

Compound Characterization List

Compounds	¹ H-NMR	¹³ C-NMR	LR-MS	HR-MS	NOESY or NOE
7	x	x	a, c		
8-Br	x	x	a, b, c		x, f
8-I	x	x	a, c		x
8-Cl	x	x	x	x	x
9	x	x	x	x	
10-Br	x	x	x	x	x, f
10-I	x	x	x	x	x, f
11	x	x	x	x	
12-Br	x	x	x	x	x
12-I	x	x	x	x	x
13	x	x	x	x	
14-Br	x	x	x	x	x, f
14-I	x	x	x	e	x
15	x	x	x	e	
16-Br	x	x	a, b, d		f
16-I	x	x	a, d		f
17	x	x	x	x	x
18	x	x	a, d		x
19	x	x	x	x	x
20	x	x	x	x	x
21	x	x	x	x	x
22	x	x	x	x	x
23	x	x	x	x	x
24	x	x	x	x	x
25 ^g	x	x			
26	x	x	x	x	x

x Done, ^a Sample decomposed in EI and CI DIP-MS; ^b Sample decomposed in FAB and electron spray MS; ^c Two major fragment ion peaks are 138 and 139; ^d Two major fragment ion peaks are 136 and 137; ^e Sample decomposed in EI HRMS; ^f The stereochemistry of the double bond was determined by measuring the coupling constants of the two vinyl protons of the vinyl ether after quenching the corresponding α -alkoxy vinyl anion with H₂O in -78°C; ^g The NMR spectra were consistent with the authentic sample.

General Methods. Unless otherwise stated, reactions were performed under argon in flame dried glassware. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium-benzophenone ketyl. Dichloromethane and benzene were distilled from calcium hydride. All other reagents were used as purchased. Flash column chromatography was carried out using 230-400 mesh silica gel from Whatman. ^1H spectra were obtained using either a Bruker WM-360 NMR spectrometer at 360 MHz or a Bruker DRX-400 NMR spectrometer at 400 MHz; and ^{13}C NMR were obtained using a Bruker WM-360 NMR spectrometer at 90 MHz. The nOe and NOESY experiments were carried out on either a Bruker DRX-400 NMR spectrometer at 400 MHz or a Varian Unity-500 NMR spectrometer at 500 MHz. ^1H NMR chemical shifts are reported in ppm relative to residual protonated solvent resonance: CHCl_3 , δ 7.26; $\text{C}_6\text{D}_5\text{H}$, δ 7.15. Coupling constants (J) are reported in Hz. ^{13}C NMR chemical shifts are reported in ppm relative to solvent resonance: CDCl_3 , δ 77.00; C_6D_6 , δ 128.00. Mass spectral data were obtained from The University of Iowa Campus-wide Mass Spectral Facility.

A typical procedure for synthesis of α -chloro vinyl ethers: To a solution of acetylenic ether (1 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added anhydrous methanol (0.99 mmol) followed by slow addition of TMSCl (0.99 mmol) under nitrogen at 25 °C. The reaction mixture was stirred at 25 °C for about 30 minutes until TLC showed the disappearance of the acetylenic ethers (Note: acetylenic ether and α -halo vinyl ethers may decompose on silica gel TLC plates). After removal of the solvent and the side product (MeOTMS) by rotary evaporation, the product can be used without any further purification.

A typical procedure for synthesis of α -bromo vinyl ethers: To a solution of acetylenic ether (1 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added anhydrous methanol (0.99 mmol) followed by slow addition of TMSBr (0.99 mmol) under nitrogen at -40 °C. The reaction mixture was stirred at -40 °C for about 10 minutes and then was allowed to warm up to 25 °C. After removal of the solvent and the side product (MeOTMS) by rotary evaporation, the product can be used without any further purification.

A typical procedure for synthesis of α -iodo vinyl ethers: To a solution of acetylenic ethers (1 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added anhydrous methanol (0.99mmol) followed by slow addition of TMSI (0.99 mmol) under nitrogen at -78 °C.

The reaction mixture was stirred at -78 °C for about 10 minutes and then was allowed to warm up to 25 °C. After removal of the solvent and the side product (MeOTMS) by rotary evaporation, the product can be used without any further purification.

A typical procedure for the generation of α -alkoxy vinyl anions. To a solution of α -bromo vinyl ether (1 mmol) in anhydrous ethyl ether (5 mL) was added *t*-BuLi (1.7 M solution in hexane, 1.9 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for about 20 minutes until TLC showed the disappearance of the α -bromo vinyl ethers.

A procedure for the low order cuprate reaction with 2-cyclohexenone. To a clear solution of CuI (65 mg, 0.35 mmol) and Me₂S (103 μ L, 1.4 mmol) in 0.5 mL THF at -40 °C was added α -alkoxy vinyl anion (0.693 mmol) which was prepared by the typical procedure. The reaction mixture was stirred at -40 °C for 30 minutes. The solution was cooled to -78 °C and 2-cyclohexen-1-one (25 μ L, 0.245 mmol) was added. The reaction mixture was stirred at -78 °C until TLC showed the disappearance of the starting material. 5 mL of saturated aqueous ammonium chloride which contained 10% ammonium hydroxide (26 degree) was added and the reaction mixture was stirred at room temperature for about 30 minutes. Extracted with ether for three times, washed with brine, the combined organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified with silicon gel flash column chromatography (deactivated 3% triethylamine-hexane) to afford 49.9 mg compound **21** (78%).

A Procedure for the high order cuprate reaction with 2-cyclohexenone. To a clear solution of CuCN (27.9 mg, 0.311 mmol) and LiCl (26.4 mg, 0.622 mmol) in 0.5 mL THF at -40 °C was added α -alkoxy vinyl anion (0.622 mmol) which was prepared by the typical procedure. The reaction mixture was stirred at -40 °C for 30 minutes, and then the solution was cooled to -78 °C. 2-cyclohexen-1-one (22 μ L, 0.218 mmol) was added. The reaction mixture was stirred at -78 °C until TLC showed the disappearance of the starting material. 5 mL of saturated aqueous ammonium chloride which contained 10% ammonium hydroxide (26 degree) was added and the reaction mixture was stirred at room temperature for about 30 minutes. Extracted with ether for three times, washed with brine, the combined organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified with silicon gel flash column chromatography (deactivated 3% triethylamine-hexane) to afford 50.3 mg compound **21** (88%).

A Procedure for the mixed high order cuprate reaction with 2-cyclohexenone. To a suspension of CuCN (41 mg, 0.464 mmol) in 1mL ethyl ether was added MeLi (0.464 mmol) in -78 °C. The reaction mixture was warmed up to about -10°C until the solid disappeared. The solution was cooled to -78 °C and α -alkoxy vinyl anion (0.464 mmol.) which was prepared by typical procedure was added. The reaction mixture was stirred at -78 °C until TLC showed the disappearance of the starting material. 5 mL of saturated aqueous ammonium chloride which contained 10% ammonium hydroxide (26 degree) was added and the reaction mixture was stirred at room temperature for about 30 minutes. Extracted with ether for three times, washed with brine, the combined organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified with silicon gel flash column chromatography (deactivated 3% triethylamine-hexane) to afford 50.7 mg compound **21** (83%).

Mass Spectra Data

Compound **8-Cl**: EI HRMS m/z 230.1425 (M^+), calcd for $C_9H_{17}OI$ 230.1437.

Compound **9**: EI HRMS m/z 112.0887 (M^+), calcd for $C_7H_{12}O$ 112.0888

Compound **10-Br**: EI HRMS m/z 192.0174 (M^+), calcd for $C_7H_{13}OBr$ 192.0150.

Compound **10-I**: EI HRMS m/z 240.0023 (M^+), calcd for $C_7H_{13}OI$ 240.0011.

Compound **11**: EI HRMS m/z 125.0973 (M^+-CH_3), calcd for $C_8H_{13}O$ 125.0966

Compound **12-Br**: EI HRMS m/z 220.0466 (M^+), calcd for $C_9H_{17}OBr$ 220.0463

Compound **12-I**: EI HRMS m/z 268.0328 (M^+), calcd for $C_9H_{17}OI$ 268.0324.

Compound **13**: EI HRMS m/z 164.1219 (M^+), calcd for $C_{11}H_{16}O$ 164.1201

Compound **14-Br**: EI HRMS m/z 244.0458 (M^+), calcd for $C_{11}H_{17}OBr$
244.0463.

Compound **14-I**: EI LRMS (50ev) m/z 292 (M^+); $C_{11}H_{17}OI$

Compound **15**: EI LRMS (50ev) m/z 206 (M^+); $C_{14}H_{22}O$

Compound **17**: EI HRMS m/z 262.1560 (M^+), calcd for $C_{16}H_{22}O_3$ 262.1569

Compound **19**: EI HRMS m/z 268.2247 (M^+), calcd for $C_{16}H_{32}OSi$ 268.2222

Compound **20**: EI HRMS m/z 343.1235 (M^+-CH_3), calcd for $C_{15}H_{29}O^{118}Sn$
343.1234

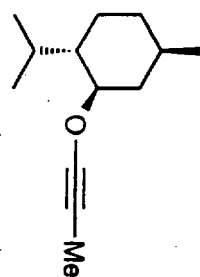
Compound **21**: EI HRMS m/z 262.1934 (M^+), calcd for $C_{17}H_{26}O_2$ 262.1933.

Compound **22**: EI HRMS m/z 222.1990 (M^+), calcd for $C_{15}H_{26}O$ 222.1984

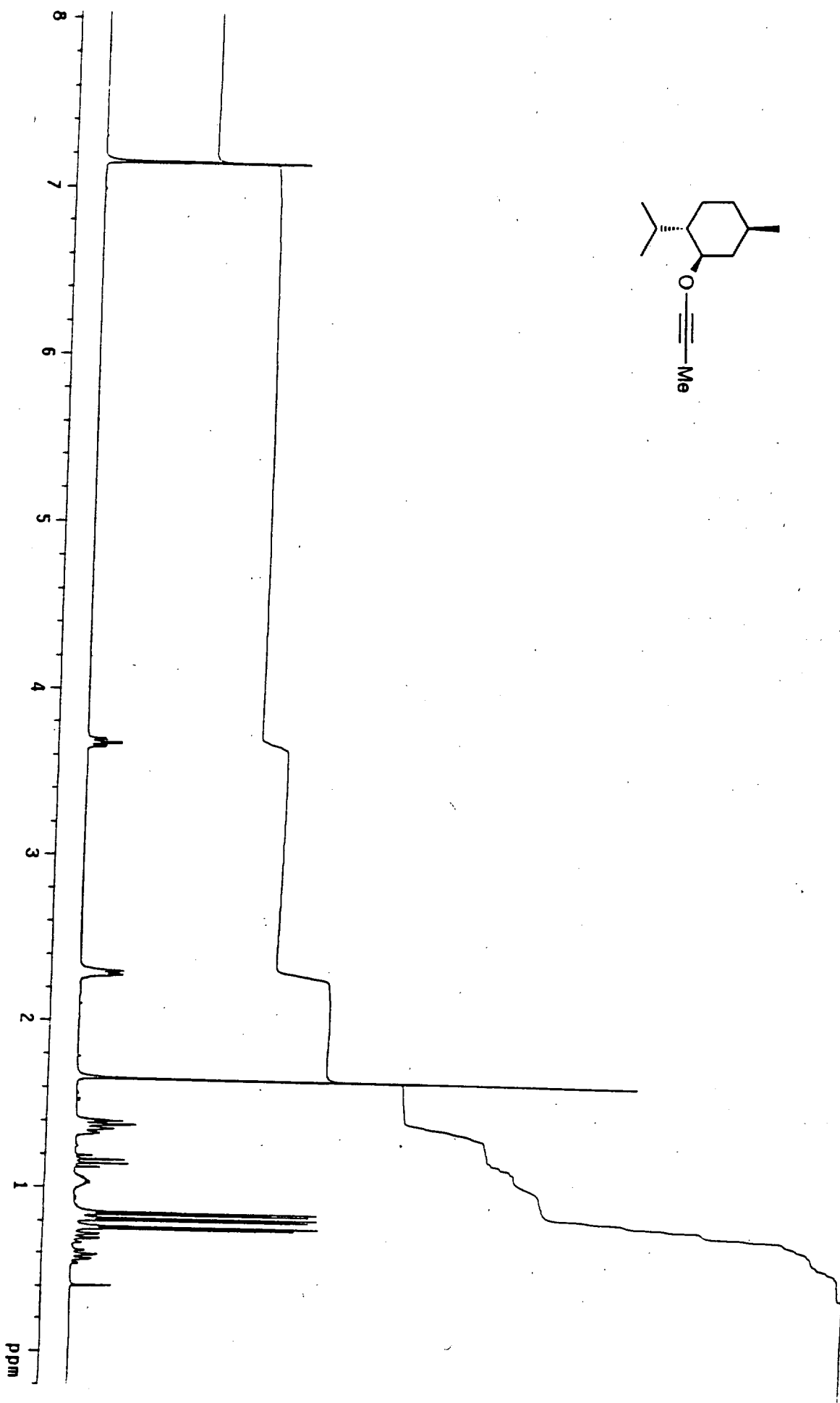
Compound **23**: EI HRMS m/z 152.1180 (M^+), calcd for $C_{10}H_{16}O$ 152.1201

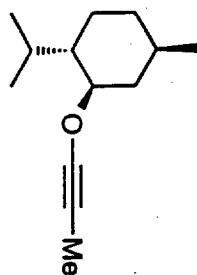
Compound **24**: EI HRMS m/z 200.1412 (M^+), calcd for $C_{11}H_{20}O_3$ 200.1412

Compound **26**: EI HRMS m/z 272.2143 (M^+), calcd for $C_{19}H_{28}O$ 272.2140

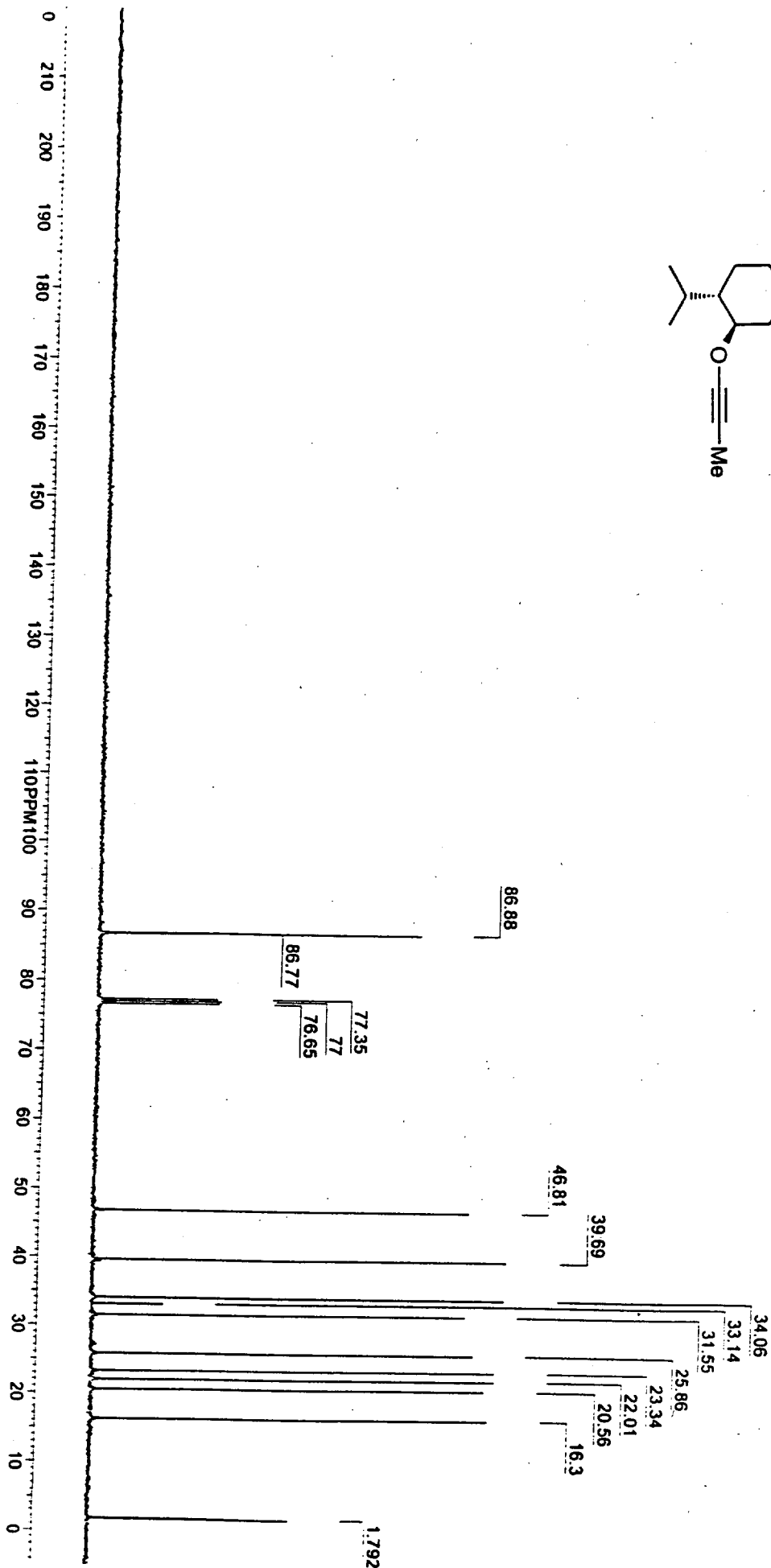


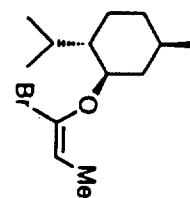
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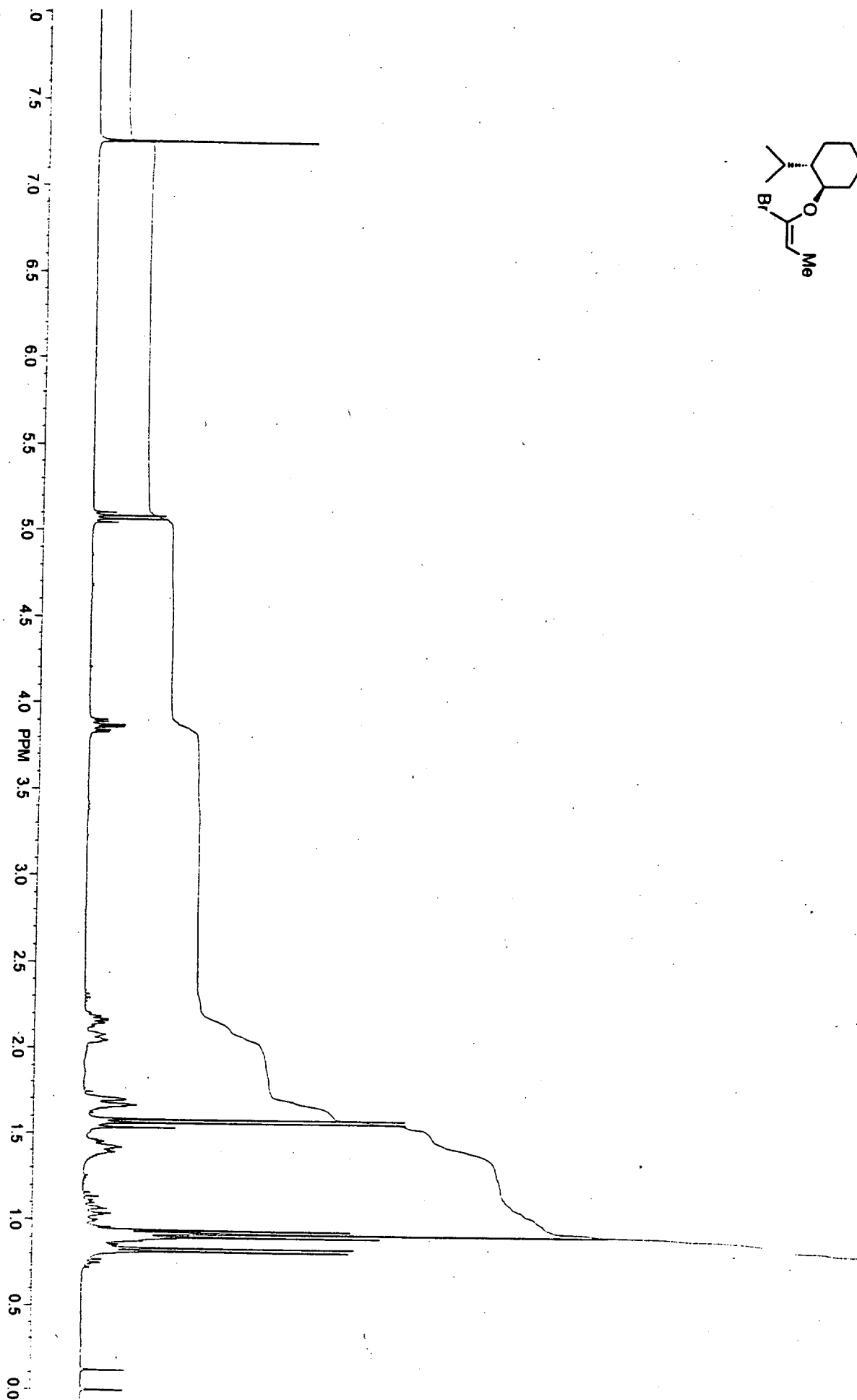


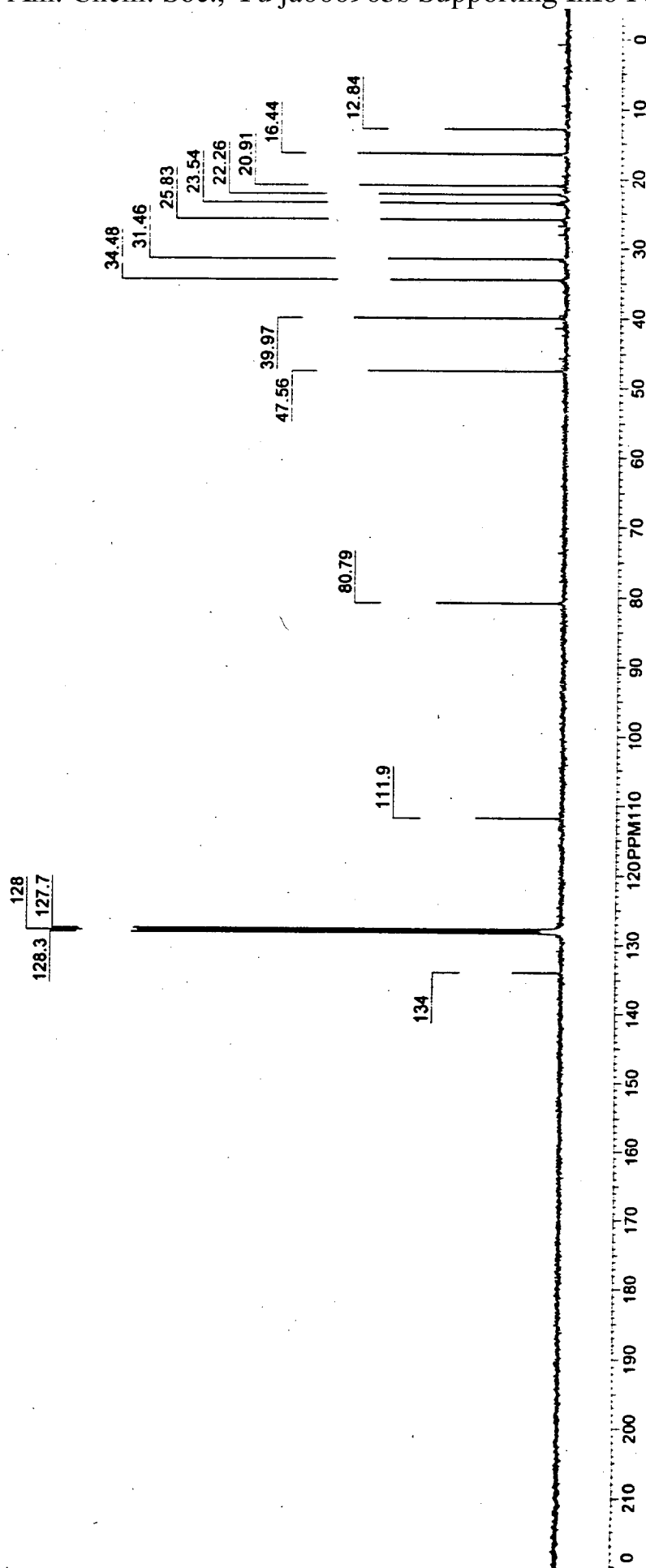
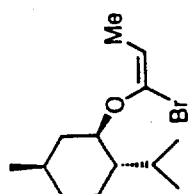
90MHz ¹³C-NMR of 7



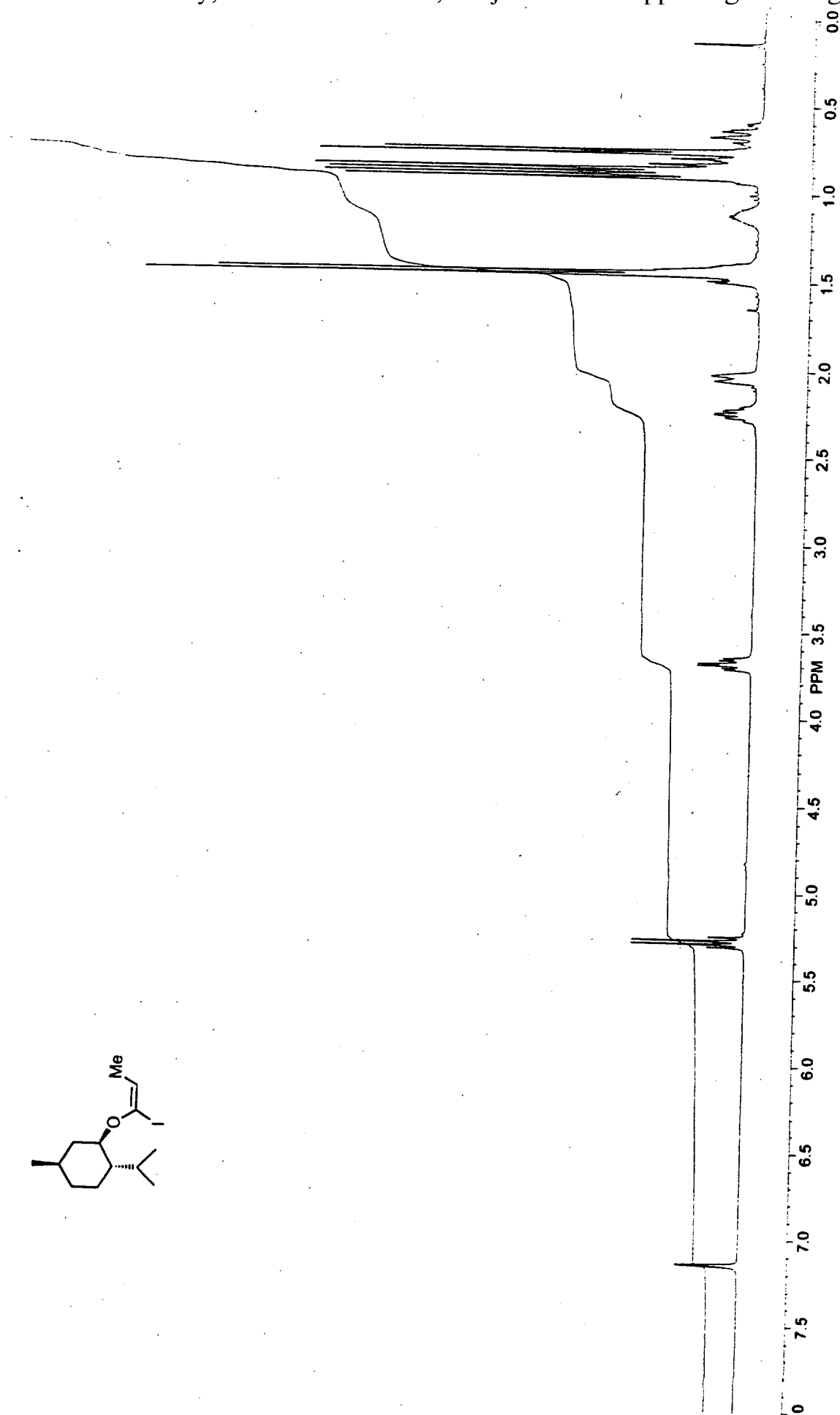
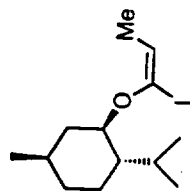


360MHz ^1H -NMR of 8-Br

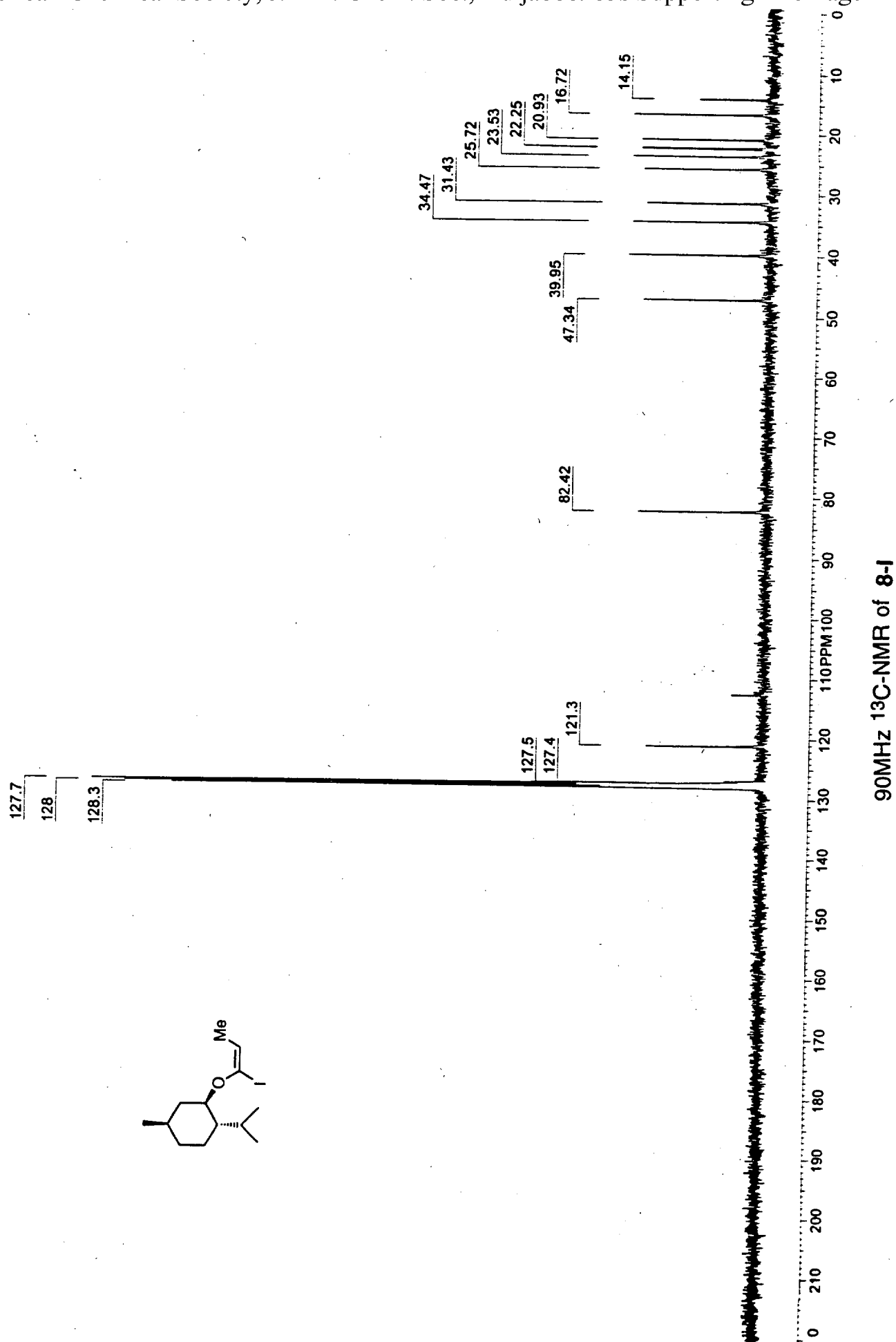


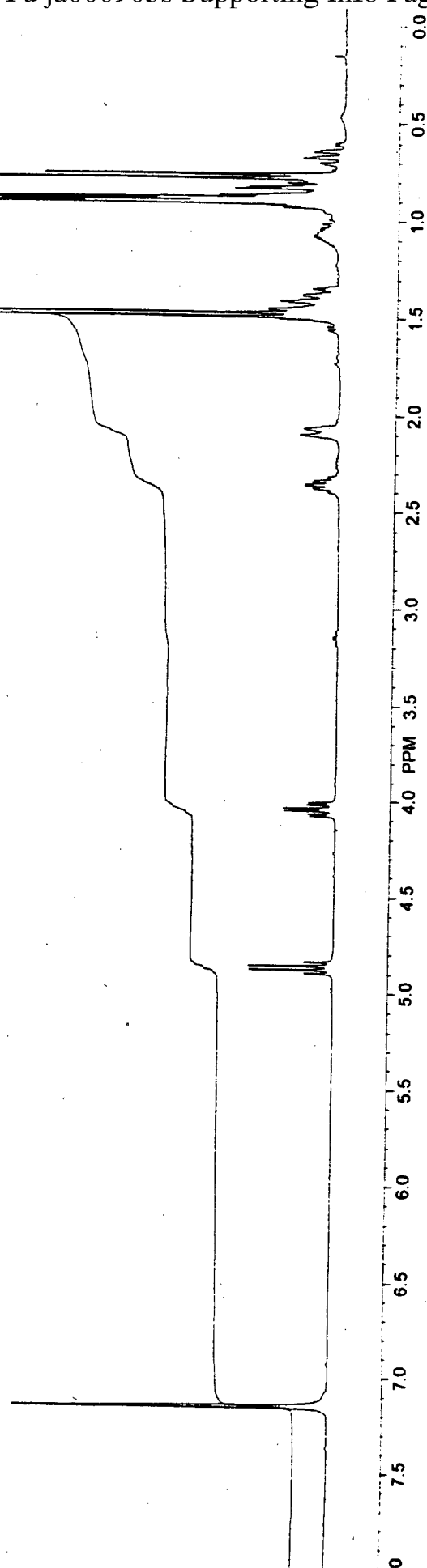
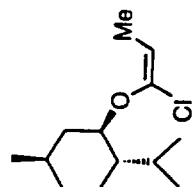


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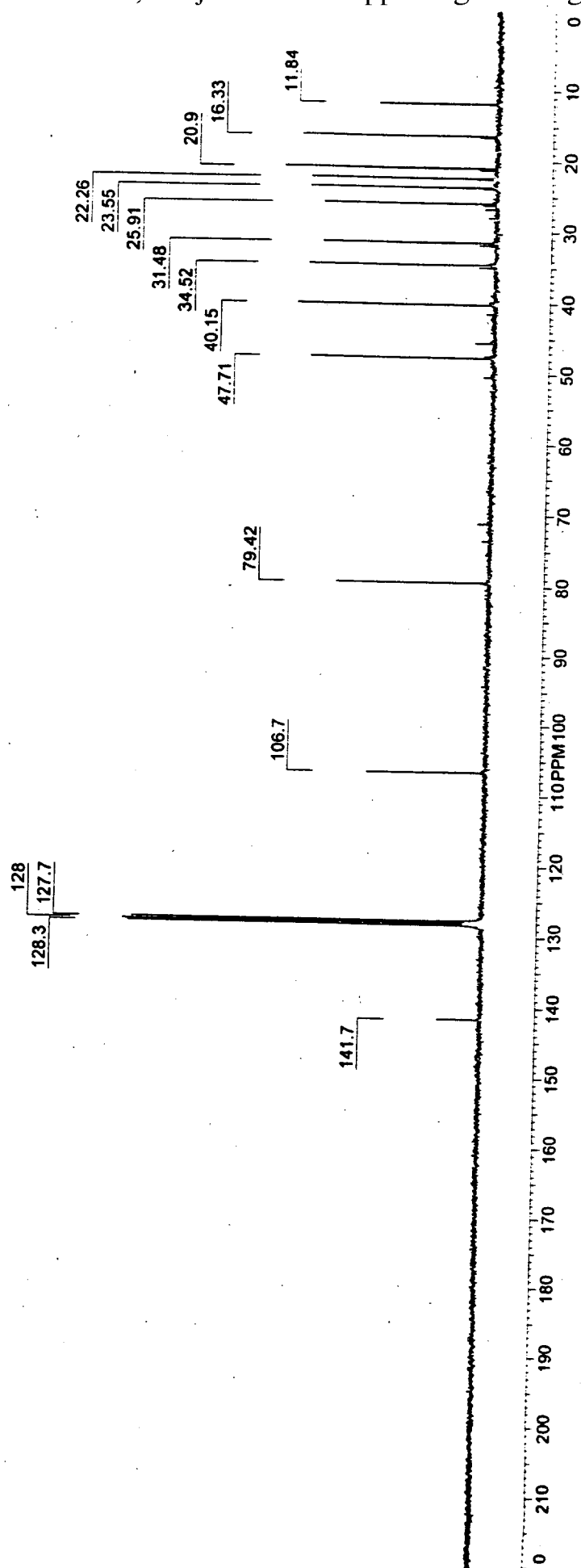
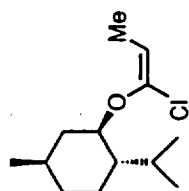


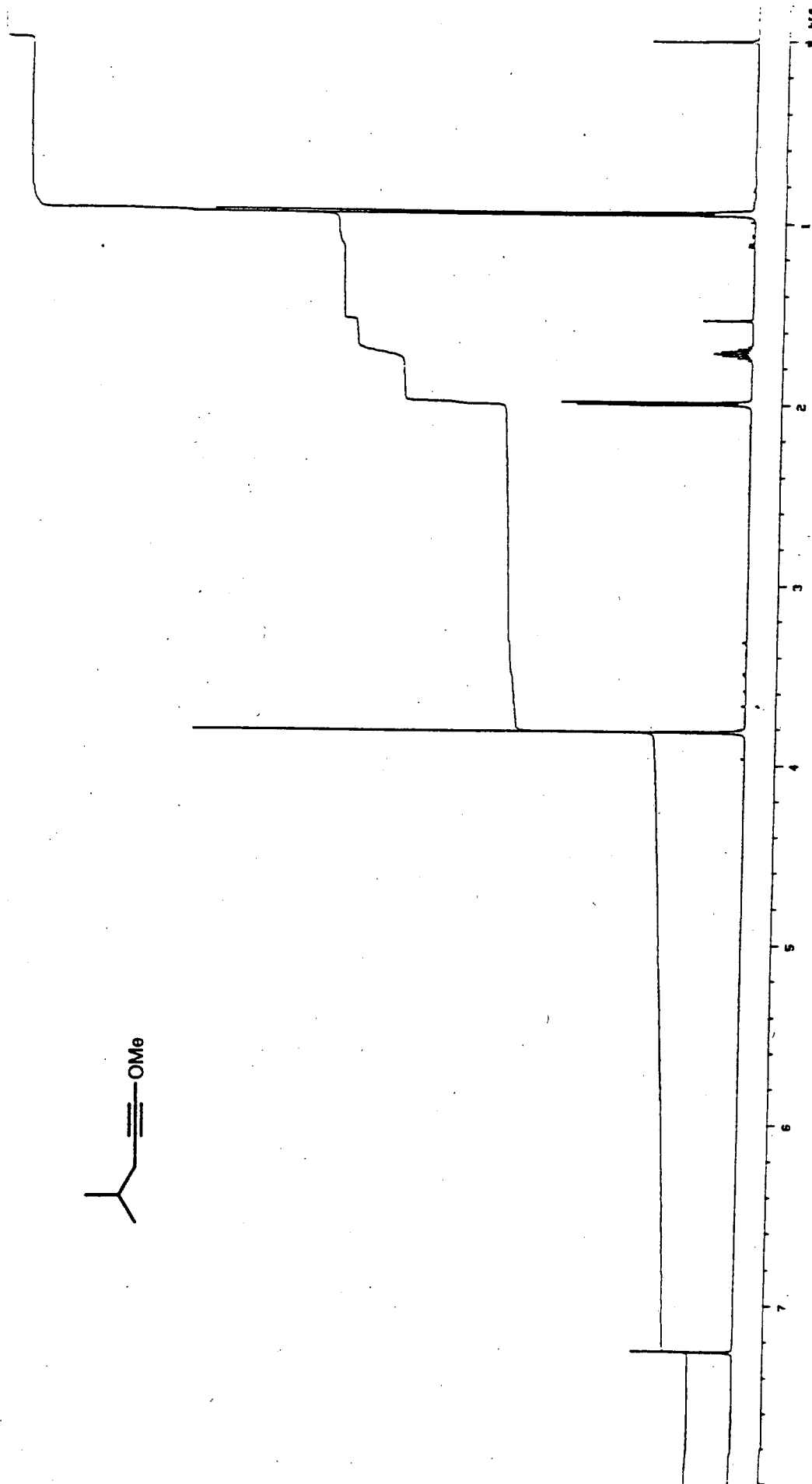
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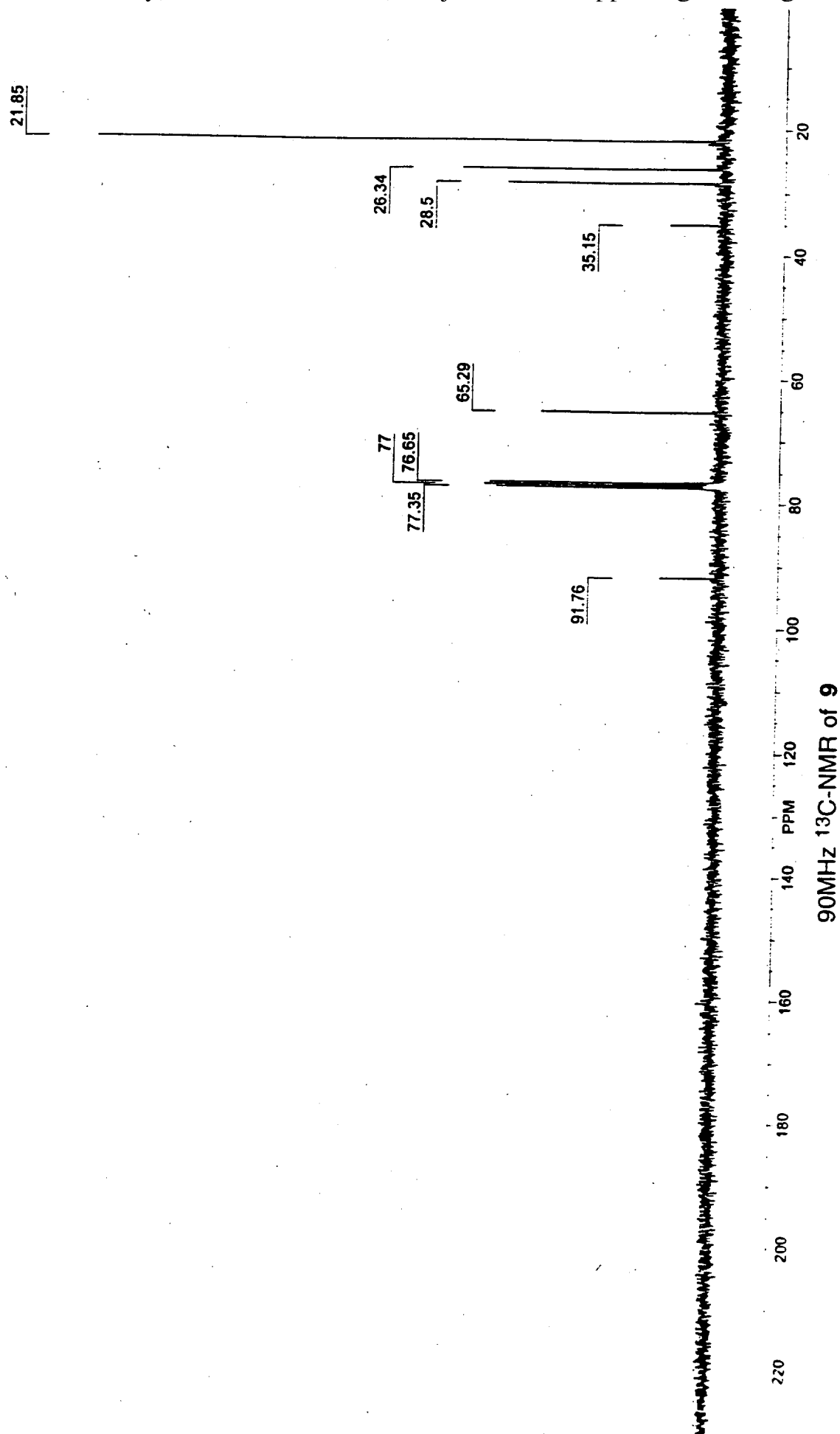


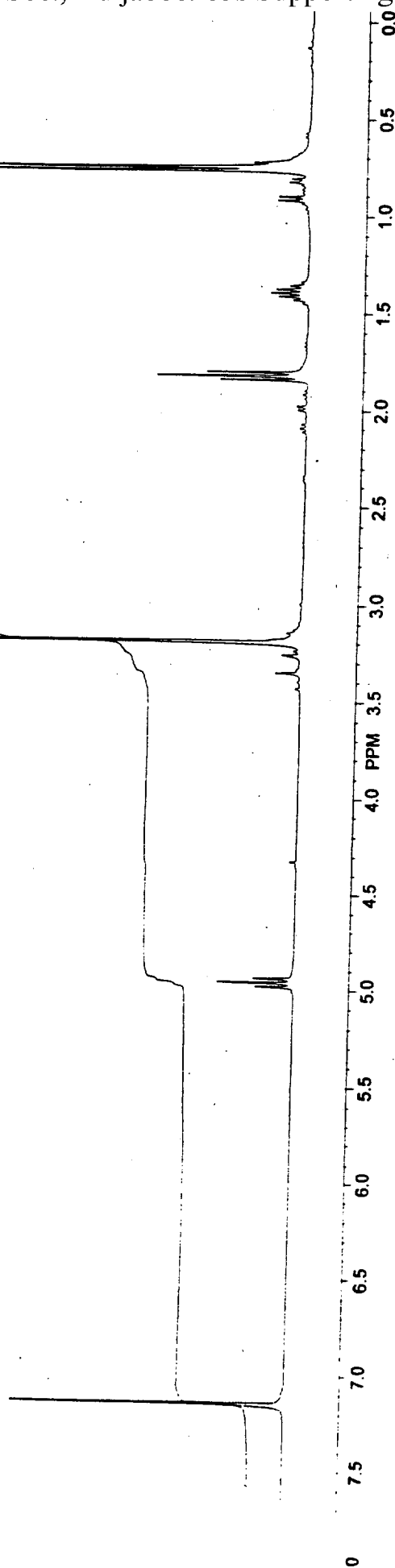
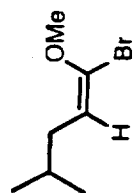
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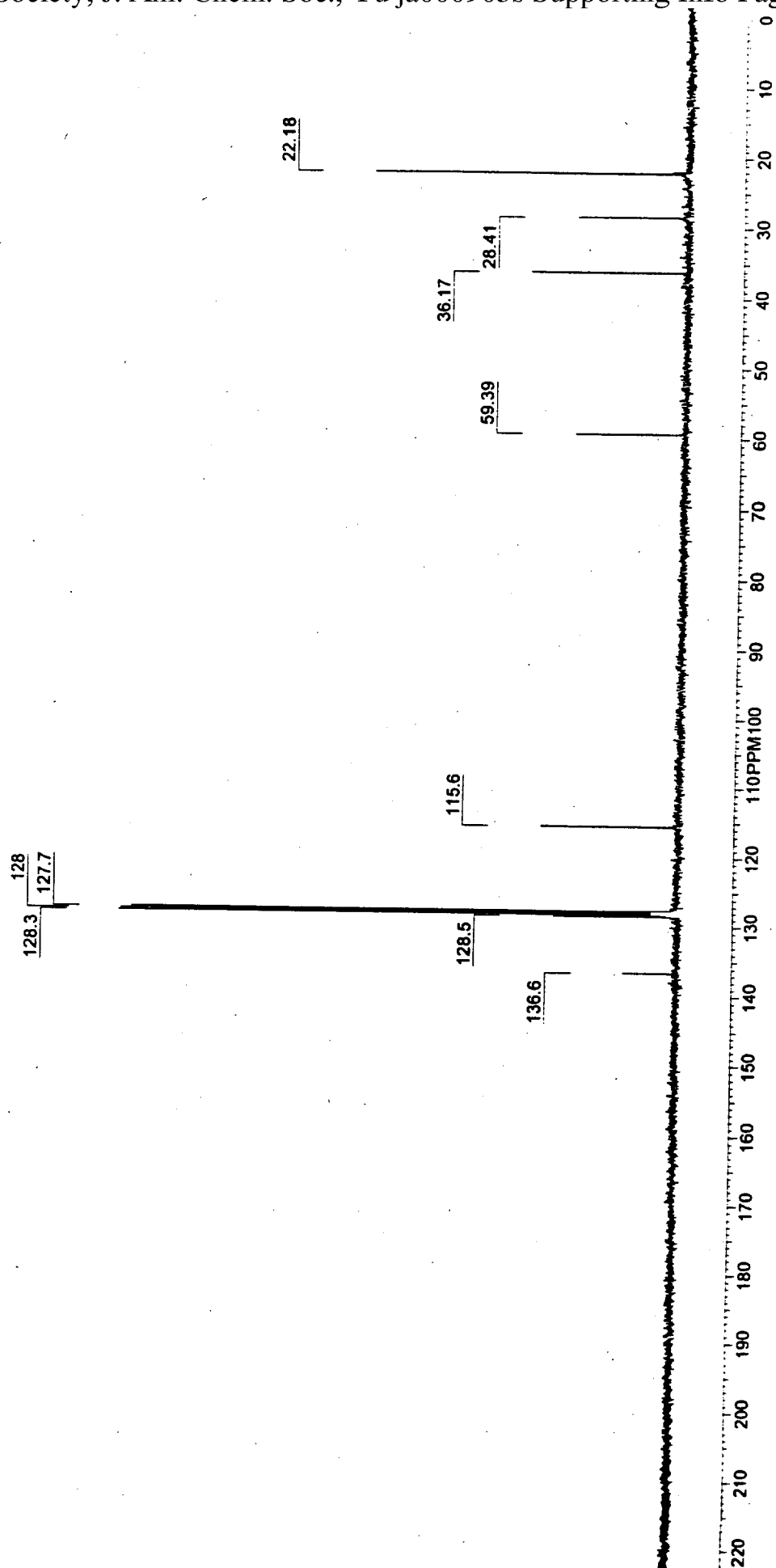
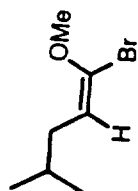


500MHz ¹H-NMR of **9**

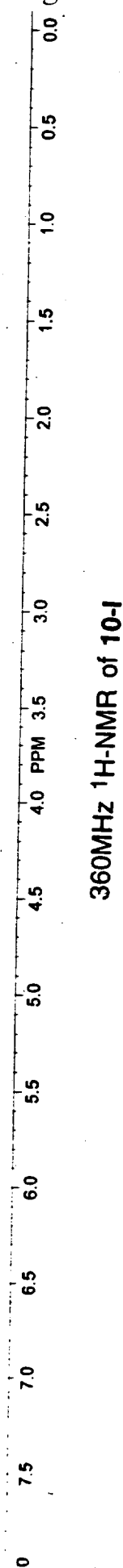
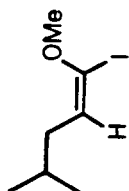


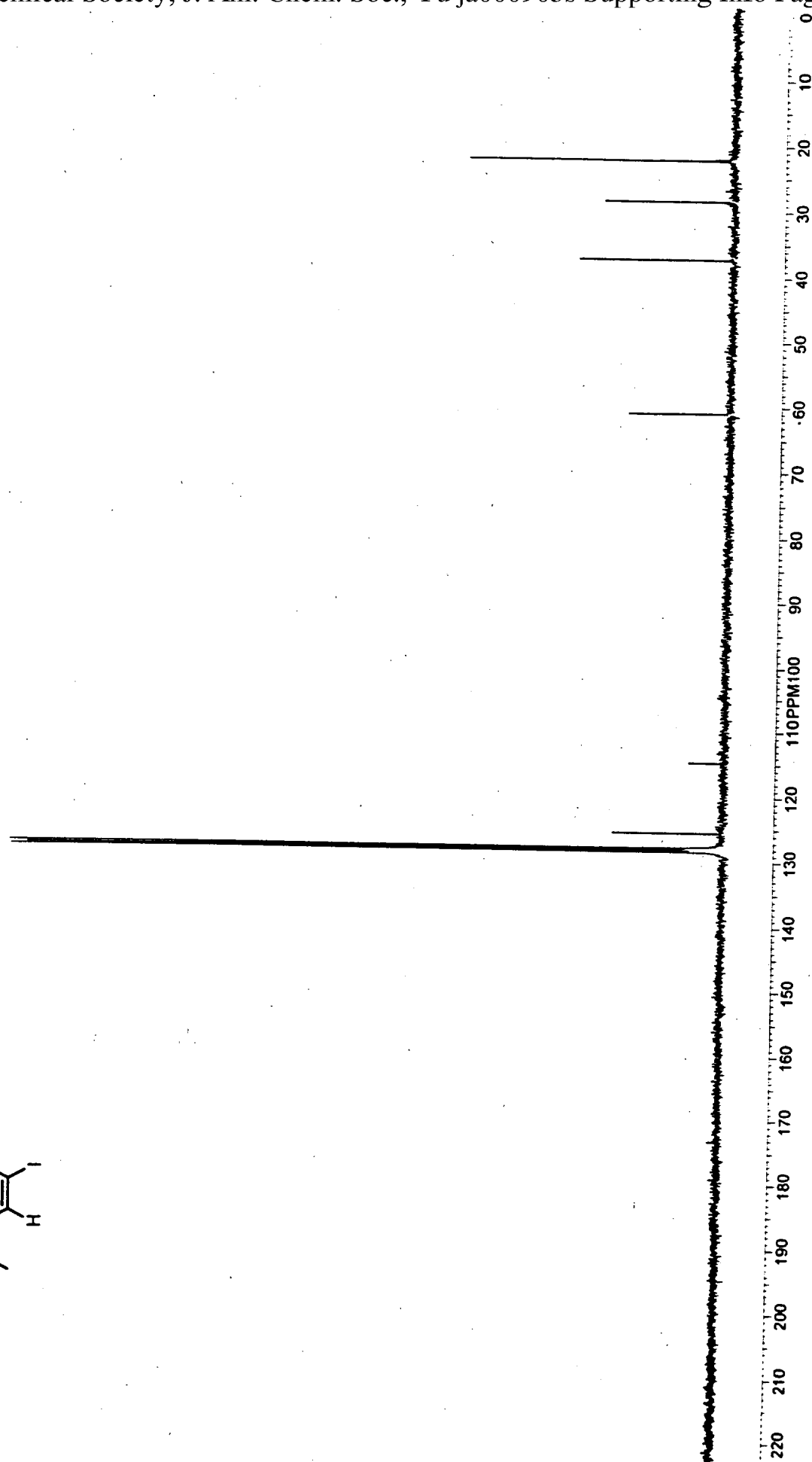
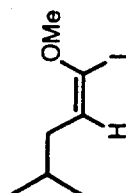


360MHz ¹H-NMR of 10-Br

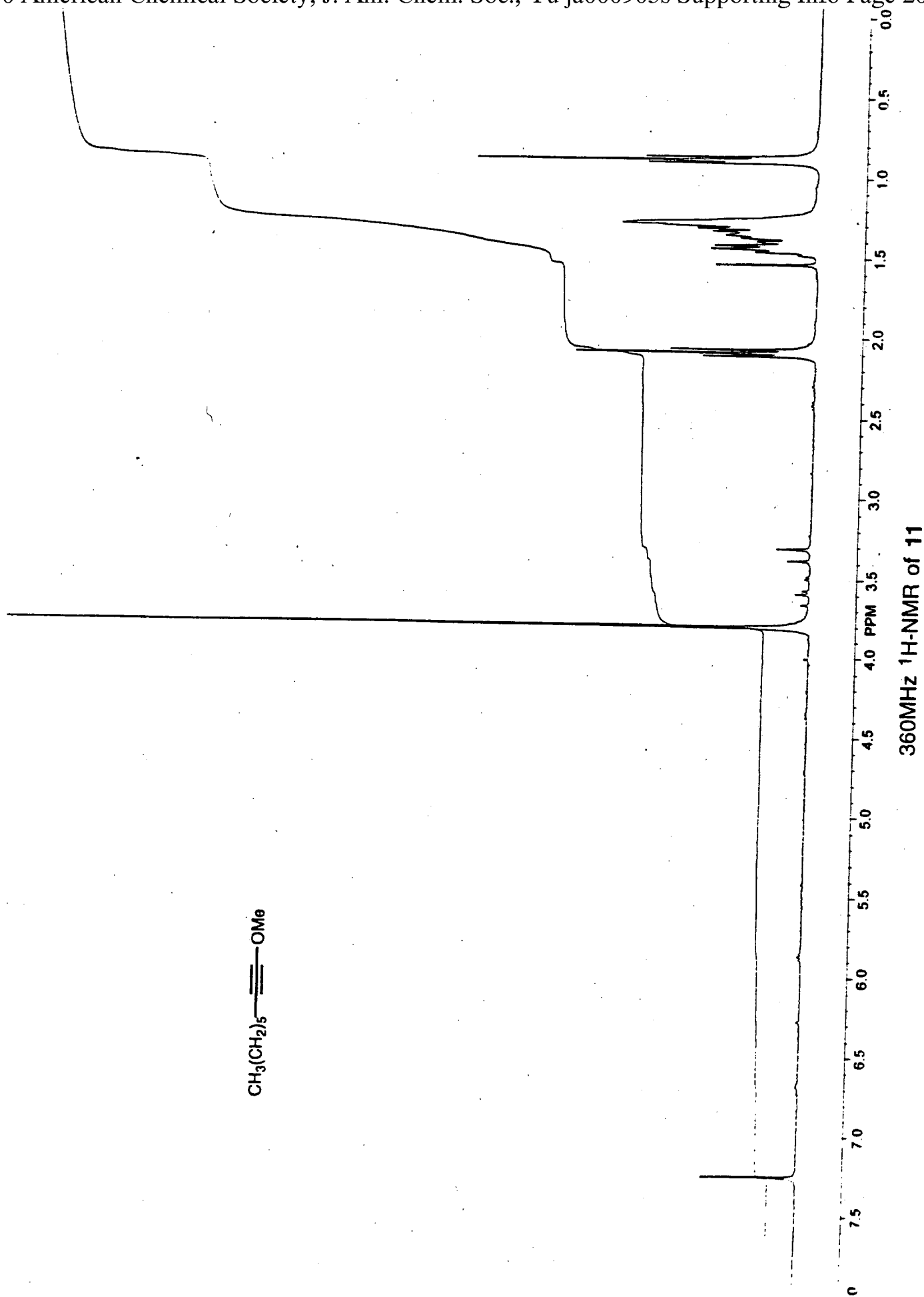


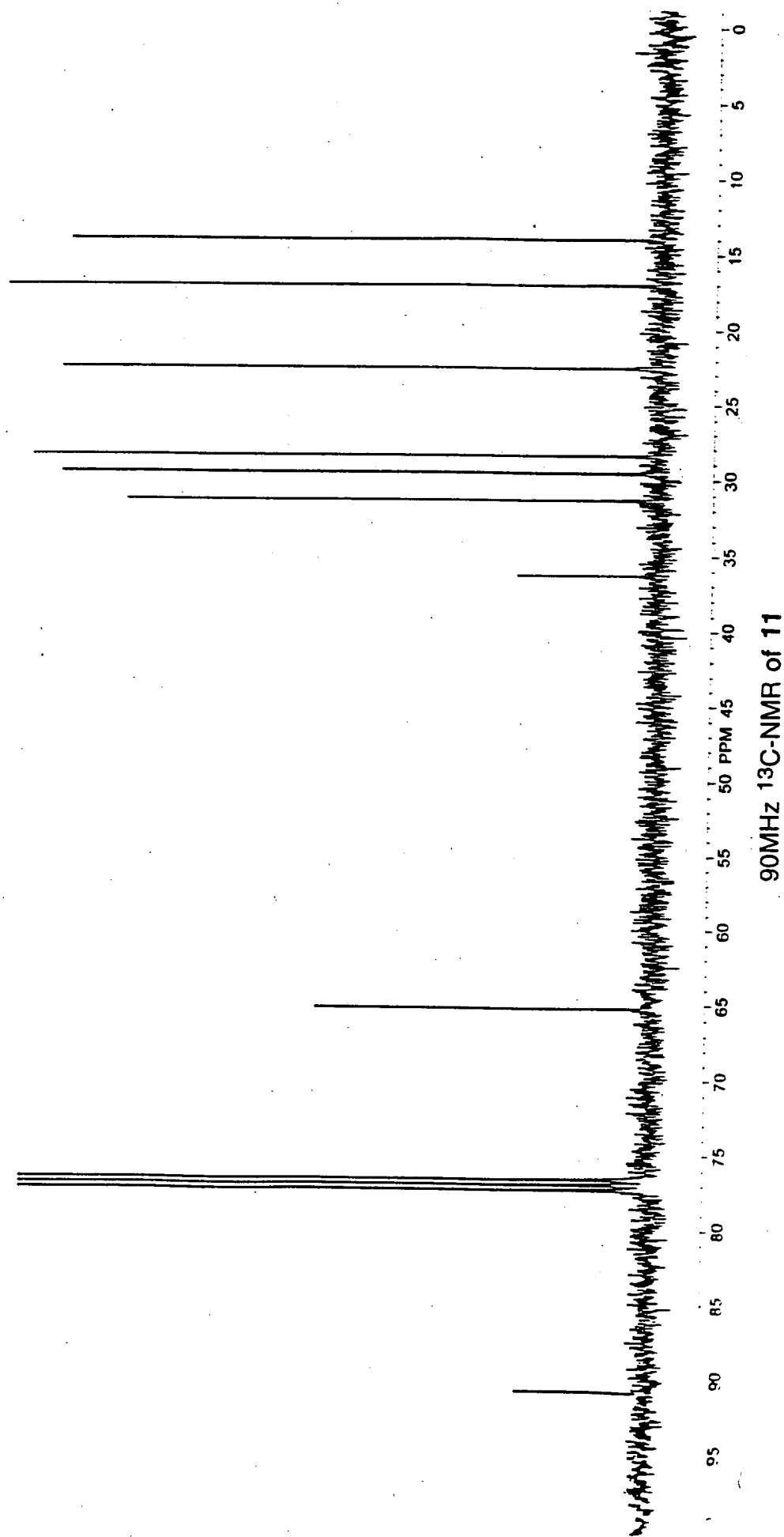
90MHz ^{13}C -NMR of 10-Br

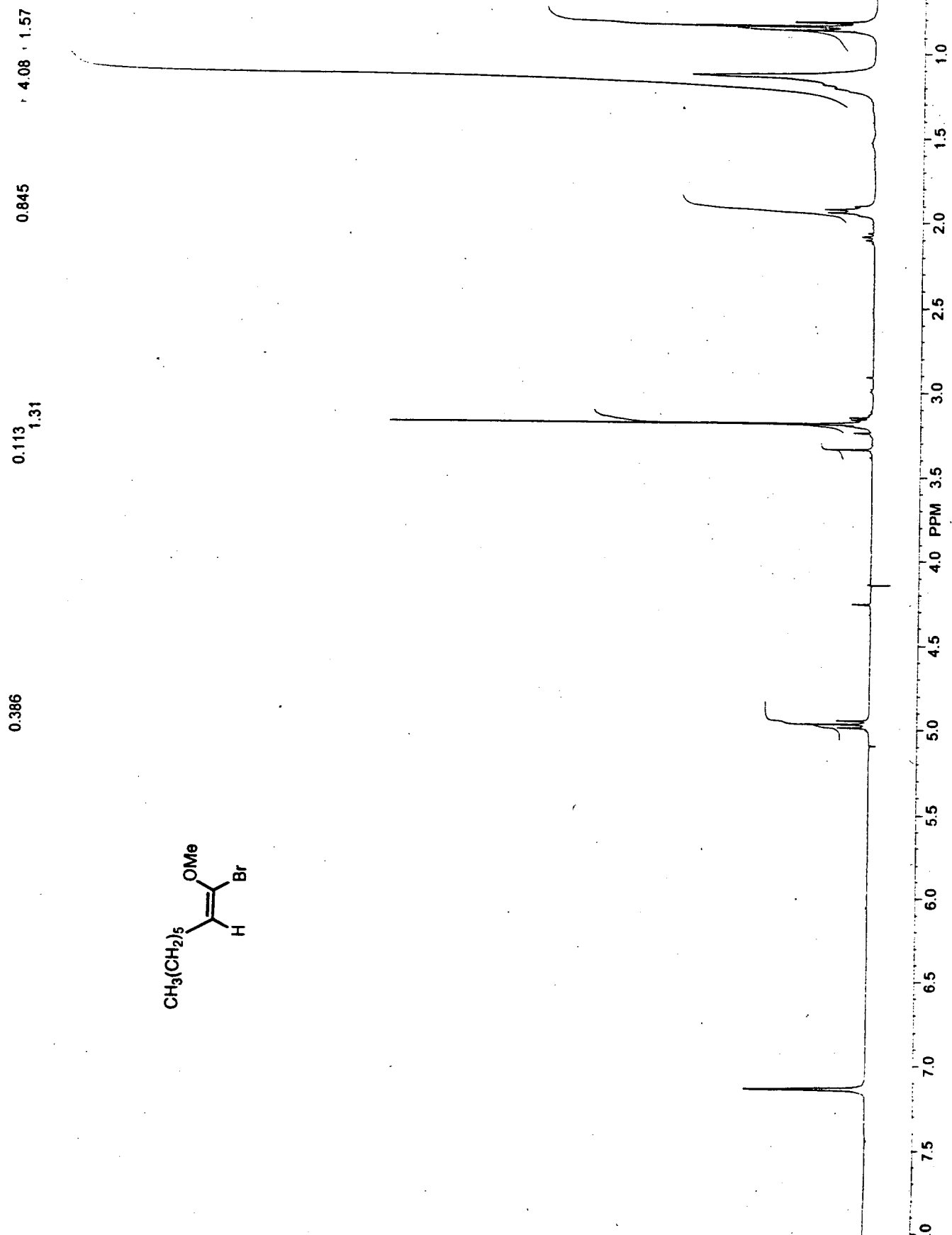
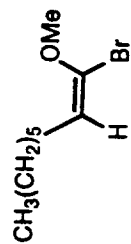




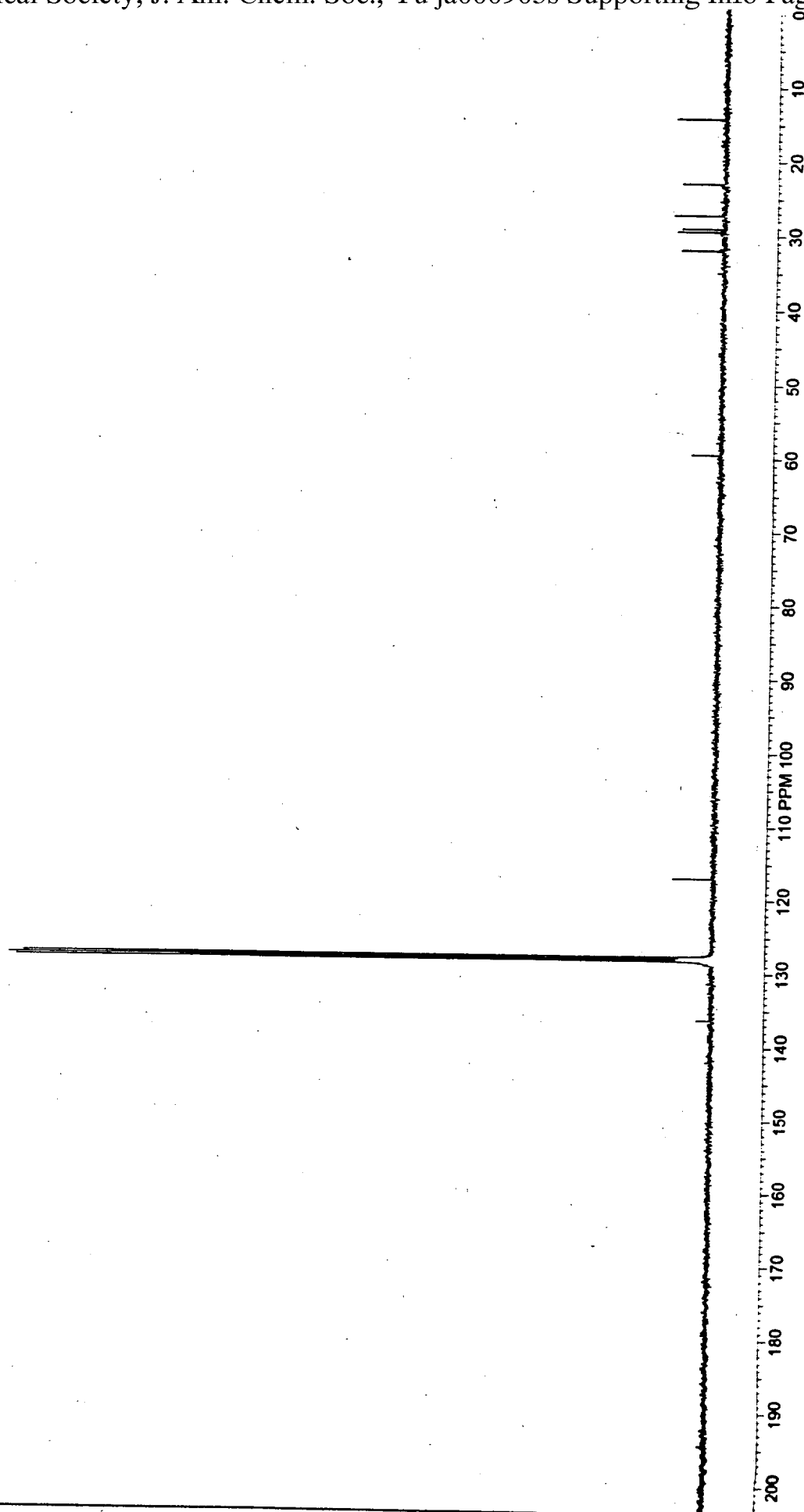
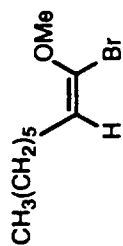
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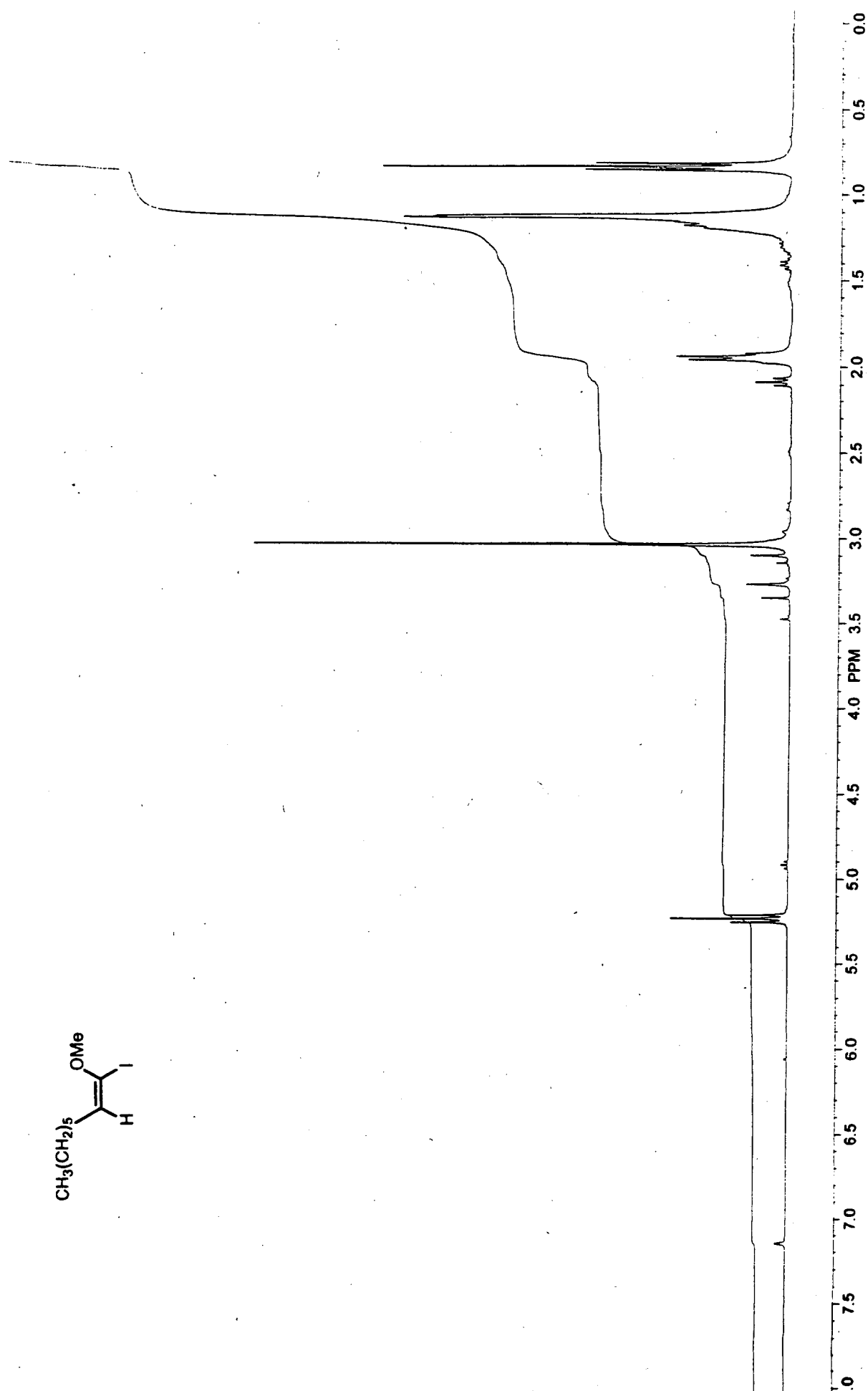
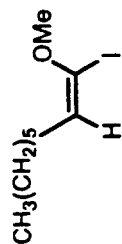




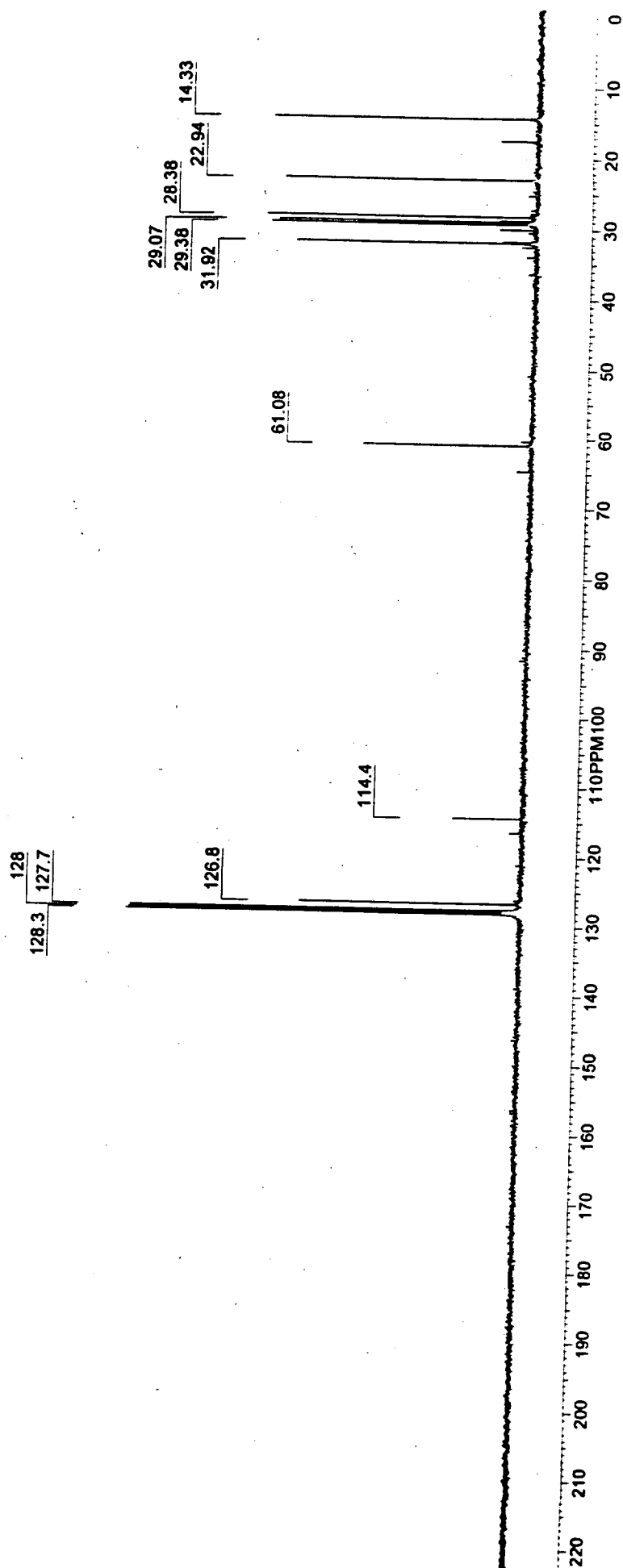
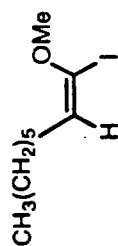
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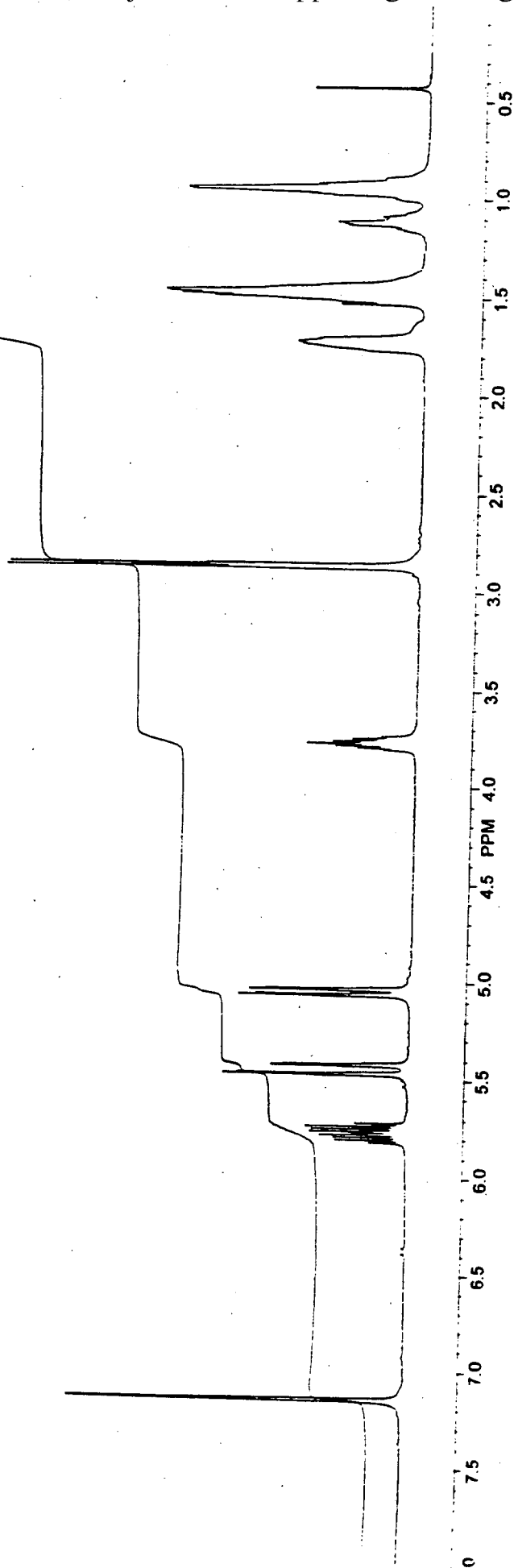
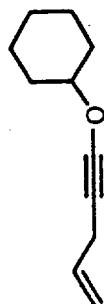
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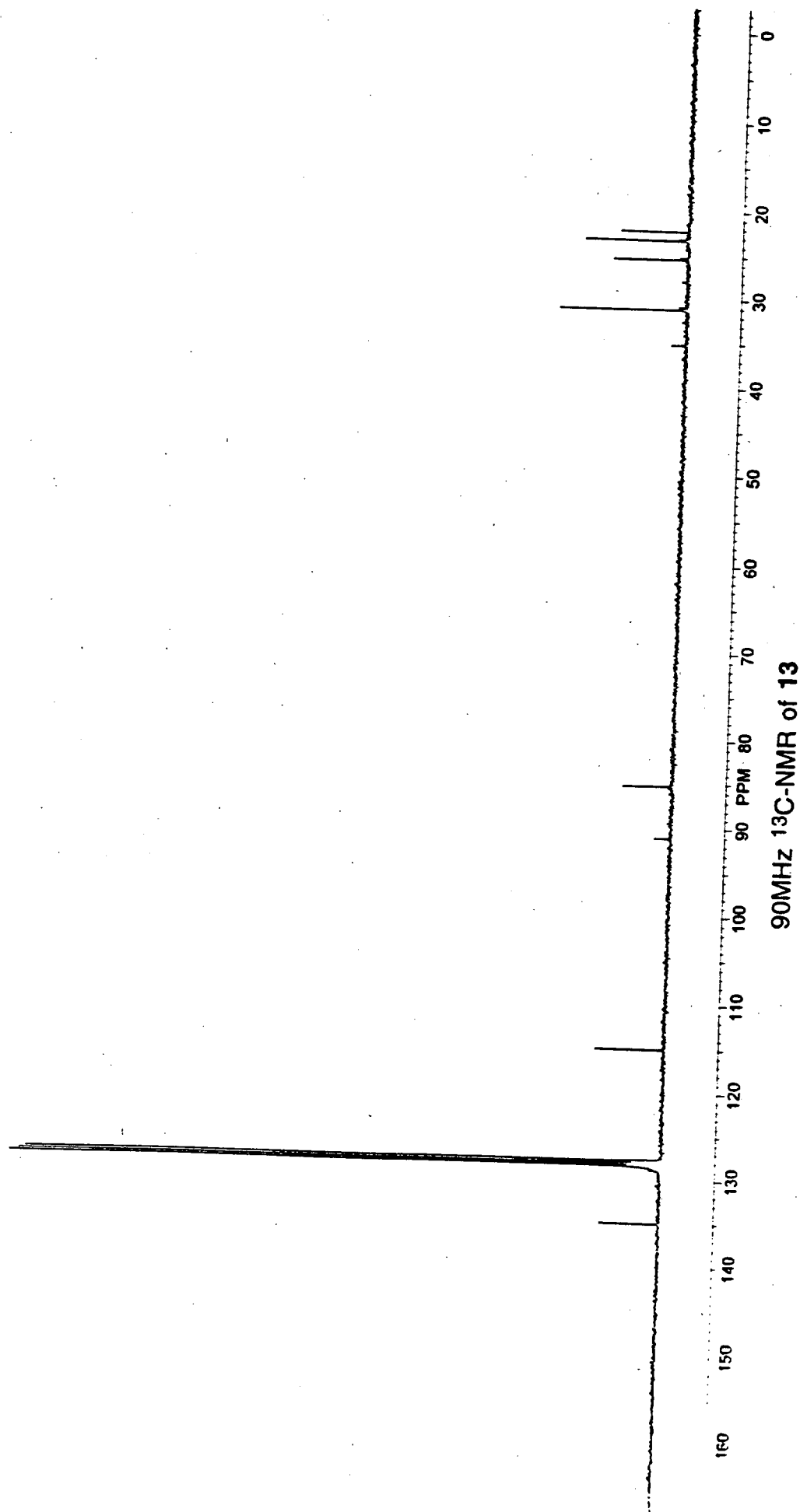
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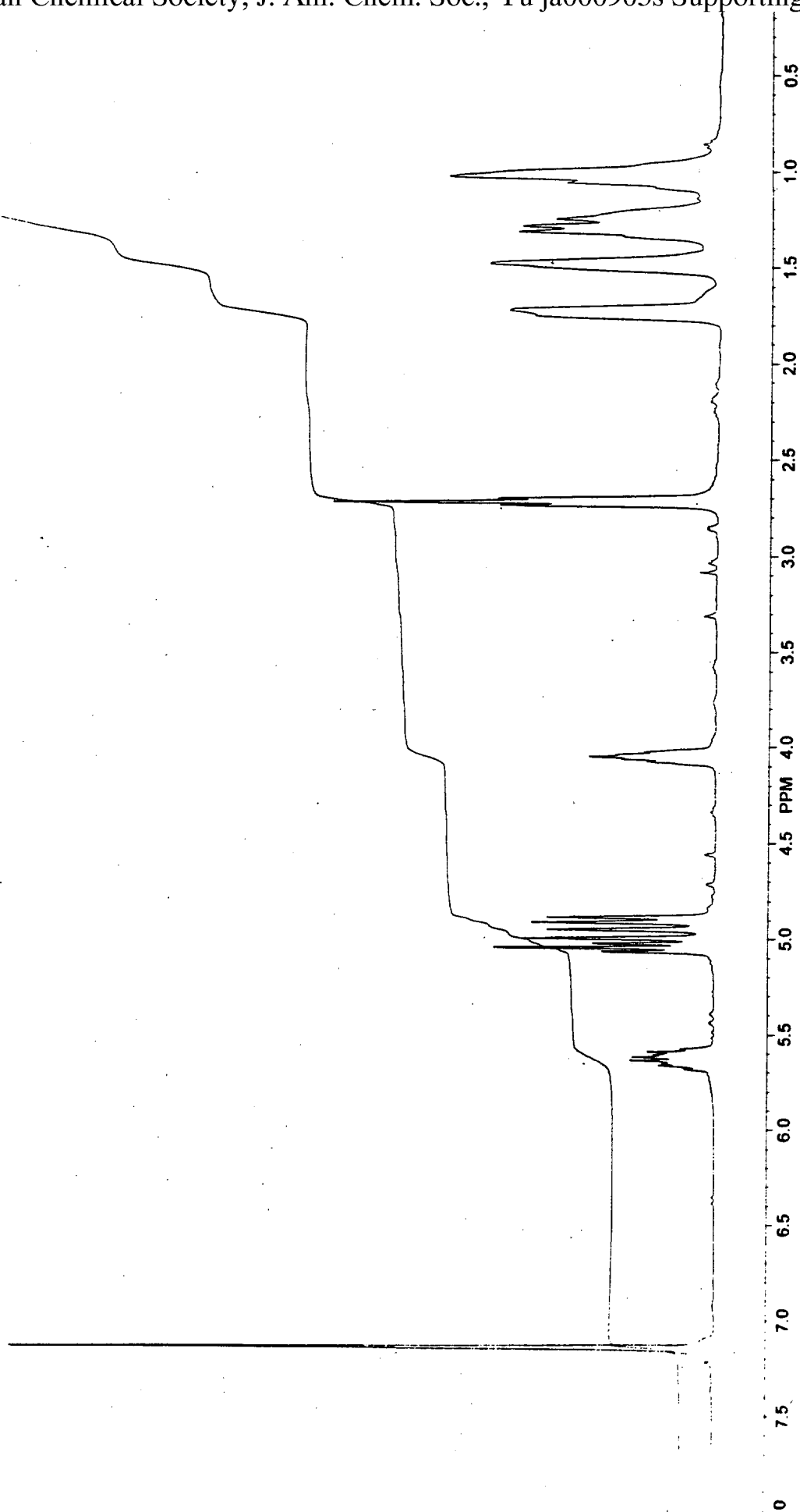
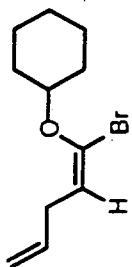


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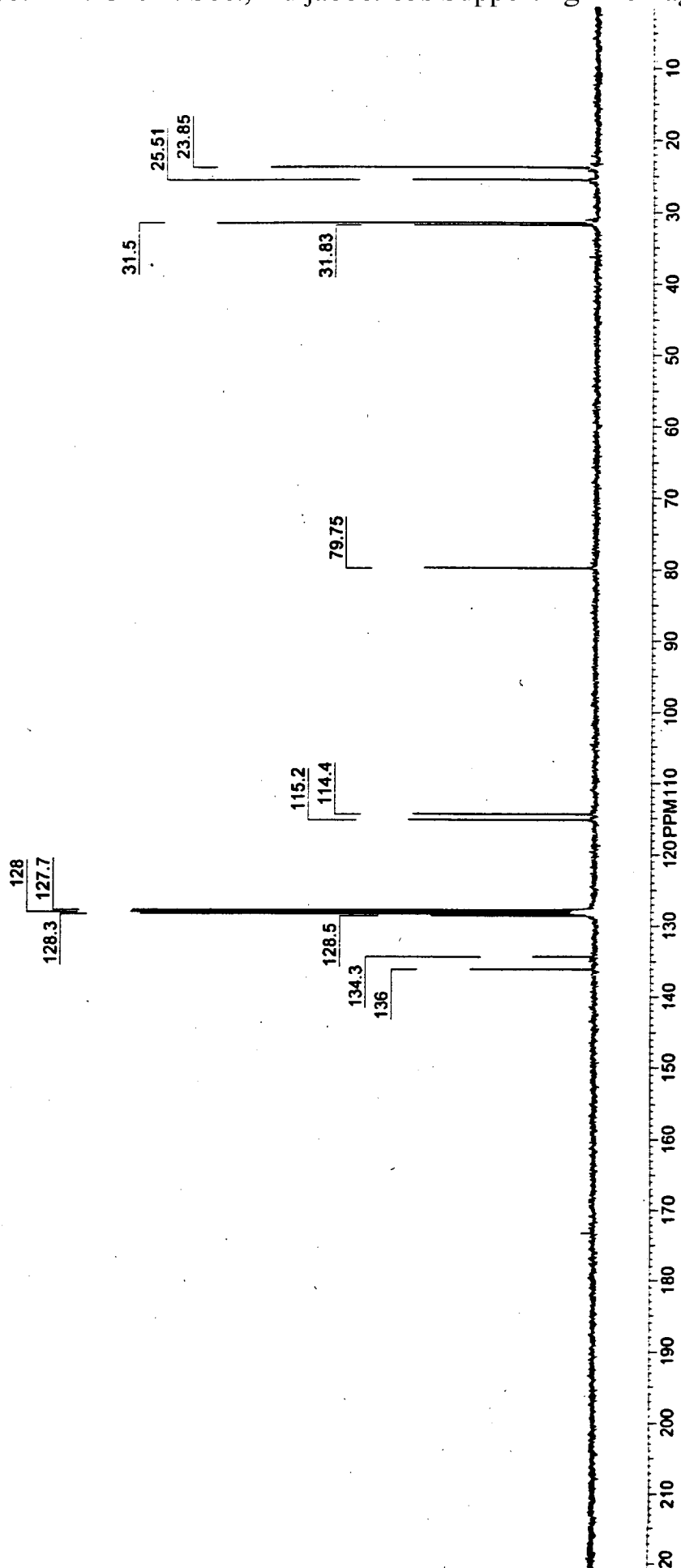
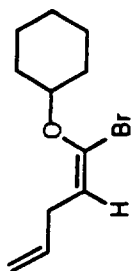


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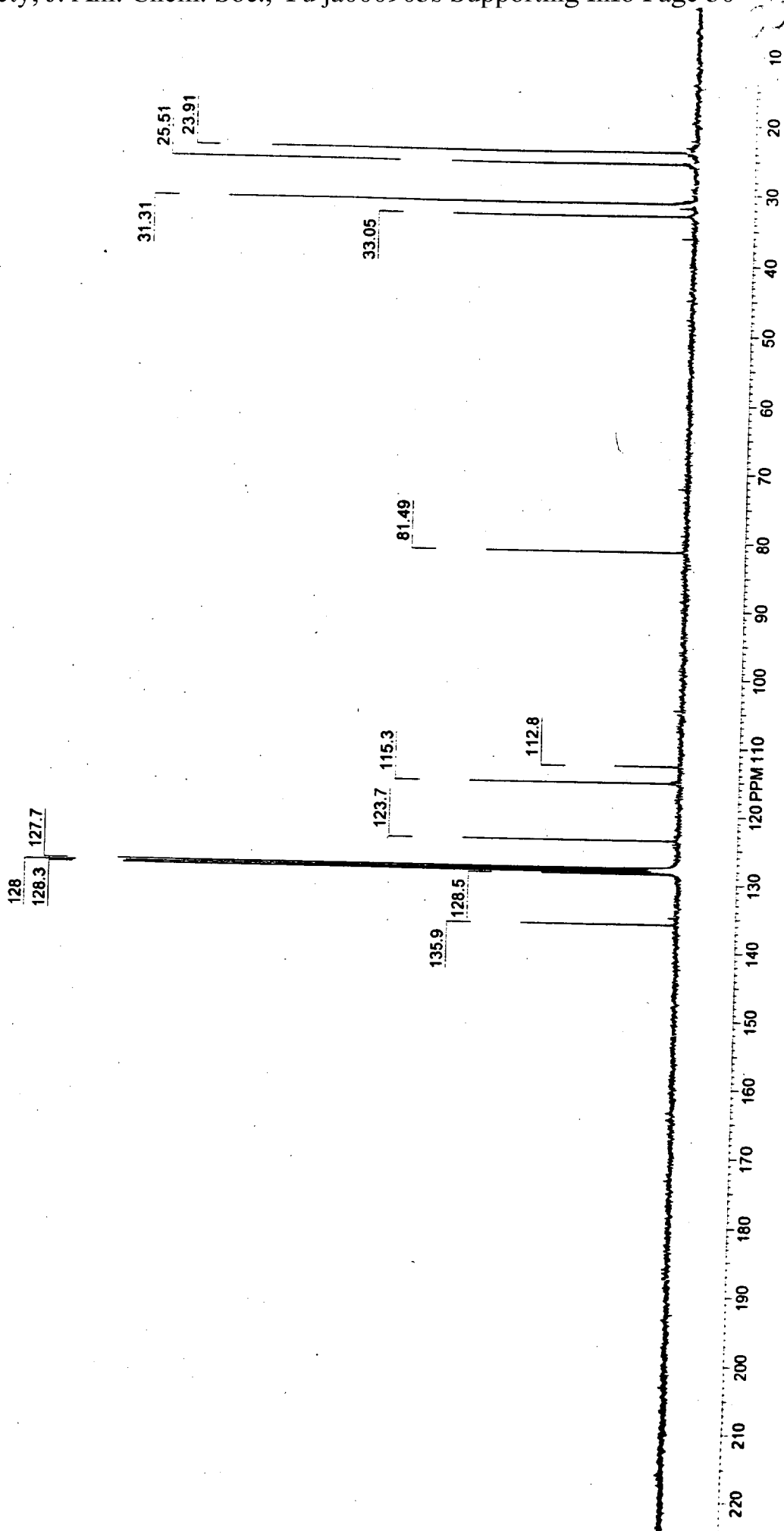
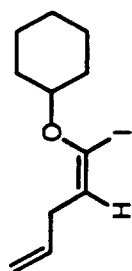


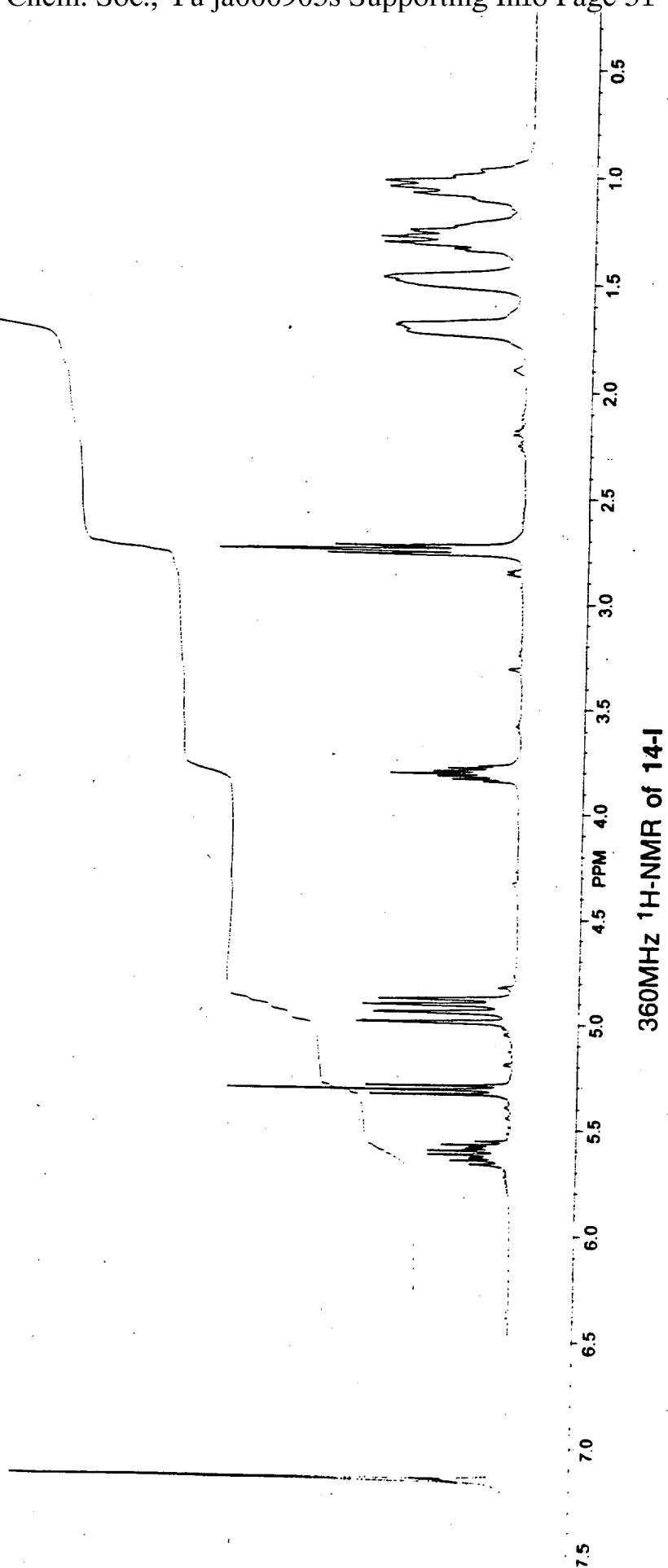


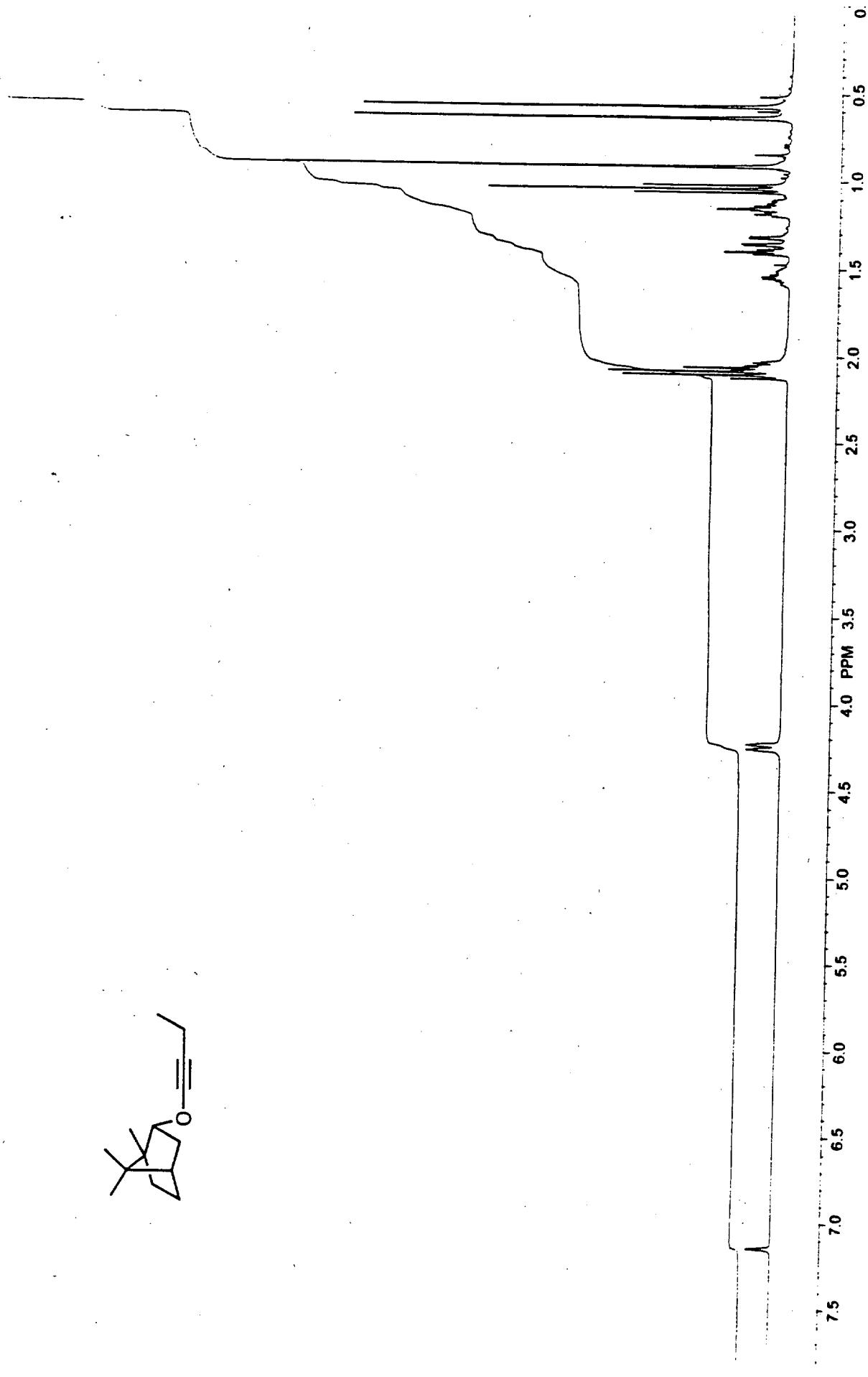
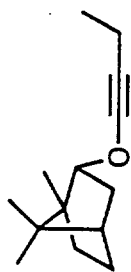
360MHz ¹H-NMR of 14-Br



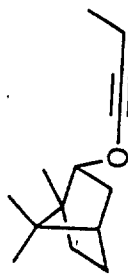
90MHz ^{13}C -NMR of 14-Br







360MHz ¹H-NMR of 15



128
128.3
127.7

26.46
19.64
18.67
15.42
13.76

35.87
28.07

38.42
44.94

48.54
49.87

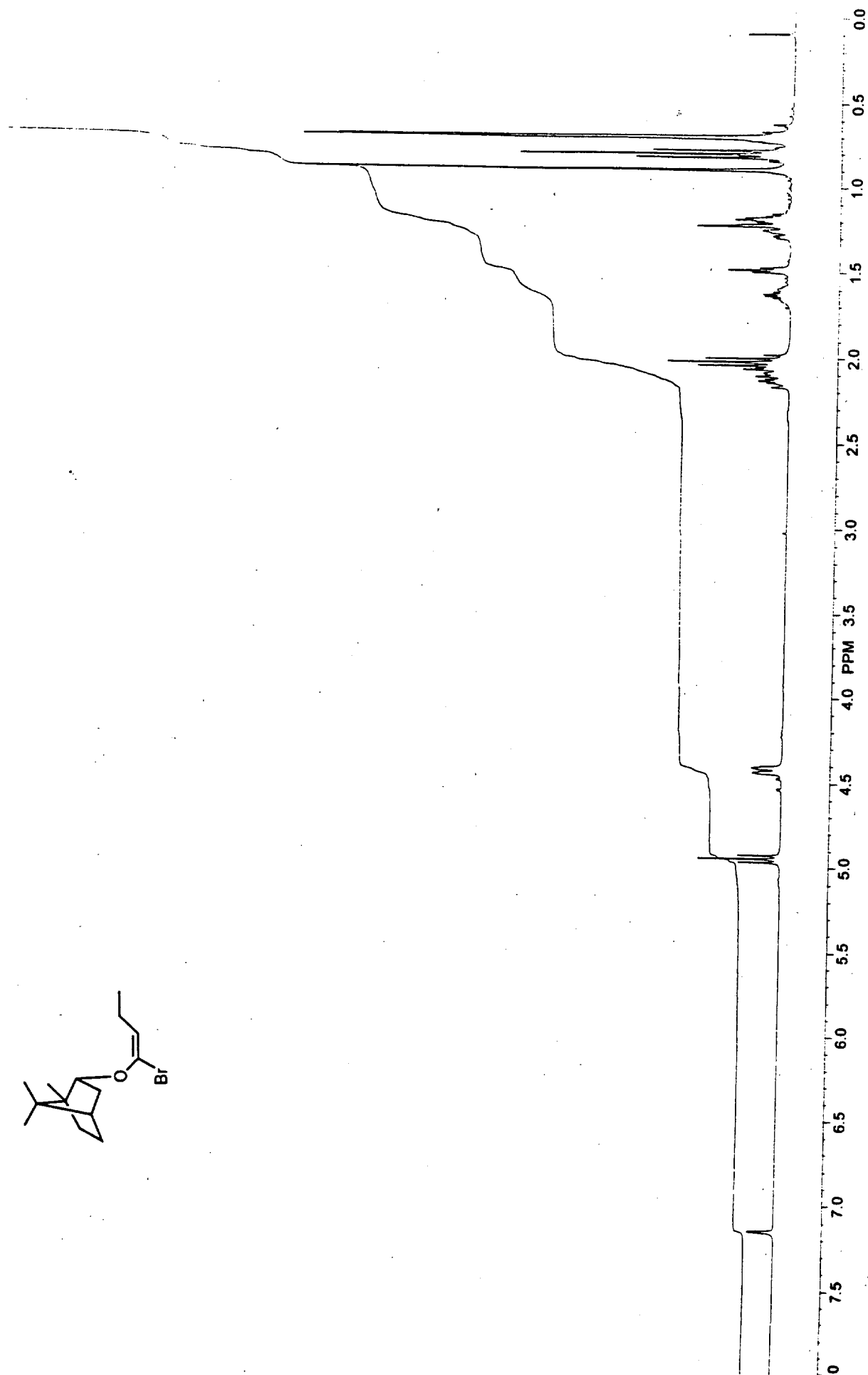
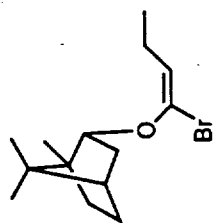
93.91

90.29

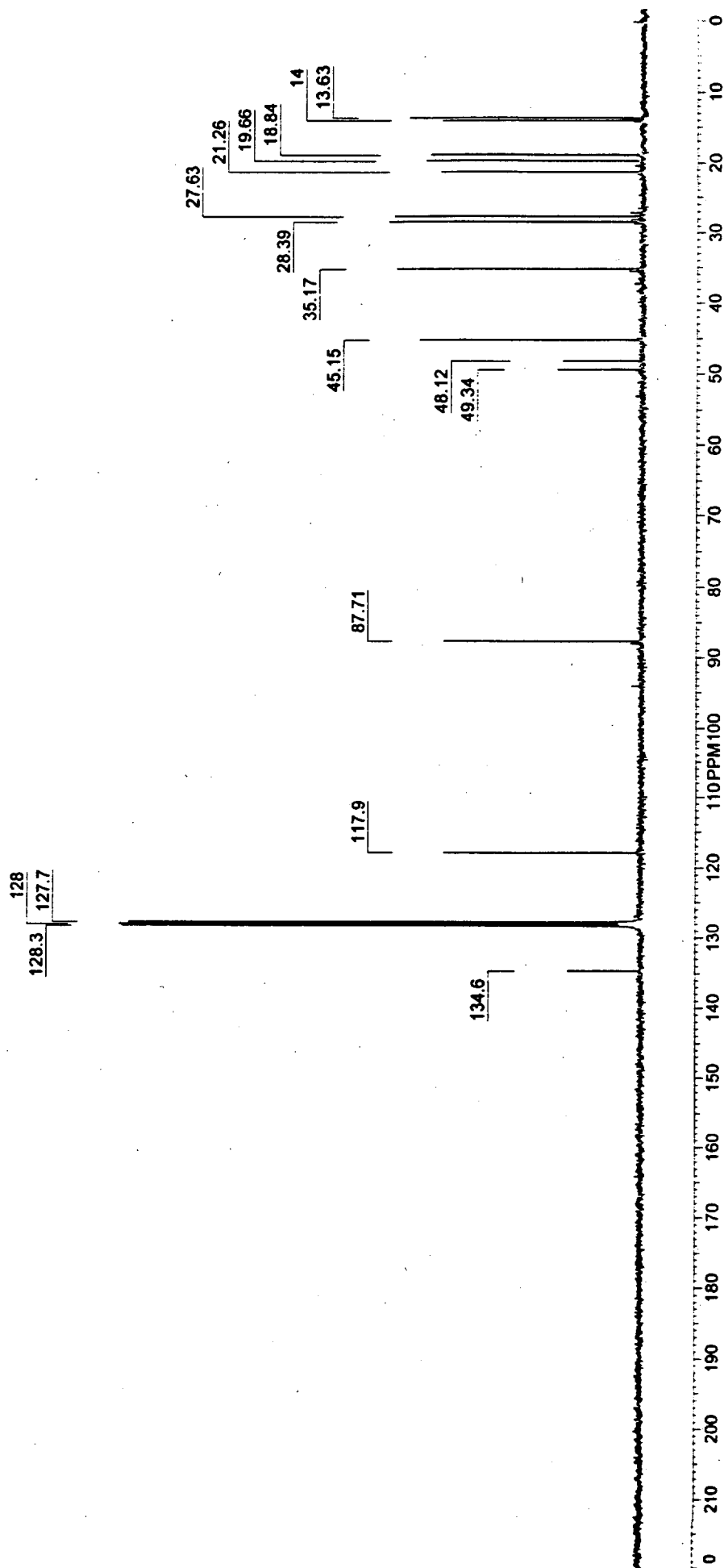
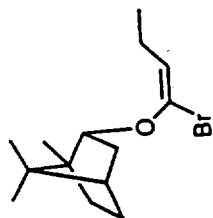
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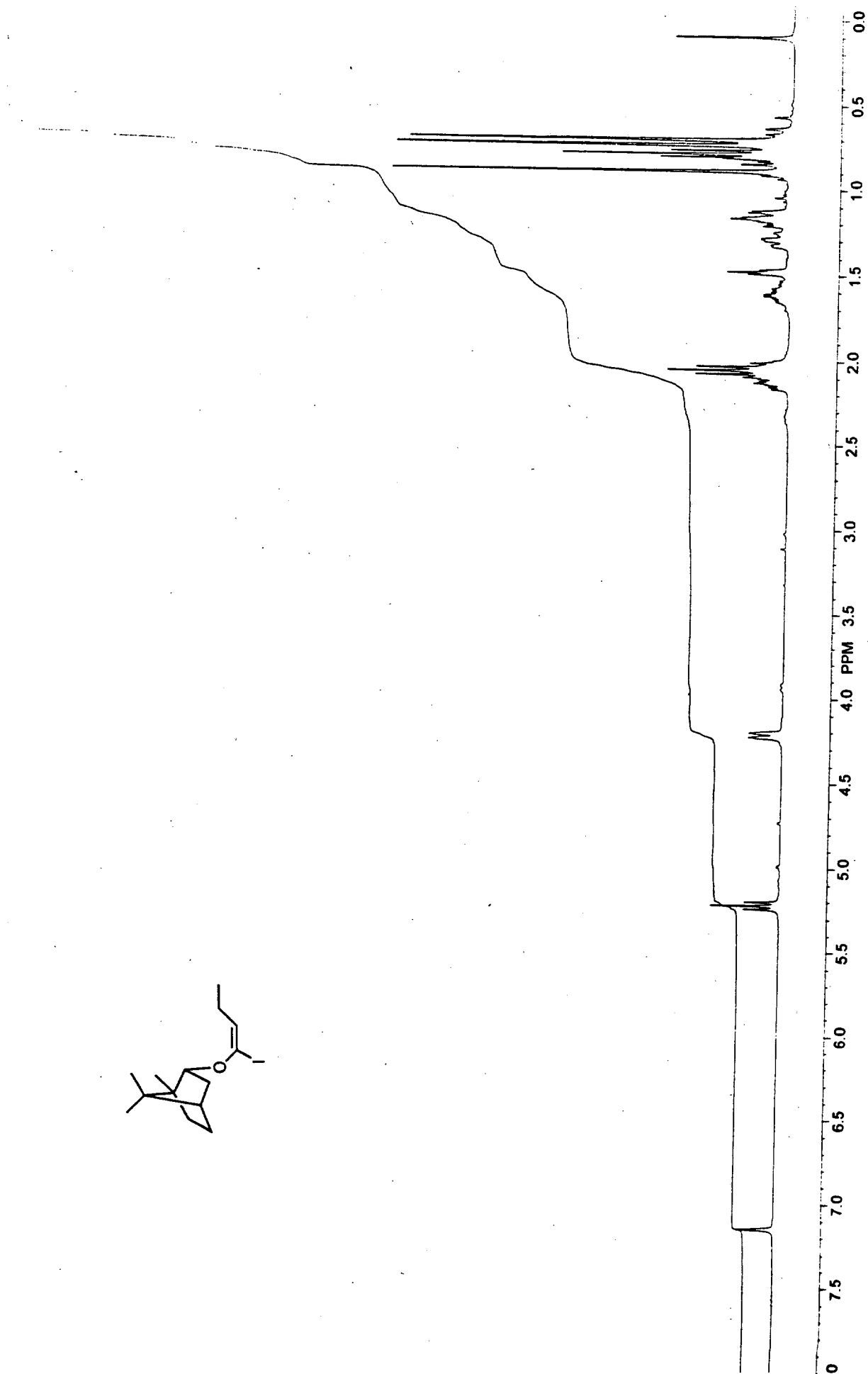
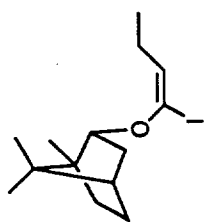
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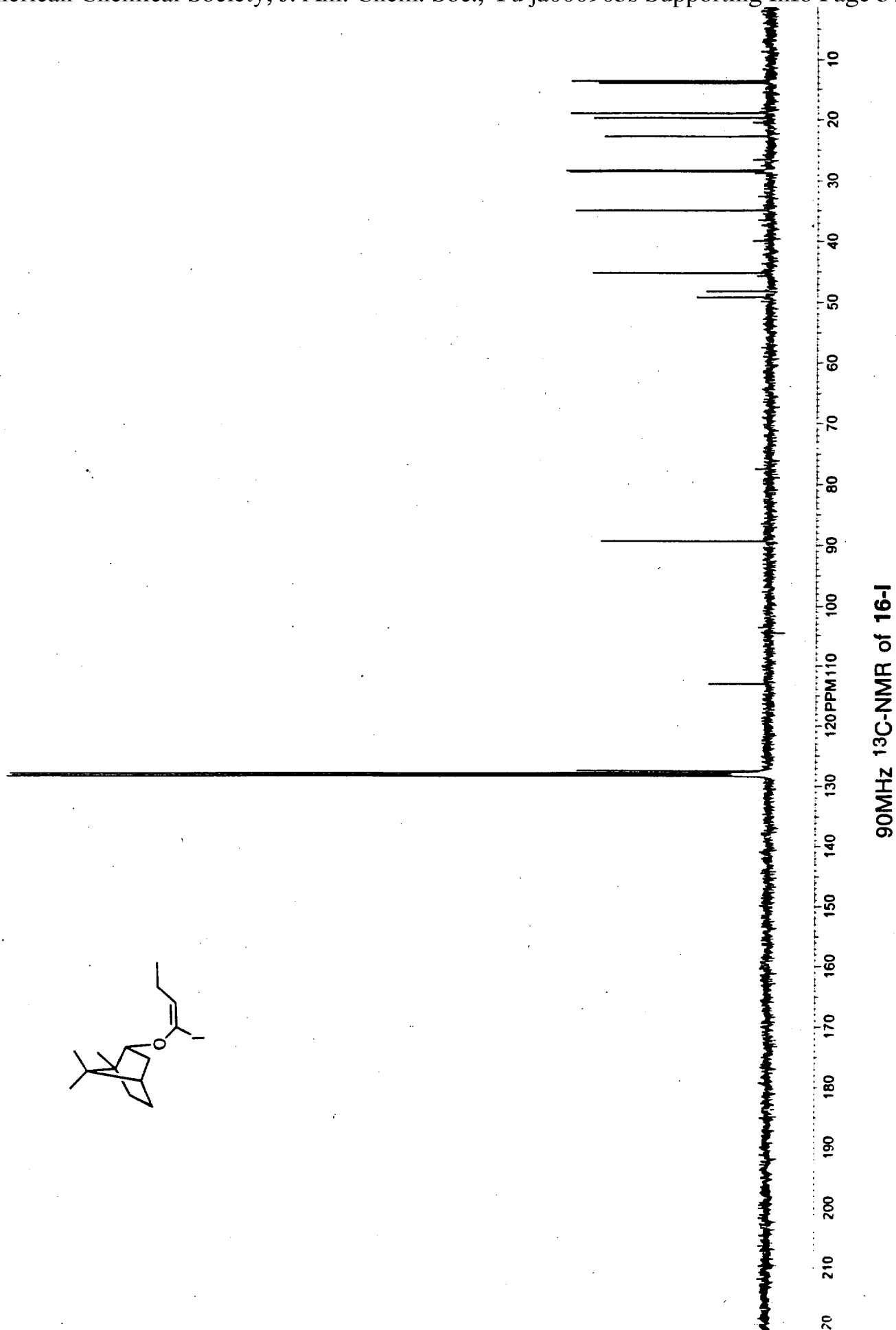
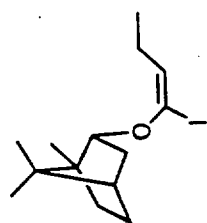


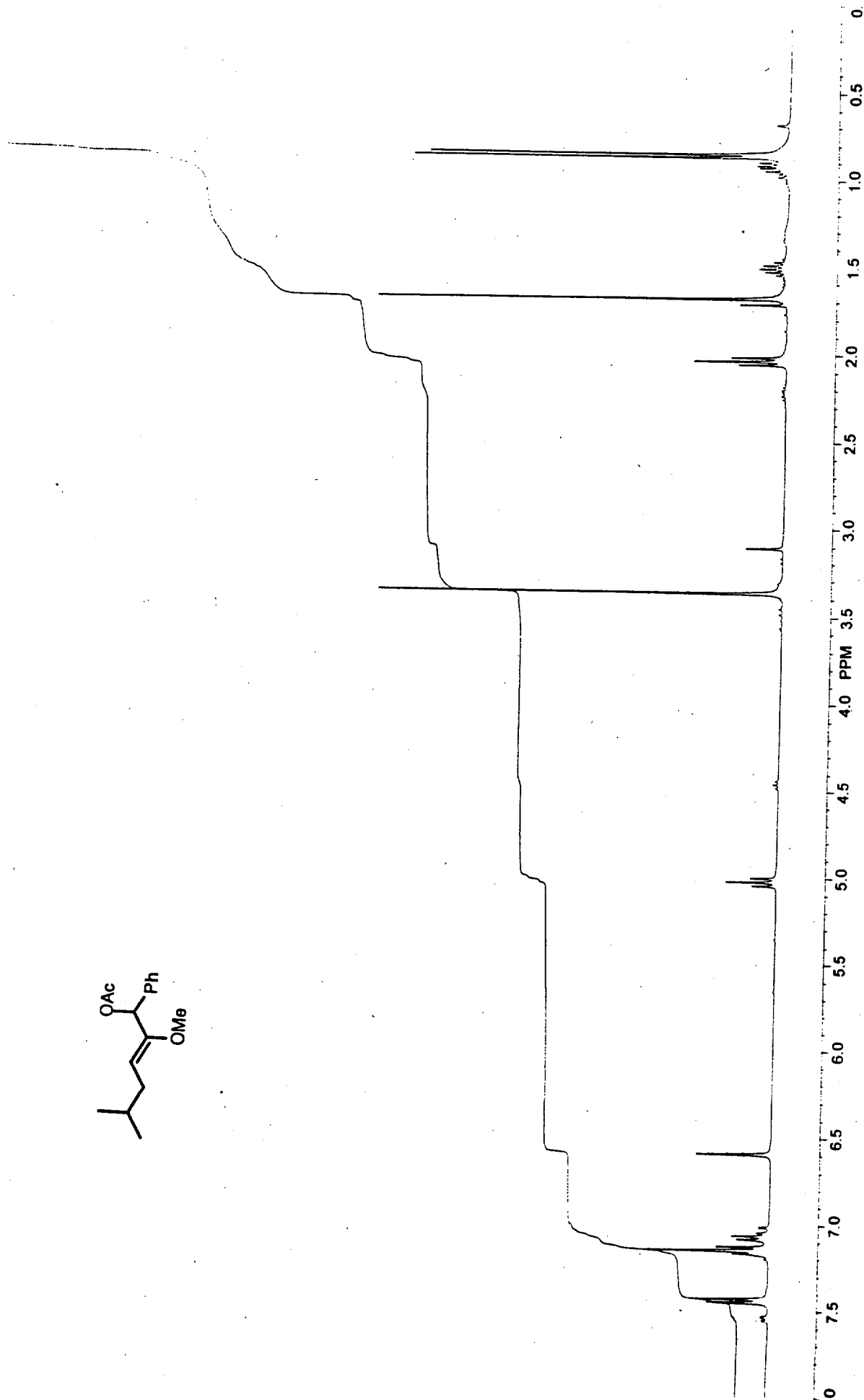
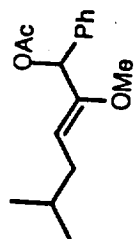
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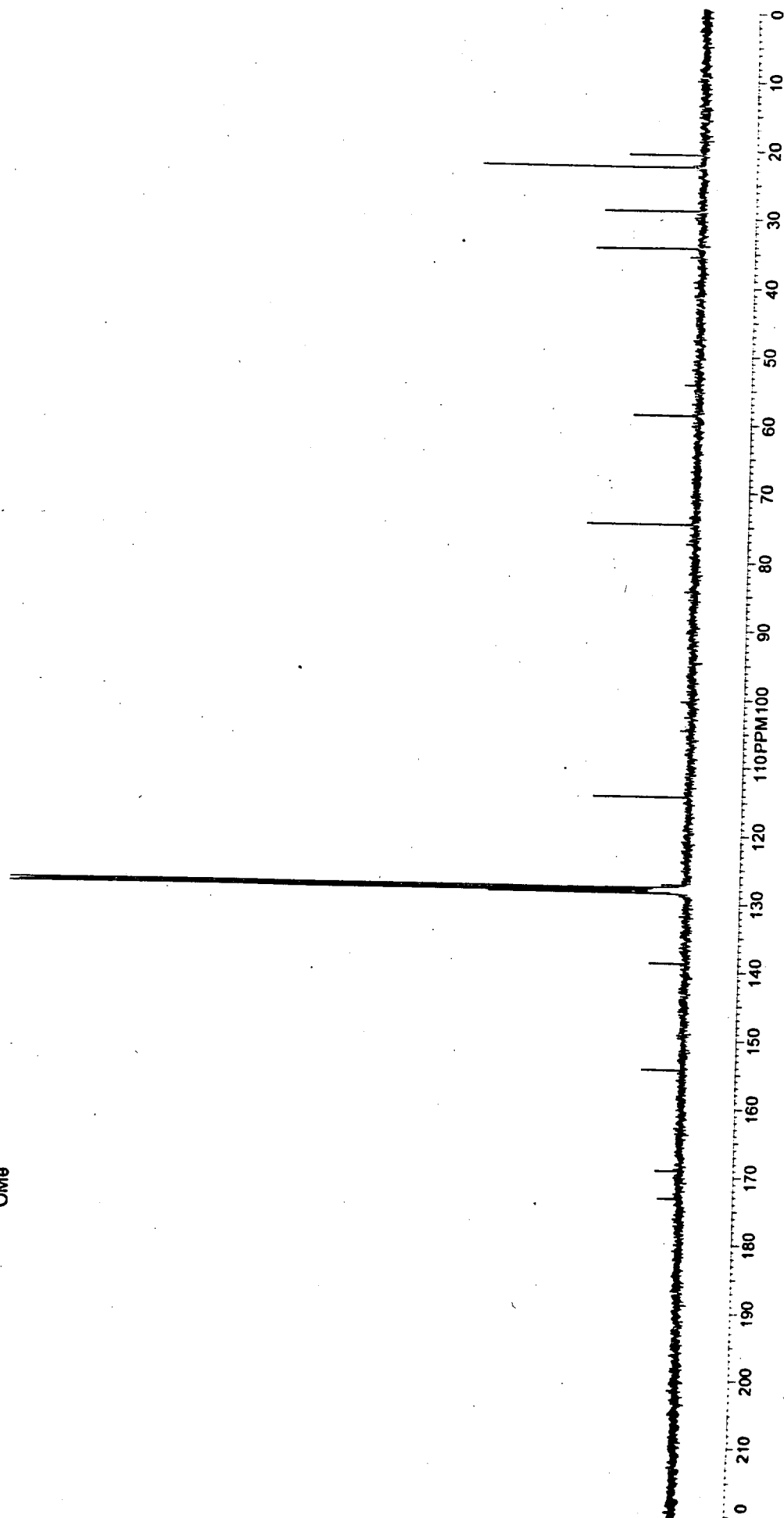
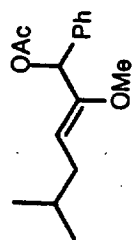


90MHz ¹³C-NMR of 16-Br









90MHz ¹³C-NMR of **17**

