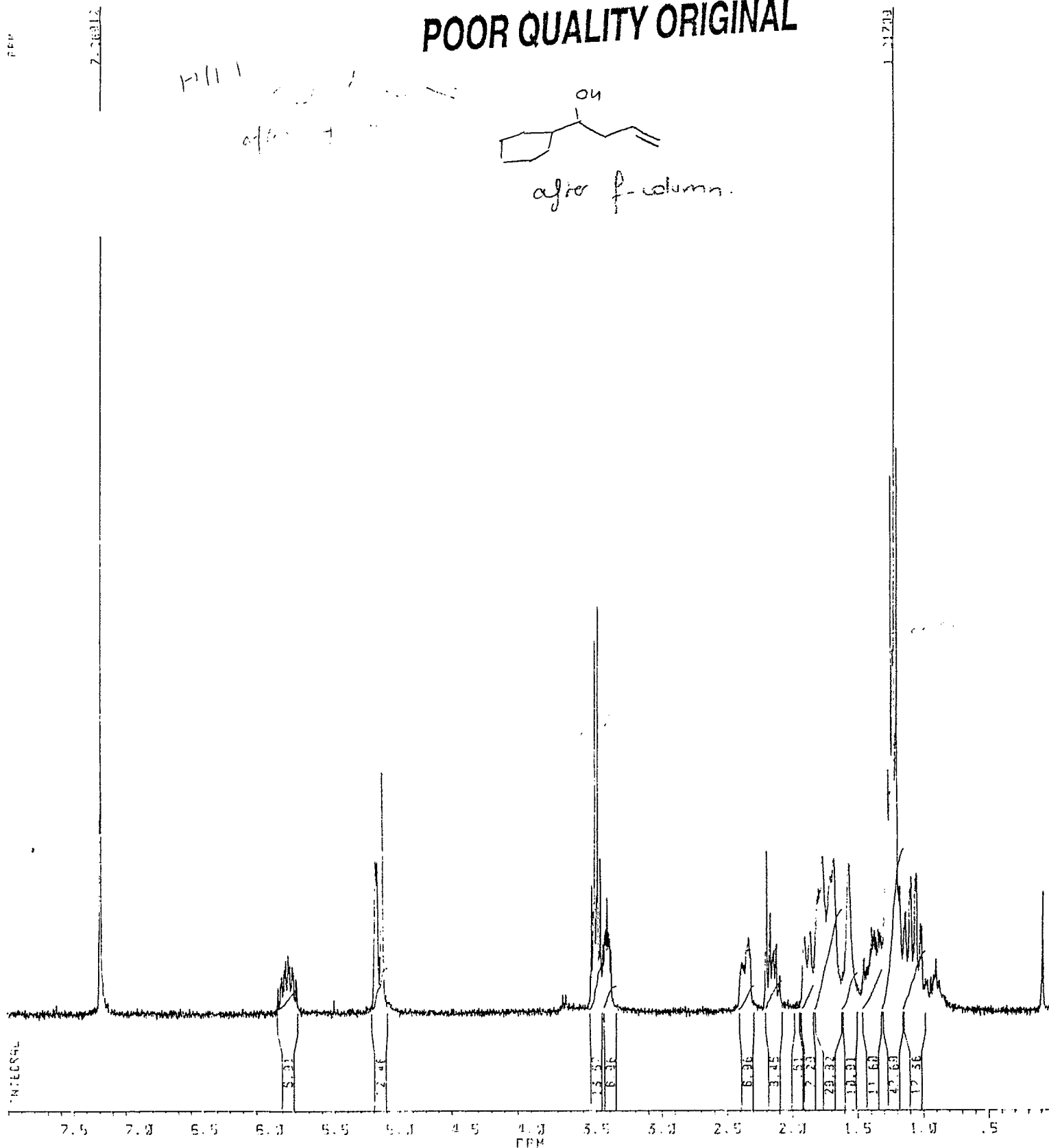
S23

POOR QUALITY ORIGINAL

1111



after f-column.

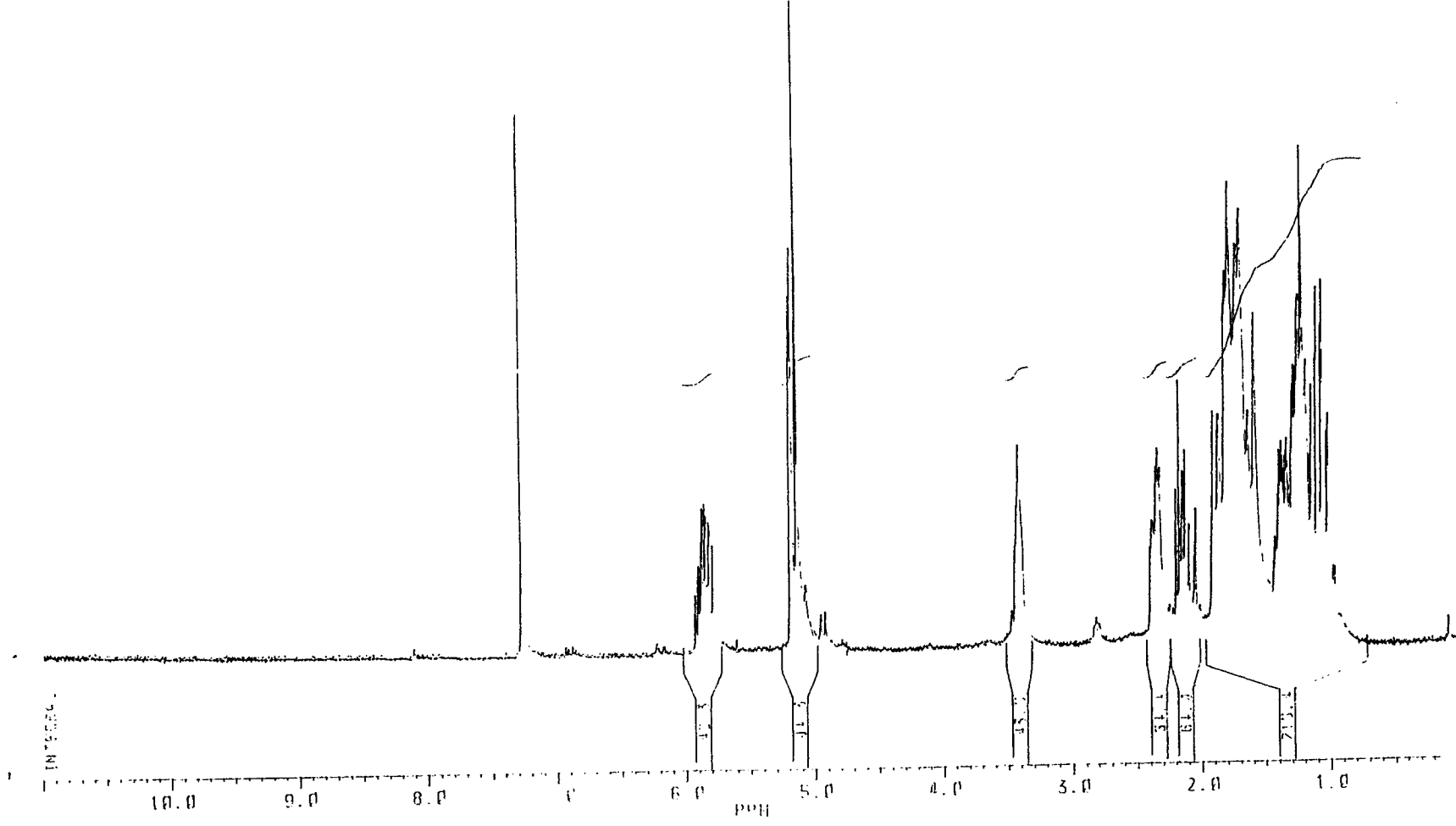


GRAPHIC CONTROLS CORPORATION

BUFFALO, NEW YORK

524

POOR QUALITY ORIGINAL



525

POOR QUALITY ORIGINAL

HEWLETT-PACKARD P/

1-7-1
2-7-1

230000 1 1

0.000 0.000 0.000

11

0.20

STOP

RUN # 45

NAME:

RT

0.20

NAME TIME

0.000 0.000

NAME

0.001

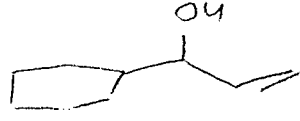
NAME

100.000

TOTAL NAME 0.000

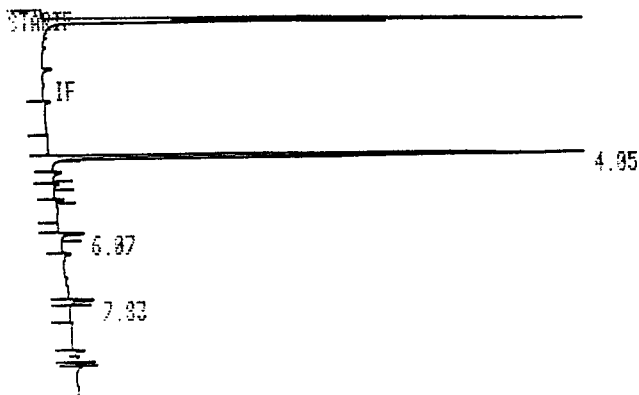
MUL FACTOR= 1.0000E+00

ACKARD PART NUMBER 5181-1219 PRINT THIS SIDE



after column

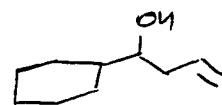
925



RUN # 10
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 WORKFILE NAME:

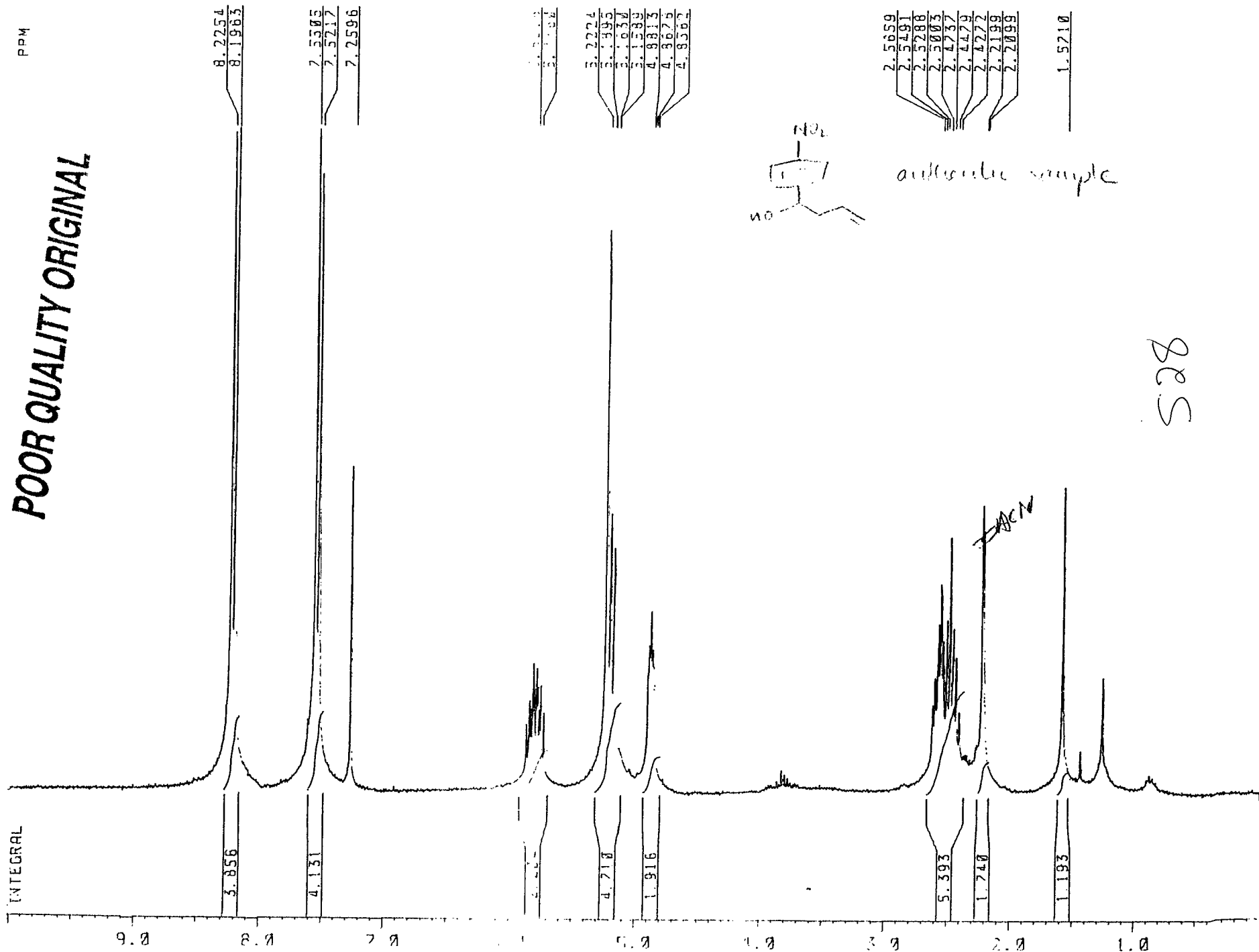
RT	AREA	TYPE	AR/HT	AREA%
4.95	2918300	PB	0.040	90.819 ←
6.07	166460	PB	0.060	5.189
7.93	128570	BB	0.046	4.001

TOTAL AREA= 3213400
 MUL FACTOR= 1.0000E+00



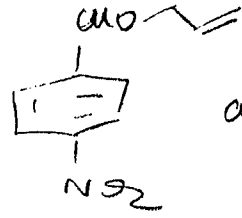
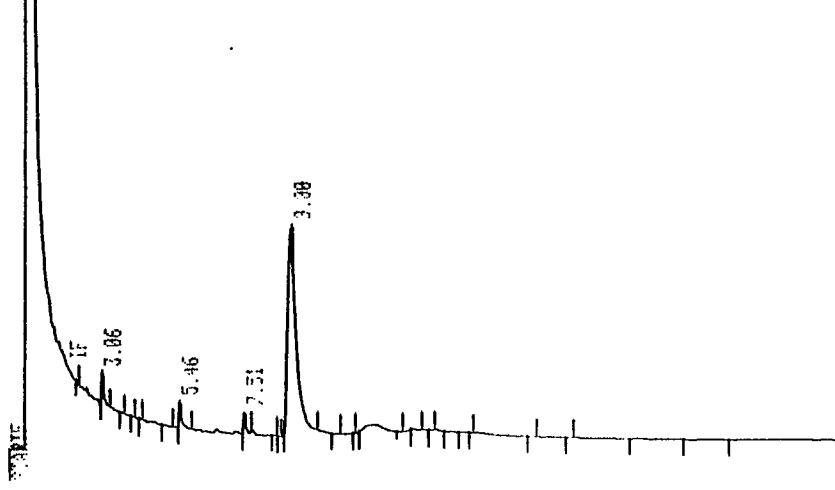
after extraction

S27



POOR QUALITY ORIGINAL

2-29-1



after column

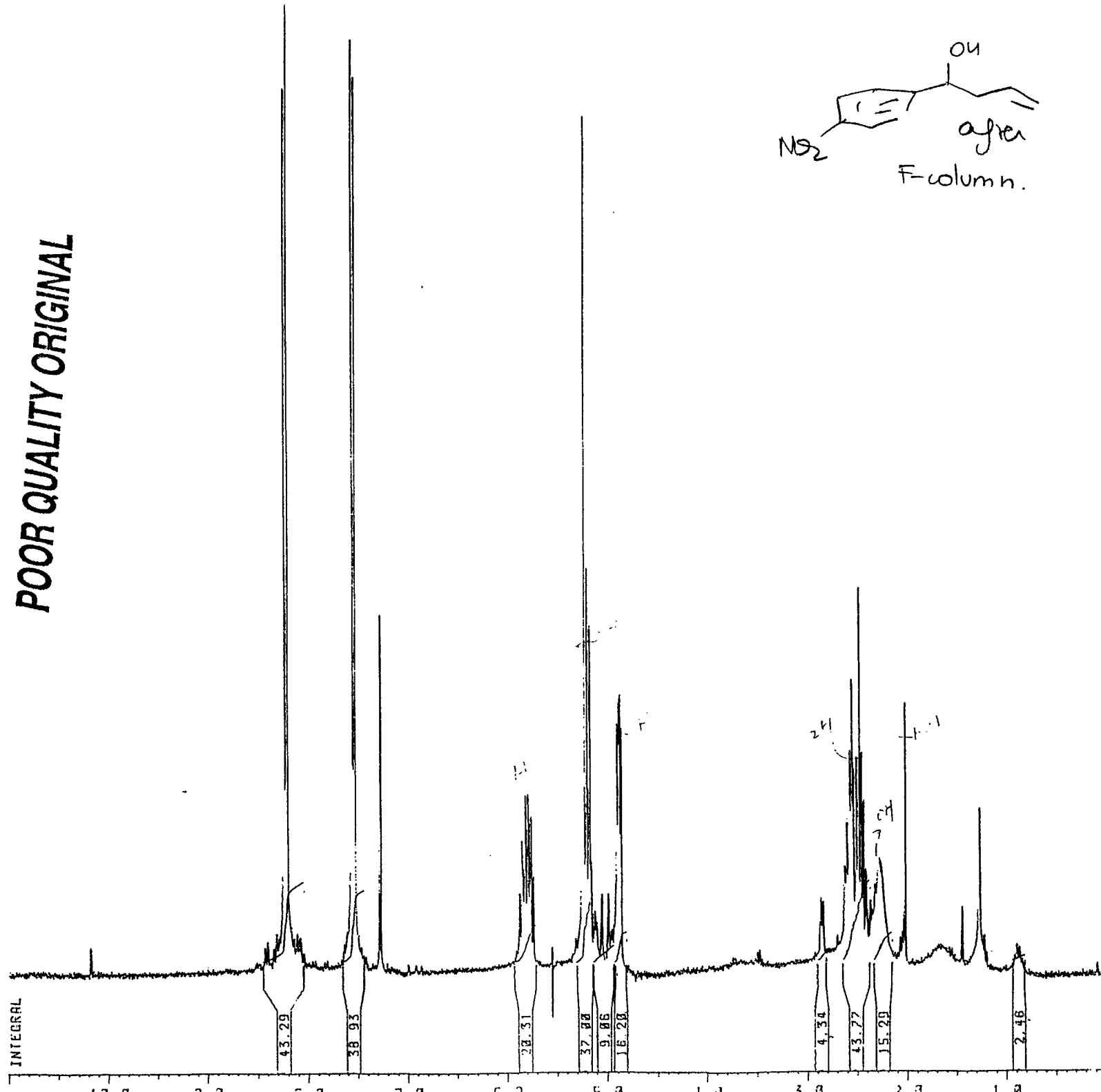
RUN # 78
WORKFILE ID: C2
WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
3.06	18626	BB	0.069	3.364	
5.46	18534	BB	0.087	3.348	
7.51	12012	PB	0.074	2.170	
9.00	584480	PB	0.289	91.119	

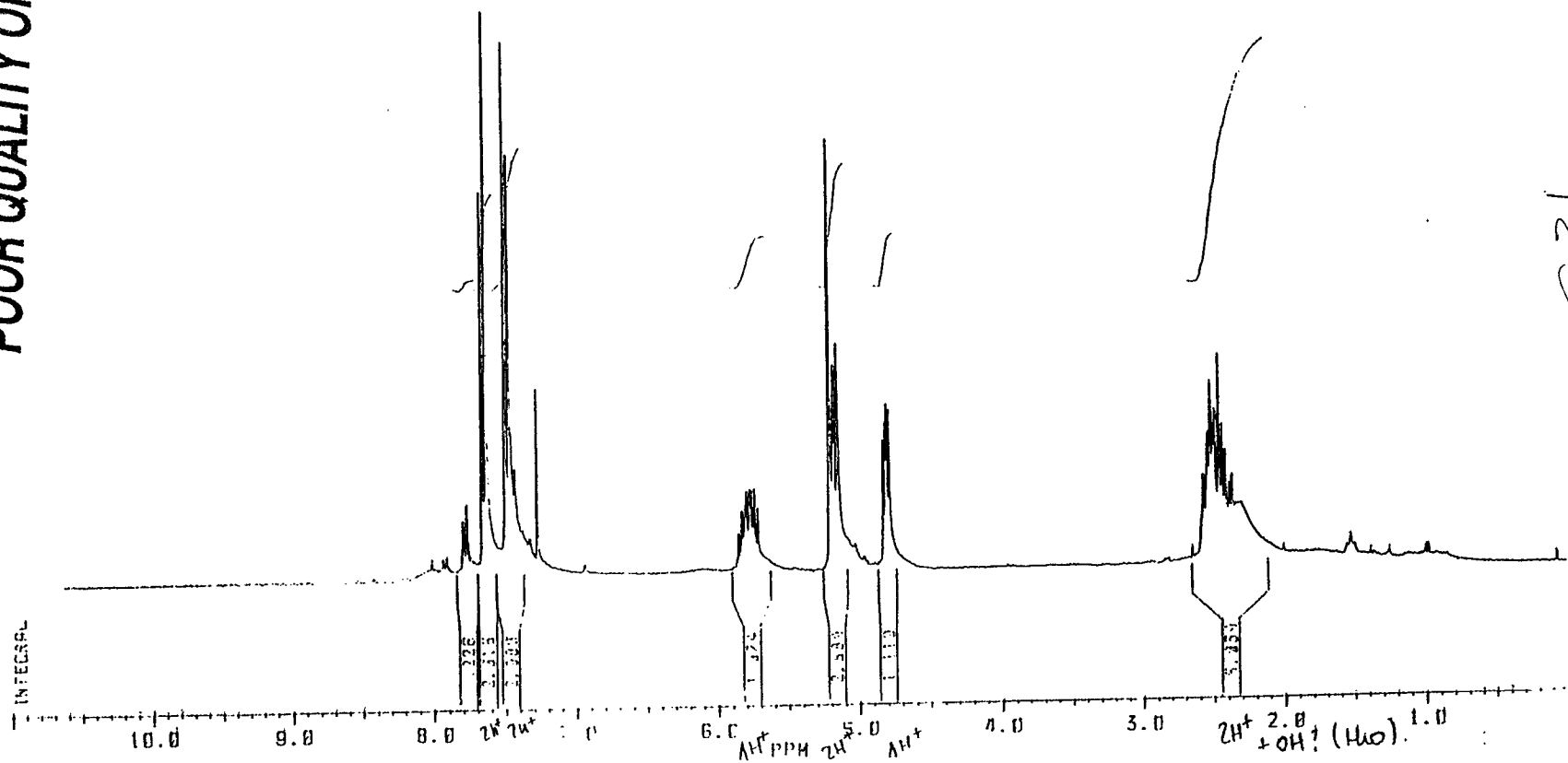
TOTAL AREA= 553650
MUL FACTOR= 1.0000E+00

629

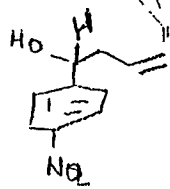
POOR QUALITY ORIGINAL



S30

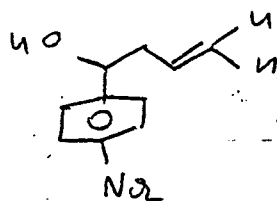


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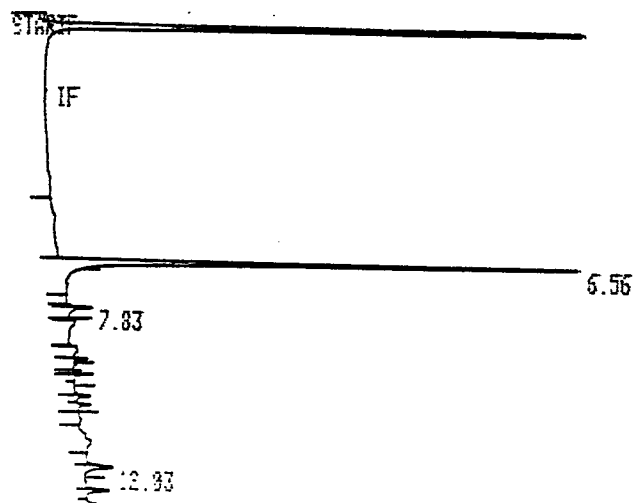


after extraction





after f extraction



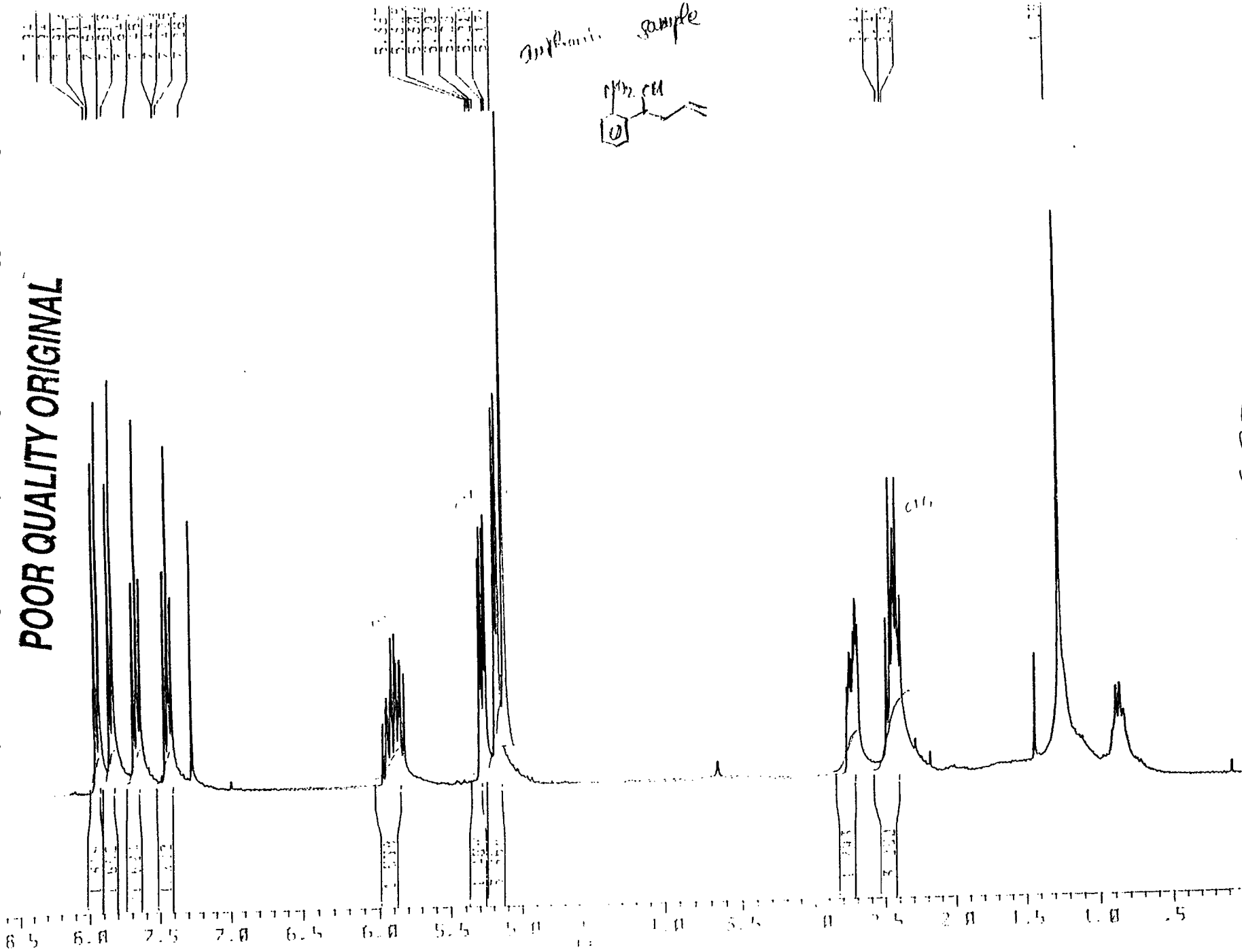
RUN # 12
 WORKFILE ID: C5
 WORKFILE NAME:

RT	AREA	TYPE	AR/HT	AREA%
6.56	4751388	PS	0.063	93.075 ←
7.83	157338	BB	0.063	3.082
12.93	196160	BB	0.071	3.843

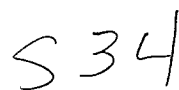
TOTAL AREA= 5184888
 MUL FACTOR= 1.0000E+00

S32

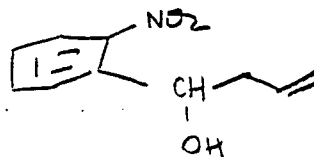
POOR QUALITY ORIGINAL



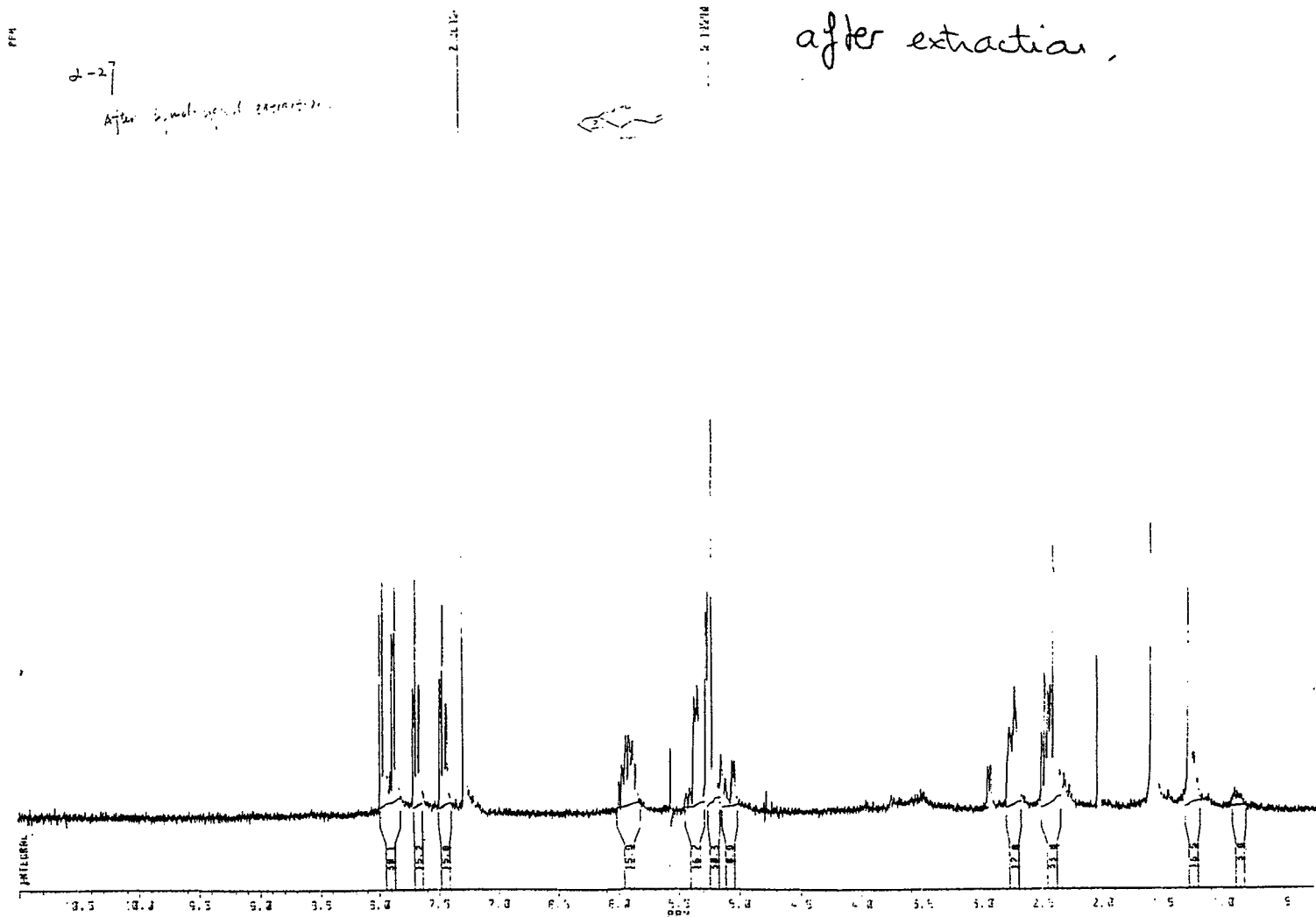
533



POOR QUALITY ORIGINAL

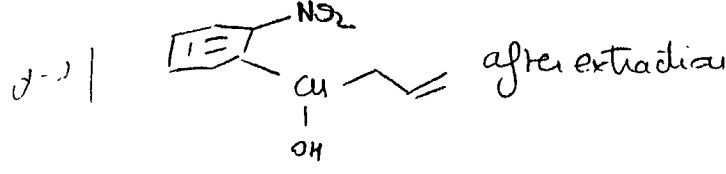
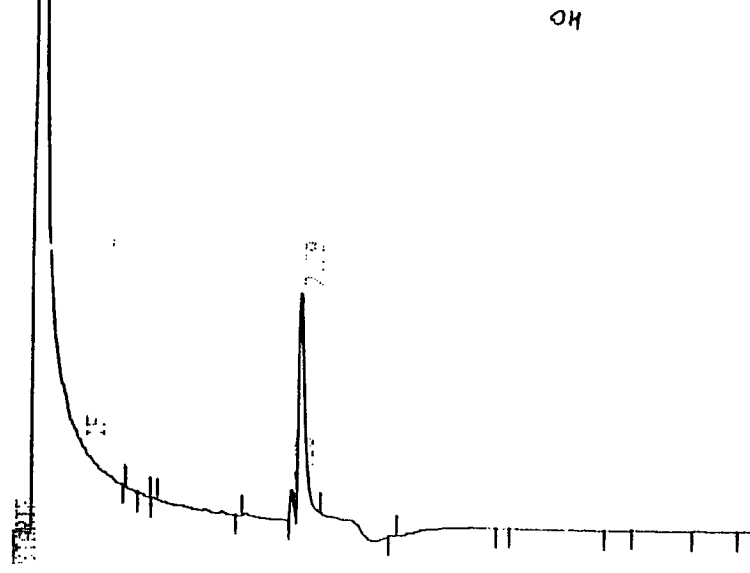


after extraction.



S35

POOR QUALITY ORIGINAL



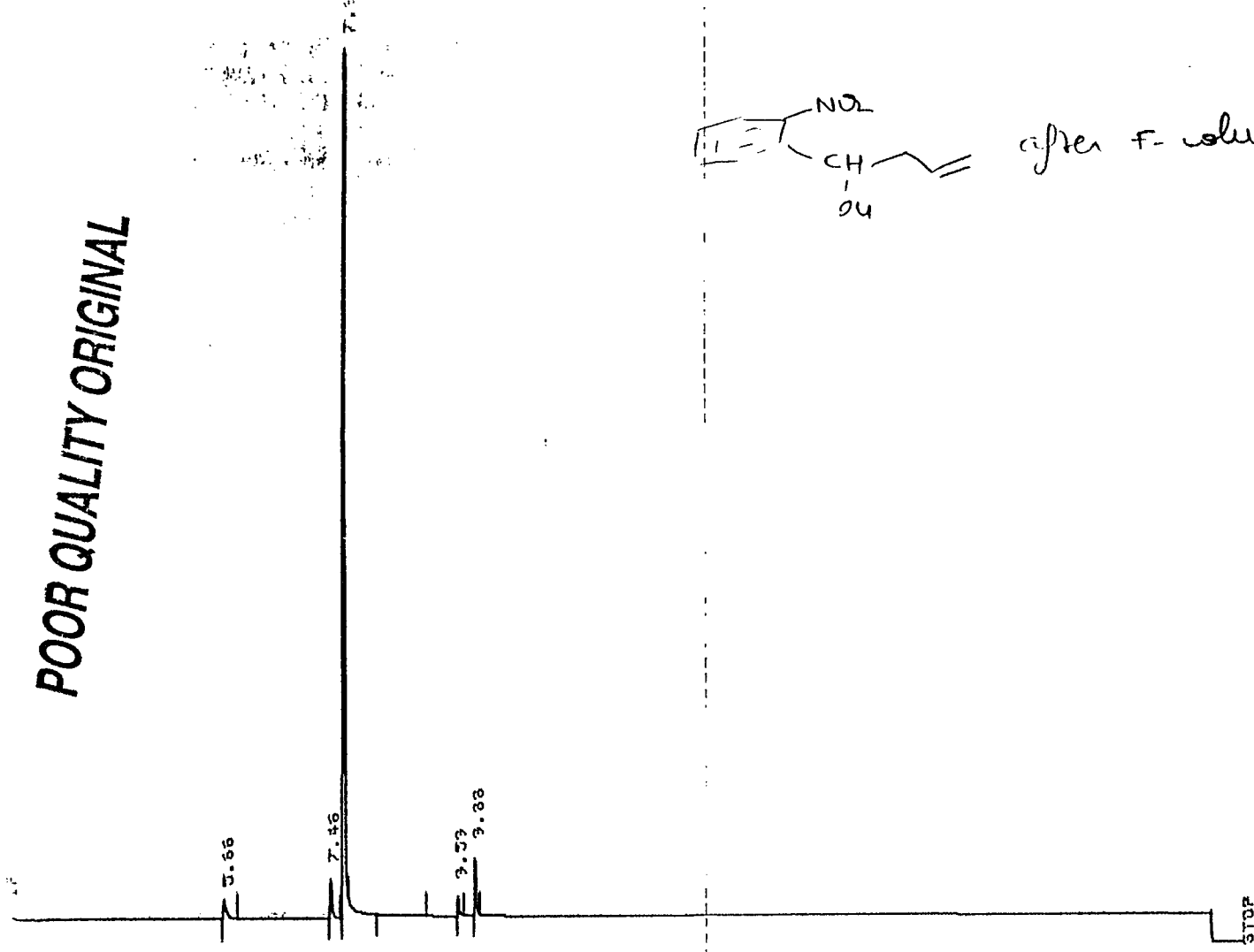
RUN # 77
WORKFILE ID: C2
WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
7.53	21086	PV	0.102	6.810	
7.79	299500	VB	0.107	93.190	

TOTAL AREA= 321390
MUL FACTOR= 1.0000E+00

S36

POOR QUALITY ORIGINAL



RUN # 325

AREA%	RT	AREA	TYPE	RR/HT	AREA%
5.66	31012	PB	0.061	1.677	
7.46	44326	PB	0.037	2.424	
7.63	1715100	PB	0.034	92.727	
9.88	50693	PB	0.030	3.173	

TOTAL AREA= 1349700
MUL FACTOR= 1.00000E+00

537