

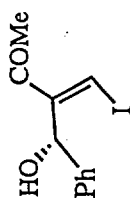
Supplement Materials (51 pages including this page):

1. Experimental Procedure
2. Copies of ^1H NMR spectra of pure isomers
3. NOE Analysis
4. Copies of ^{13}C NMR spectra of pure isomers
5. Chromatographic analysis of enantiomerically enriched products

Supplemental Materials

Typical Procedure

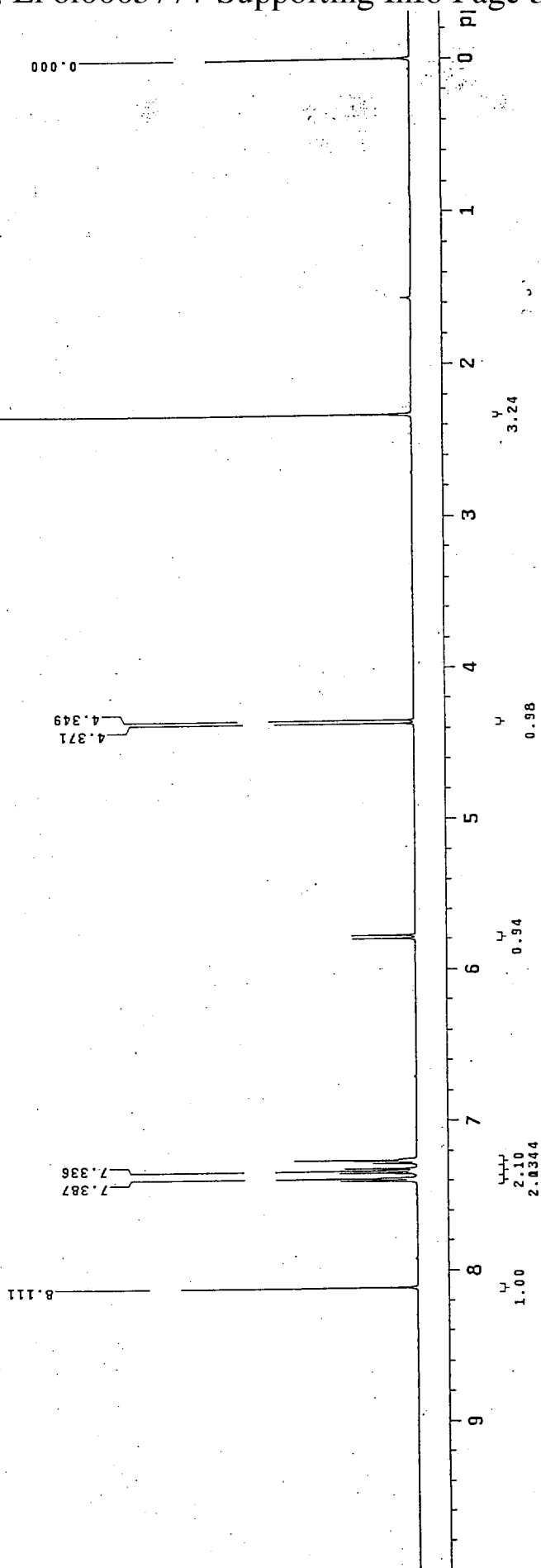
The representative procedure was illustrated by entry 1 of Table 3. Into a dry, nitrogen flushed flask was added (*S*)-*N*-heptafluoropropyl phenylalanine (58 mg, 0.22 mmol) and freshly distilled propionitrile (1.5 mL). The resulting solution was added by $\text{BH}_3 \cdot \text{THF}$ (0.20 mL, 1.0 M in THF, 0.2 mmol). The reaction mixture was stirred for 10 min at room temperature, and at 50 °C for 1 h before cooled down to -78 °C. Into another flask was dissolved methyl ethynyl ketone (0.10 mL, 1.3 mmol) in propionitrile (1.5 mL) and cooled to -78 °C followed by dropwise addition of trimethylsilyl iodide (0.18 mL, 1.2 mmol). The resulting mixture was stirred at -78 °C for 1 h to afford β -iodo TMS-allenolate which was transferred into the stirring solution of the first flask via Teflon cannula in one-portion. The solution of benzaldehyde (107 mg, 1.0 mmol) in propionitrile (1.6 mL) was added into the above combined mixture which was maintained at -78 °C via a syringe pump over a period of 10 h. The reaction was continued for addition 7 h after addition of benzaldehyde. The reaction was finally quenched by dropwise addition of 10 mL of aqueous HCl solution (1 M), and the resulting mixture was allowed to stand for 15 min. The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to dryness which was determined by ^1H -NMR. Purification by flash chromatography (EtOAc/hexane, 1/5, v/v) provided *E* isomer (71.4 mg) and *Z* isomer (143 mg) as colorless oils (71 % combined yield).

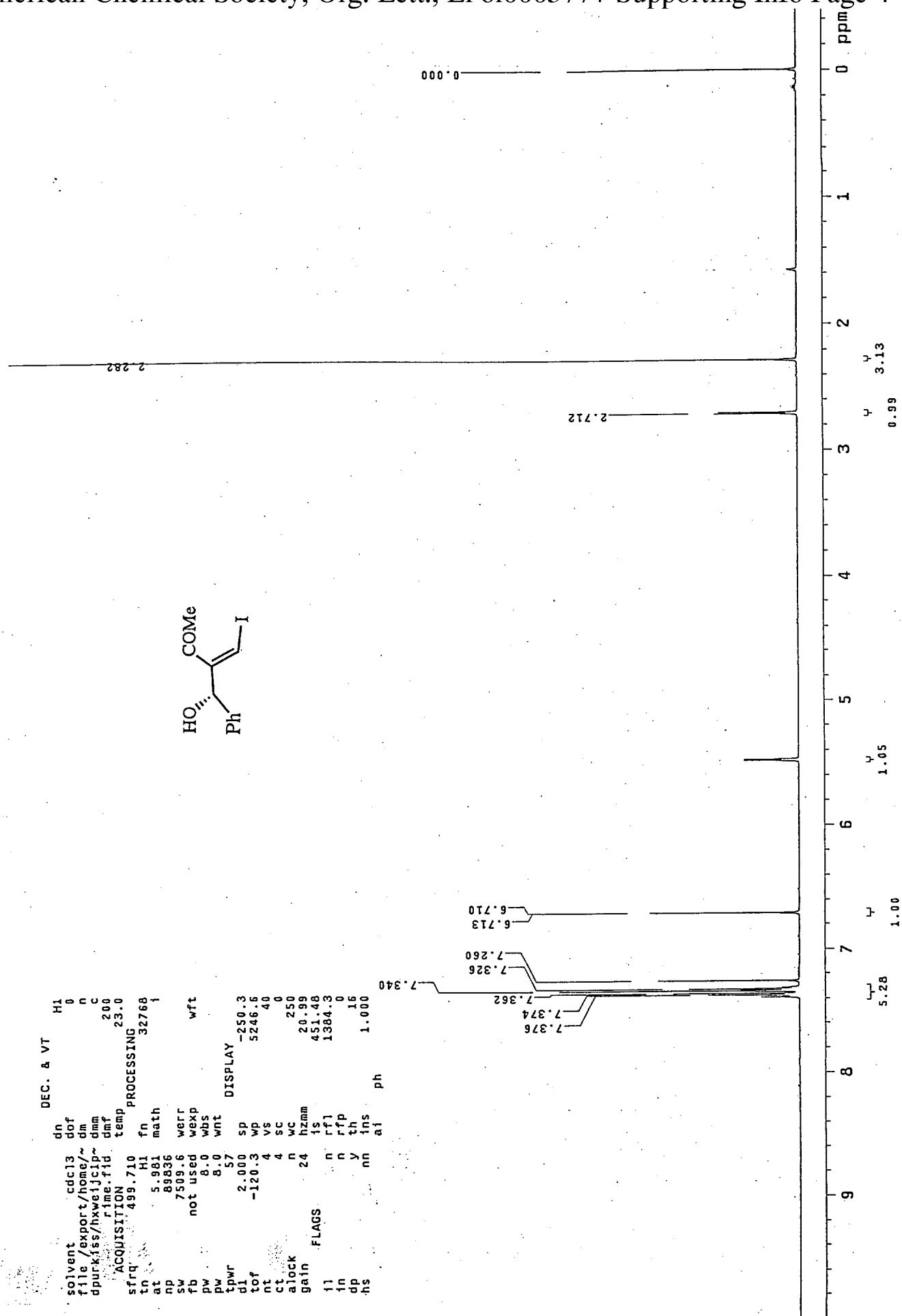


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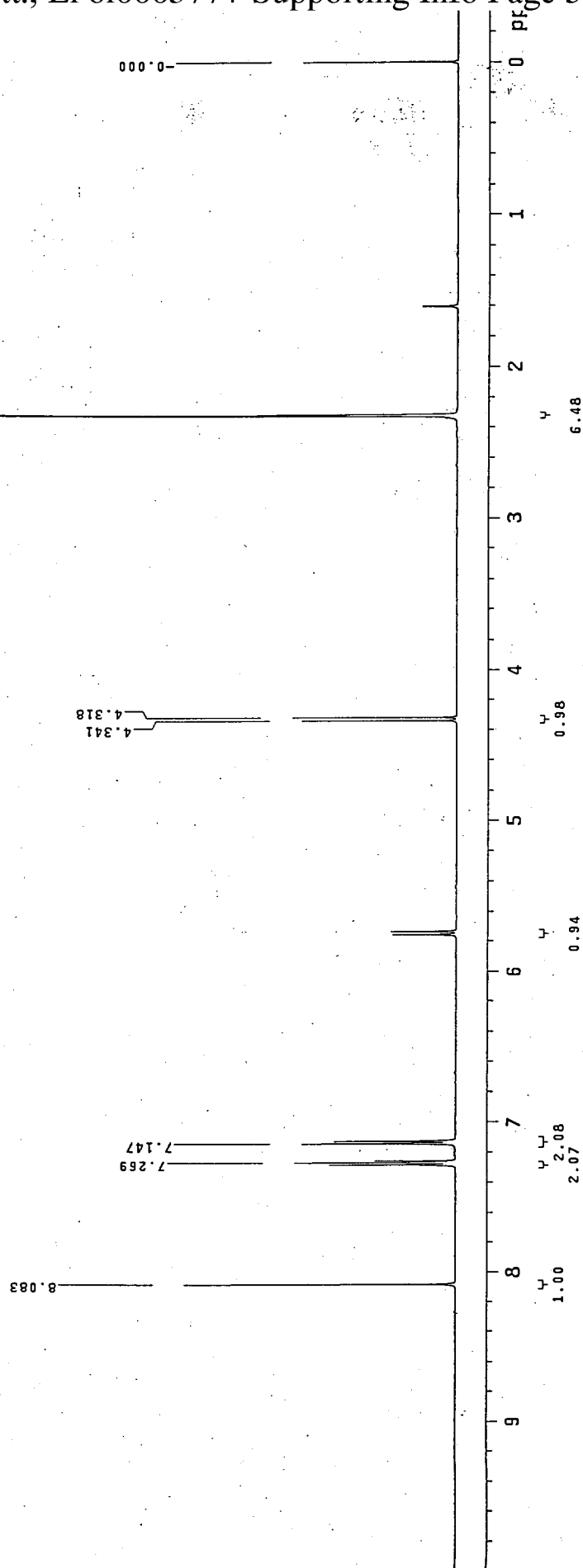
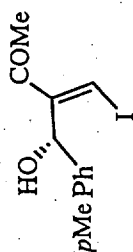
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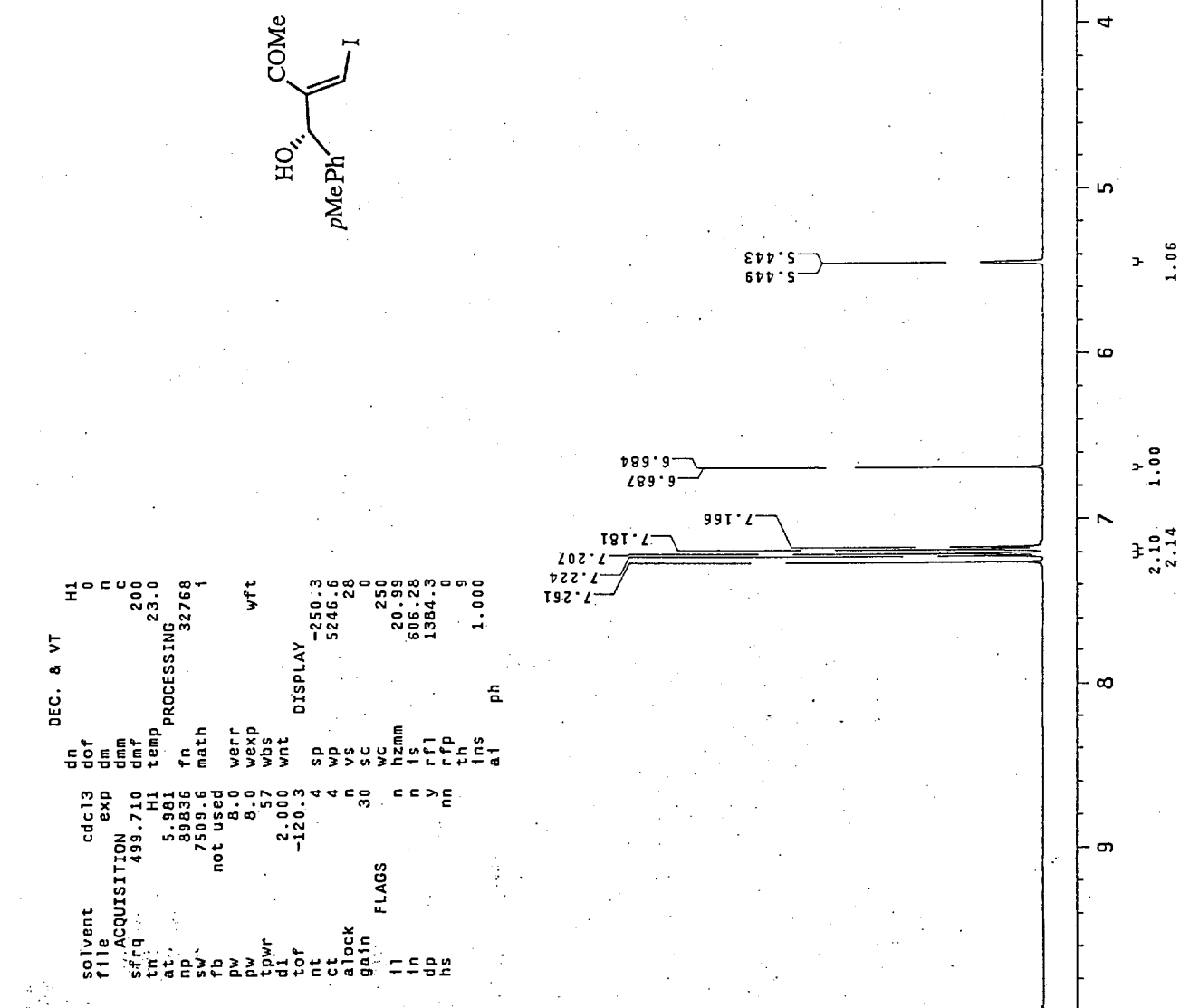
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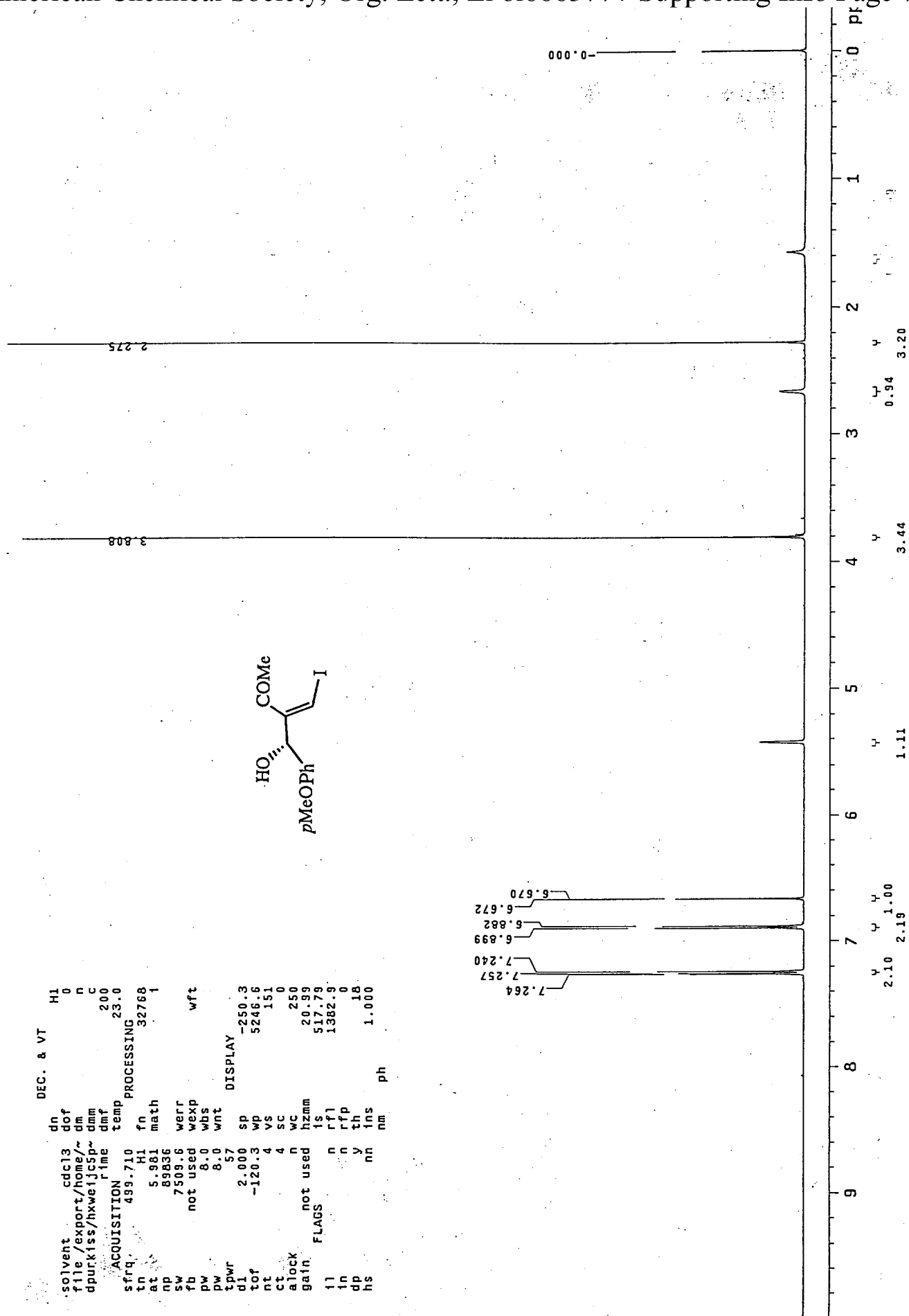
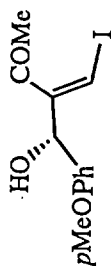


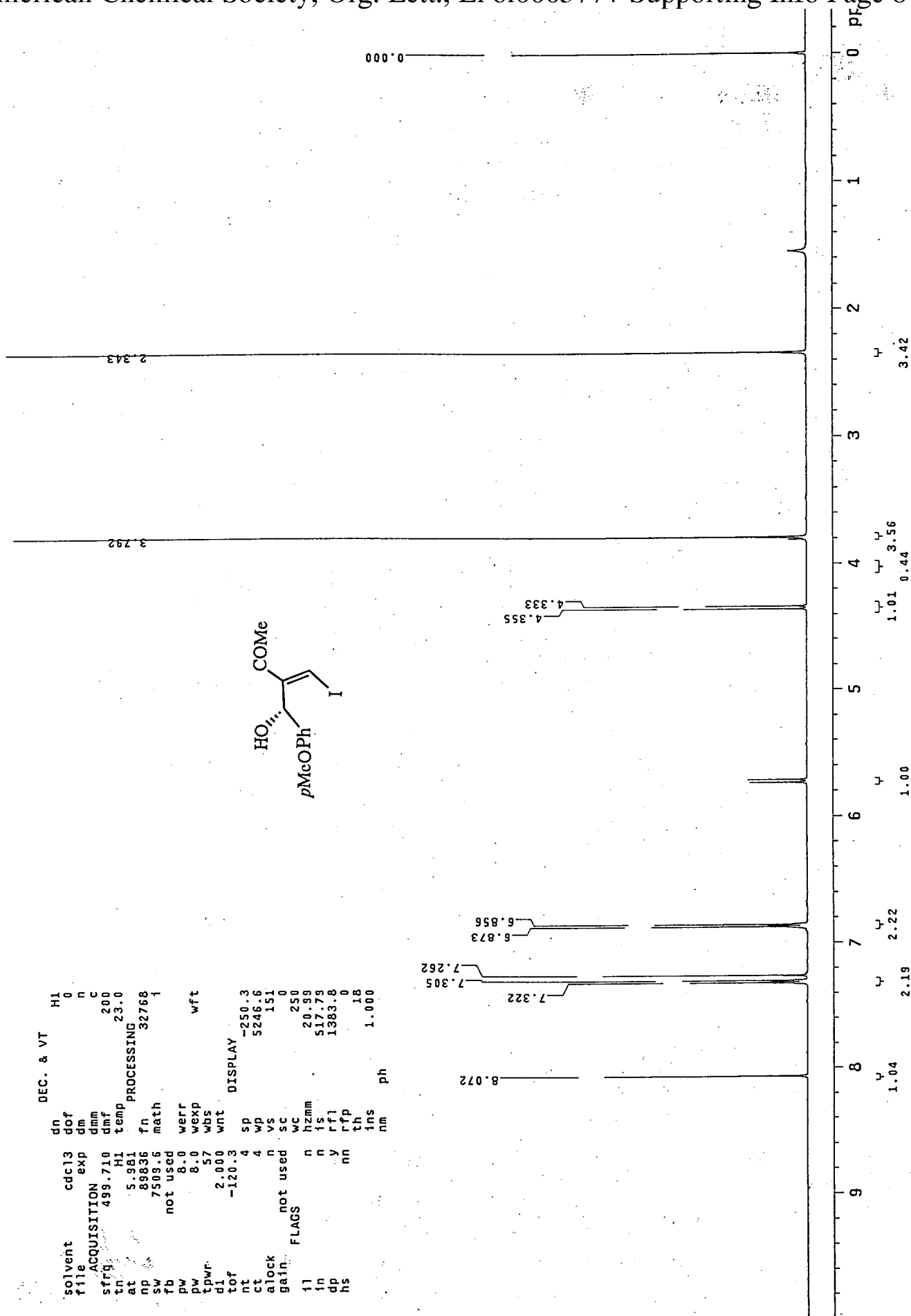
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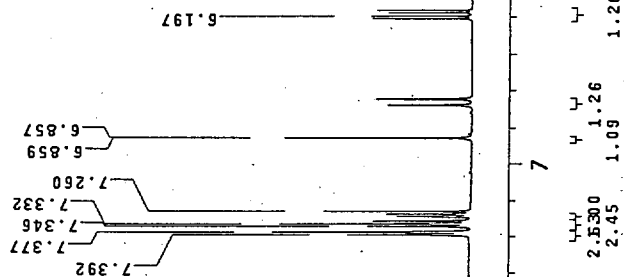
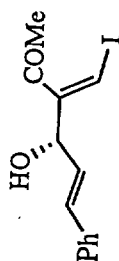
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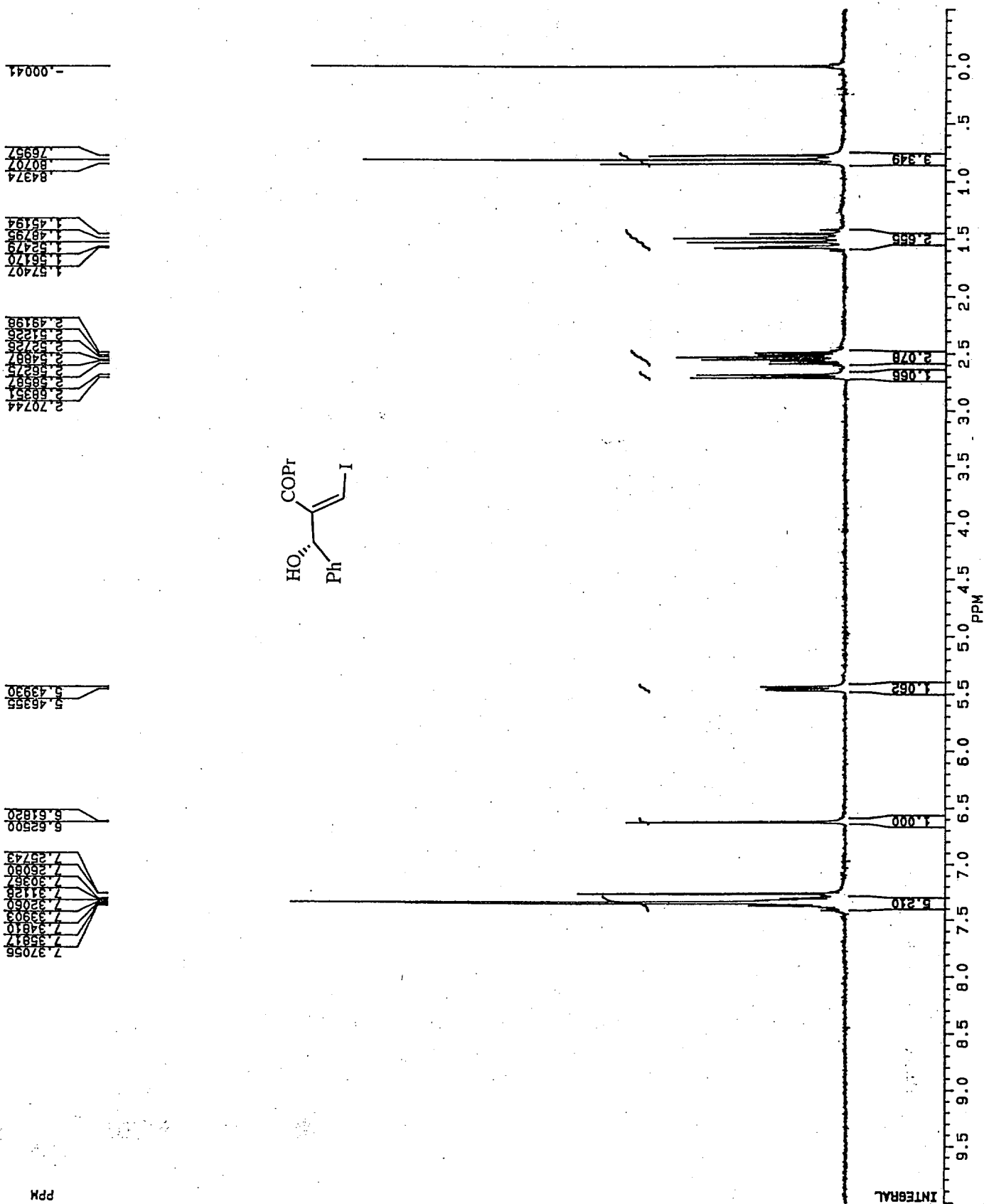
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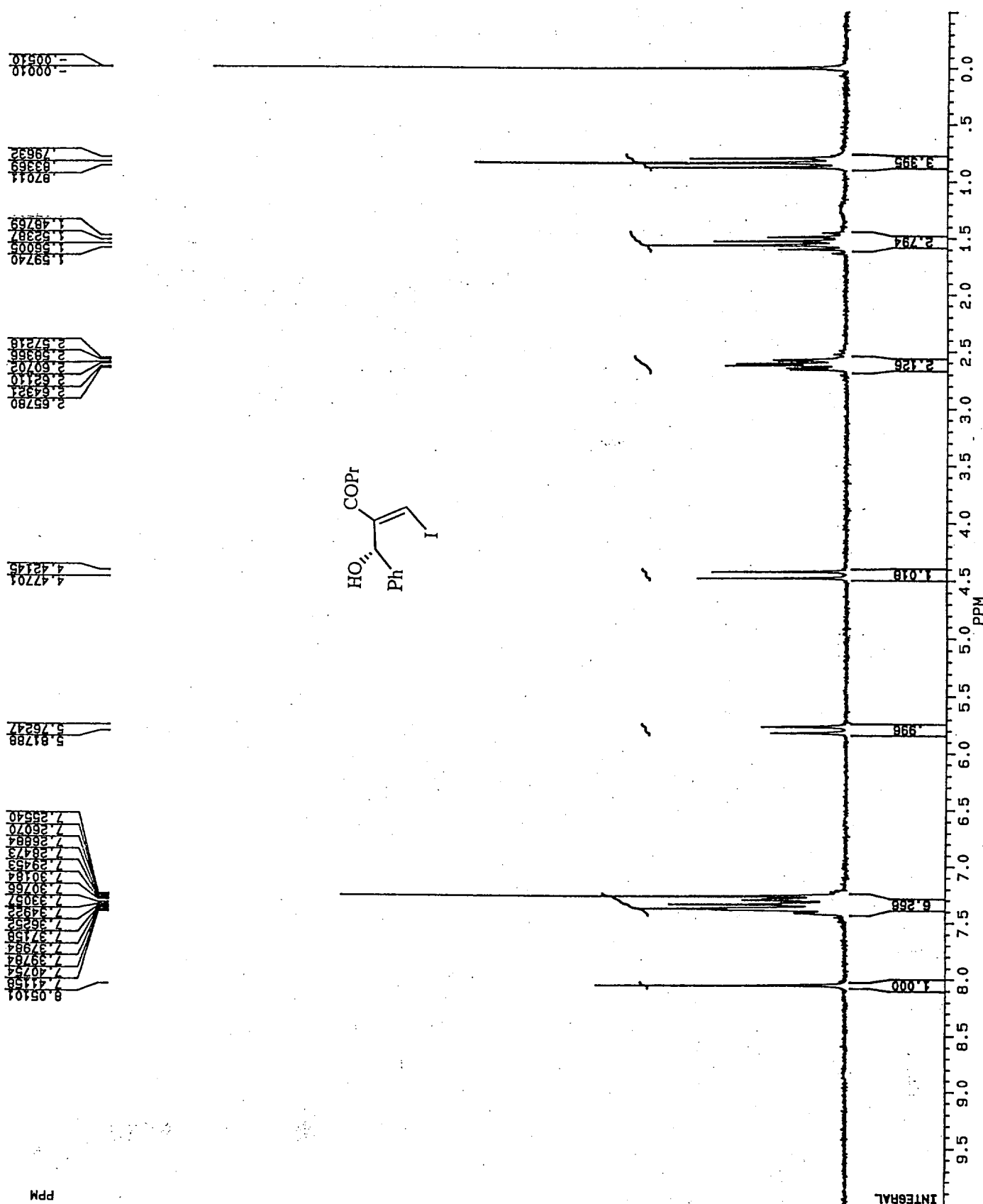


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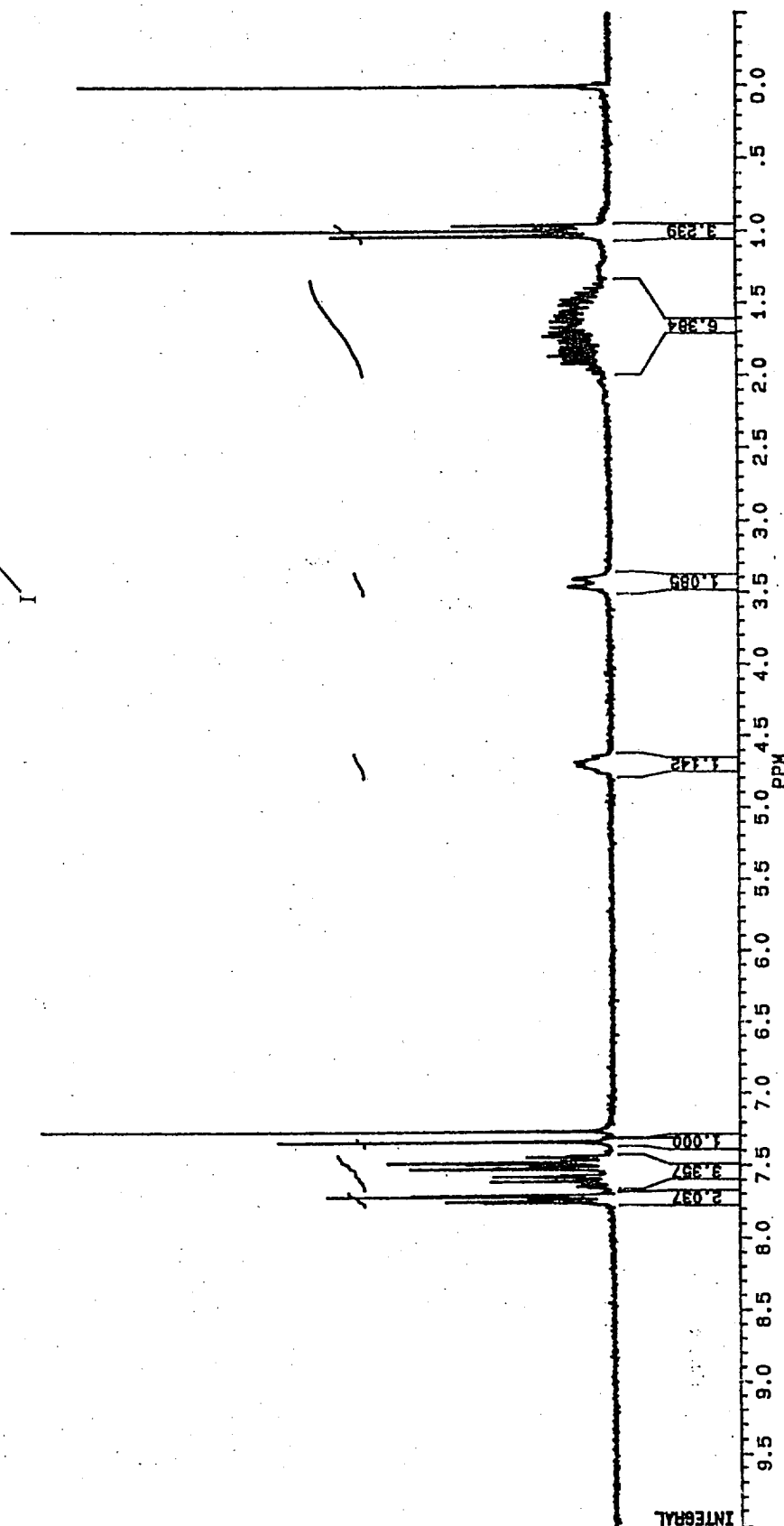
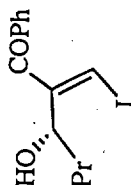
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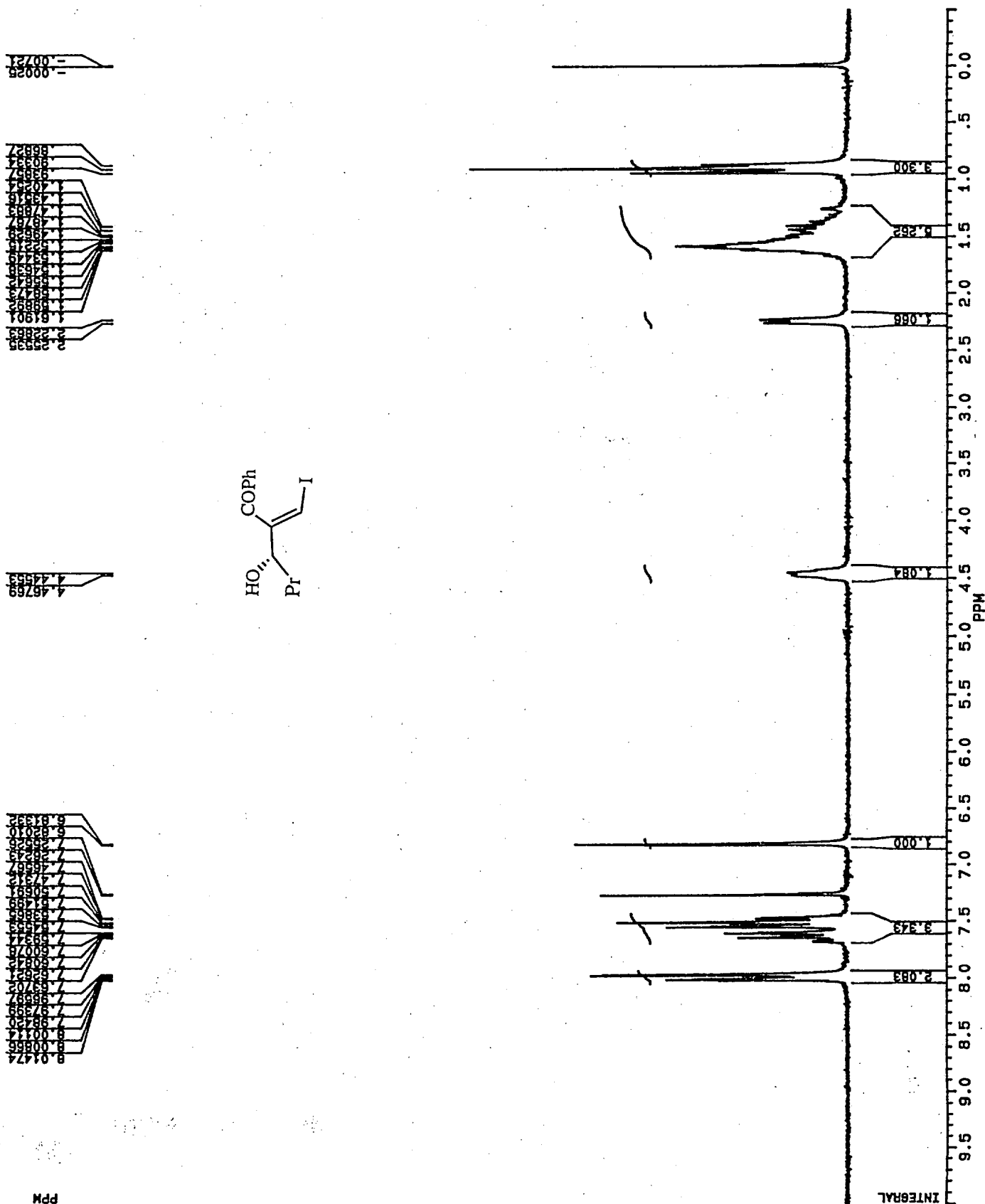
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INTEGRAL



BRUKER

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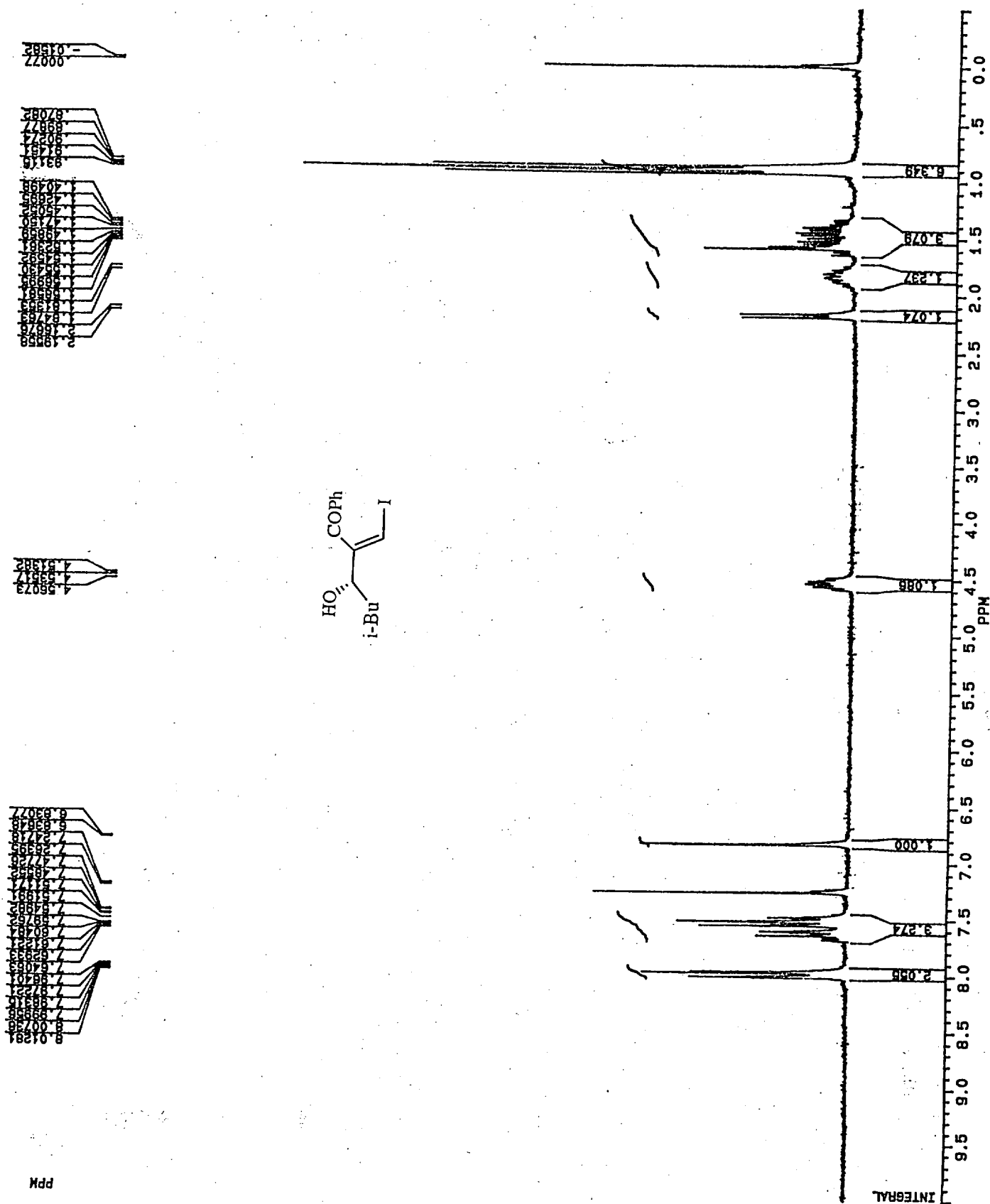
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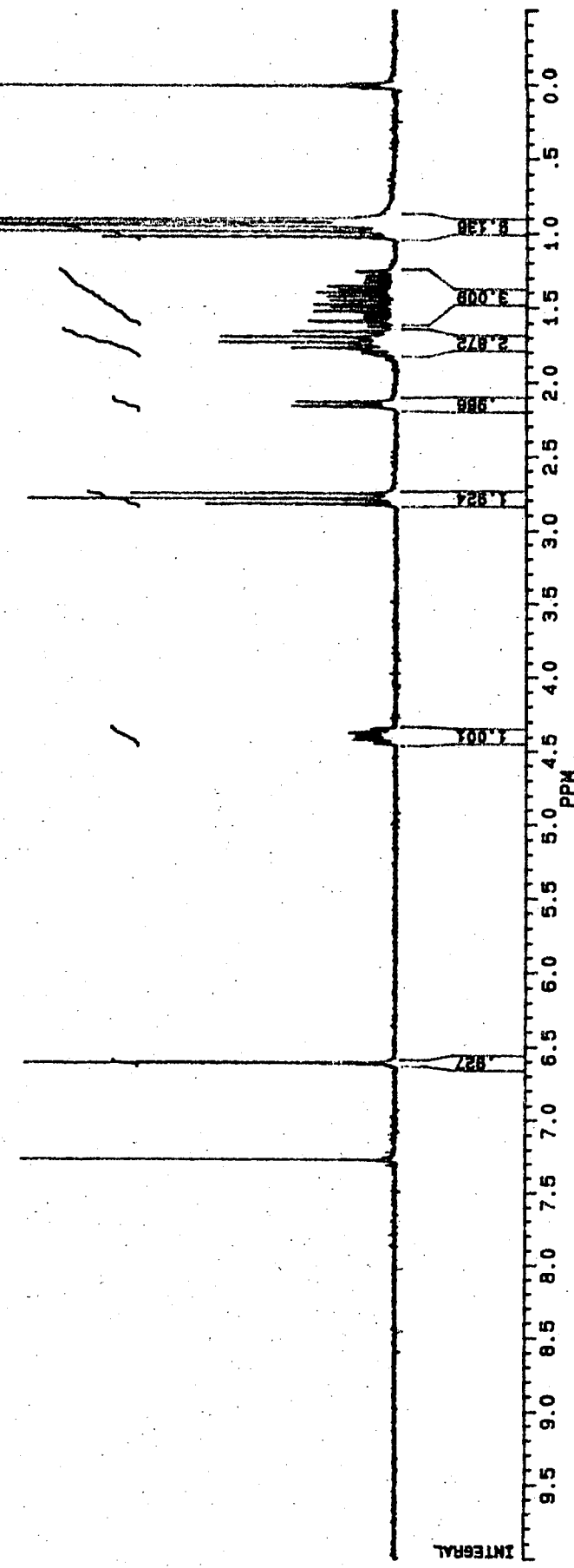
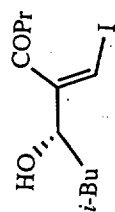
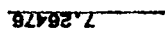
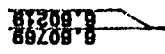
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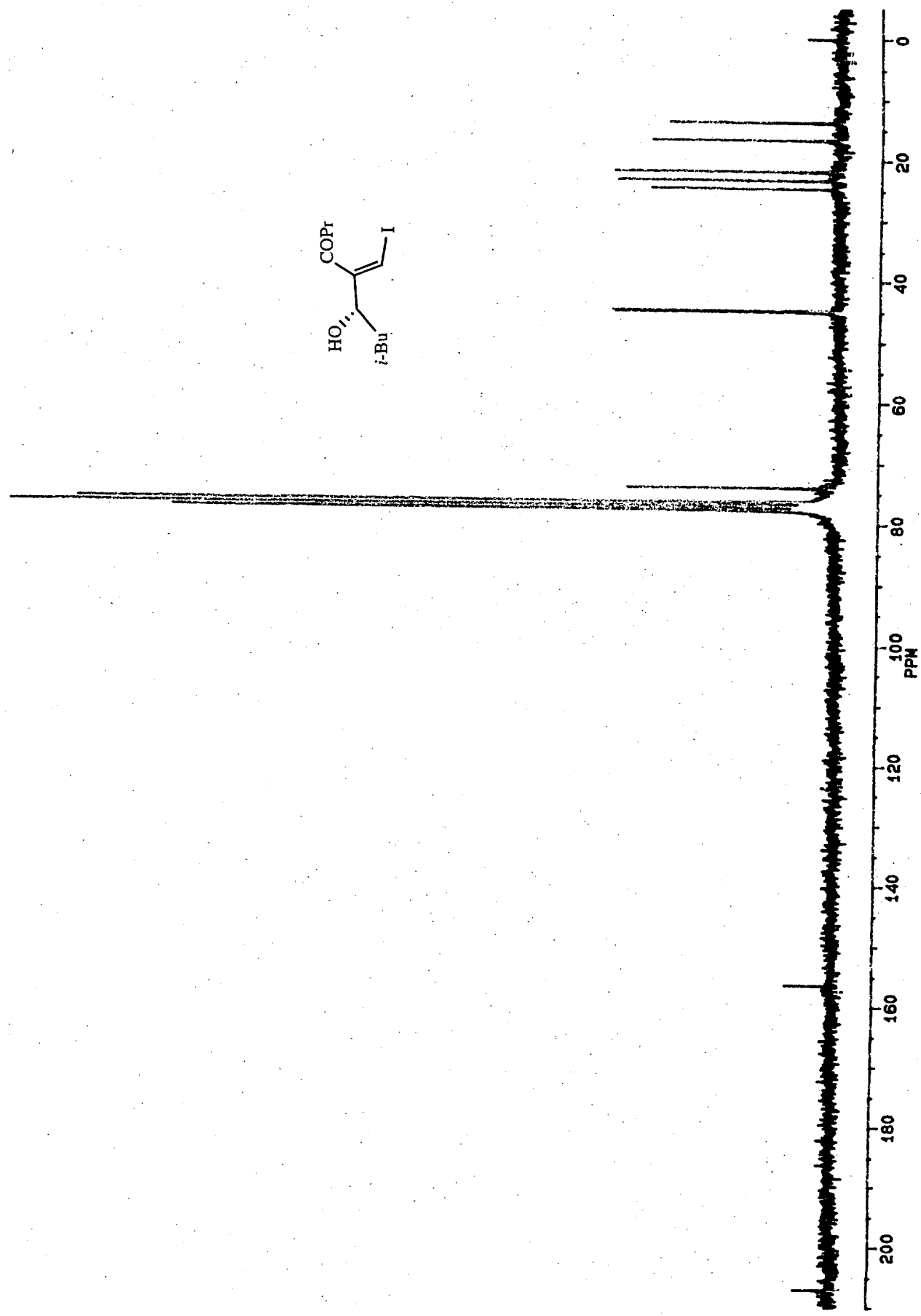
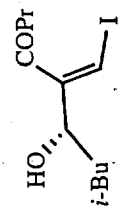


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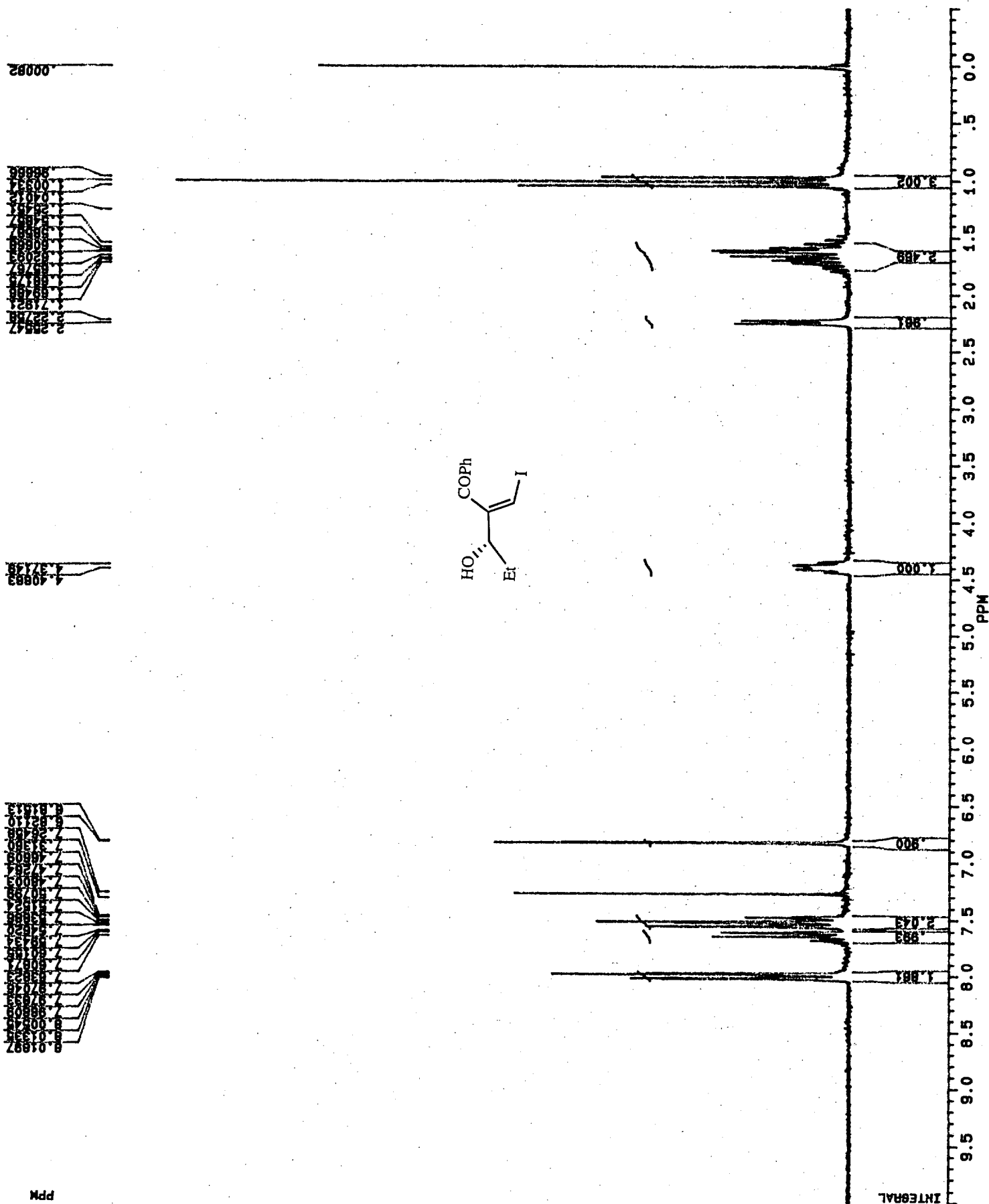
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F2
HZ/CM
PPM/C
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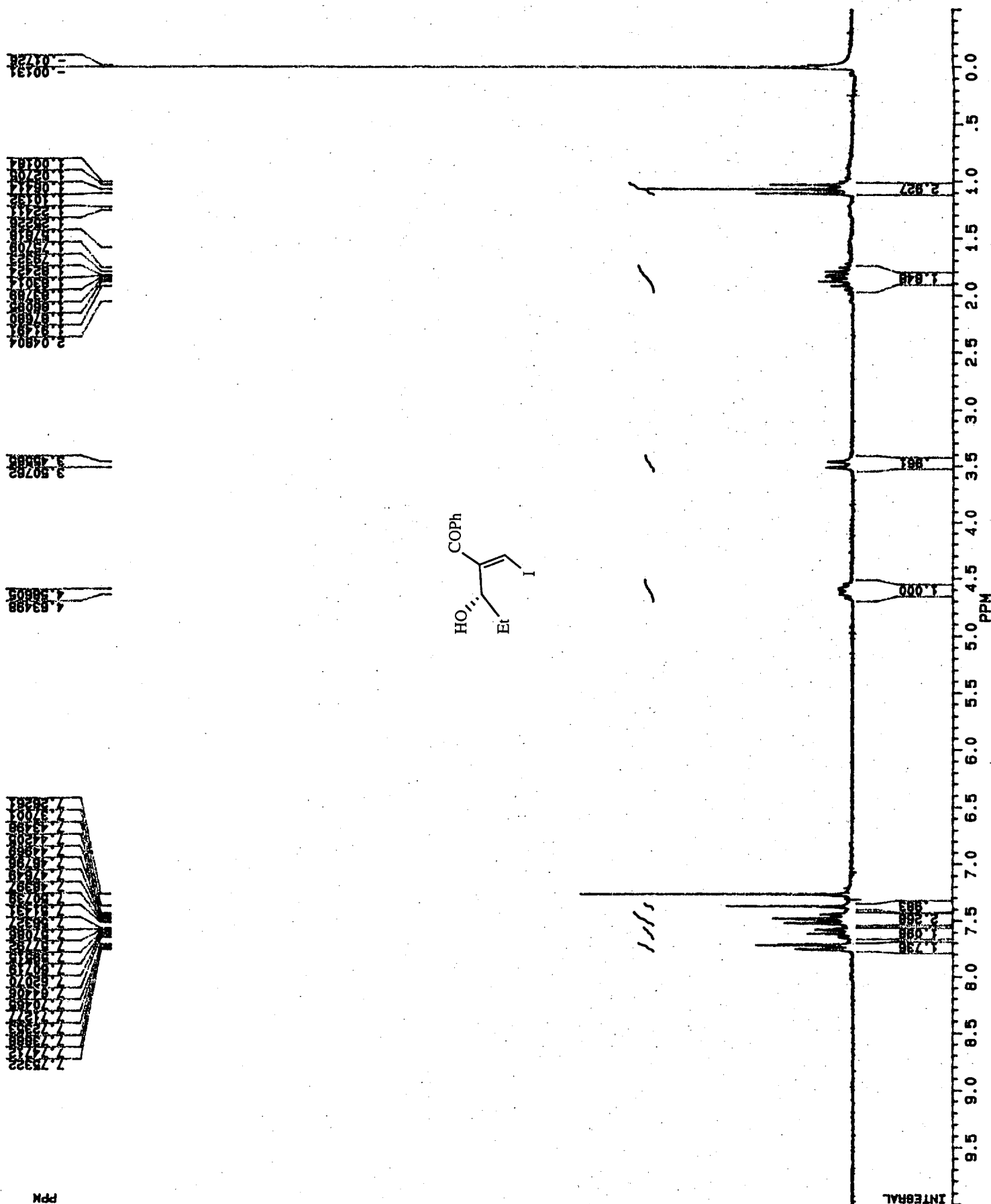


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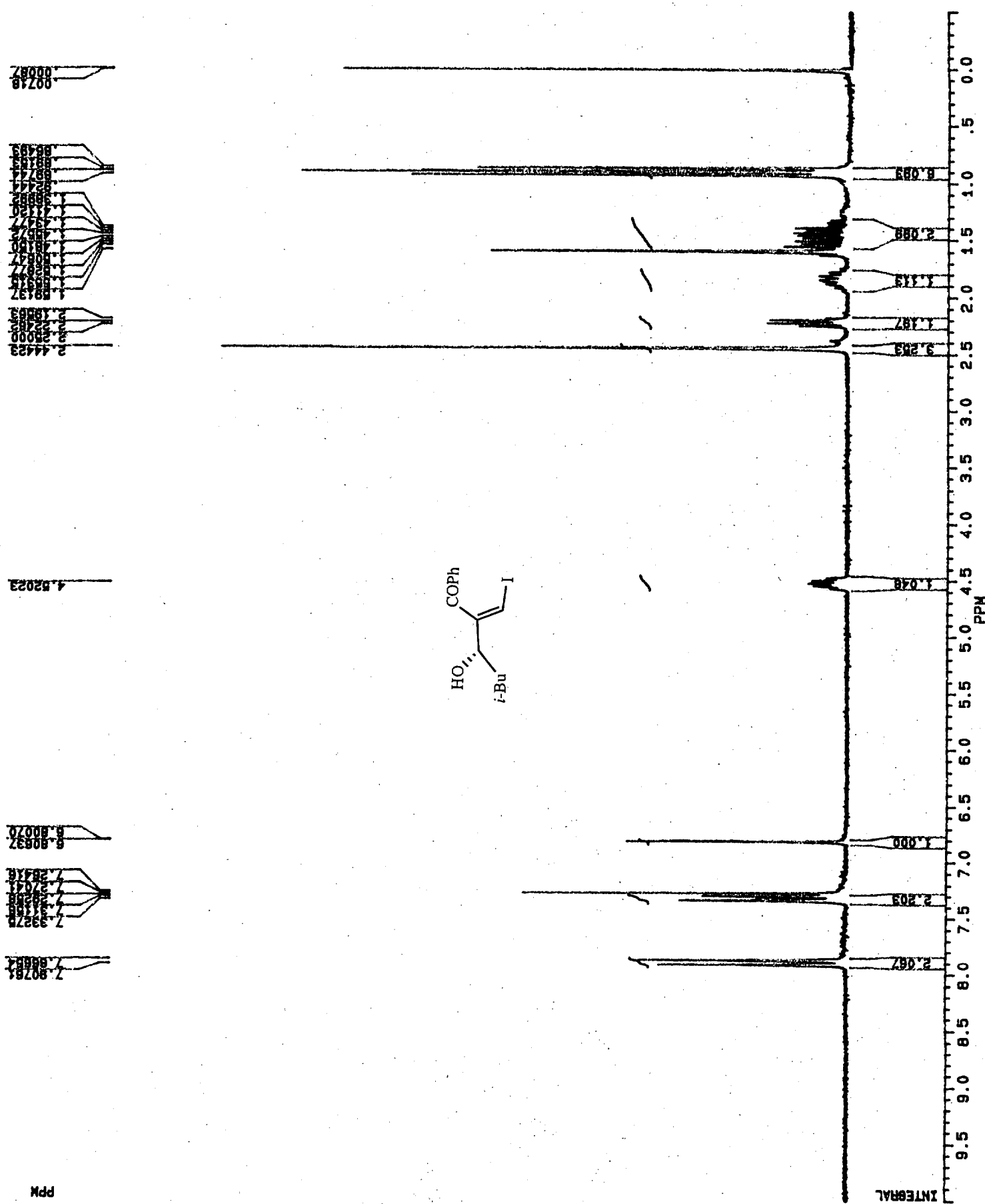


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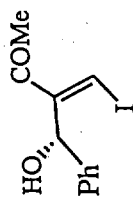
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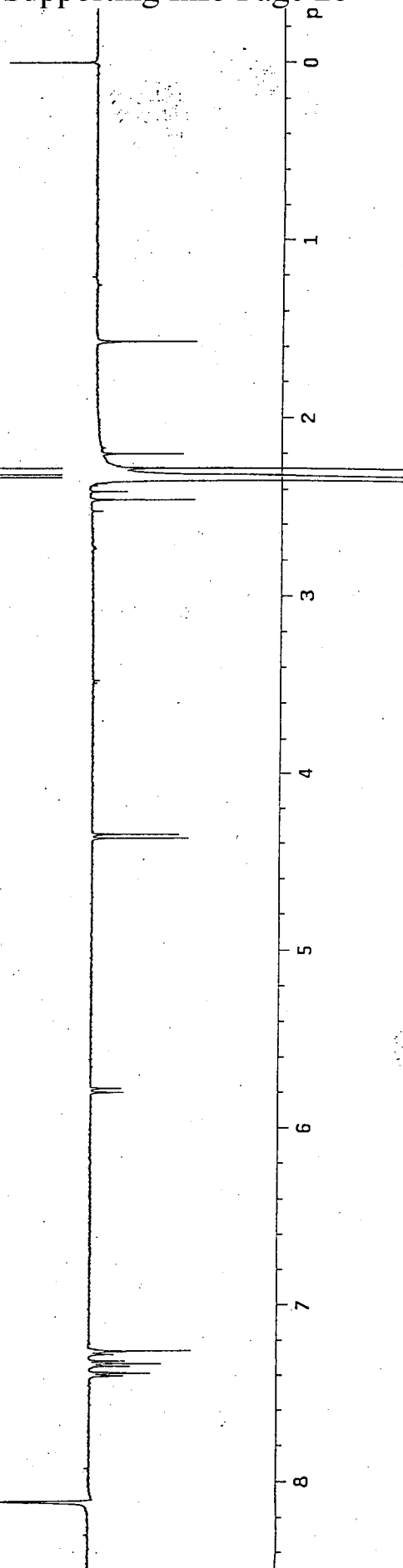


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 2.) Irradiated at 2.33 ppm
 HX Wet

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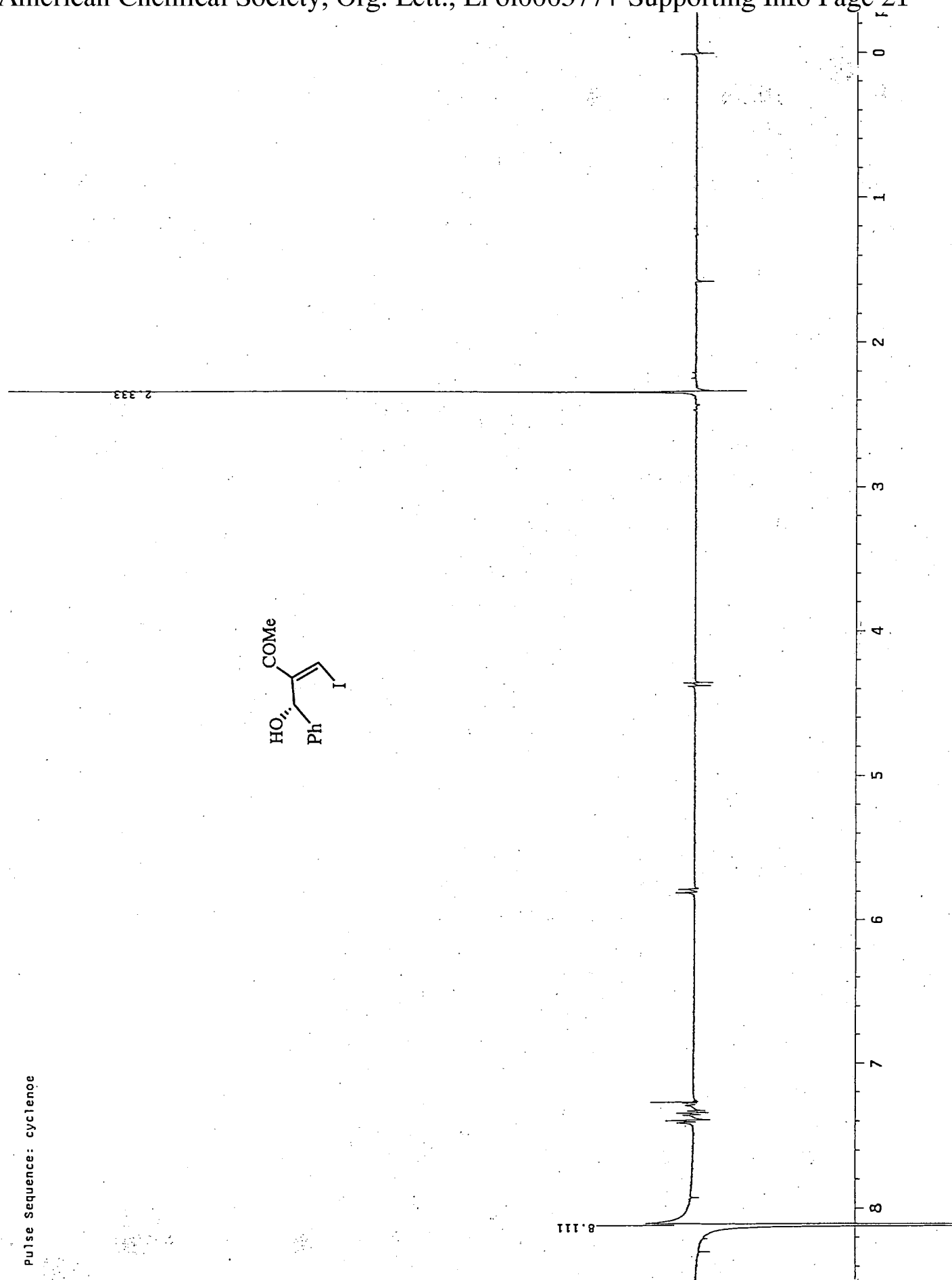


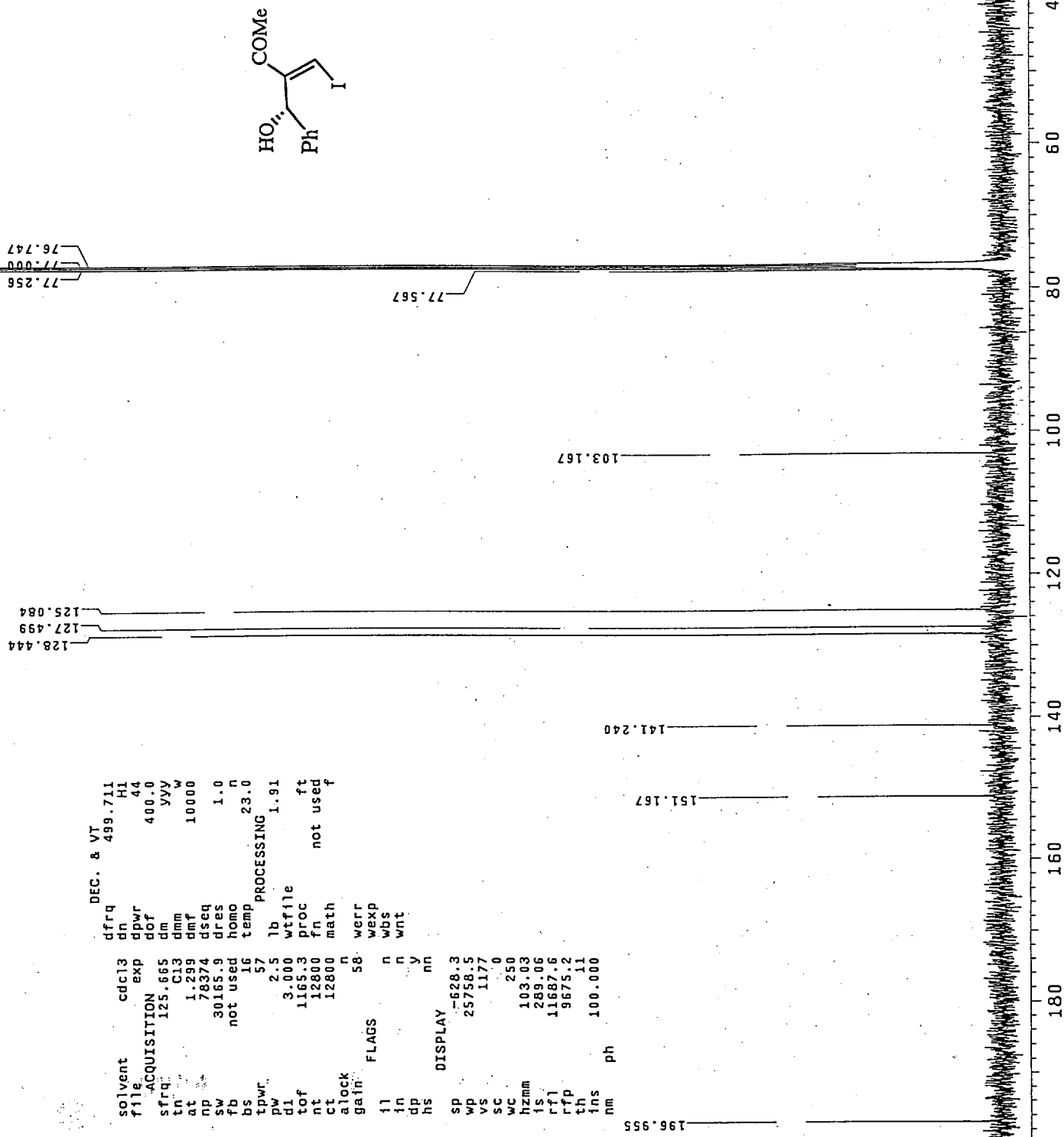
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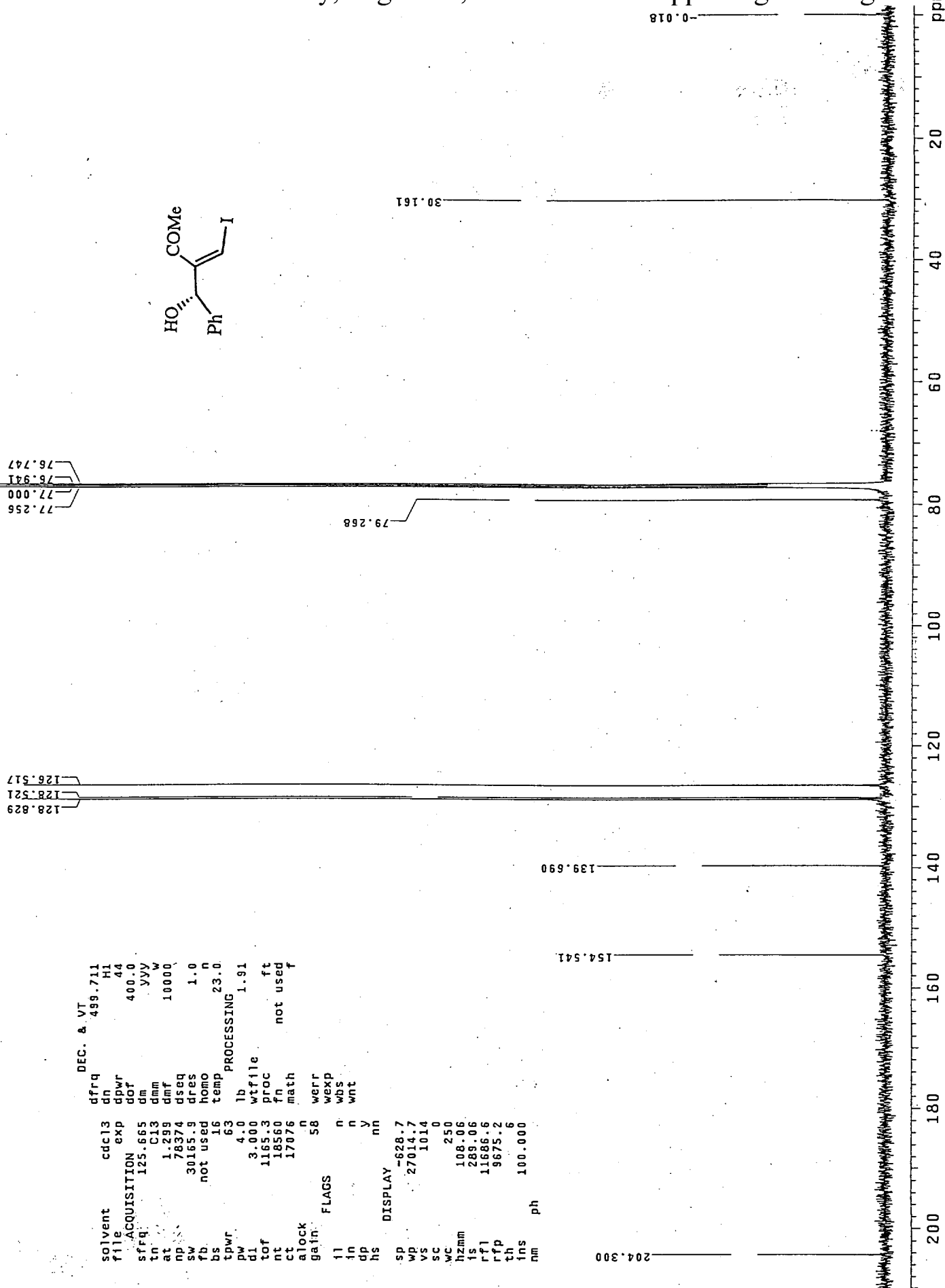


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 HX Ver1

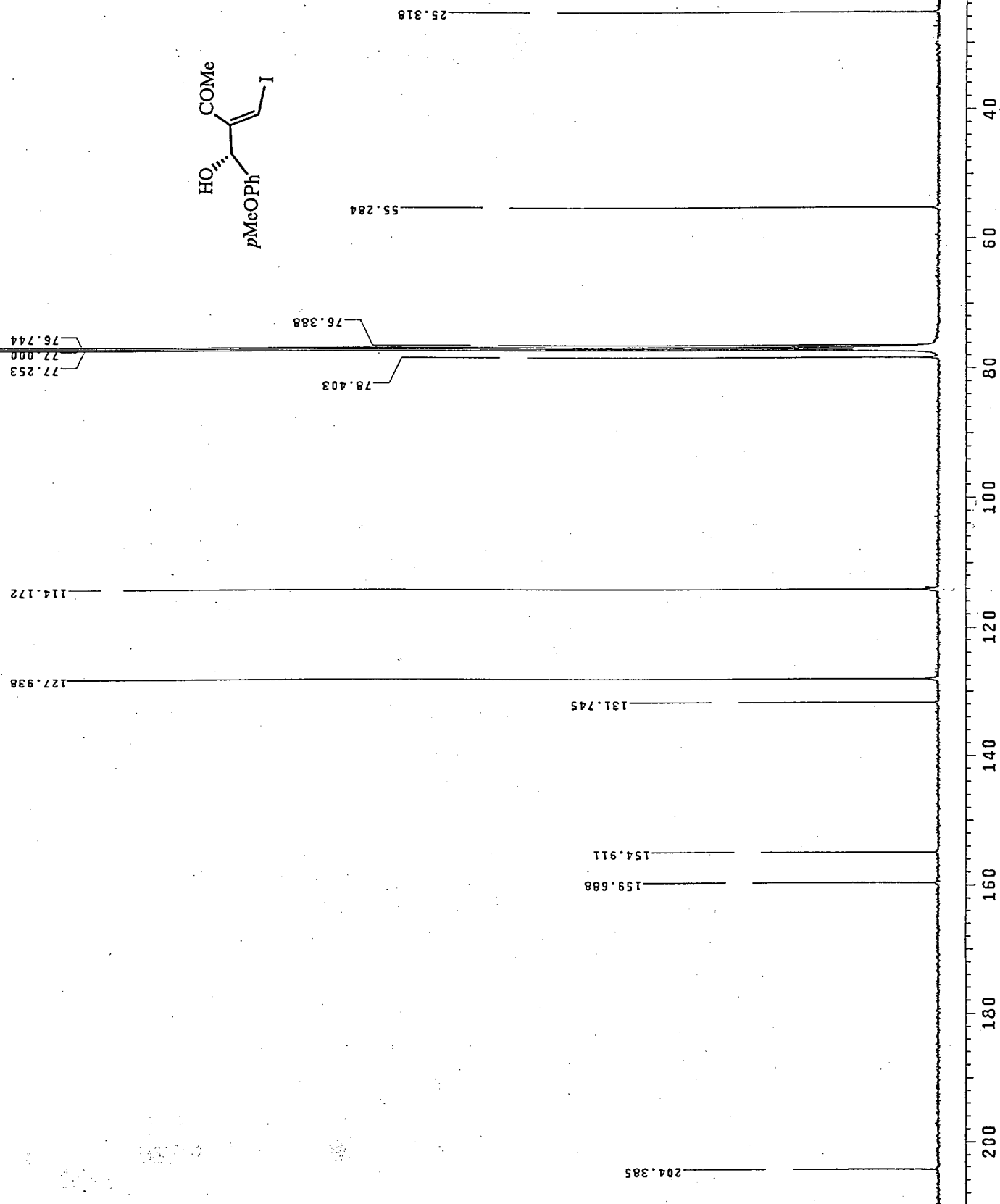
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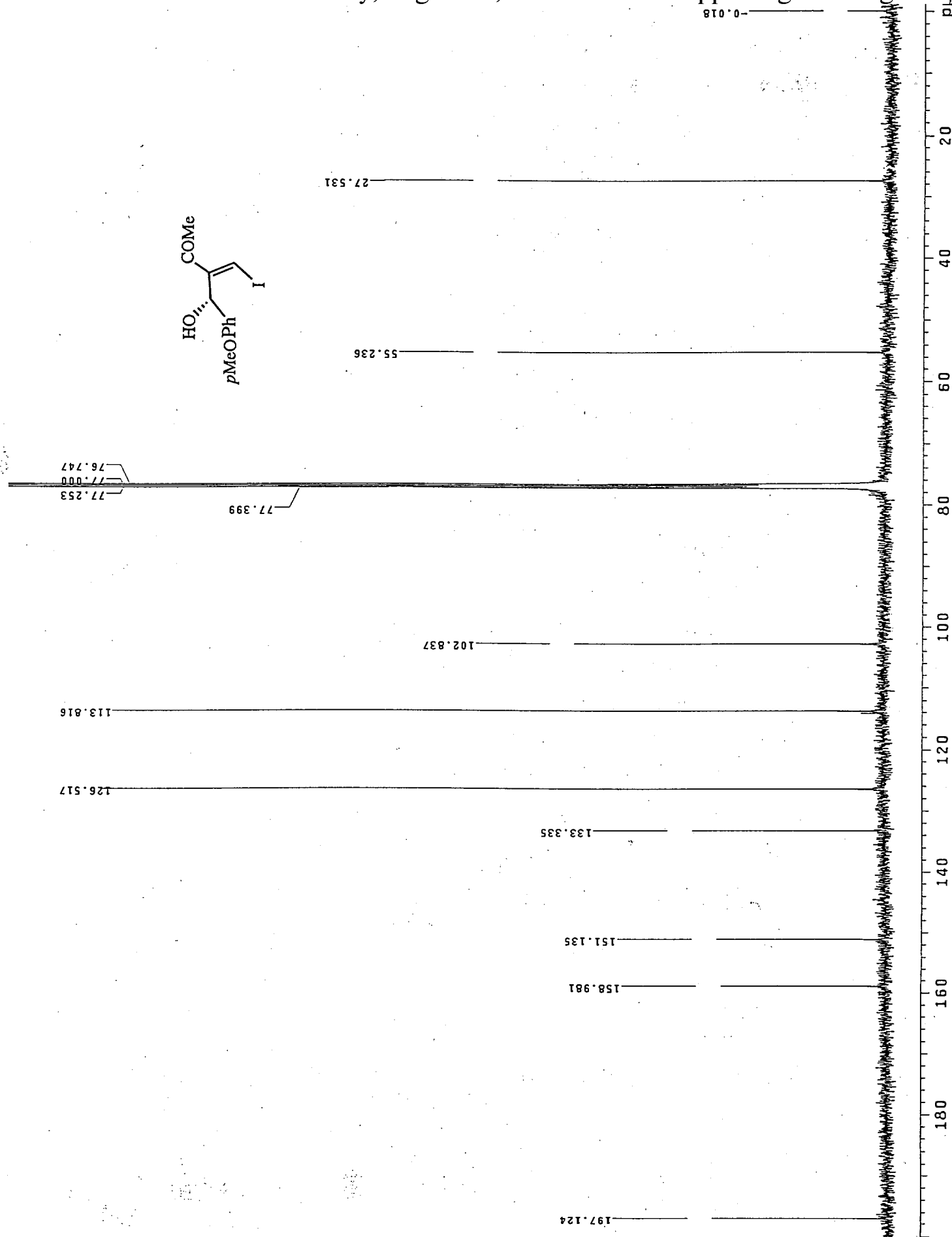


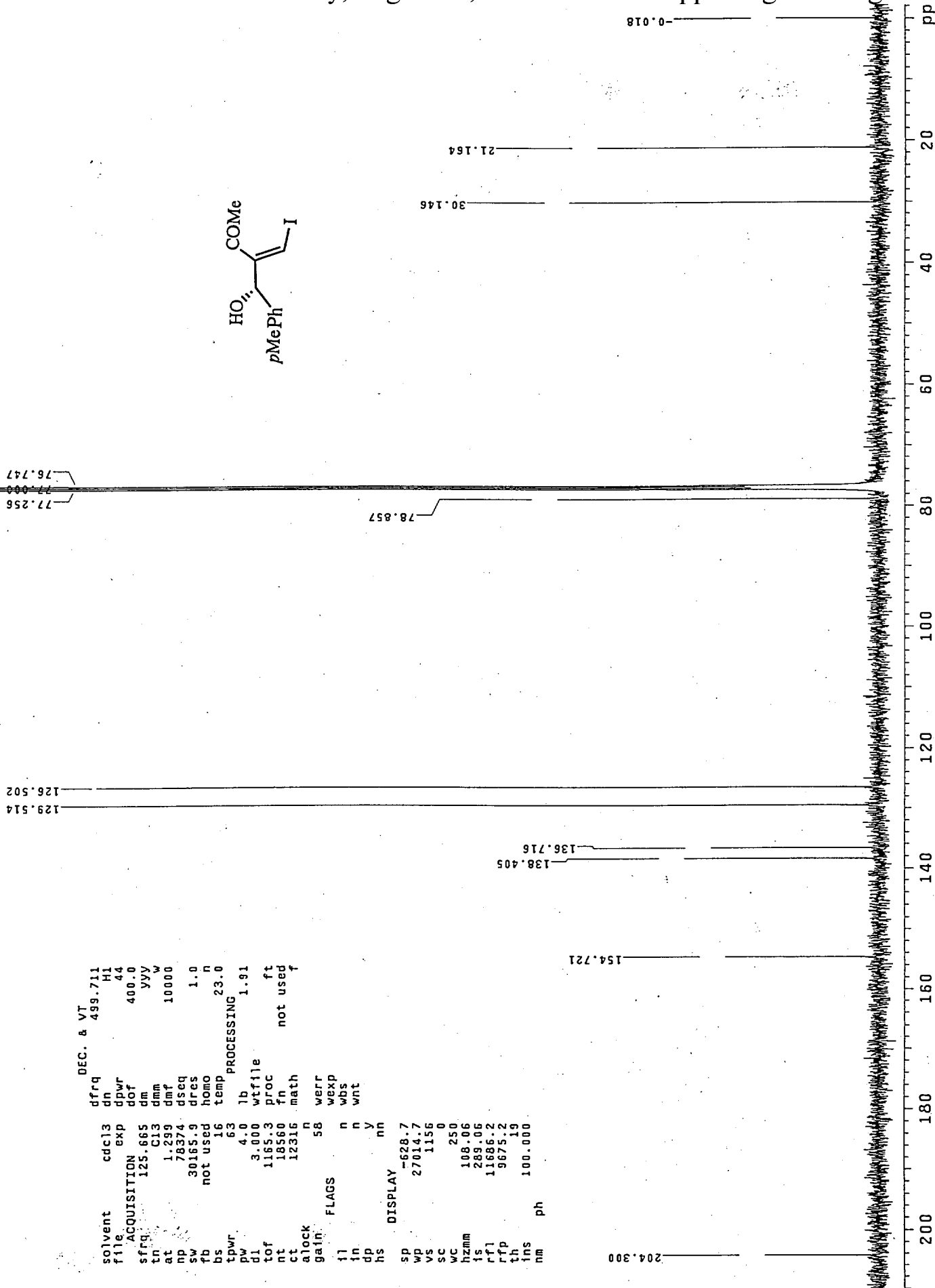




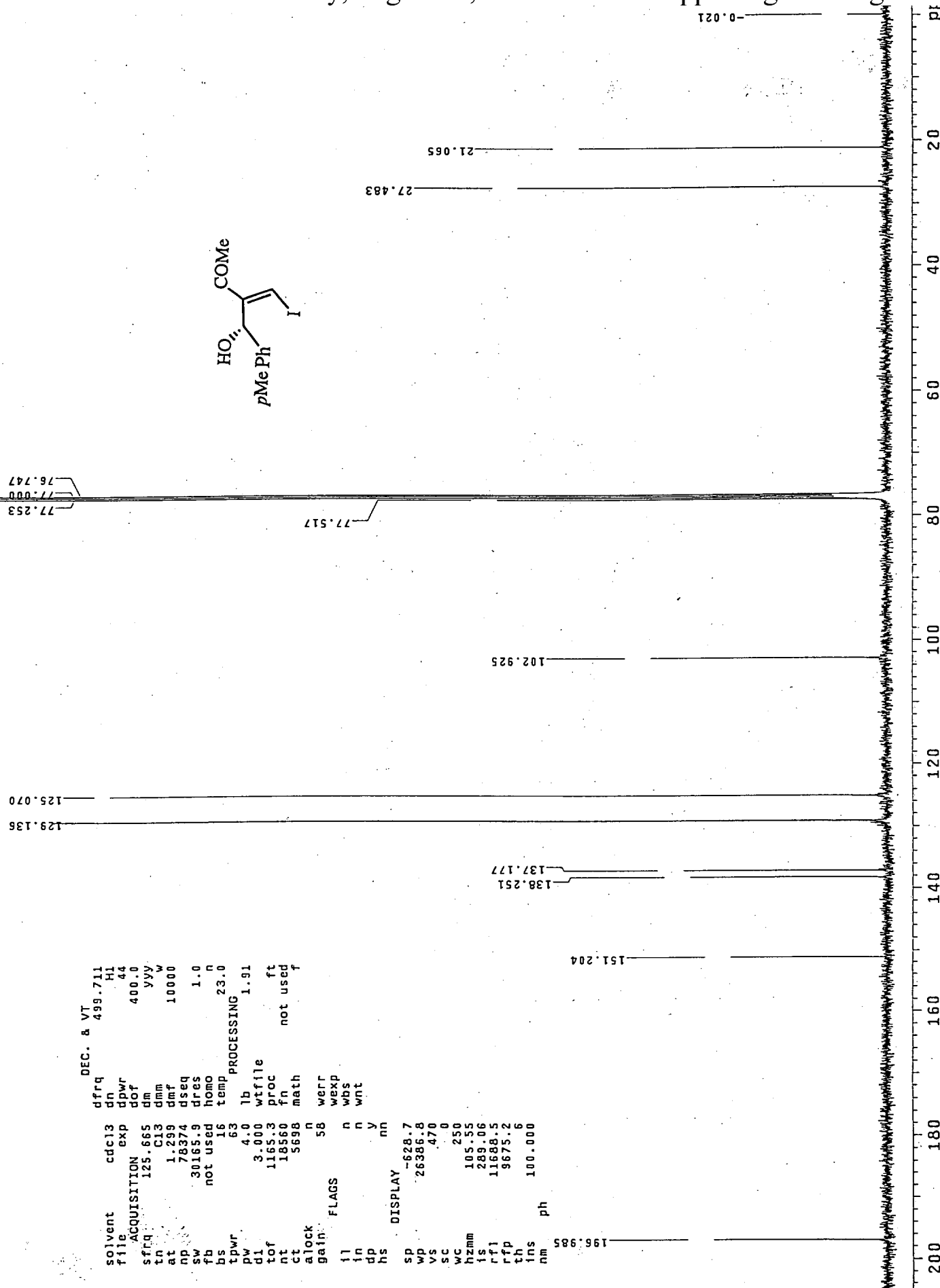
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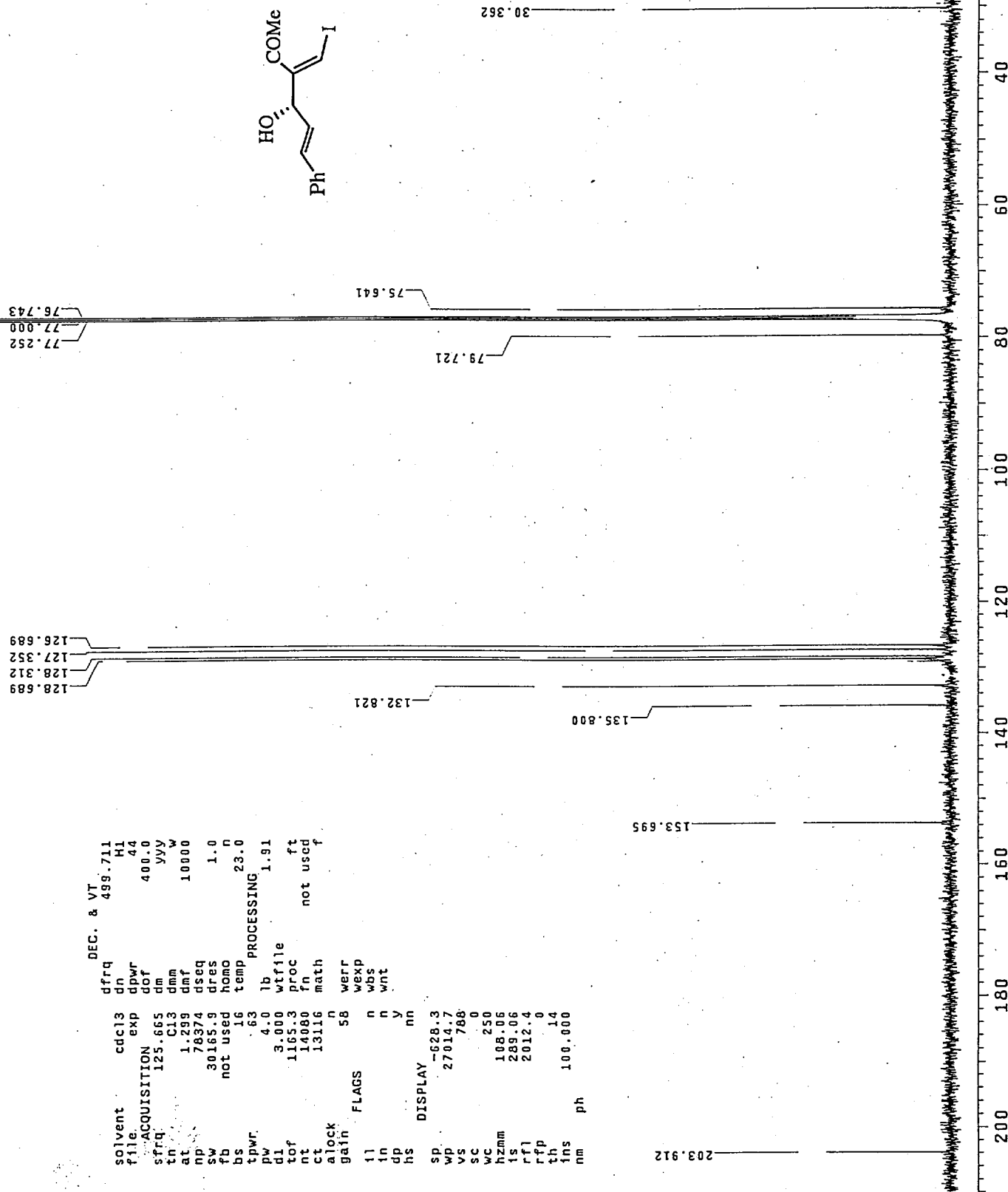






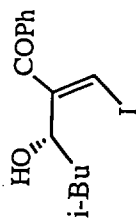
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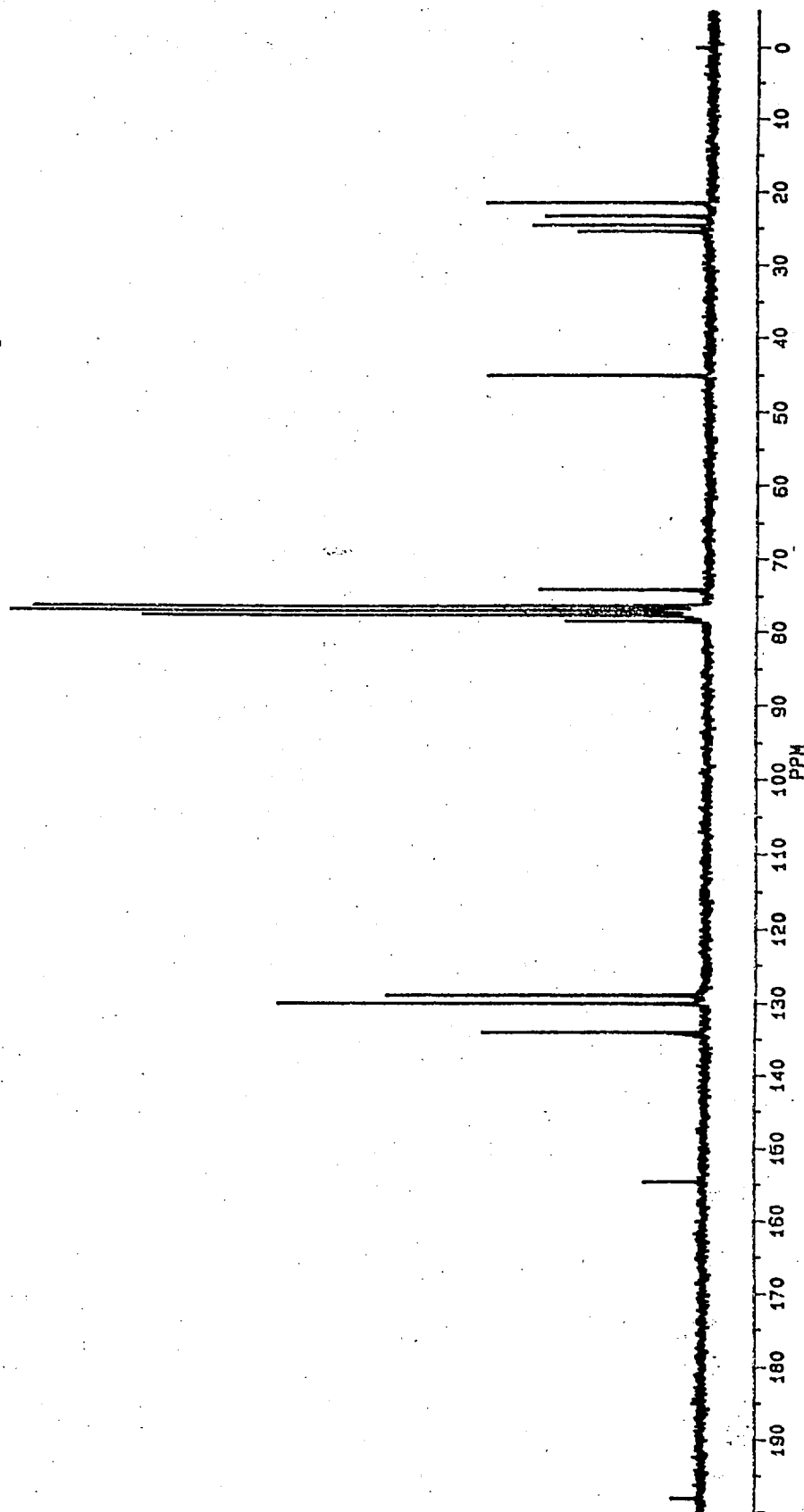
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 PPM



~~BRUKER~~

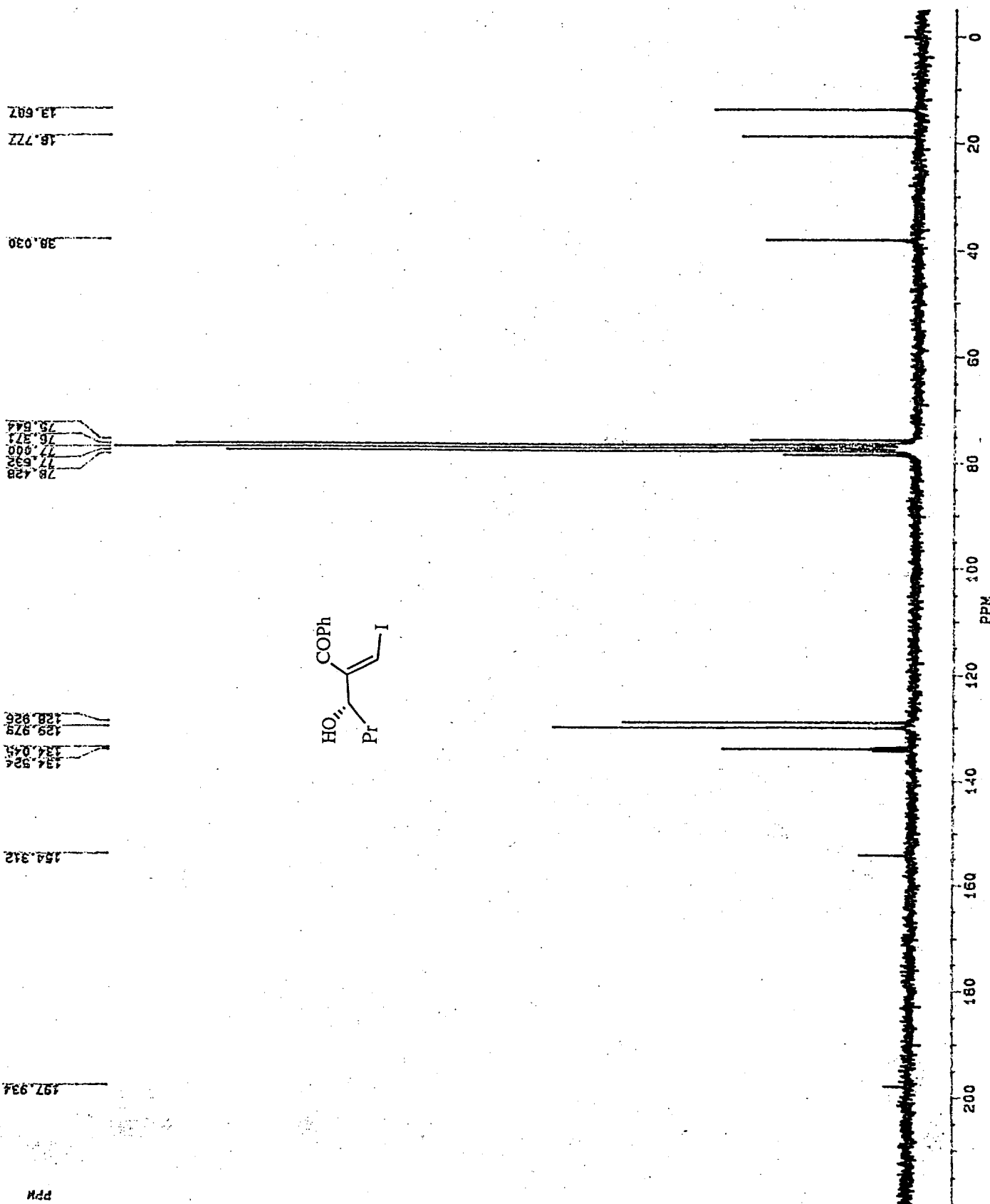
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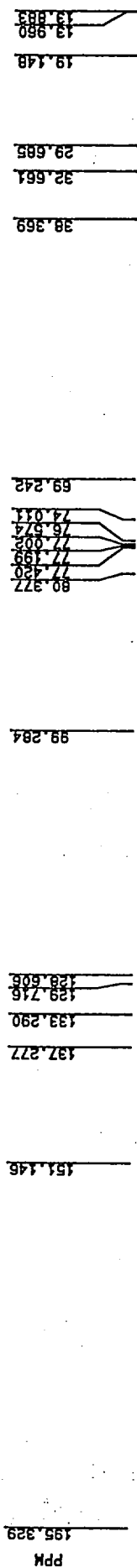
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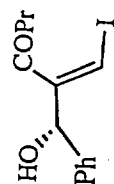
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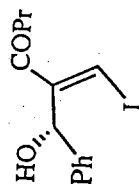
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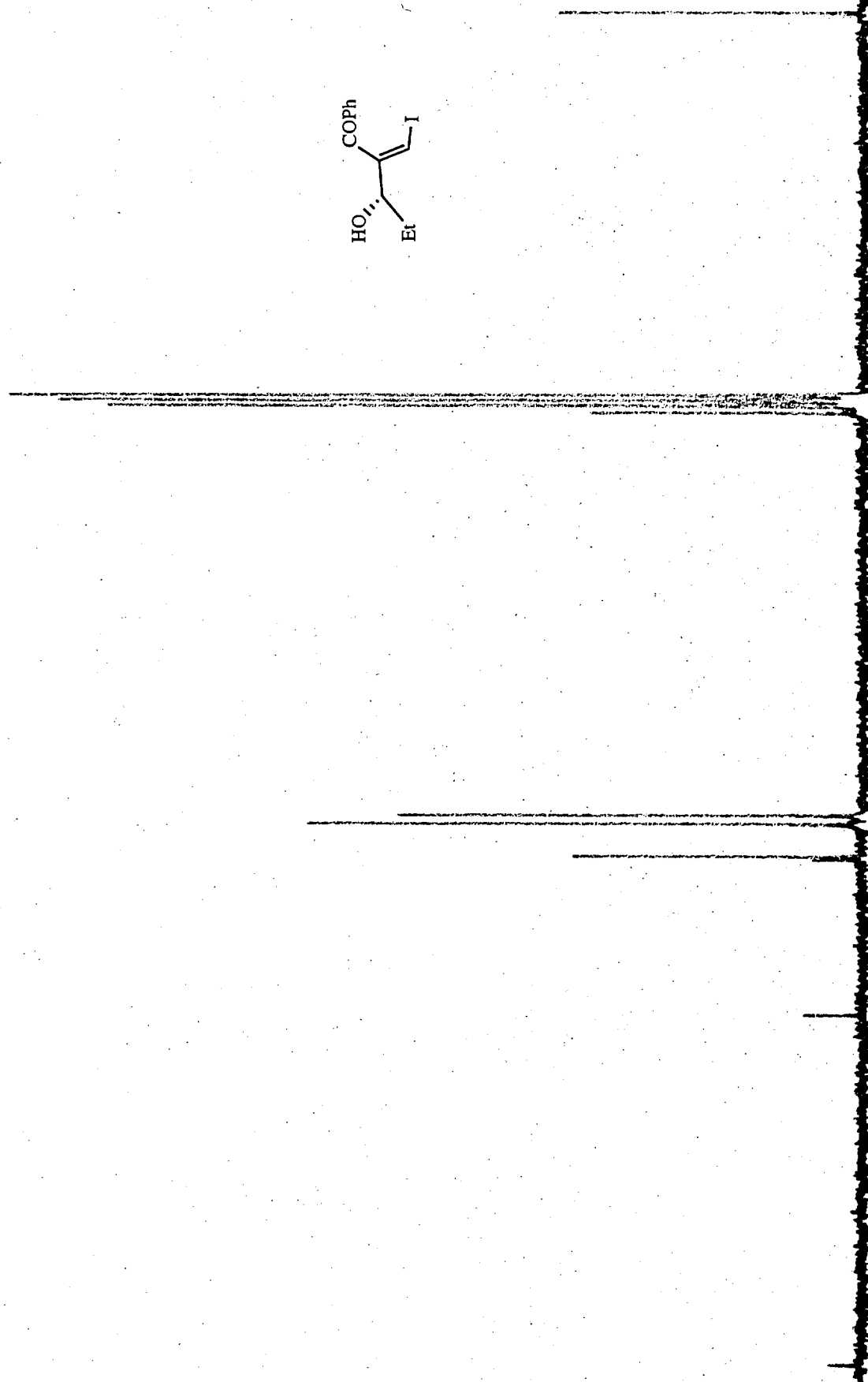
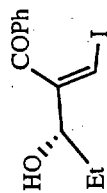
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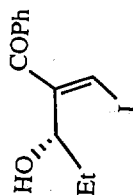


0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
180.0
200.0
PPM



190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 PPM

29.682
29.438



76.686
77.415
76.991
76.884
76.808
76.348
74.010

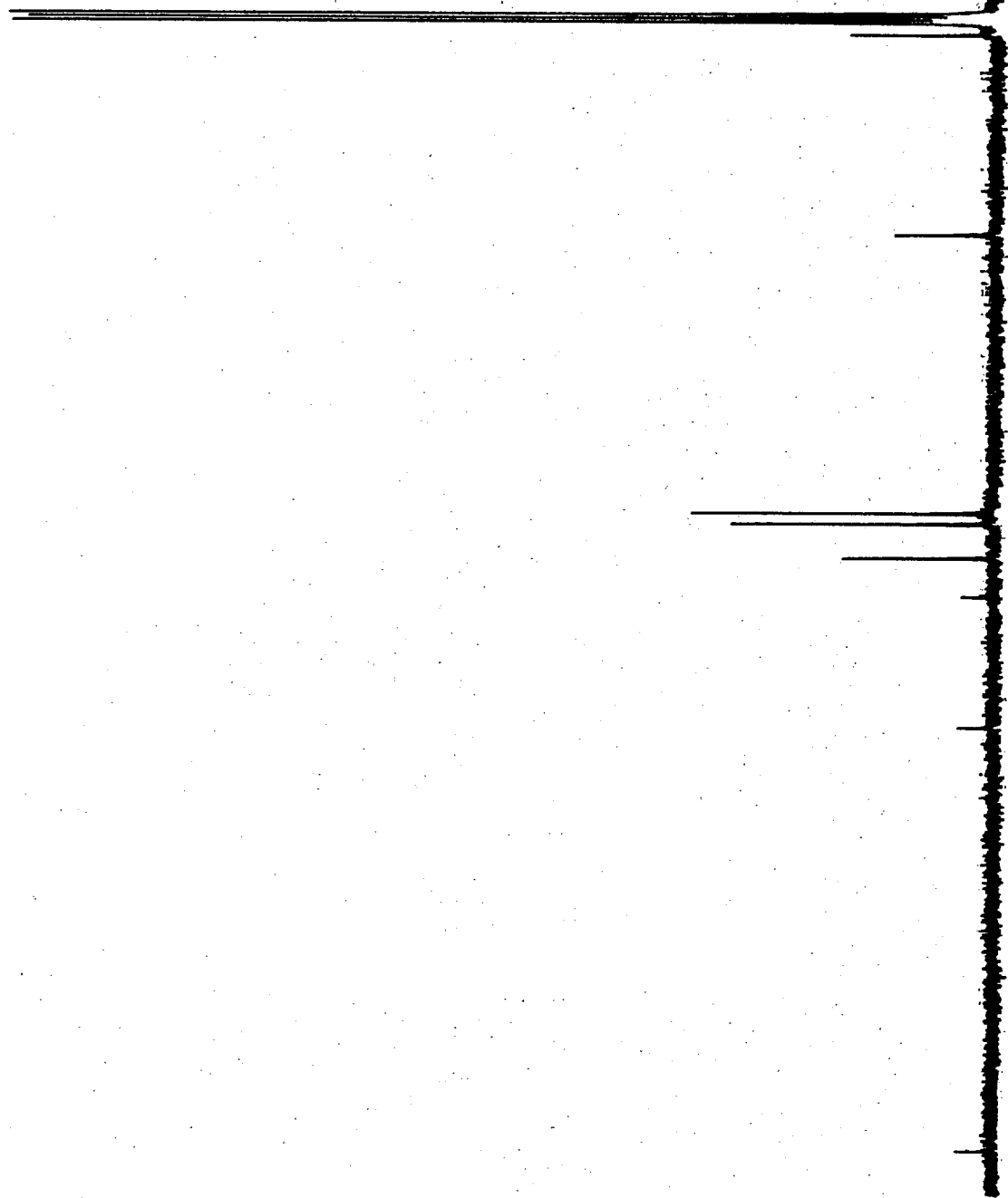
99.589

137.260
133.289
128.715
128.603

150.953

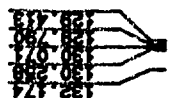
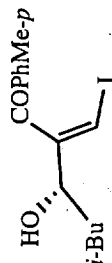
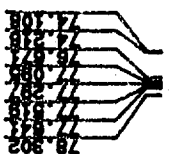
185.318
ppm

20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0





48.084



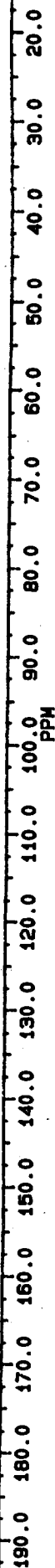
148.330

154.739

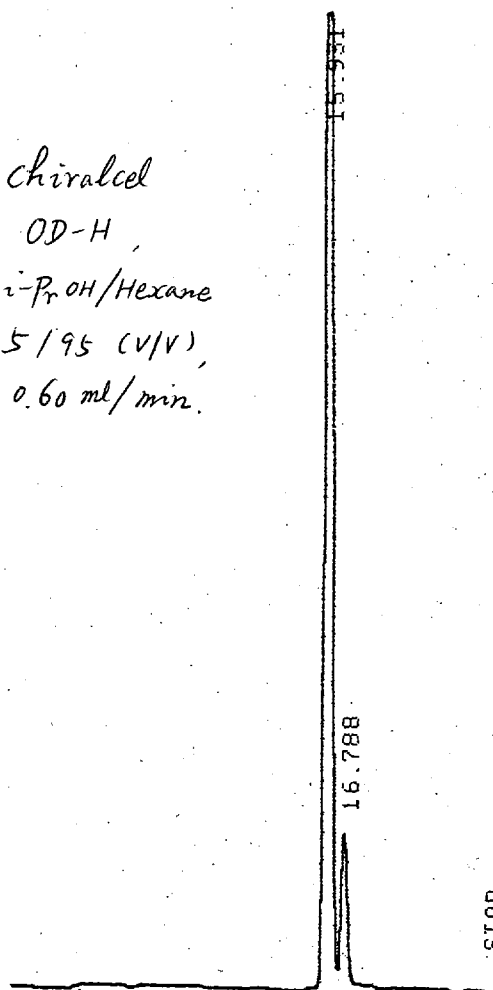
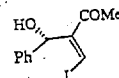
177.774



197.867



Chiralcel
OD-H,
i-PrOH/Hexane
5/95 (v/v),
0.60 ml/min.



RT	AREA	TYPE	WIDTH	PU	UU	AREA%
15.931	39930784	PU	.403			92.55412
16.788	3212389	UU	.250			7.44588

