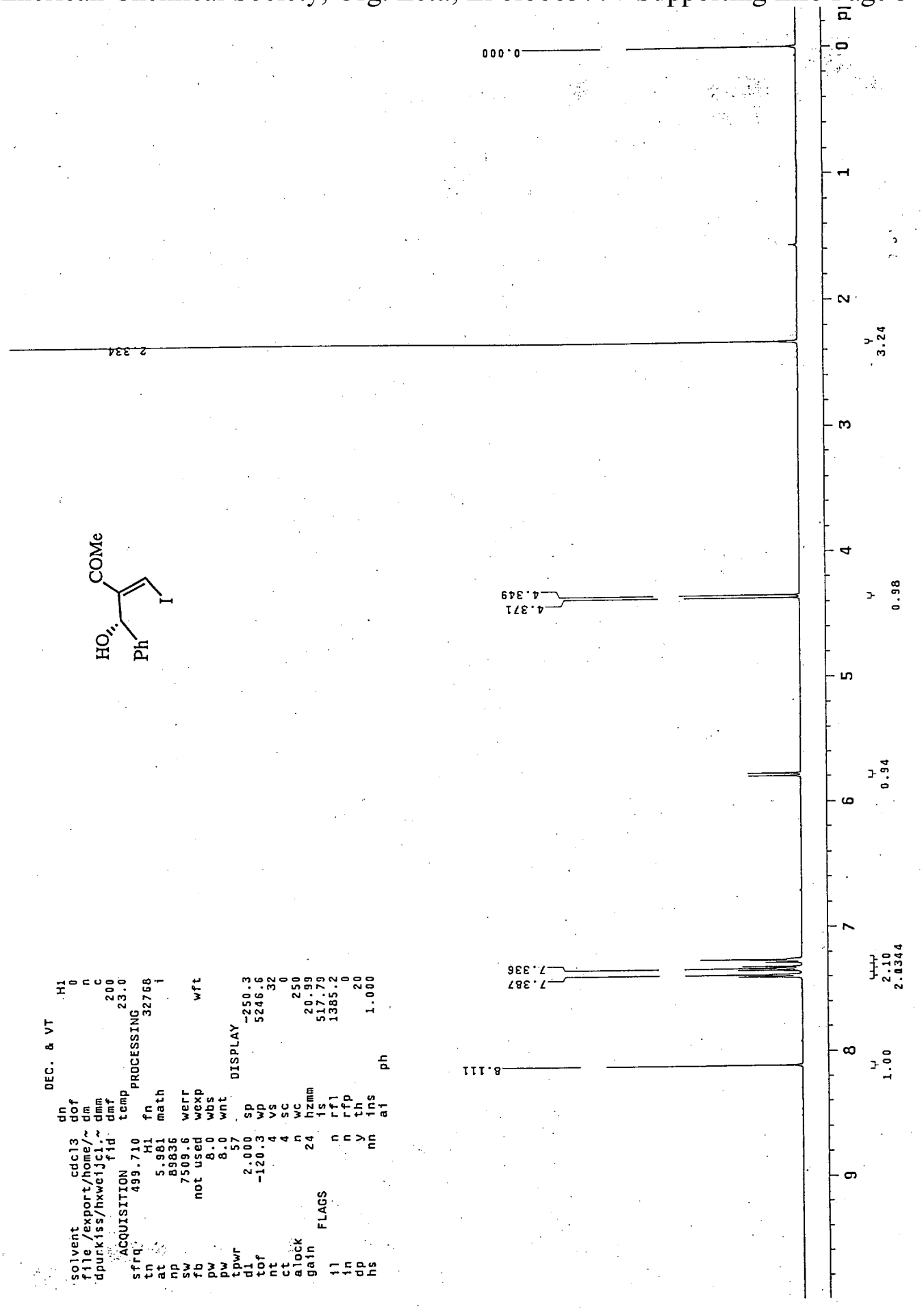
Supplement Materials (51 pages including this page):

1. Experimental Procedure
2. Copies of ^{1}H 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*-heptaflouropropyl phenyalanine (58 mg, 0.22 mmol) and freshly distilled propionitrile (1.5 mL). The resulting solution was added by BH_3·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 ethynl 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 stirrred 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 ^{1}H-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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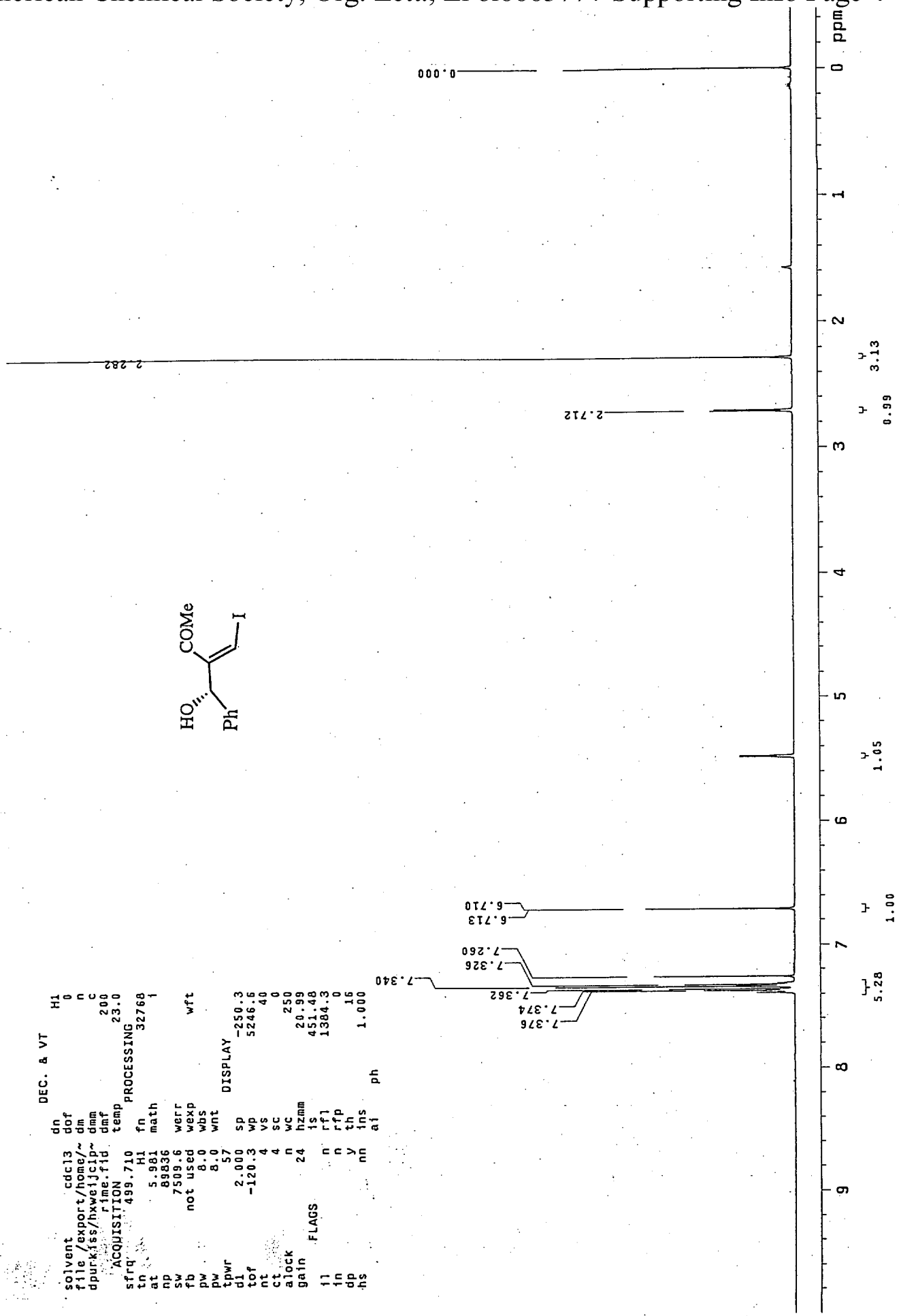
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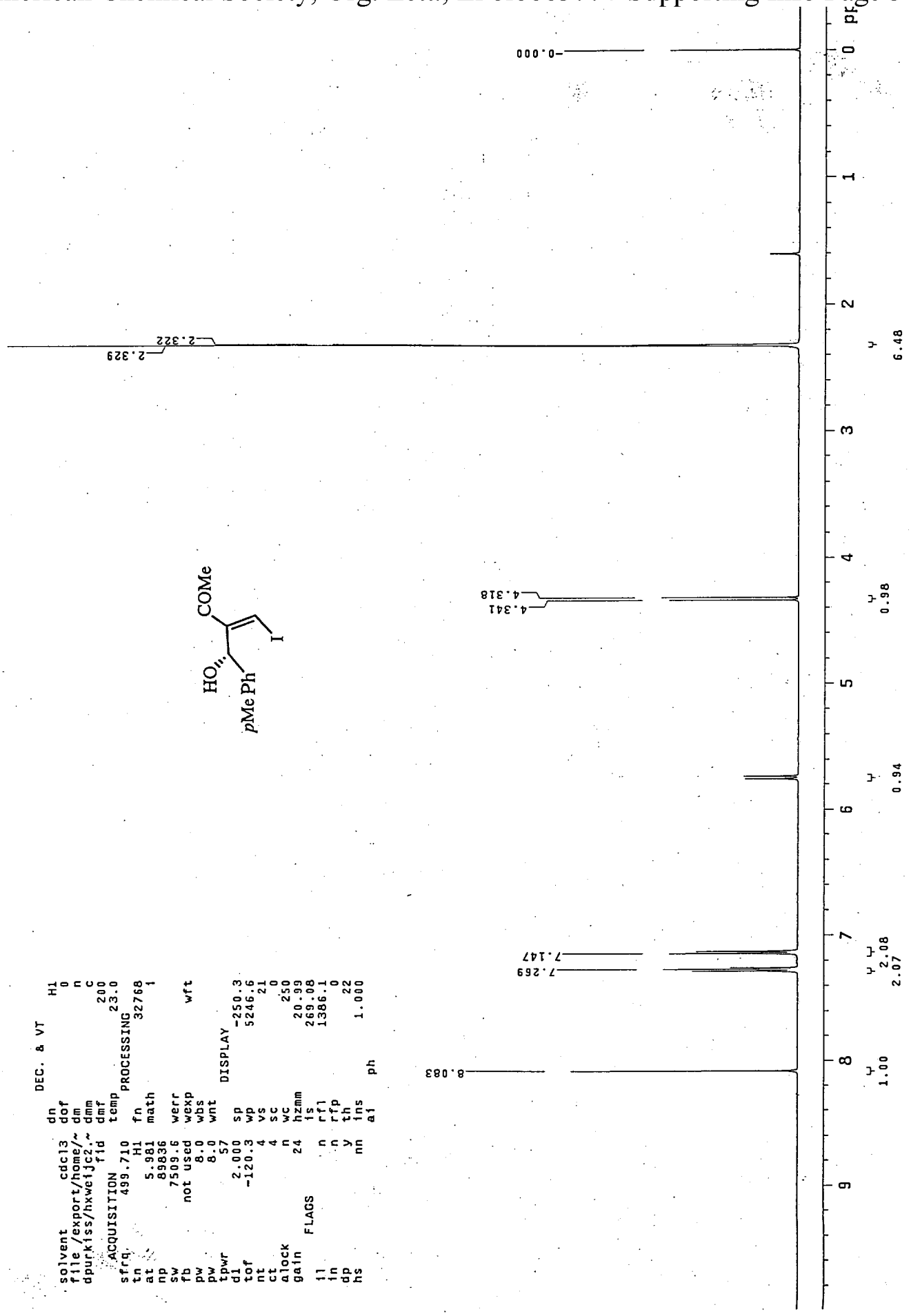
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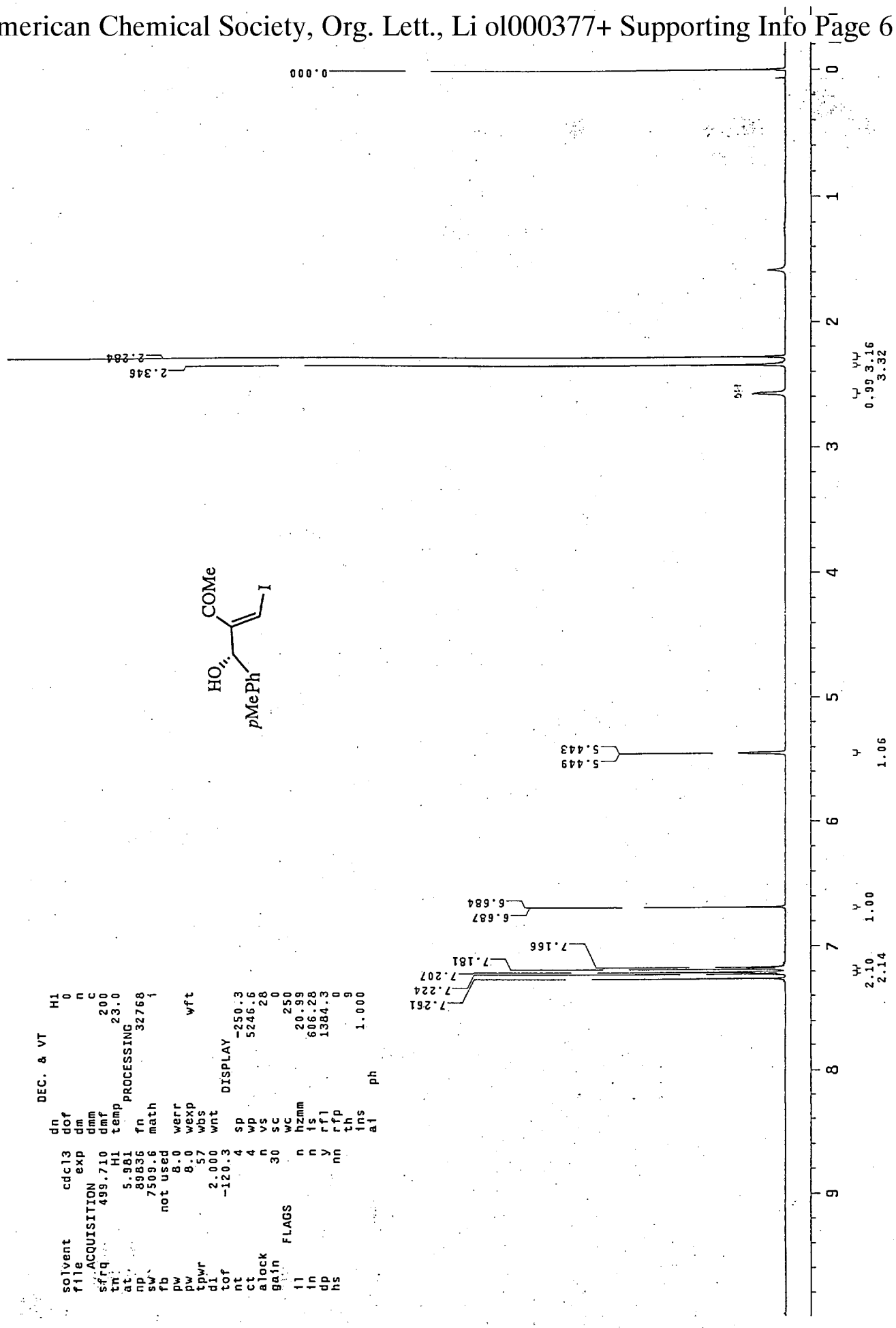

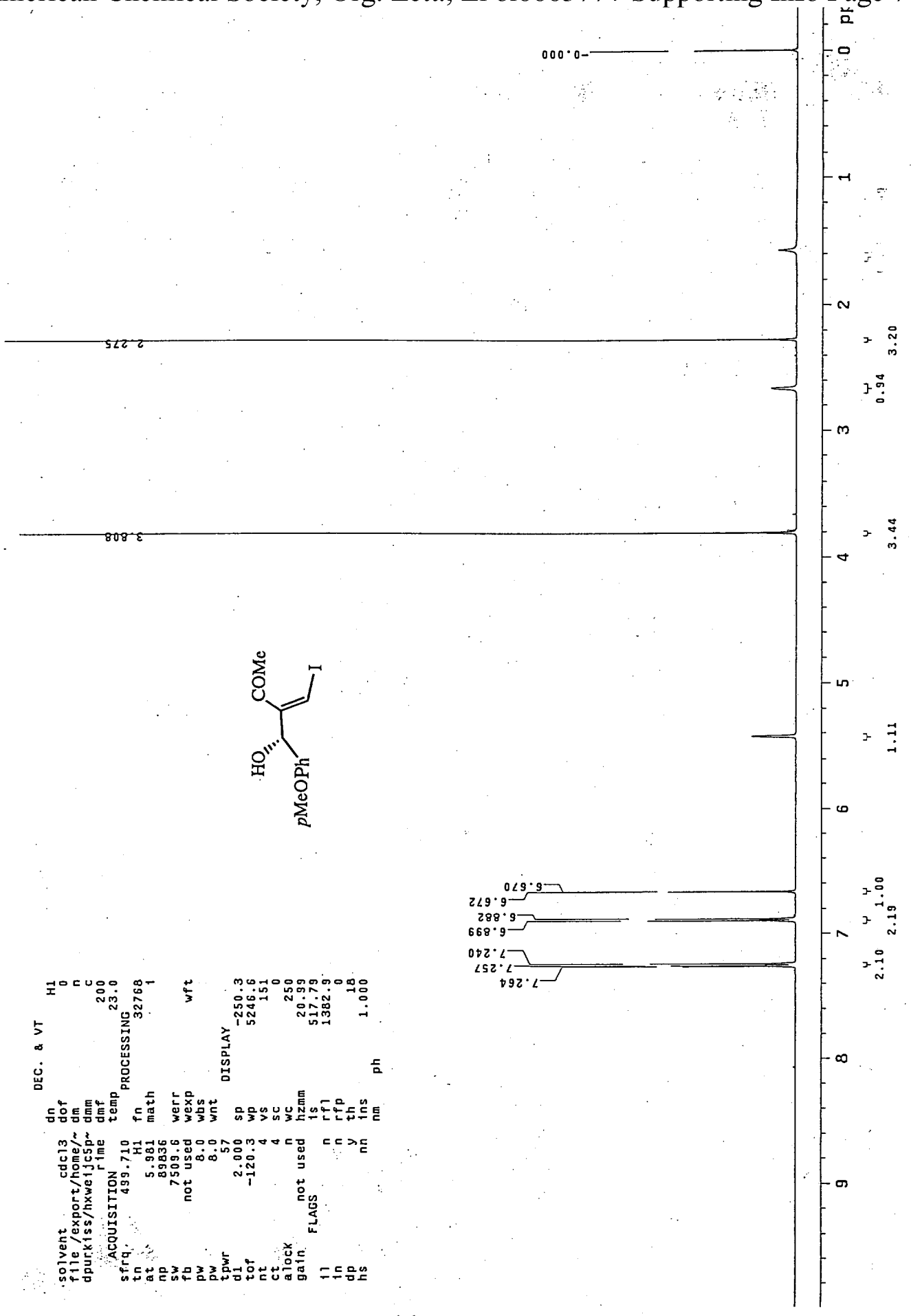

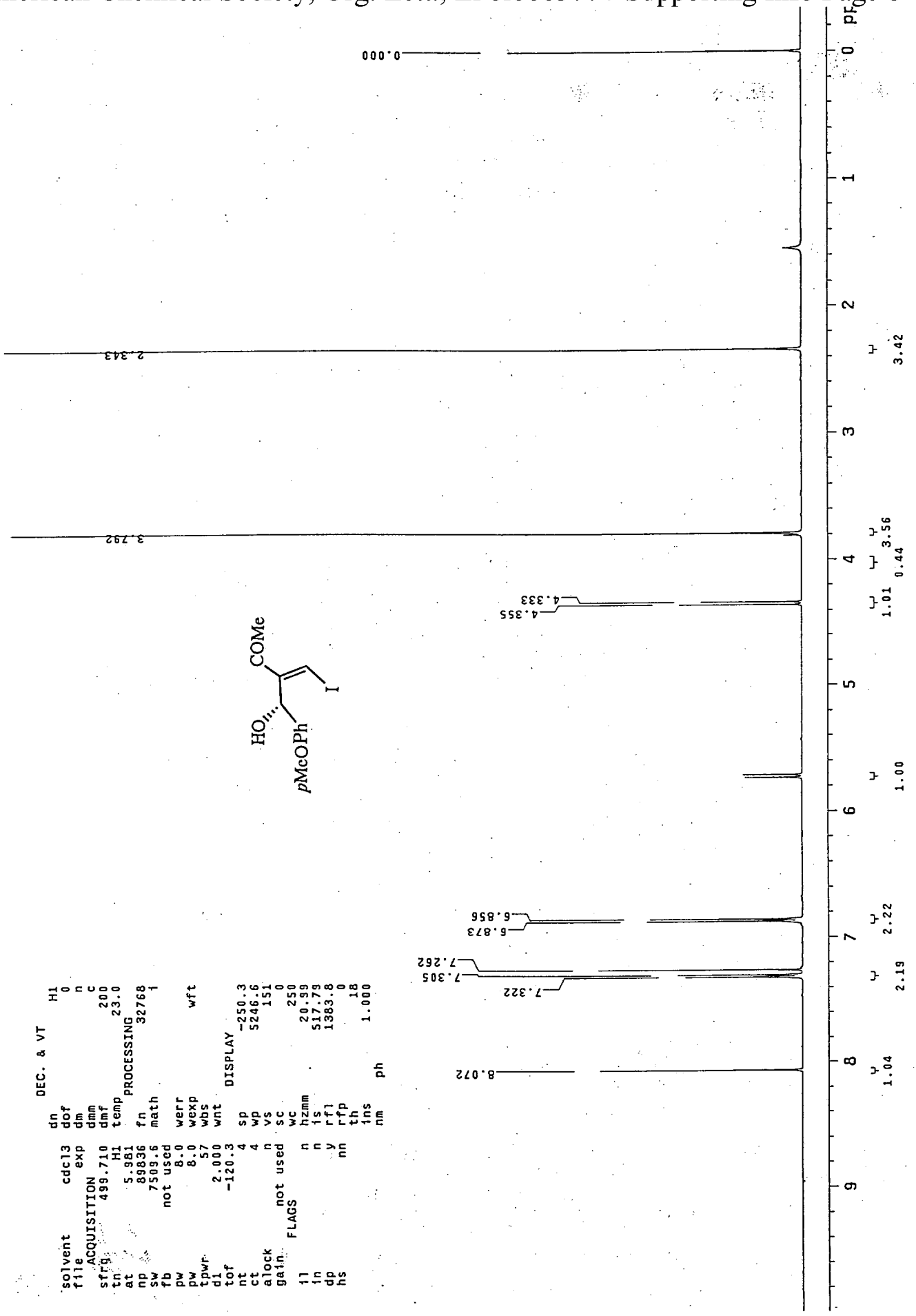
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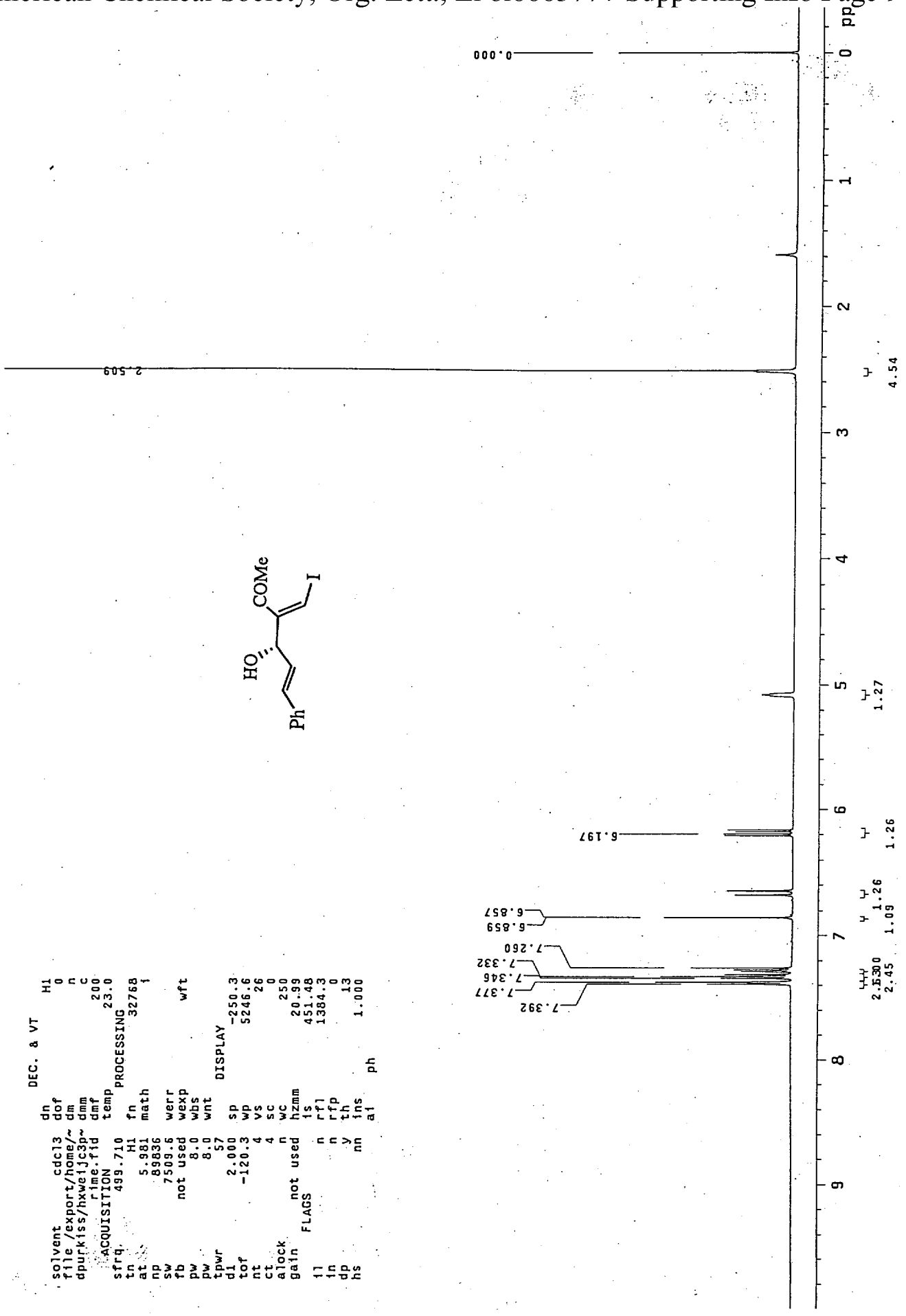

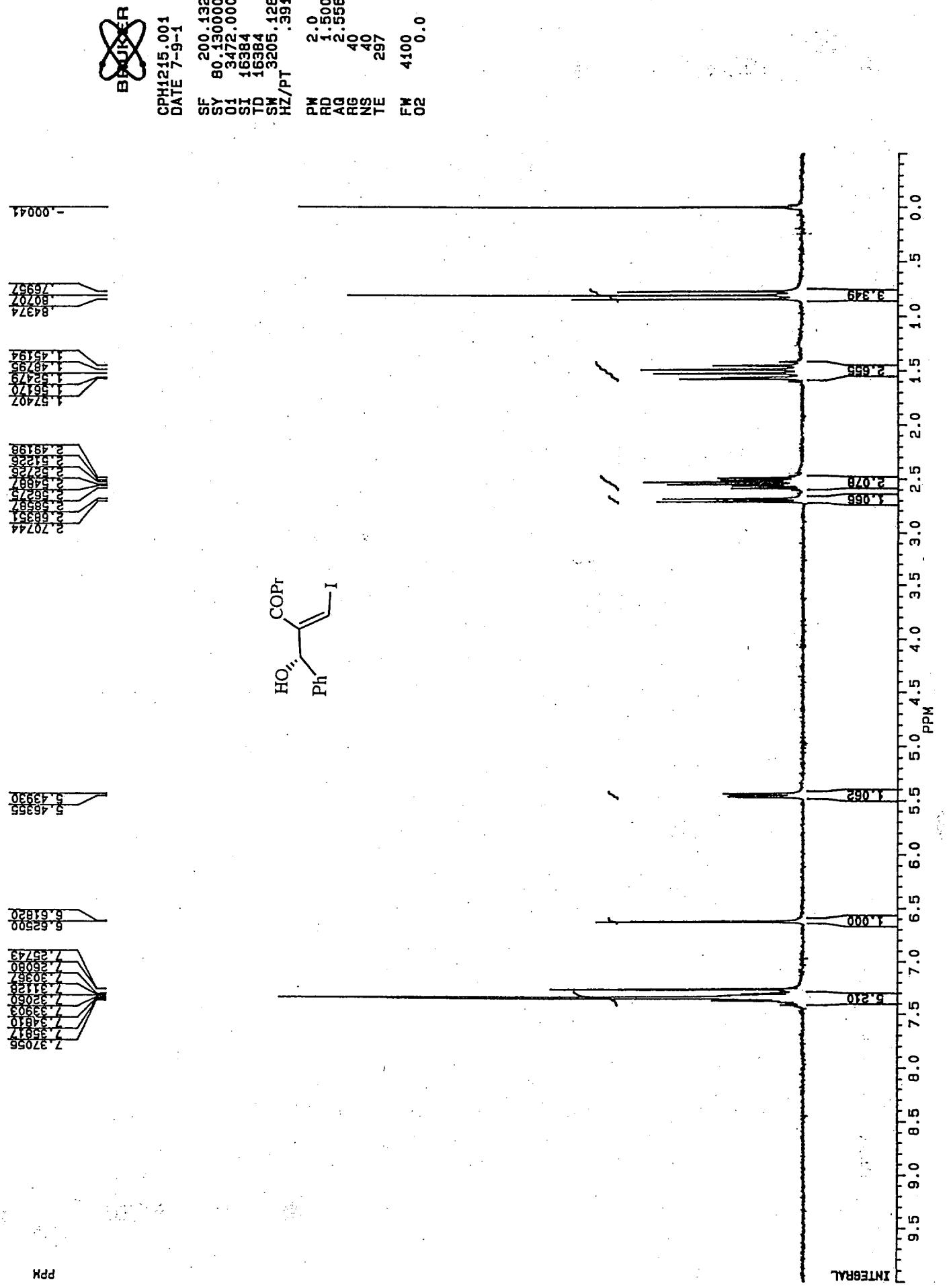

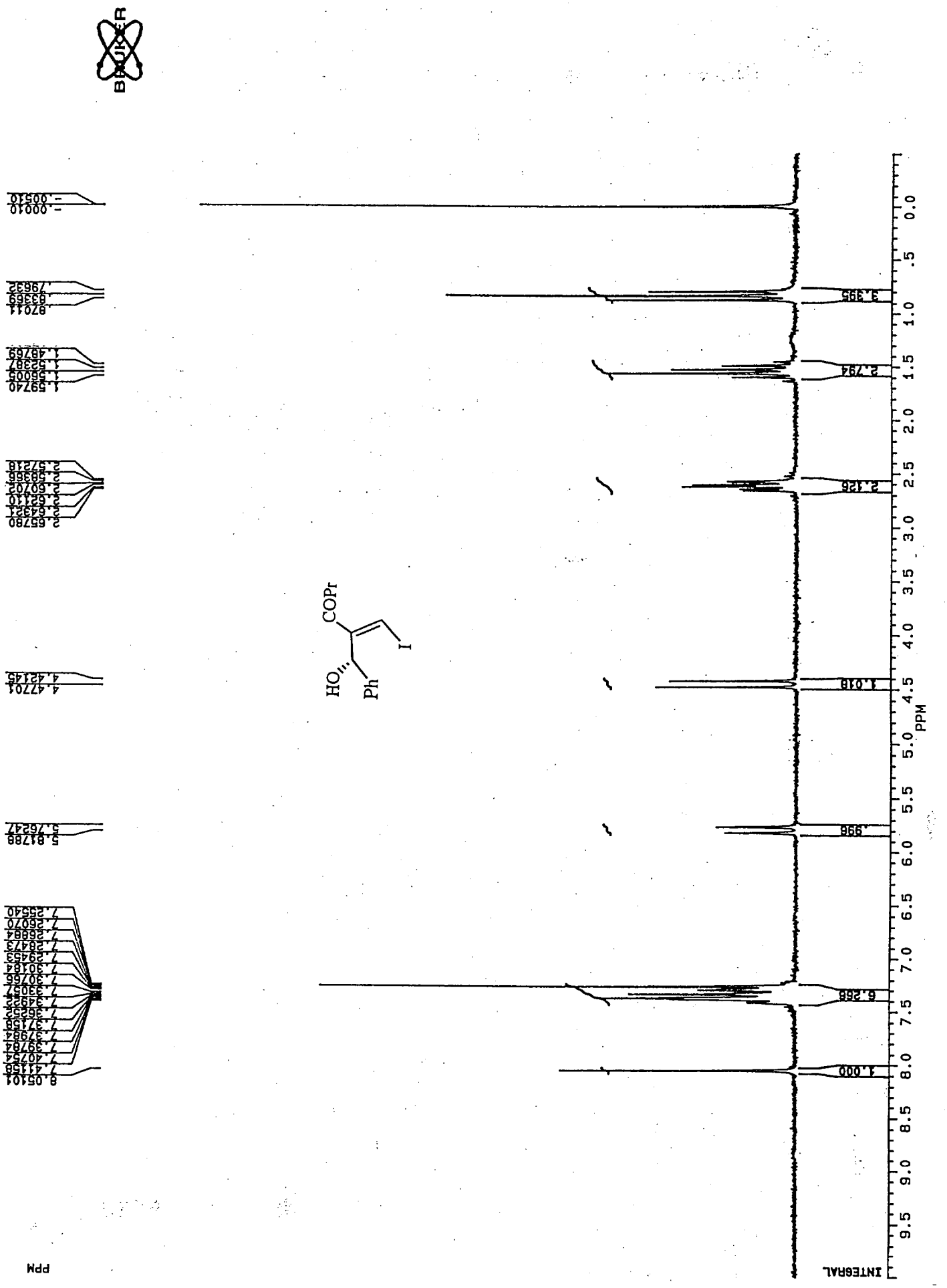
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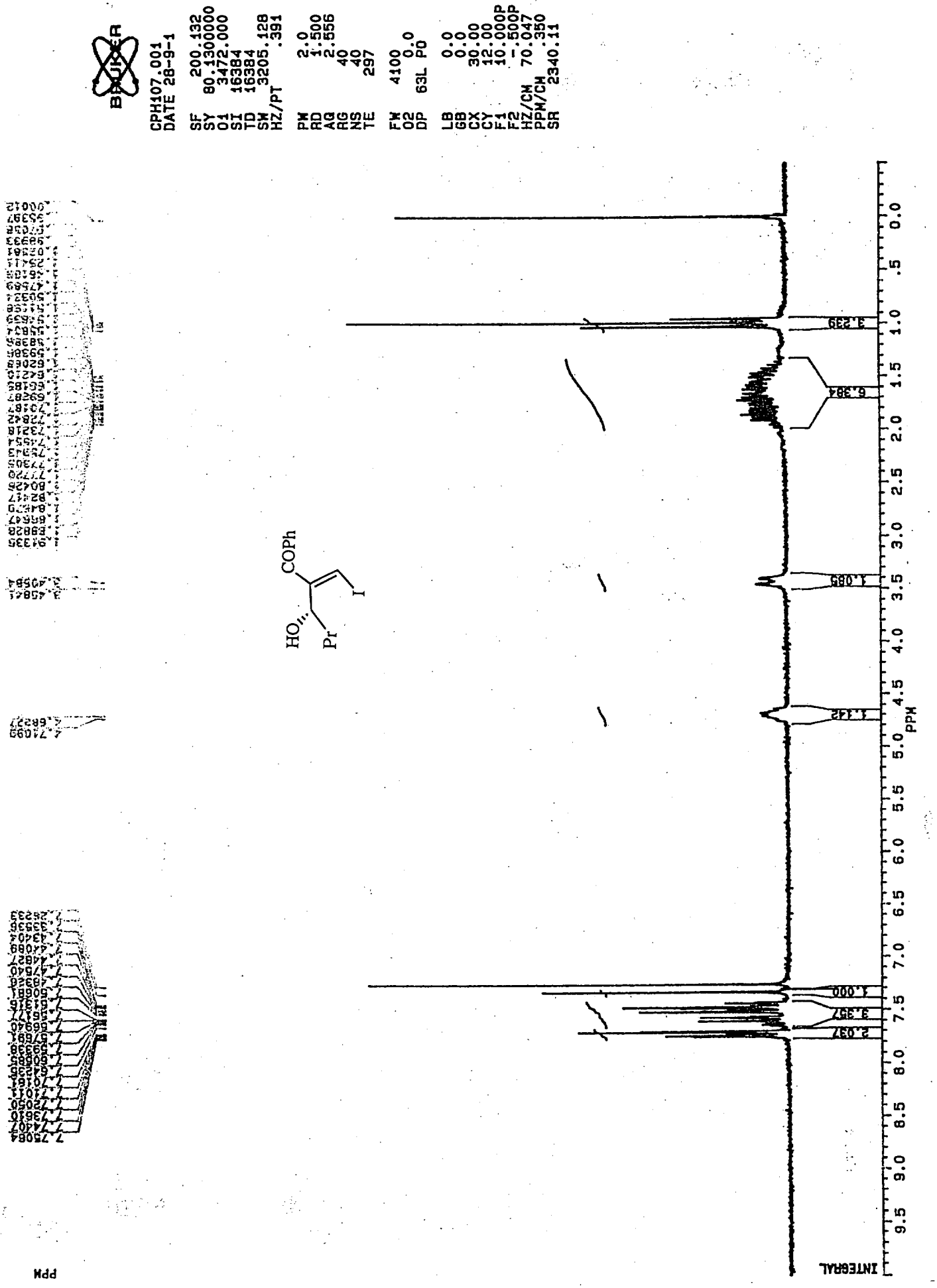

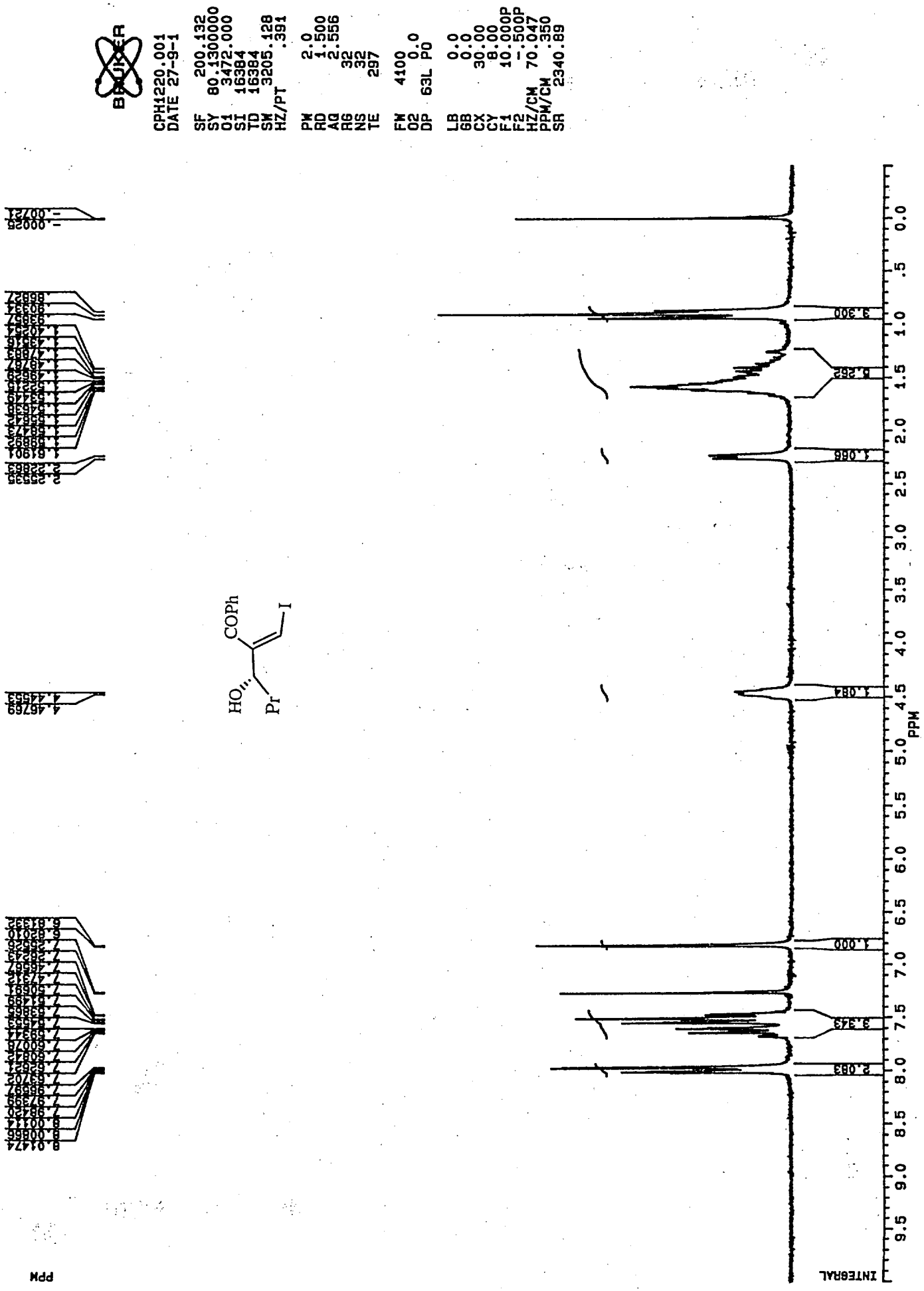

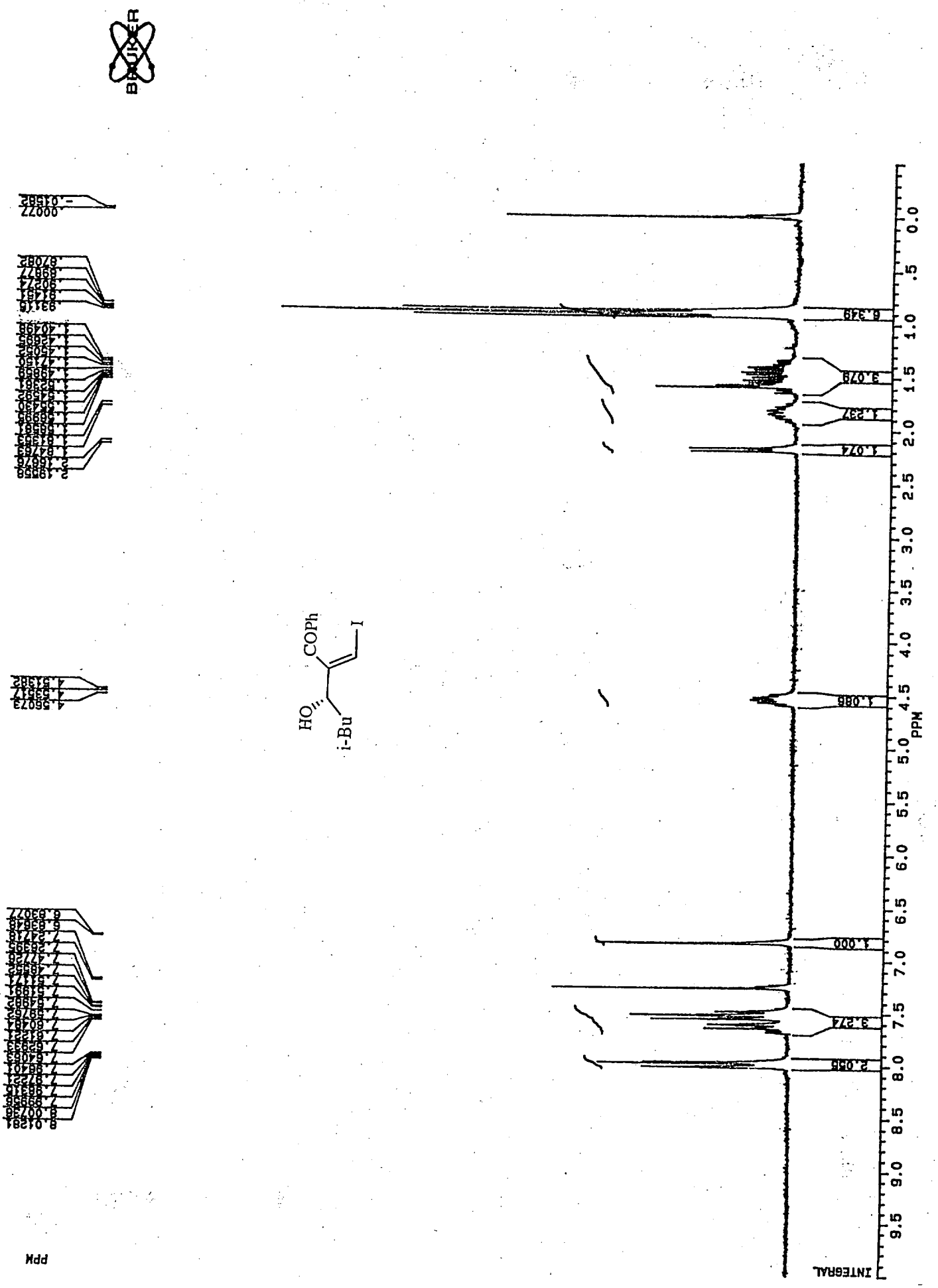
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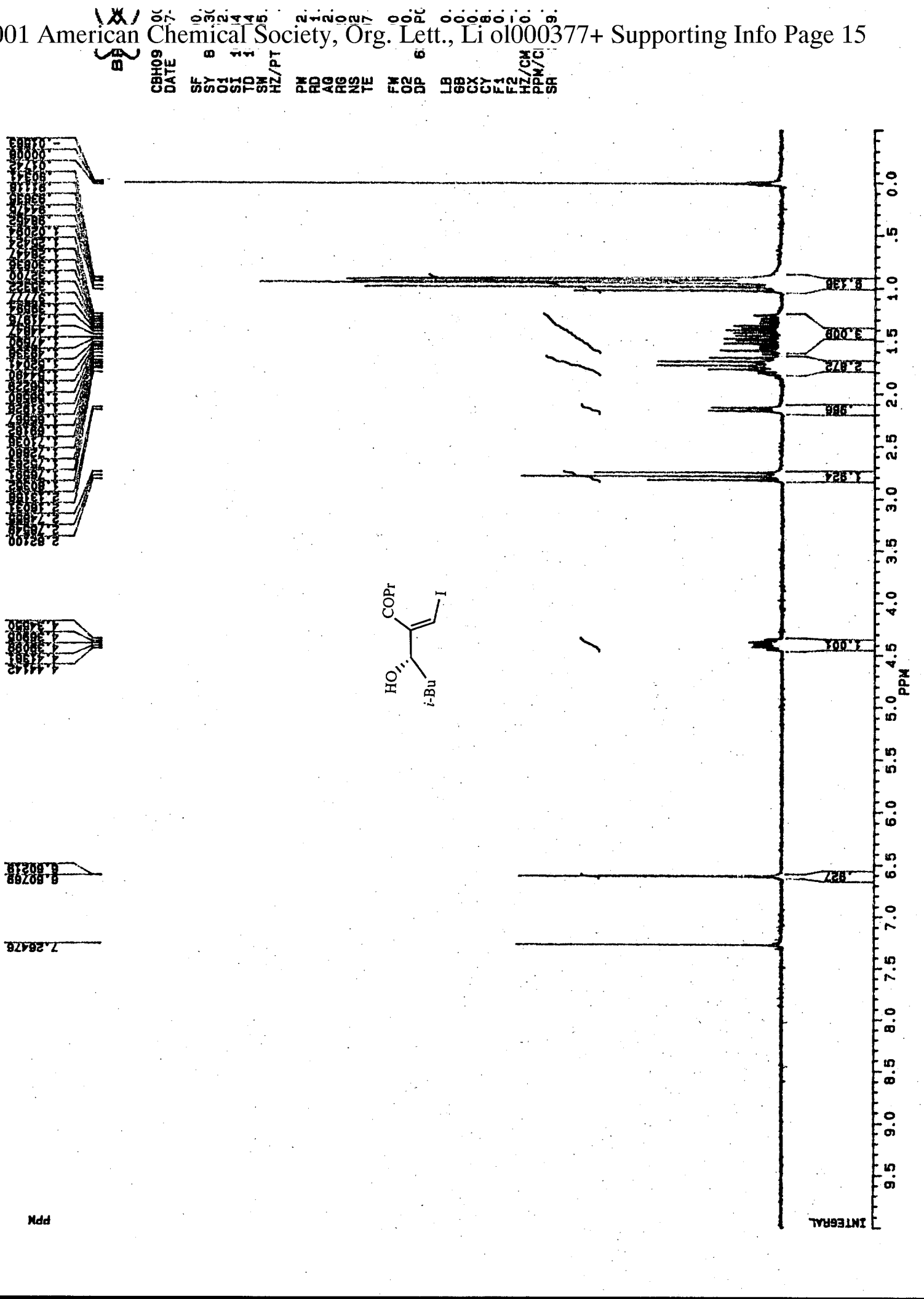
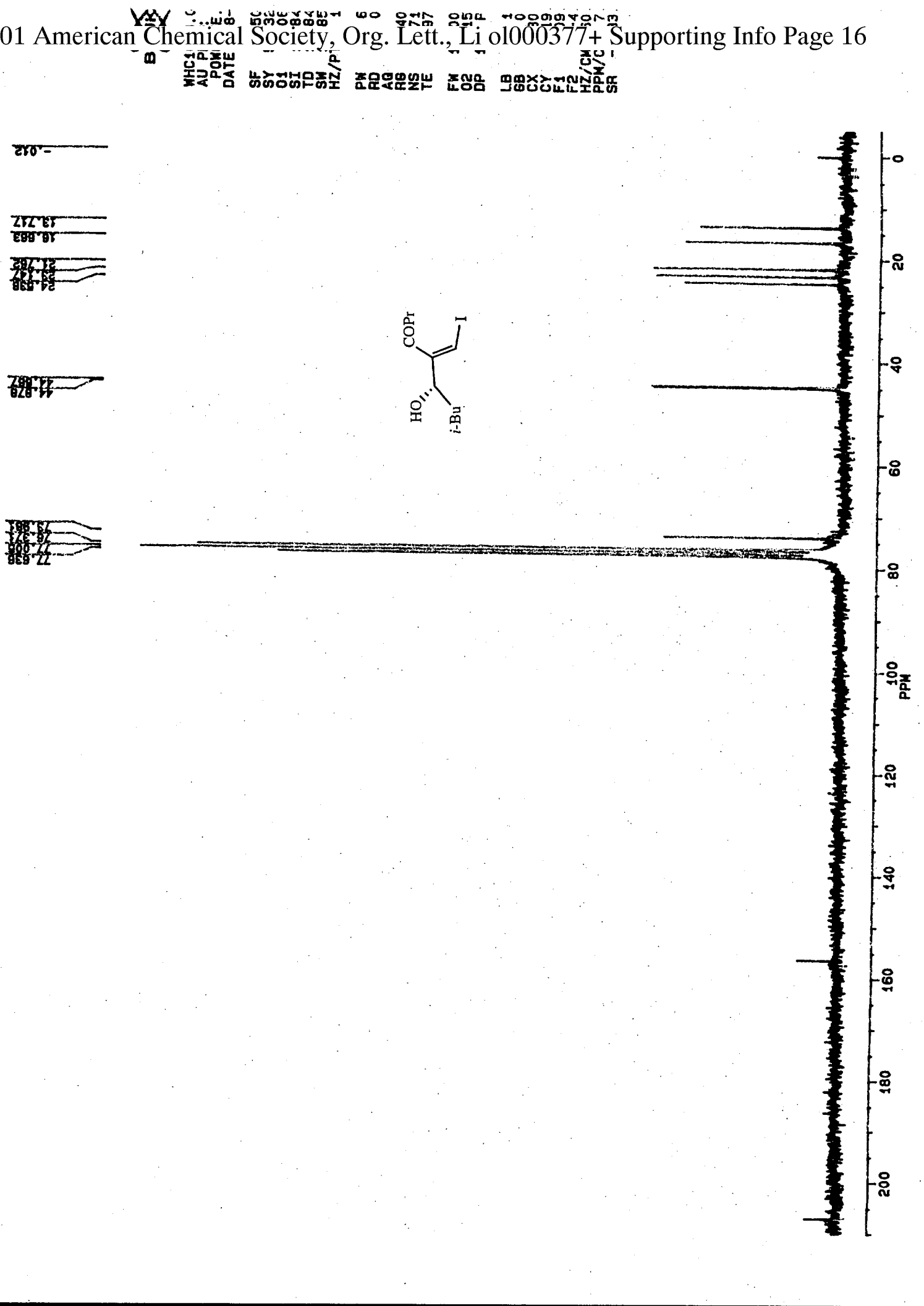
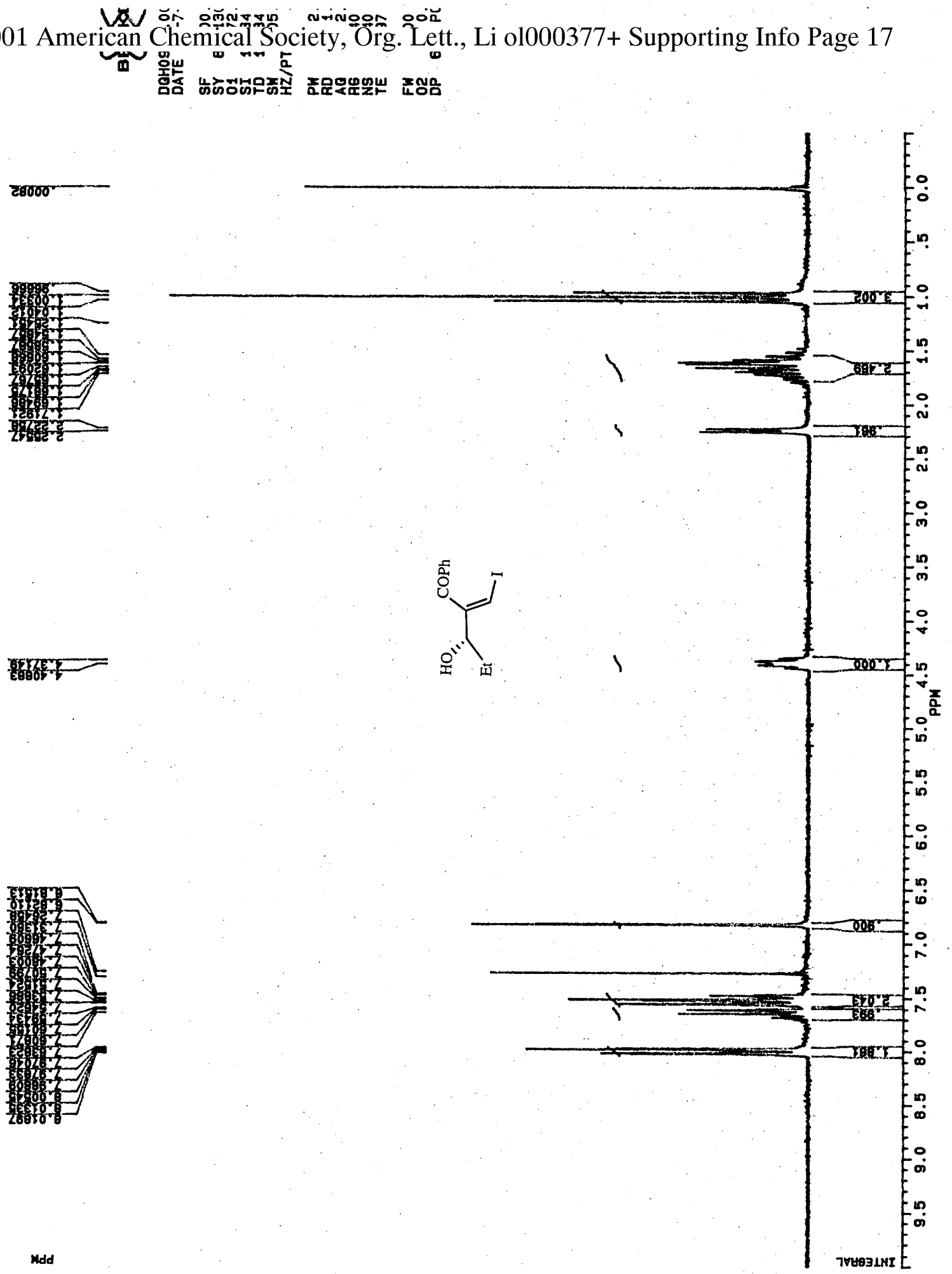
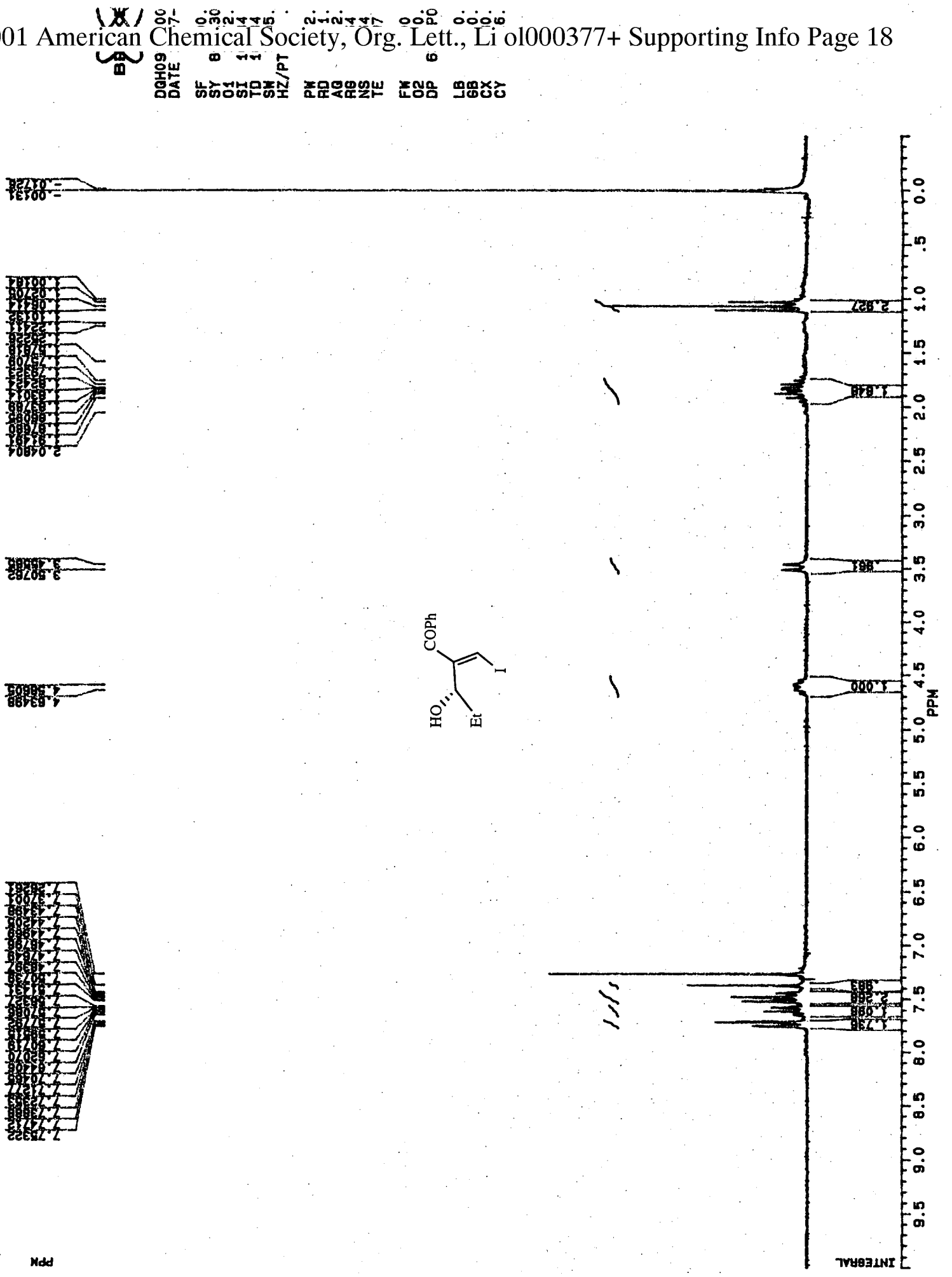
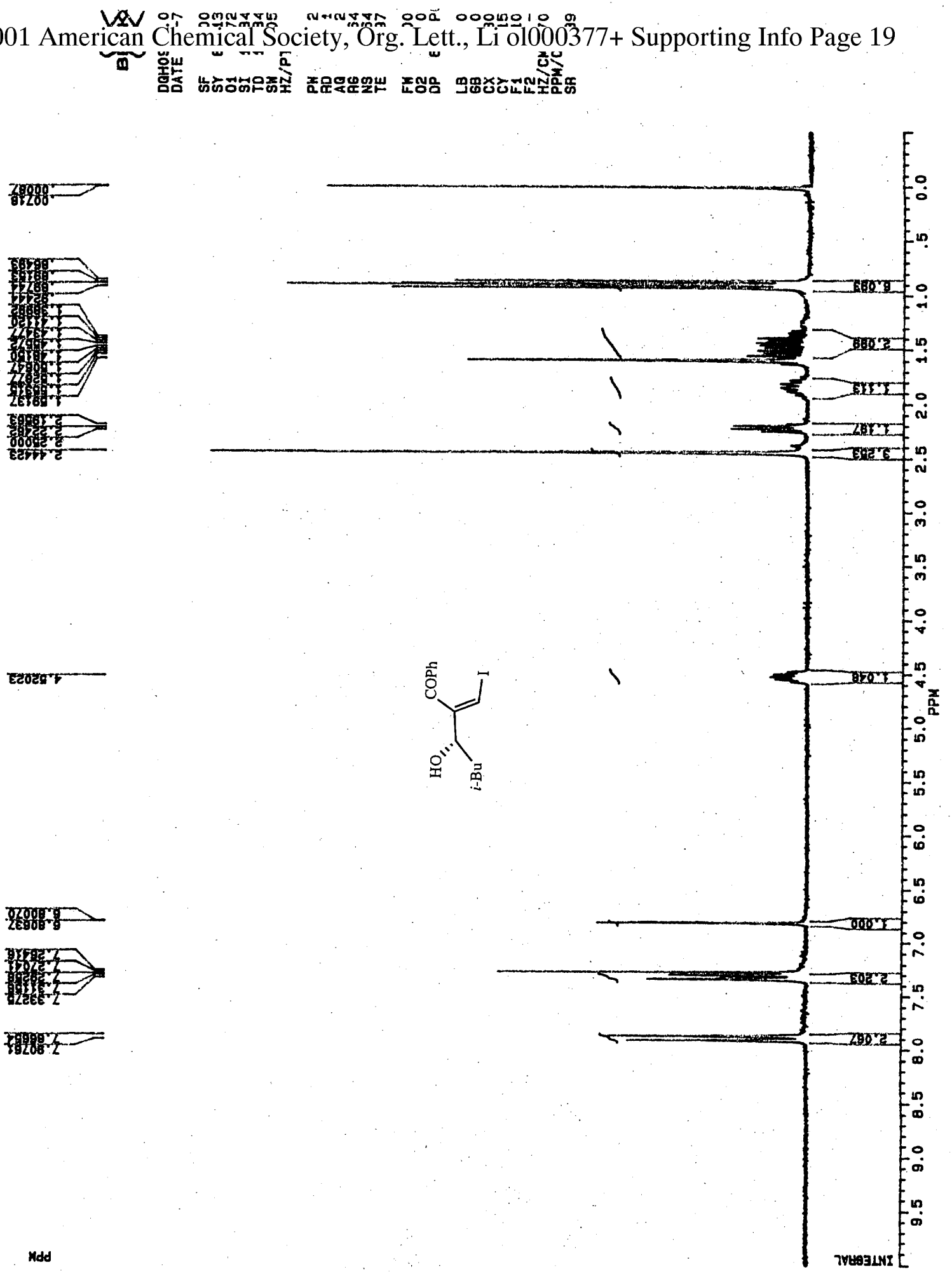
ppm

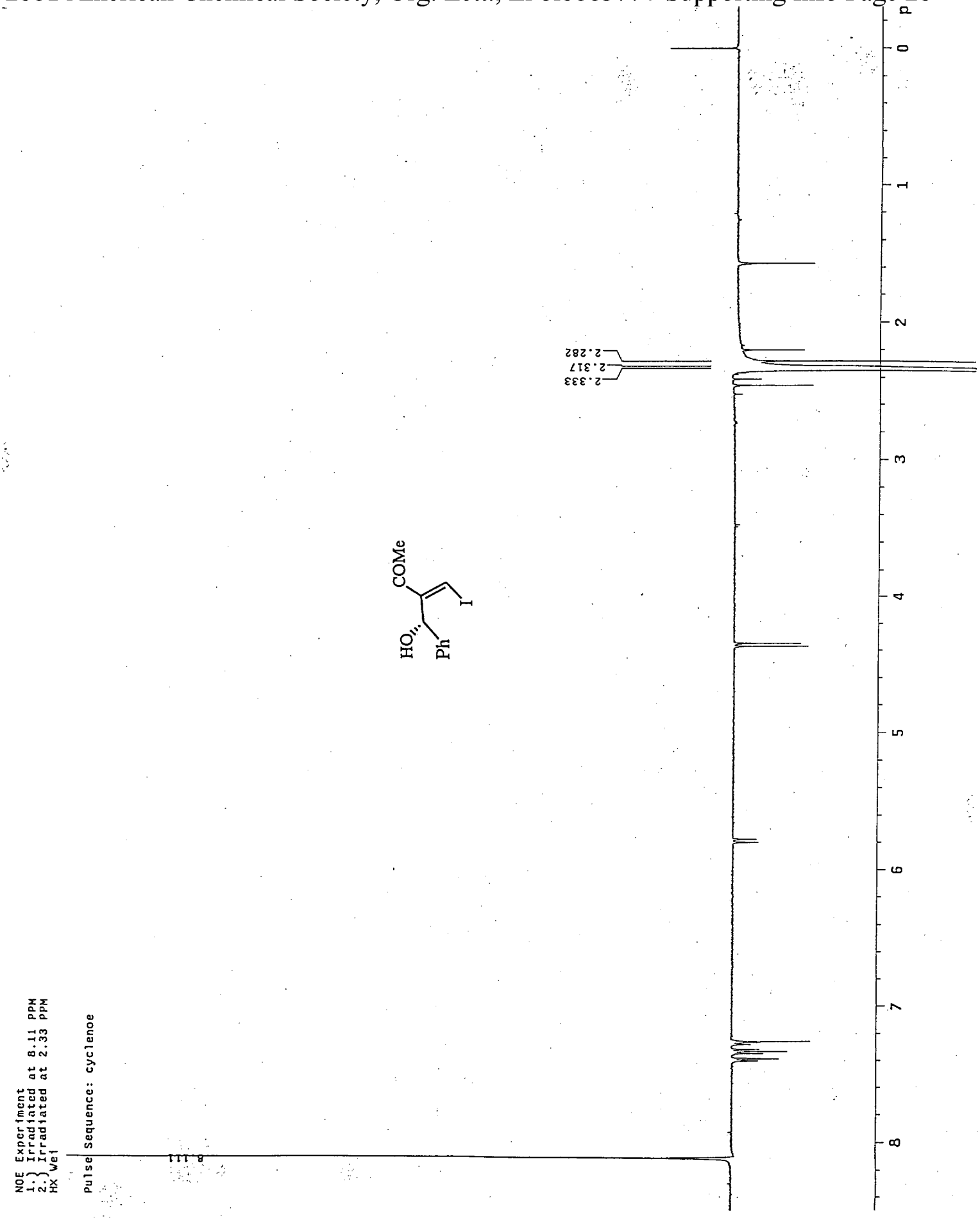








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2.) Irradiated at 2.33 PPM
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HO
Ph
p
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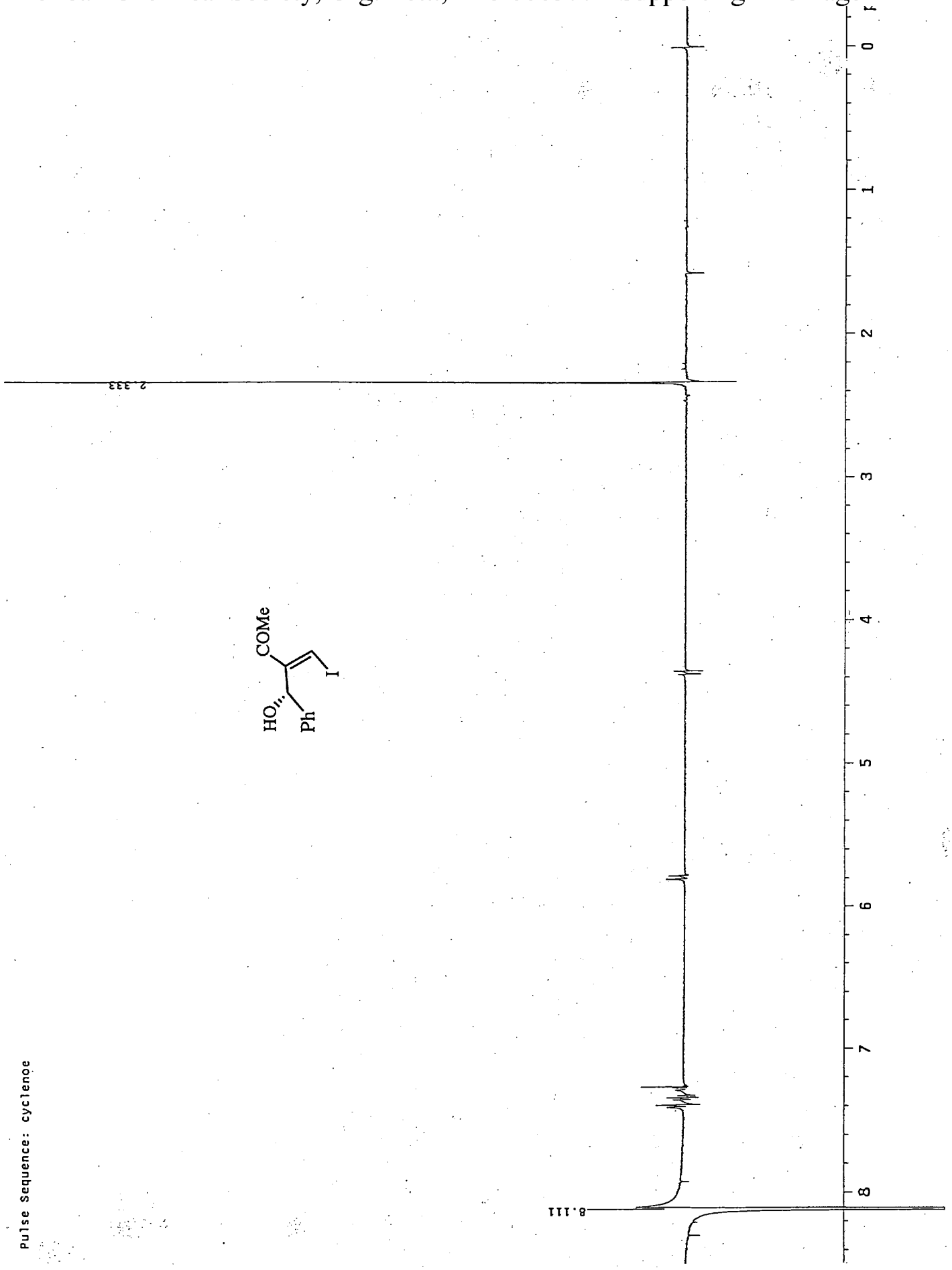
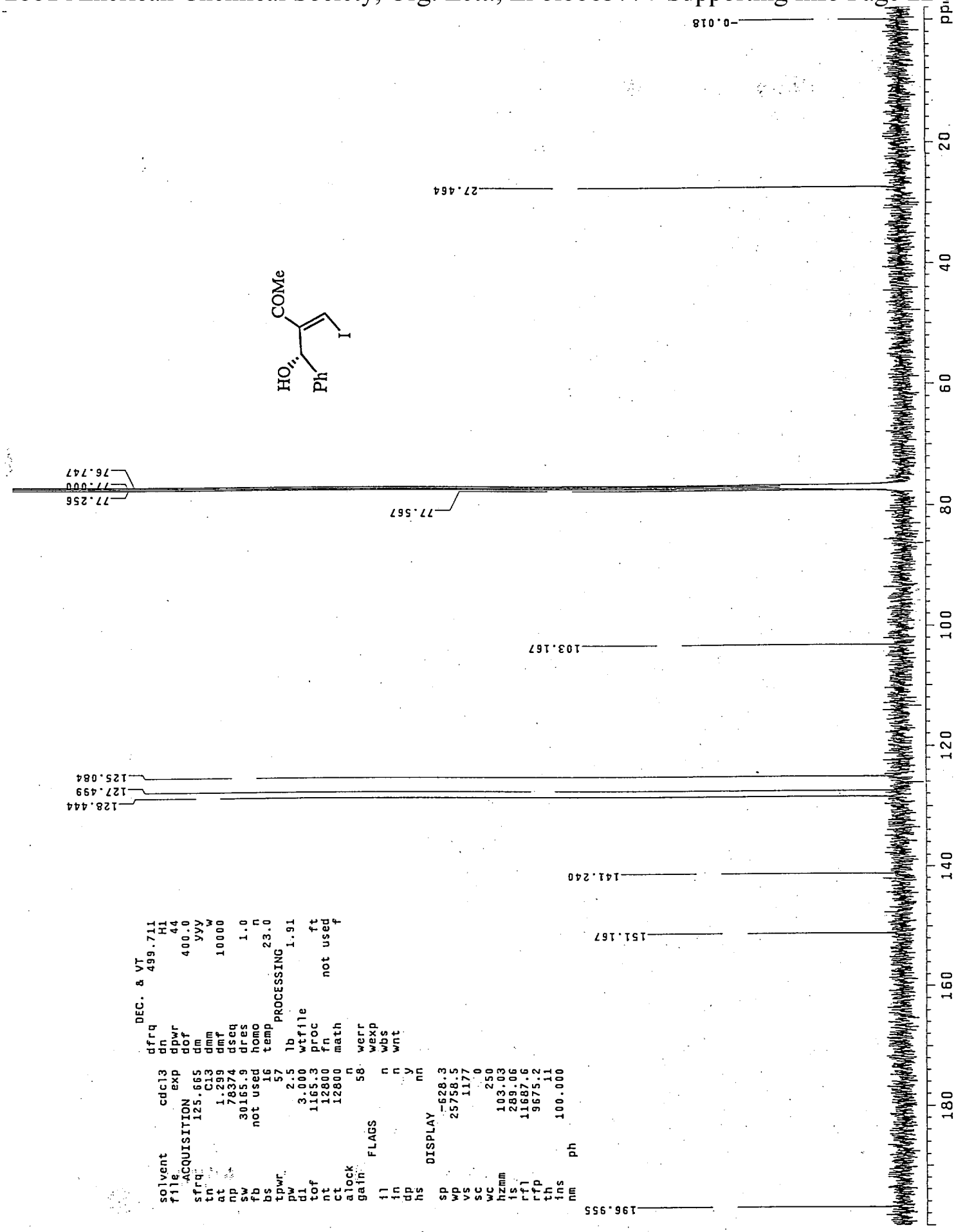
2
3
4
5
6
7
8

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140
160
180
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Ph
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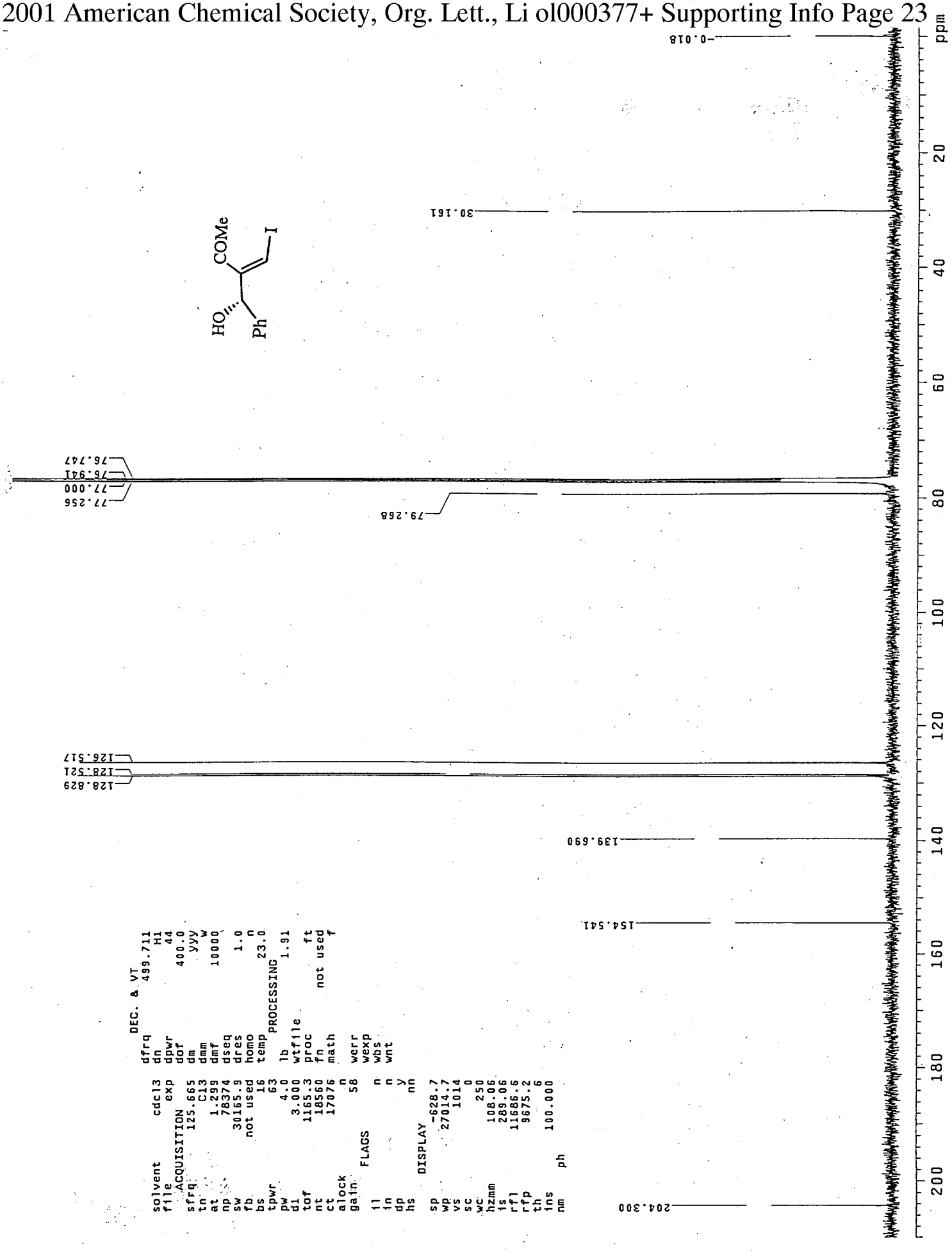

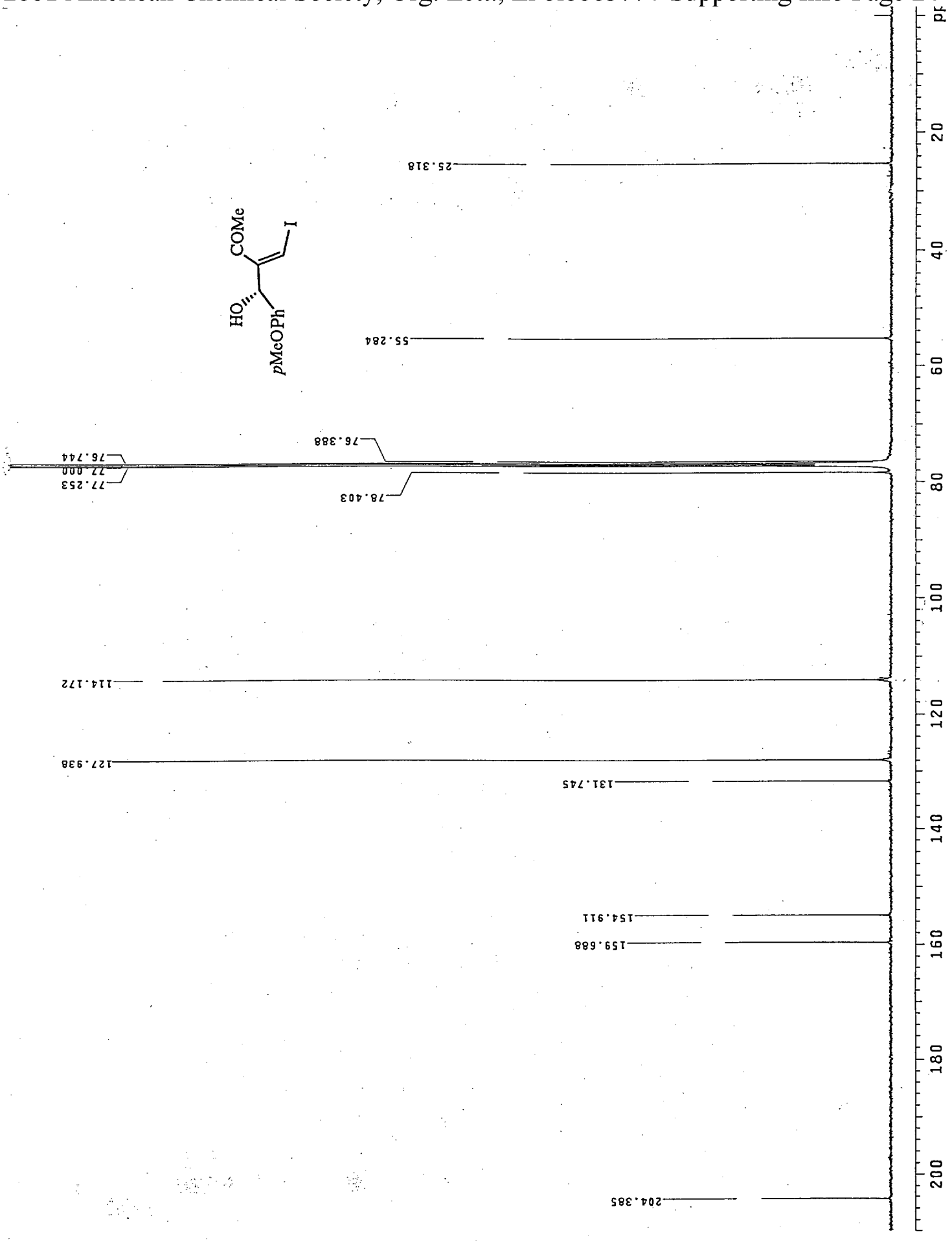
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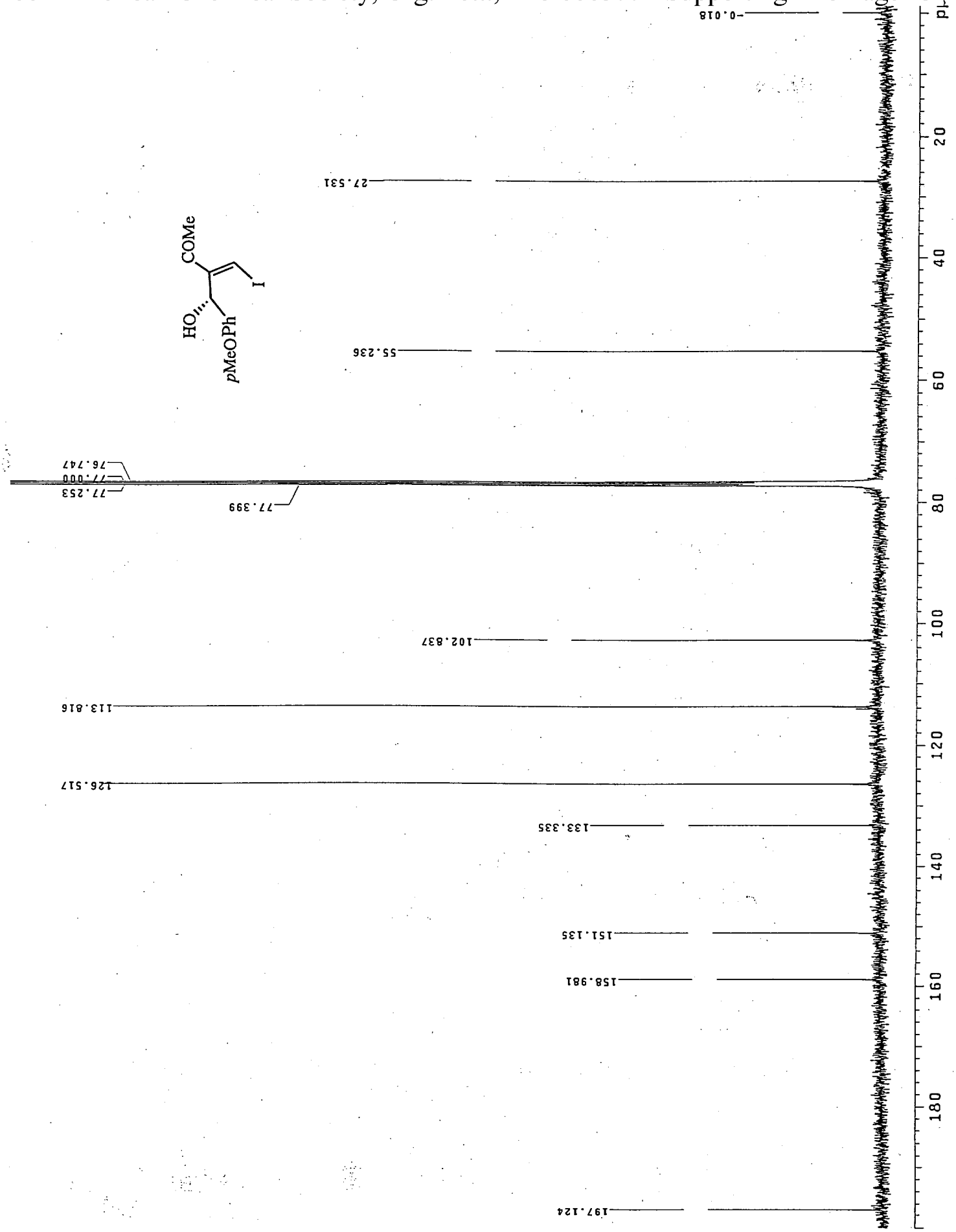
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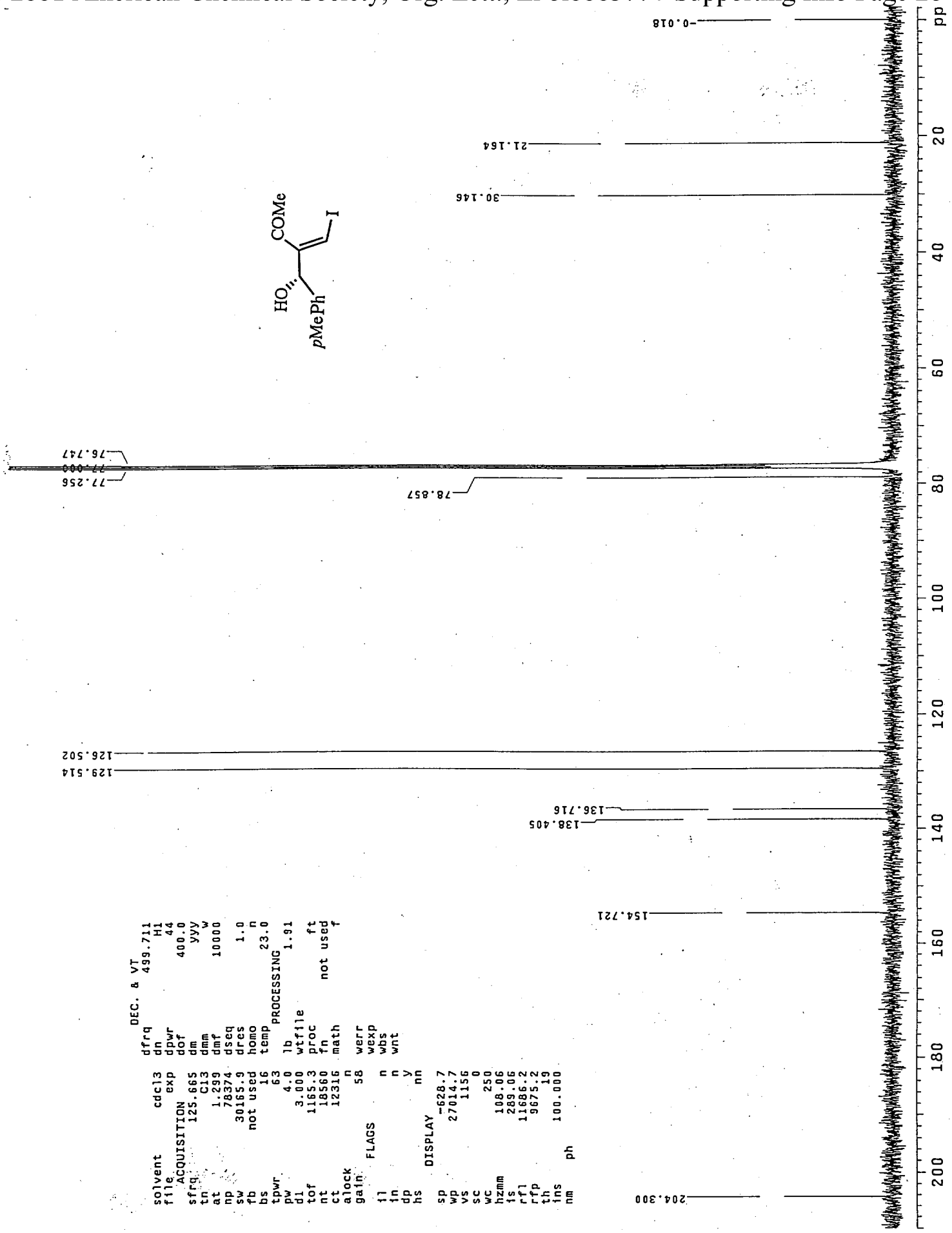
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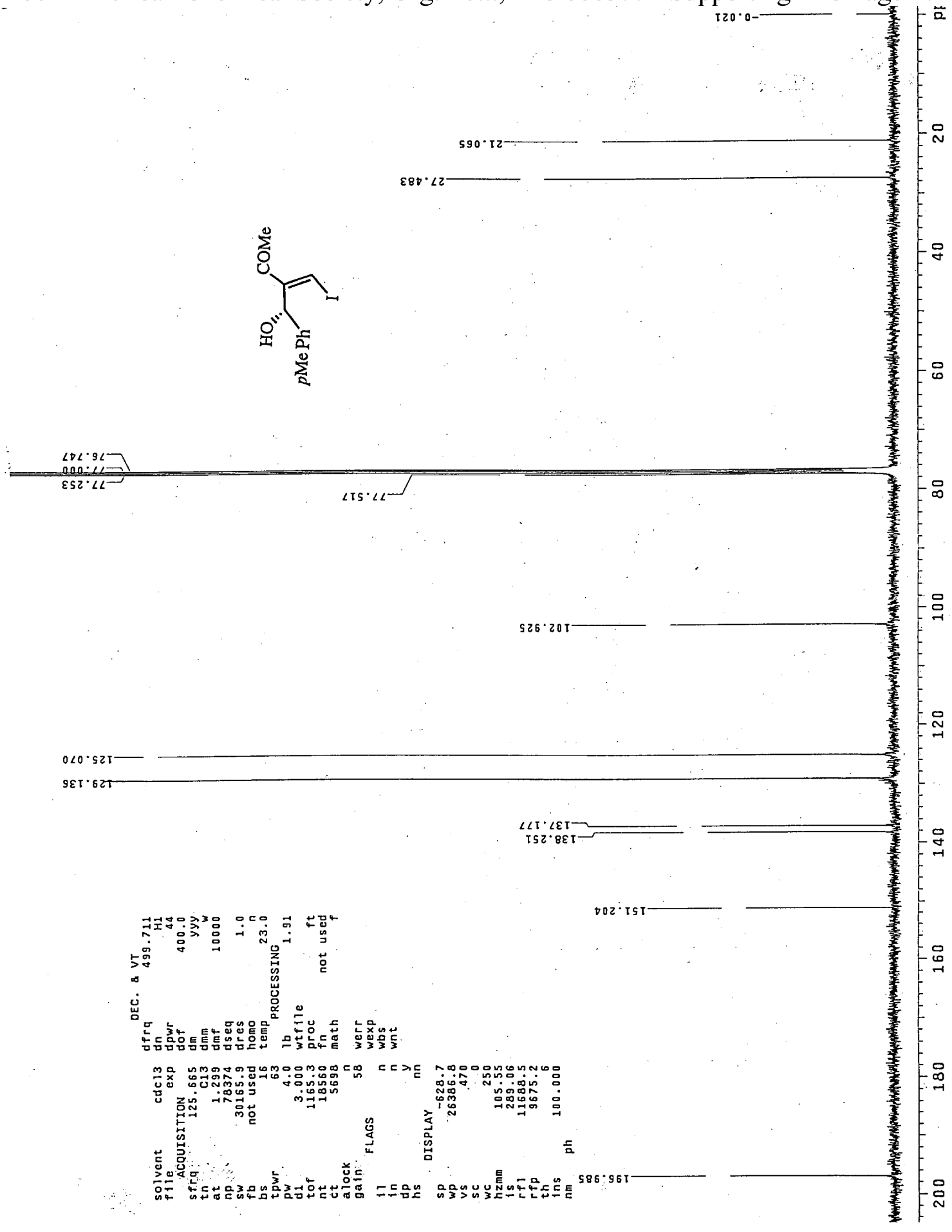

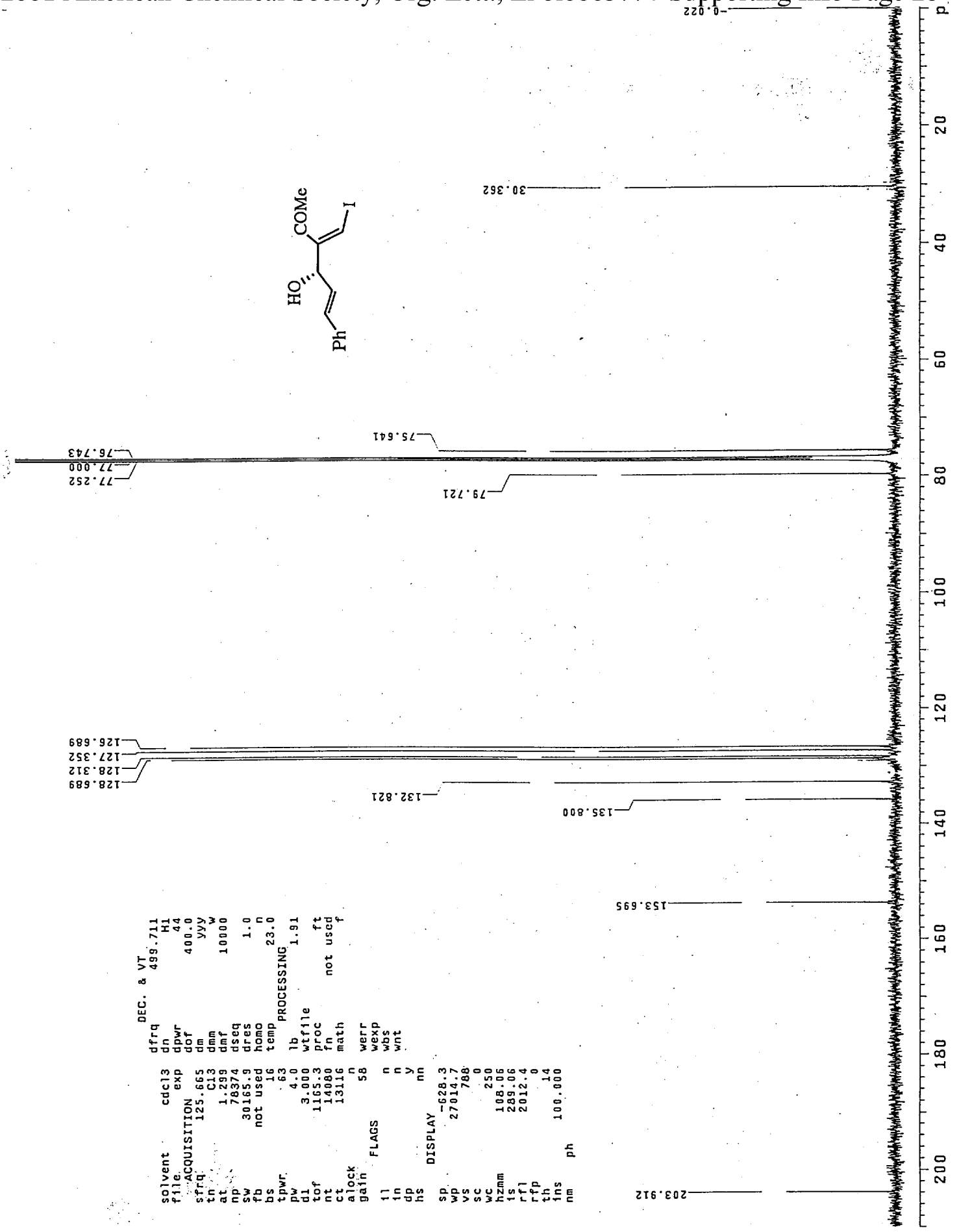

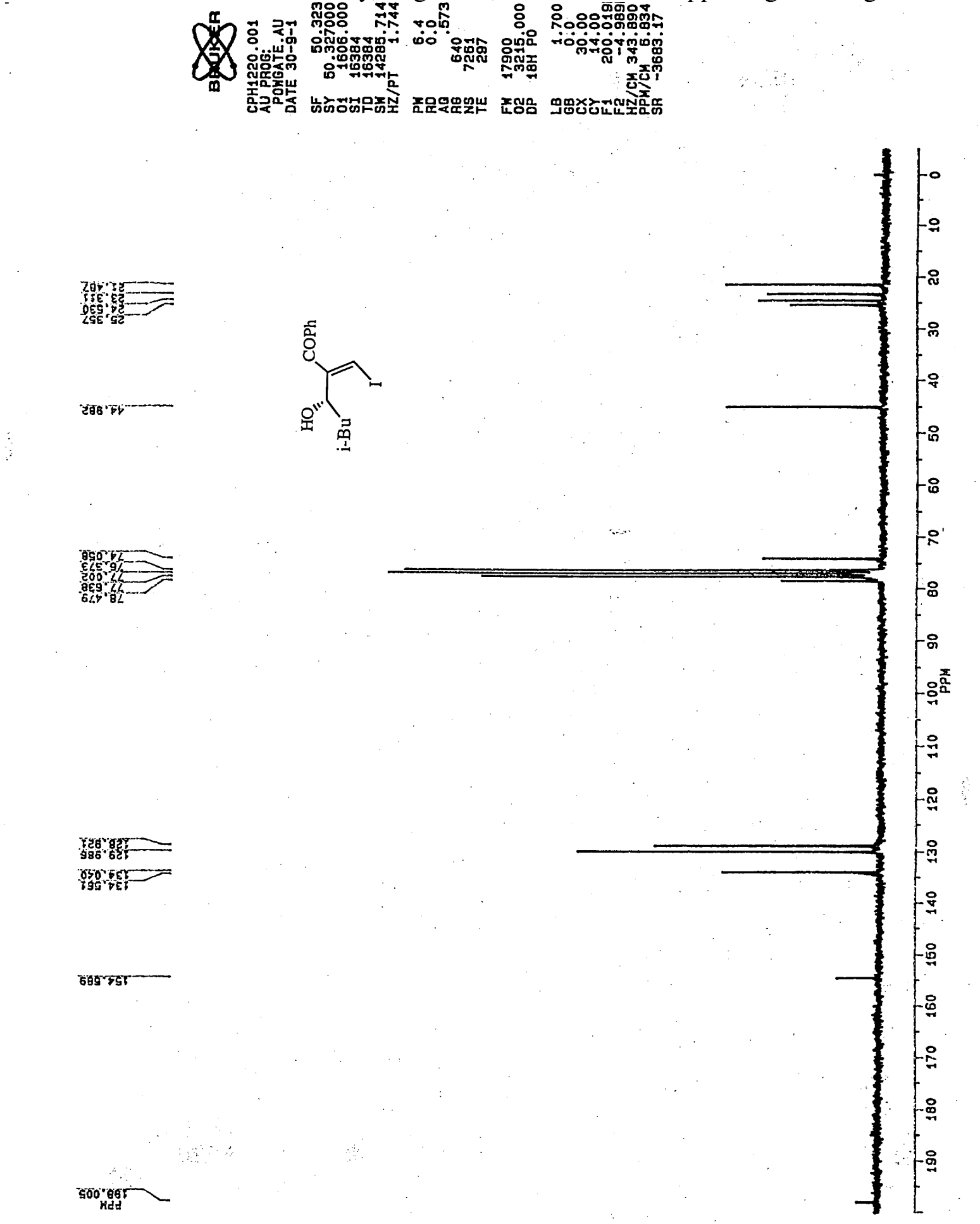

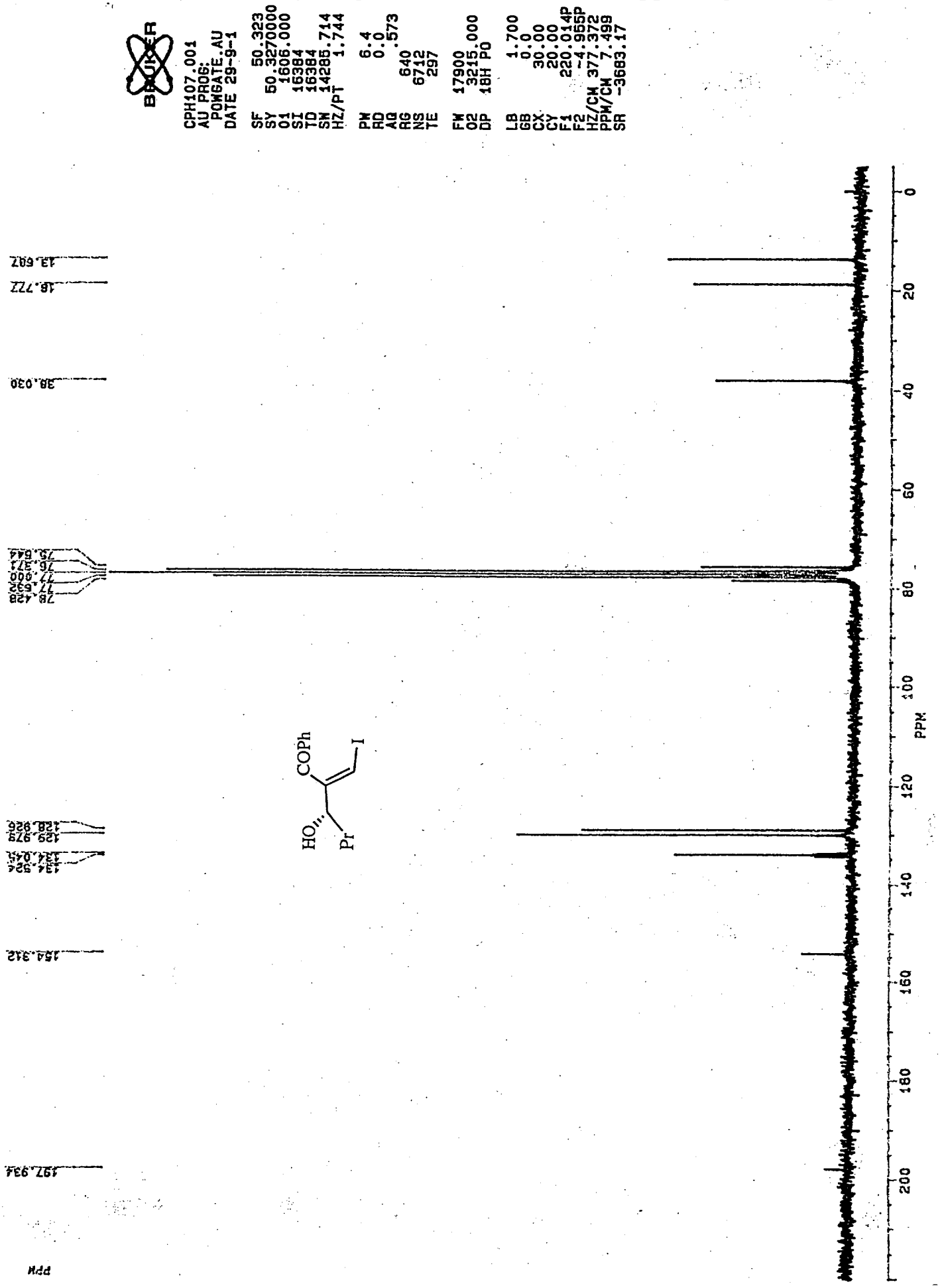

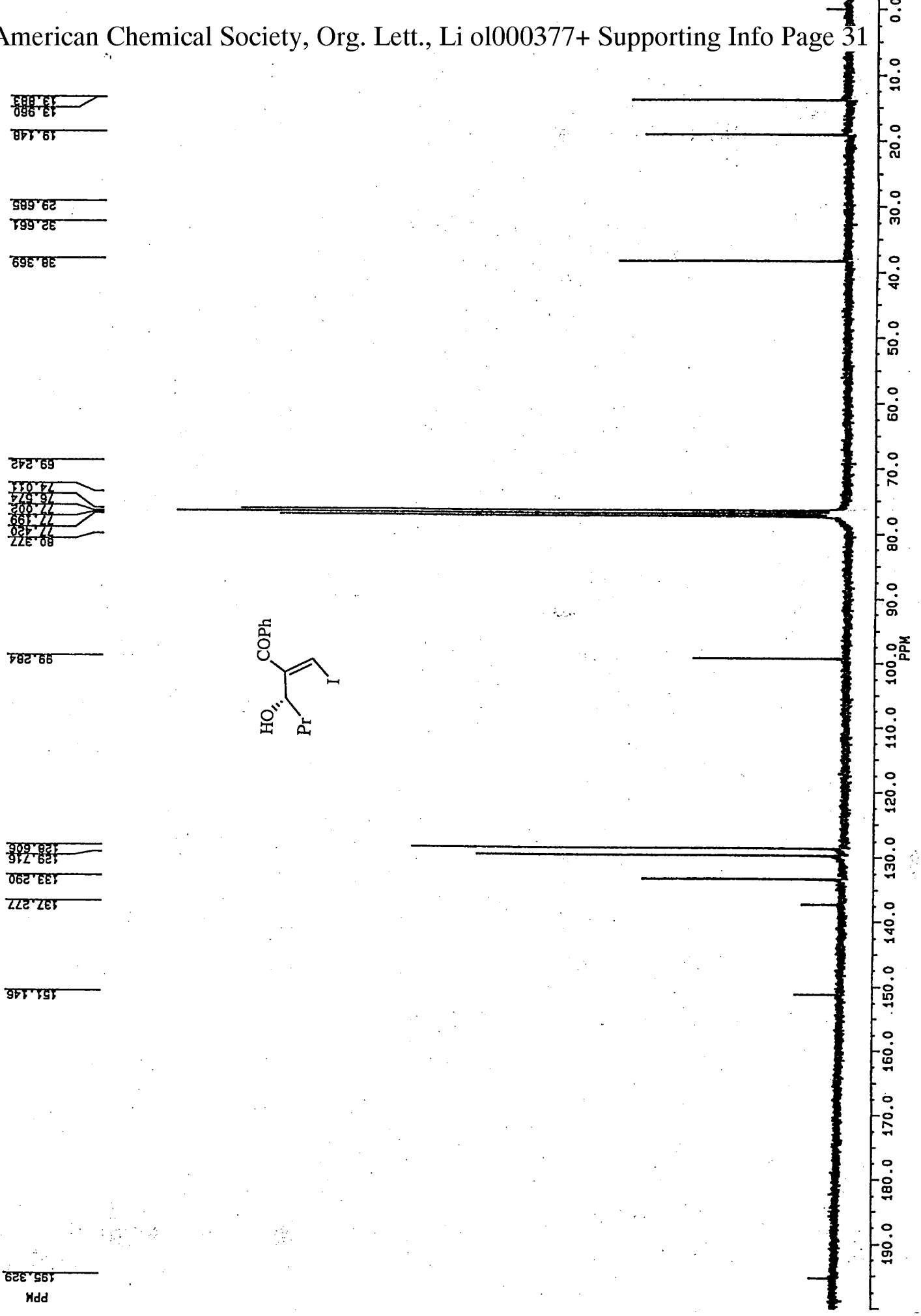
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99.284
128.606
129.716
133.290
137.277
151.146
195.329
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HO
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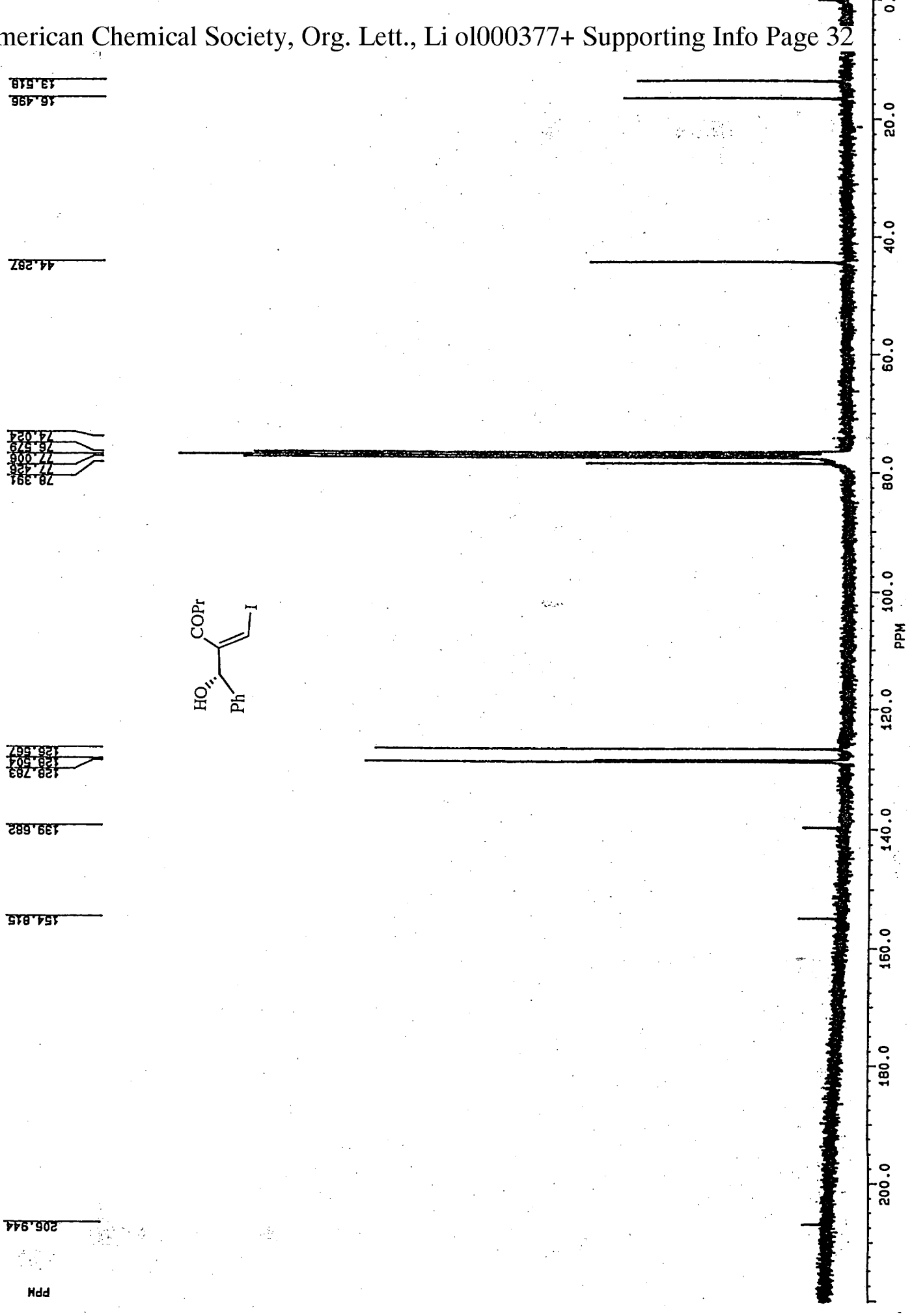
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HO
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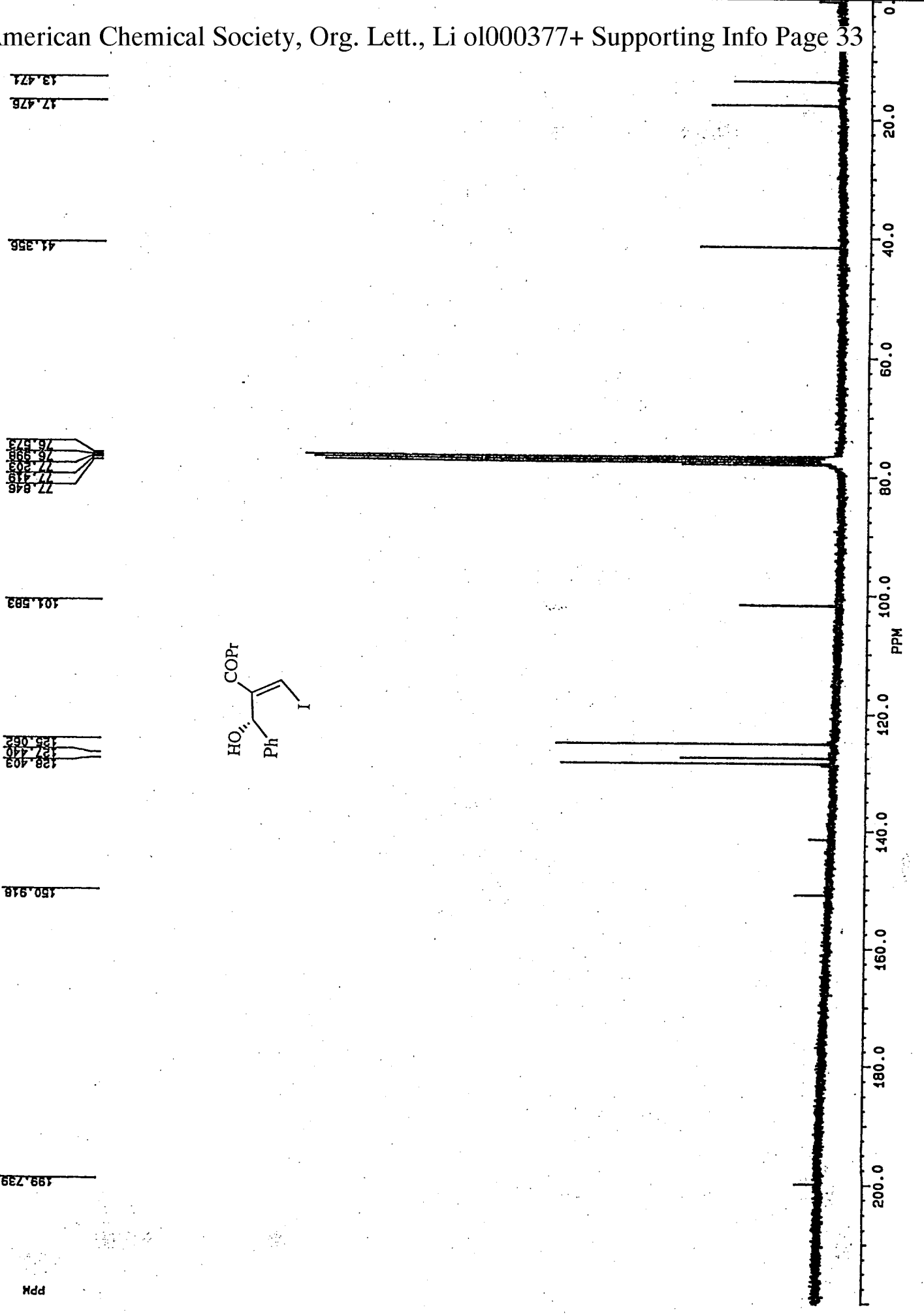

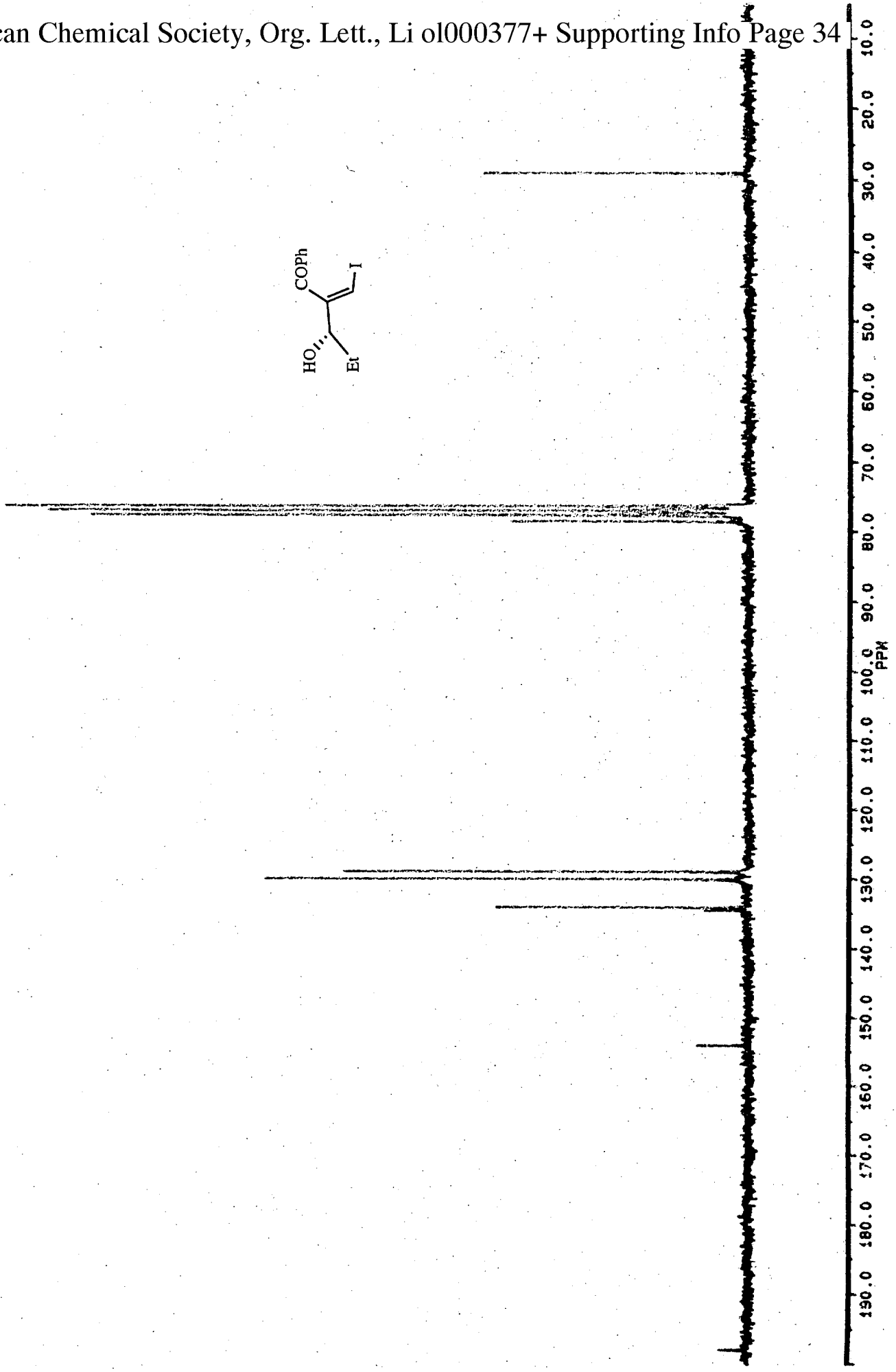
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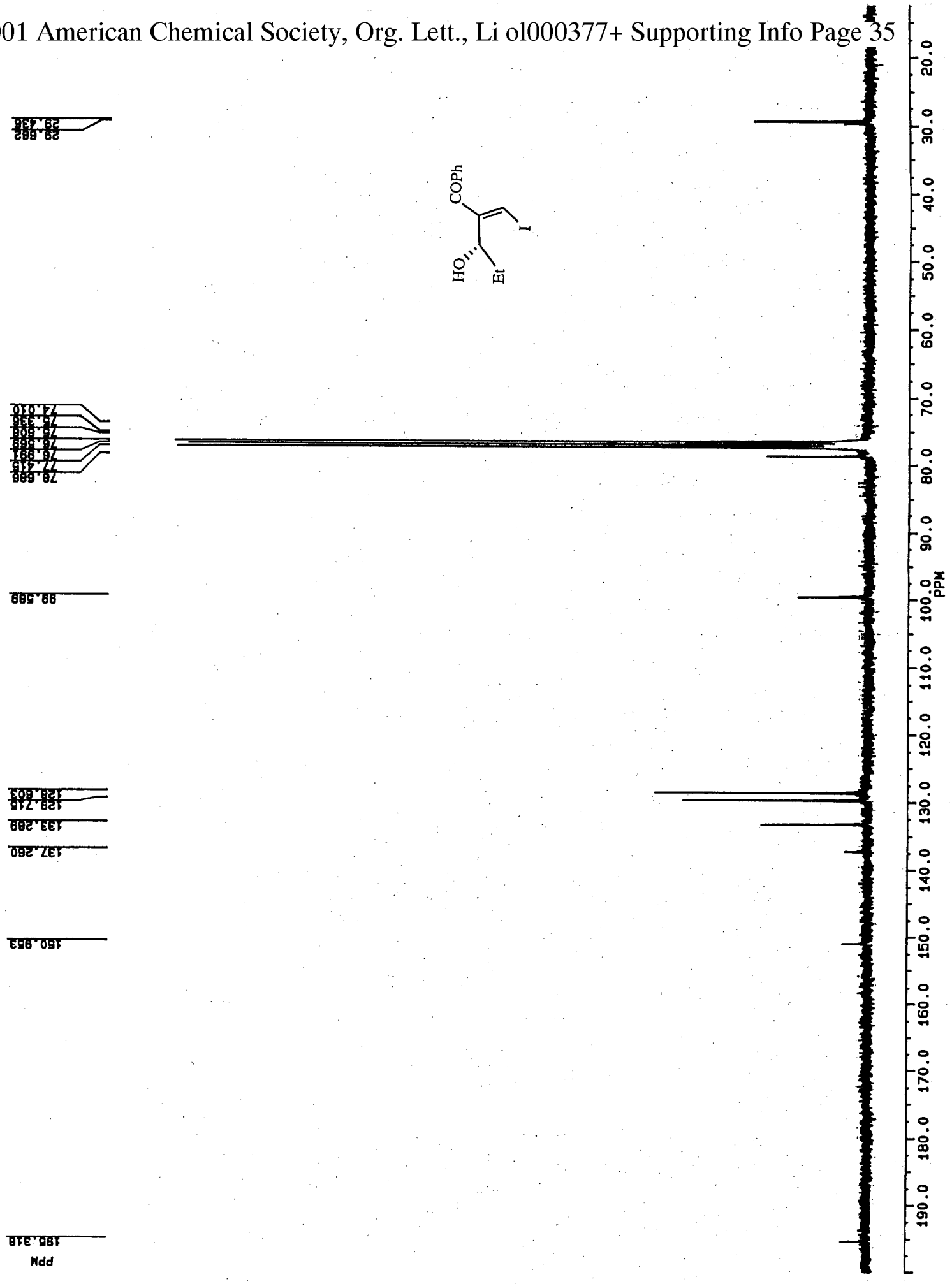
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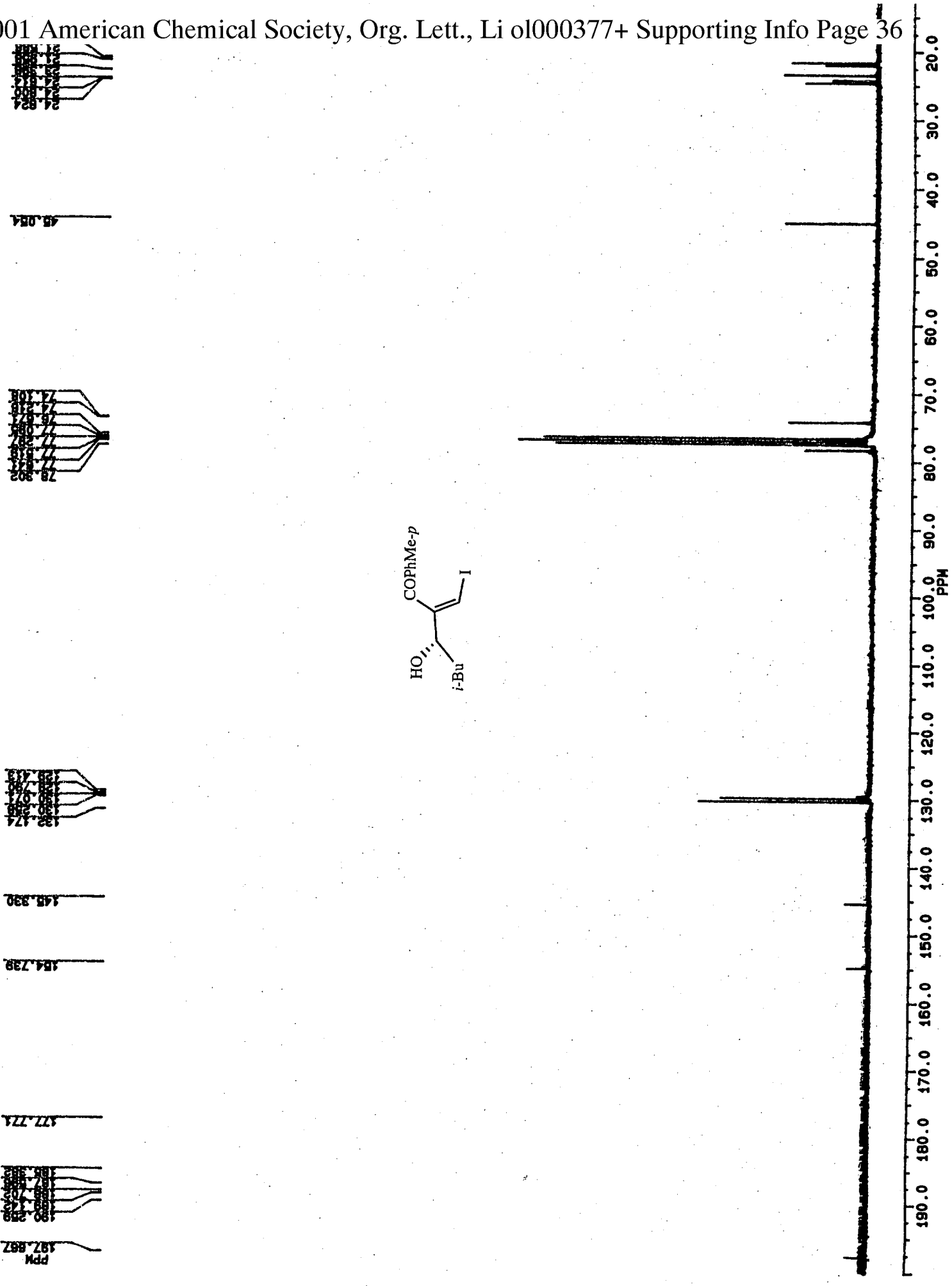
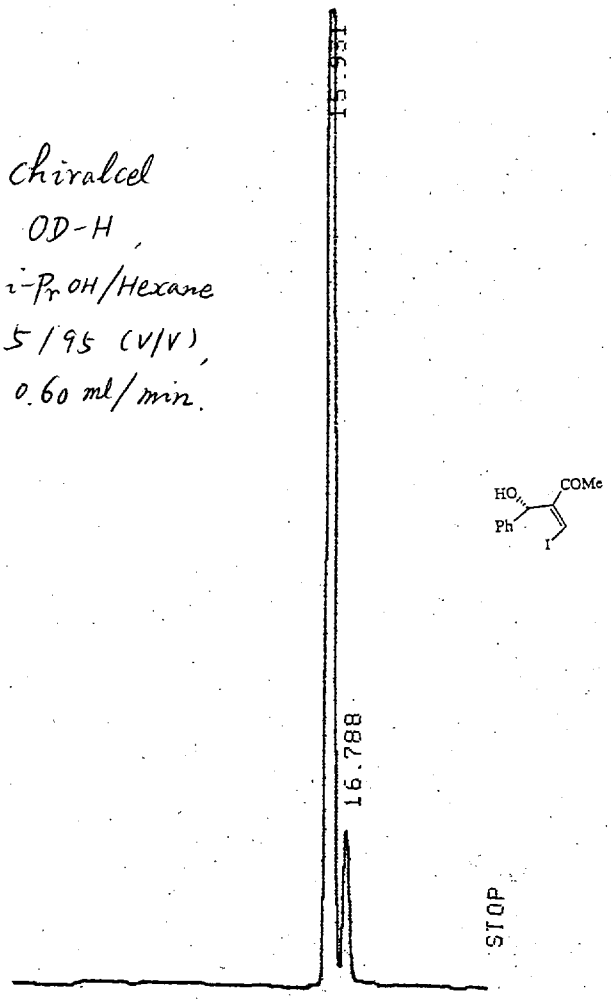
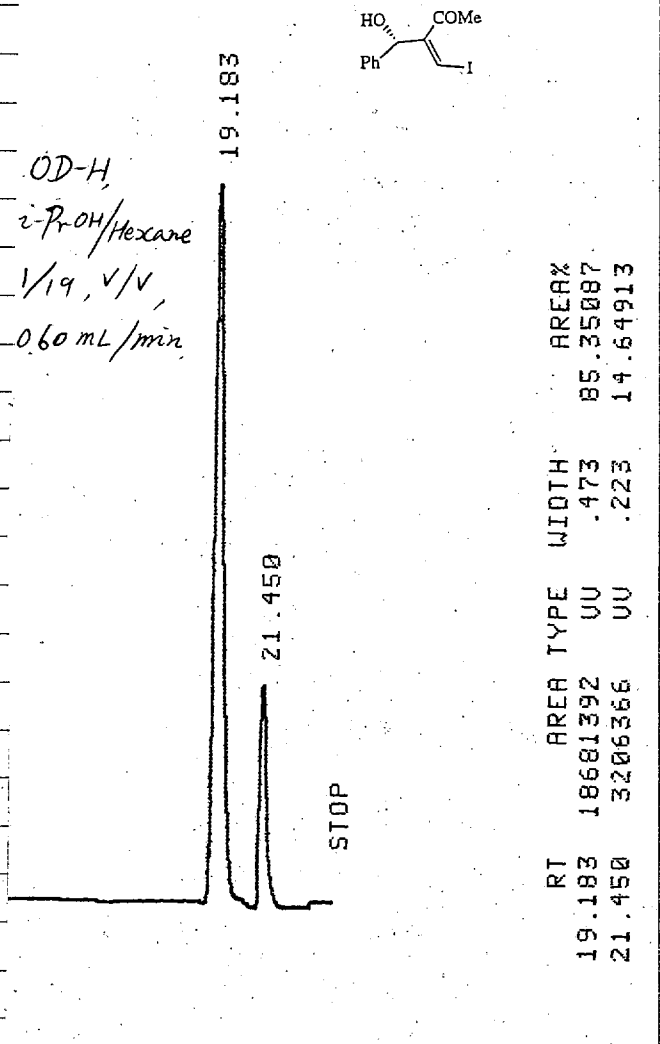
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
PPM


COPhMe-p
I
HO
i-Bu
PPM

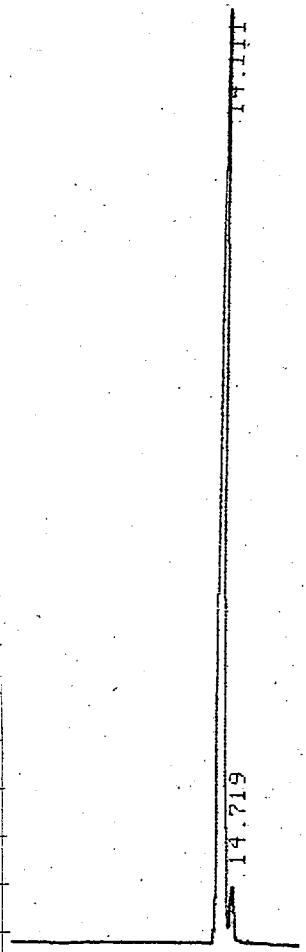
Chiralcel
OD-H,
i-PrOH/Hexane
5/95 (V/V),
0.60 ml/min.

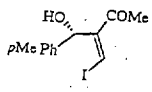


RT	AREA	TYPE	WIDTH	AREA%
15.931	39930784	PU	.403	92.55412
16.788	3212389	UU	.250	7.44588


HO
COMe
Ph
I
19.183
21.450
STOP
OD-H,
i-PrOH/Hexane
1/19, v/v,
0.60 mL/min
RT AREA TYPE WIDTH AREA%
19.183 18681392 UU .473 85.35087
21.450 3206366 UU .223 14.64913

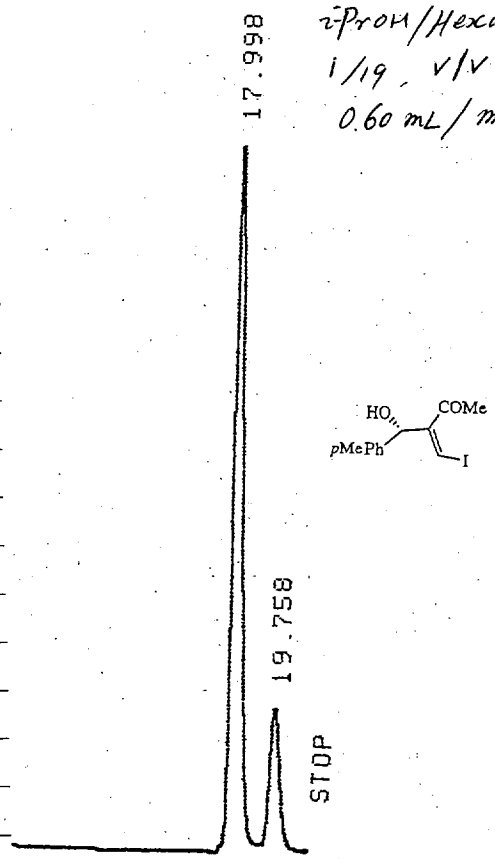
OD-H
i-PrOH/Hexane
(1/19, V/V),
0.60 mL/min





RT	AREA	TYPE	WIDTH	AREA%
14.111	20883680	VV	.338	98.93994
14.719	223751	PV	.175	1.06006

OD-H,
i-PrOH/Hexane
1/19, v/v,
0.60 mL/min.



RT	AREA	TYPE	WIDTH	AREA%
17.998	17798976	PU	.463	82.62481
19.758	3698191	VV	.200	17.37519