Supporting Information

Experimental Procedures and Characterization

General: Acetonitrile, methanol and ethanol were dried using standard methods. TLC plates POLYGRAM SIL G/UV$_{245}$ (Macherey-Nagel) were used for monitoring reactions. Chromatographic separations were performed on silica gel 60 (Fluka, 230 - 400 mesh). Melting points are uncorrected. IR spectra were taken on a Nicolet DX-320 FT-IR spectrometer. ^{1}H and ^{13}C nmr spectra were recorded on Bruker AM 400 or AC 200 spectrometers at 400 or 200, and 100 or 50 MHz. ^{13}C nmr assignments were abtained from DEPT experiments, connectivity by ^{1}H-^{1}H COSY experiments. Mass spectra were recorded on a Finnigan MAT 8430 spectrometer at 70 eV or FAB in the positive mode with NBA as matrix. Elemental analyses were performed at the Microanalytical Laboratories of the Technical University of Braunschweig.

The precursors for amines **1a-i** were prepared by literature procedures:
5-Bromo-1,1-diphenylpent-1-ene,[1] 5-bromo-1-phenylpent-1-ene,[2] hex-4-enyl and 5-methylhex-4-enyl tosylates were prepared by standard tosylation of hex-4-en-1-ol[3] or 5-methylhex-4-en-1-ol.[4,5]

***N,N*,5-Substituted Pent-4-enylamines** (General procedure):
A mixture of 1 g (1 equiv.) of the appropriate 5-bromopent-1-ene or pent-4-enyl tosylate, 2 equiv. K_2CO_3, 5 equiv. dialkylamine and 0.4 equiv. NaI in 50 ml dry acetonitrile was refluxed under N_2 until the reaction was complete by TLC. The solvent was evaporated and the residue was partitioned between water and ether. The layers were separated and the aqueous layer was washed three times with ether. The combined organic layers were dried over a mixture of Na_2SO_4 and K_2CO_3. The solvent was evaporated and the amine was purified by flash column chromatography.

***N,N*-Diethyl-5,5-diphenylpent-4-enylamine (1a)**: Hexane/EtOAc 10:1, then hexane/EtOAc/NEt$_3$ 20:10:1; yield 0.90 g (96%) of a colorless oil. ^{1}H nmr (200 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.1 Hz, 6 H), 1.55 (tt, J = 7.5, 7.7 Hz, 2 H), 2.06 (dt, J = 7.4, 7.5 Hz, 2 H), 2.41 (m, 6 H), 6.05 (t, J = 7.4 Hz, 1 H), 7.23 (m, 10 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 11.7 (q), 27.5 (t), 27.9 (t), 46.9 (t), 52.6 (t), 126.8 (d), 126.8 (d), 127.2 (d), 128.0 (d), 128.1 (d), 129.6 (d), 129.9 (d), 140.2 (s), 141.9 (s), 142.8 (s).

***N*-(5,5-Diphenylpent-4-enyl)pyrrolidine (1b)**: Hexane/EtOAc 10:1, then hexane/EtOAc/NEt$_3$ 20:10:1; yield 0.96 g (97%) of a colorless oil. IR (film): 3080, 3056, 3023, 2964, 2930, 2875, 1598, 1495 cm^{-1}. - ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.60 (m, 6 H), 2.10 (dt, J = 7.4, 7.5 Hz, 2 H), 2.37 (m, 6 H), 6.06 (t, J = 7.5 Hz, 1 H), 7.23 (m, 10 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 23.4 (t), 28.0 (t), 29.5 (t), 54.2 (t), 56.1 (t), 126.8 (d), 126.8 (d), 127.2 (d), 128.0 (d), 128.1 (d), 129.6 (d), 129.9 (d), 140.2 (s), 141.8 (s), 142.7 (s). - MS (70 eV); m/z (%): 291 (58) [M$^+$], 186 (14), 110 (38), 96 (16), 84 (100) [M$^+$-

$Ph_2CCH(CH_2)_2$]. - Anal. Calcd. for $C_{21}H_{25}N$ (291.43): C 86.55, H 8.65, N 4.80; Found: C 86.38, H 8.78, N 4.67.

***N,N*-Diallyl-5,5-diphenylpent-4-enylamine (1c)**: Hexane/EtOAc 10:1, then hexane/EtOAc/NEt_3 20:10:1; yield 1.0 g (97%) of a colorless oil. ^{1}H nmr (200 MHz, acetone-d_6): δ = 1.48 (tt, *J* = 7.1, 7.6 Hz, 2 H), 1.92 (dt, *J* = 7.5, 7.6 Hz, 2 H), 2.27 (t, *J* = 7.1 Hz, 2 H), 2.89 (m, 4 H), 4.97 (m, 4 H), 5.65 (m, 2 H), 6.01 (t, *J* = 7.5 Hz, 1 H), 7.16 (m, 10 H). - ^{13}C nmr (50 MHz, acetone-d_6): δ = 28.0 (t), 28.2 (t), 53.3 (t), 57.3 (t), 116.8 (t), 127.5 (d), 127.7 (d), 127.8 (d), 128.8 (d), 129.0 (d), 130.4 (d), 130.5 (d), 137.3 (d), 141.2 (s), 142.6 (s), 143.6 (s).

***N,N*-Dibenzyl-5,5-diphenylpent-4-enylamine (1d)**: Hexane/EtOAc 20:1; yield 1.25 g (91%) of a colorless oil. IR (film): 3082, 3060, 3026, 2927, 2892, 2859, 1599, 1494 cm^{-1}. - ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.59 (m, 2 H), 2.07 (dt, *J* = 7.5, 7.6 Hz, 2 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 3.47 (s, 4 H), 5.93 (t, *J* = 7.5 Hz, 1 H), 7.14 (m, 20 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.3 (t), 27.5 (t), 52.8 (t), 58.2 (t), 126.7 (d), 126.8 (d), 127.2 (d), 128.0 (d), 128.1 (d), 128.8 (d), 129.8 (d) 129.9 (d), 139.8 (s), 140.2 (s), 141.6 (s), 142.7 (s). - MS (70 eV); m/z (%): 417 (40) [M^+], 326 (24) [M^+-Bn], 236 (22), 210 (53) [M^+-$Ph_2CCH(CH_2)_2$], 146 (19), 120 (16), 91 (100) [Bn]. - Anal. Calcd. for $C_{31}H_{31}N$ (417.59): C 89.17, H 7.48, N 3.35; Found: C 89.23, H 7.51, N 3.22.

***N*-(5,5-Diphenylpent-4-enyl)-*N*-methylaniline (1e)**: Hexane/EtOAc 10:1, then hexane/EtOAc/NEt_3 20:10:1; yield 0.97 g (90%) of a colorless oil. IR (film): 3079, 3056, 3025, 2940, 2910, 2883, 1599, 1574, 1506 cm^{-1}. - ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.67 (m, 2 H), 2.11 (dt, *J* = 7.4, 7.5 Hz, 2 H,), 2.81 (s, 3 H), 3.22 (t, *J* = 7.5 Hz, 2 H), 6.04 (t, *J* = 7.4 Hz, 1 H), 6.64 (m, 3 H), 7.23 (m, 12 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 26.9 (t), 27.4 (*t*), 38.3 (q), 52.3 (t), 112.2 (d), 116.4 (d), 126.9 (d), 127.0 (d), 127.2 (d), 128.1 (d), 128.2 (d), 129.1 (d), 129.2 (d), 129.9 (d), 140.1 (s), 142.3 (s), 142.7 (s), 149.2 (s). - MS (70 eV); m/z (%): 327 (38) [M^+], 146 (42), 120 (100) [M^+-$Ph_2CCH(CH_2)_2$], 107 (30) [$PhNHCH_3$], 77 (13) [Ph]. - Anal. Calcd. for $C_{24}H_{25}N$ (327.46): C 88.03, H 7.69, N 4.28; Found C 87.88, H 7.81, N 4.20.

***(Z)*-*N,N*-Diethyl-5-phenylpent-4-enylamine (1g)**: Hexane/EtOAc 5:1, then hexane/EtOAc/NEt_3 10:10:1; yield 0.88 g (92%) of a colorless oil. IR (film): 3057, 2969, 2934, 2800, 1494, 1383, 1202, 1073 cm^{-1}. - ^{1}H nmr (200 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.2 Hz, 6 H), 1.56 (m, 2 H), 2.23-2.52 (m, 8 H), 5.63 (dt, *J* = 7.2, 11.6 Hz, 1 H), 6.38 (d, *J* = 11.6 Hz, 1 H), 7.21 (m, 5 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 11.7 (q), 26.7 (t), 27.4 (t), 46.9 (t), 52.5 (t), 125.9 (d), 128.1 (d), 128.7 (d), 129.0 (d), 132.7 (d), 137.7 (s). - MS (70 eV); m/z (%): 217 (14) [M^+], 202 (11) [M^+-CH_3], 112 (16), 91 (8), 86 (100) [CH_2NEt_2], 72 (12) [NEt_2], 58 (9). - Anal. Calcd. for $C_{15}H_{23}N$ (217.35): C 82.89, H 10.67, N 6.44; Found C 82.58, H 10.97, N 6.34.

***N,N*-Dibenzyl-5-methylhex-4-enylamine (1h)**: Hexane/EtOAc 20:1; yield 1.2 g (82%) of a colorless oil. IR (film): 3063, 3047, 2927, 2795, 1494, 1453, 1127, 1029, 744, 698 cm^{-1}. - ^1H nmr (200 MHz, $CDCl_3$): δ = 1.88 (m, 2 H), 1.89 (s, 3 H), 1.97 (s, 3 H), 2.29 (dt, *J* = 7.3, 7.4 Hz, 2 H), 2.75 (t, *J* = 7.4 Hz, 2 H), 3.88 (s, 4 H), 5.37 (m, 1 H), 7.52 (m, 10 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 17.7 (q), 25.7 (q), 25.8 (t), 27.3 (t), 53.1 (t), 58.3 (t), 124.5 (d), 126.7 (d), 128.1 (d), 128.8 (d), 131.4 (s), 140.0 (s). - MS (70 eV); m/z (%): 293 (27) [M^+], 236 (18), 210 (77) [CH_2NBn_2], 202 (24) [M^+-Bn], 181 (9), 91 (100) [Bn]. - Anal. Calcd. for $C_{21}H_{27}N$ (293.45): C 85.95, H 9.27, N 4.77; Found: C 85.92, H 9.41, N 4.75.

***N,N*-Dibenzylhex-4-enylamine (1i)**: Hexane/EtOAc 10:1; yield 3 g (93%) of a colorless oil. IR (film): 3027, 2934, 2795, 1494, 1453, 966, 698 cm^{-1}. - ^1H nmr (400 MHz, $CDCl_3$): δ = 1.49 (m, 5 H), 1.90 (m, 2 H), 2.36 (t, *J* = 7.1 Hz, 2 H), 3.49 (s, 4 H), 5.28 (m, 2 H), 7.23 (m, 10 H). - ^{13}C nmr (100 MHz, $CDCl_3$): δ = 17.9 (q), 27.0 (t), 30.2 (t), 52.9 (t), 58.3 (t), 124.8 (d), 126.7 (d), 128.1 (d), 128.8 (d), 131.2 (d), 140.0 (s). - MS (70 eV); *m/z* (%): 279 (10) [M^+], 210 (84) [CH_2NBn_2], 188 (14) [M^+-Bn], 91 (100) [Bn]. - Anal. Calcd. for $C_{20}H_{25}N$ (279.42): C 85.97, H 9.02, N 5.01; Found. C 85.79, H 9.05, N 5.04.

***(E)*-*N,N*-Diethyl-5-phenylpent-4-enylamine (1f)**: A solution of **1g** (1.5 g, 6.9 mmol) in 120 ml benzene was irradiated (150 W mercury lamp) in the presence of 30 mg (0.14 mmol) diphenyl disulfide in 120 ml benzene for two hours. The solvent was evaporated and the amine was purified by flash column chromatography (hexane/EtOAc 5:1, then hexane/EtOAc/NEt_3 10:10:1). Yield 1.3 g (90%) of a colorless oil. IR (film): 3082, 3060, 3026, 2969, 2934, 2800, 1599, 1578, 1466, 1382, 1071 cm^{-1}. ^1H nmr (200 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.5 Hz, 6 H), 1.57 (tt, *J* = 7.5, 7.6 Hz, 2 H), 2.17 (m, 2 H), 2.46 (m, 6 H), 6.20 (dt, *J* = 6.5, 15.8 Hz, 1 H), 6.36 (d, *J* = 15.8 Hz, 1 H), 7.21 (m, 5 H). - ^{13}C nmr (50 MHz, $CDCl_3$): δ = 11.7 (q), 26.7 (t), 31.0 (t), 46.9 (t), 52.5 (t), 126.0 (d), 127.0 (d), 128.5 (d), 130.0 (d), 132.7 (d), 137.7 (s). - MS (70 eV); m/z (%): 217 (26) [M^+], 202 (13) [M^+-CH_3], 157 (12), 137 (11), 121 (98), 112 (20), 86 (100) [CH_2NEt_2], 72 (13) [NEt_2], 58 (10). - Anal. Calcd. for $C_{15}H_{23}N$ (217.35): C 82.89, H 10.67, N 6.44; Found C 82.64, H 10.86, N 6.56.

Tris(p-bromophenyl)aminium hexafluorophosphate (2a): Nitrogen was bubbled vigorously into a solution of 3.2 g (18.3 mmol) nitrosyl hexafluorophosphate in 20 ml dry CH_2Cl_2 for 30 min. A solution of 8.8 g (18.3 mmol) tris(p-bromophenyl)amine in 30 ml dry CH_2Cl_2 was added dropwise at room temperature with further bubbling of N_2 to remove NO. When the addition was complete, N_2 bubbling was continued for 15 min. 150 ml Ether was added to the solution to precipitate the product which was filtered, washed with ether and dried under vacuum to give 7.1 g (62%) of a blue-black solid. UV (CH_3CN): λ_{max} (lg ε) = 206 nm (9.06), 228 (8.01), 306 (7.48), 362 (7.77), 374 (7.61), 498 (6.10), 592 (7.13), 618 (7.28), 706

(8.33). - Anal. Calcd. for $C_{18}H_{12}Br_3F_6NP$ (626.96): C 34.48, H 1.93, N 2.23; Found. C 34.94, H 2.08, N 2.18.

Oxidation of Tertiary Amines (1a-i) with 2a in the Presence of Water (General procedure): Amine **1** (0.35 mmol) was dissolved in acetonitrile [50m*M*] and 10 equiv. water. **2a** (1-1.5 equiv.) was added in small portions at -20°C until the color of the reaction mixture changed to blue. K_2CO_3 (1 equiv) was added and the color of the mixture changed to brown. Addition of **2a** (0.5-1.5 equiv.) in small portions was continued until the color of the reaction mixture changed to blue again, followed by addition 0.5 equiv. K_2CO_3. This addition cycle was repeated until the reaction was complete by tlc. (The oxidant was always added in small portions until the color of the reaction mixture changed to blue (total maximum amount: 3.5 equiv. **2a**. The amount of K_2CO_3 was always reduced to half the amount of the foregoing cycle). Acetone was added to dissolve precipitated triarylamine. The inorganic salts were removed by filtration, the solvent was evaporated under reduced pressure, and the residue was dissolved in a minimum amount of acetone. This solution was added dropwise into an ether/hexane mixture (70 ml, 1:1) to precipitate the product which was filtered and purified by flash column chromatography and/or recrystallization.

2-(1-Hydroxydiphenylmethyl)-1,1-diethylpyrrolidinium hexafluorophosphate (3aa): Recrystallization from i-PrOH/CH_2Cl_2 gave 140 mg (88%) of a colorless salt. mp. 227°C. - IR (Nujol): 3556 (s, OH), 1495, 1463, 1140, 1074, 1007, 881, 850, 841, 821 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.23 (t, *J* = 7.2 Hz, 3 H), 1.42 (t, *J* = 7.1 Hz, 3 H), 2.23 (m, 2 H), 2.40 (m, 1 H), 2.68 (m, 1 H), 2.87 (dq, *J* = 7.2, 13.5 Hz, 1 H), 3.19 (dq, *J* = 7.1, 13.9 Hz,1 H), 3.60 (dq, *J* = 7.1, 13.9 Hz, 1 H), 3.77 (dq, *J* = 7.3, 13.6 Hz, 1 H), 3.88 (m, 2 H), 5.51 (dd, *J* = 6.0, 9.1 Hz, 1 H), 6.19 (s, 1 H), 7.23 (m, 2 H), 7.33 (m, 4 H), 7.70 (m, 2 H), 7.83 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 9.0 (q), 9.7 (q), 20.5 (t), 27.4 (t), 53.7 (t), 55.9 (t), 63.8 (t), 77.4 (d), 80.7 (s), 125.7 (d), 125.8 (d), 128.1 (d), 128.1 (d), 129.5 (d), 129.7 (d), 145.9 (s), 147.9 (s). - MS (FAB); *m/z* (%): 310 (100) [M^+], 237 (2), 192 (3), 98 (6), 77 (4). - Anal. Calcd. for $C_{21}H_{28}F_6NOP$ (455.42): C 55.38, H 6.20, N 3.08; Found: C 55.30, H 6.16, N 2.95.

1-(Hydroxydiphenylmethyl)-5-azoniaspiro[4,4]nonane hexafluorophosphate (3ba): Purification by recrystallization from iPrOH/CH_2Cl_2. Yield: 117 mg (74%). mp. 216°C. - IR (KBr): 3542 (s, OH), 3024, 2971, 1637, 856, 833, 558 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.65 (m, 1 H), 1.97 (m, 3 H), 2.22 (m, 2 H), 2.33 (m, 1 H), 2.52 (m, 1 H), 3.49 (m, 1 H), 3.59 (m, 1 H), 3.70 (m, 3 H), 3.80 (m, 1 H), 5.54 (dd, *J* = 7.1, 7.3 Hz, 1 H), 6.08 (s, 1 H), 7.34 (m, 2 H), 7.36 (m, 4 H), 7.67 (m, 2 H), 7.85 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 21.1 (t), 21.3 (t), 22.3 (t), 28.2 (t), 60.4 (t), 65.5 (t), 66.6 (t), 78.5 (d), 80.5 (s), 125.8 (d), 126.1 (d), 128.1 (d), 128.3 (d), 129.5 (d), 129.8 (d), 145.3 (s) 147.5 (s). - MS (FAB); *m/z* (%): 308 (100) [M^+], 230 (2), 105 (6), 84 (4). - Anal. Calcd. for $C_{21}H_{26}F_6NOP$ (453.40): C 55.63, H 5.78, N 3.09; Found: C 55.05, H 5.68, N 2.86.

1,1-Diallyl-2-(1-hydroxydiphenylmethyl)pyrrolidinium hexafluorophosphate (3ca): Purification by flash column chromatography (acetone/MeOH 10:1 gradient to 1:1) gave 137 mg (82%) of a brown oil that crystallized slowly. mp 148°C. - IR (film): 3558 (s, OH), 3062, 2985, 1703, 1494, 1451, 1426, 1365, 1033, 1004, 958, 843, 838, 751, 710 cm^{-1}. - ^1H nmr (400 MHz, acetone-d_6): δ = 2.25 (m, 2 H), 2.45 (m, 1 H), 2.67 (m, 1 H), 3.65 (m, 2 H), 3.78 (m, 1 H), 3.90 (m, 2 H), 4.36 (dd, *J* = 7.1, 13.6 Hz, 1 H), 5.51 (m, 3 H), 5.74 (m, 2 H), 6.10 (m, 1 H), 6.20 (s, 1 H), 6.22 (m, 1 H) 7.27 (m, 2 H), 7.38 (m, 4 H), 7.70 (m, 2 H), 7.82 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 20.2 (t), 26.8 (t), 62.0 (t), 63.8 (t), 64.5 (t), 78.3 (d), 80.2 (s), 125.9 (d), 126.2 (d), 127.0 (d), 127.3 (t), 127.8 (d), 128.3 (d), 128.4 (d), 128.8 (t), 129.5 (d), 129.7 (d), 145.2 (s), 147.4 (s). - MS (FAB); *m/z* (%): 334 (100) [M^+], 292 (3), 237 (6), 167 (1), 150 (2), 110 (16), 105 (6), 77 (2), 70 (2), 55 (1). - Anal. Calcd. for $C_{23}H_{28}F_6NOP$ (479.44): C 57.62, H 5.89, N 2.92; Found: C 57.70, H 5.81, N 2.47.

1,1-Dibenzyl-2-(1-hydroxydiphenylmethyl)pyrrolidinium hexafluorophosphate (3da): Purification by flash column chromatography (CH_2Cl_2/acetone 20:1) followed by recrystallization from i-PrOH/CH_2Cl_2 gave 178 mg (88%) of a colorless salt. mp. 123°C. - IR (KBr): 3549 (s, OH), 2972, 2929, 1586, 1310, 1214, 850, 836, 706, 558 cm^{-1}. - ^1H nmr (400 MHz, acetone-d_6): δ = 2.18 (m, 2 H), 2.51 (m, 2 H), 3.48 (m, 1 H), 4.00 (m, 1 H), 4.40 (d, *J* = 11.4 Hz, 1 H), 4.43 (d, *J* = 11.3 Hz, 1 H), 4.87 (d, *J* = 13.4 Hz, 1 H), 4.96 (d, *J* = 13.2 Hz, 1 H), 5.45 (t, *J* = 8.4 Hz, 1 H), 6.66 (s, 1 H), 7.23-7.79 (m, 20 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 20.5 (t), 27.2 (t), 62.6 (t), 63.2 (t), 65.2 (t), 77.2 (d), 81.0 (s), 126.0 (d), 126.6 (d), 128.4 (d), 128.5 (d), 129.5 (d), 129.6 (s), 129.8 (d), 130.0 (s), 130.1 (d), 130.5 (d), 131.4 (d), 131.8 (d), 133.9 (d), 134.3 (d), 145.9 (s), 146.5 (s). - MS (FAB); *m/z* (%): 434 (100) [M^+], 342 (4) [M^+-Bn], 326 (3), 237 (3), 210 (3), 160 (23), 105 (4), 91 (28) [Bn], 77 (3) [Ph].

1,1-Diethyl-2-(1-hydroxybenzyl)pyrrolidinium hexafluorophosphate (3fa) and 2-Benzoyl-1,1-diethylpyrrolidinium hexafluorophosphate (5): Purification by flash column chromatography (CH_2Cl_2/acetone 10:1 gradient to 0:1) gave 65 mg (49%) of a diastereomeric mixture of **3fa** as a brown oil and 24 mg (18%) of **5** as a brown oil. **3fa:** IR (KBr): 3531 (m, OH), 2989, 1605, 1037, 839, 707, 558 cm^{-1}. - MS (FAB); *m/z* (%): 234 (100) [M^+], 98 (4), 55 (4). - **Major diastereomer**: ^1H nmr (400 MHz, acetone-d_6): δ = 1.47 (t, *J* = 7.2 Hz, 3 H), 1.56 (m, 3 H), 1.99 (m, 1 H), 2.16 (m, 2 H), 2.49 (m, 1 H), 3.54 (m, 1 H), 3.64-3.99 (m, 5 H), 4.06 (m, 1 H), 5.41 (s, 1 H), 5.61 (s, 1 H), 7.32 (m, 1 H), 7.39 (m, 2 H), 7.50 (d, *J* = 7.2 Hz, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 8.6 (q), 9.5 (q), 20.9 (t), 21.1 (t), 51.2 (t), 54.7 (t), 62.2 (t), 69.8 (d), 77.3 (d), 126.9 (d), 128.8 (d), 129.4 (d), 141.8 (s). - **Minor diastereomer**: ^1H nmr (400 MHz, acetone-d_6): δ = 1.56 (m, 6 H), 4.21 (m, 1 H), 5.19 (d, *J* = 10.0 Hz, 1 H), 5.32 (s, 1 H) 7.32 (m, 1 H), 7.39 (m, 2 H), 7.50 (d, *J* = 7.2 Hz, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 8.7 (q), 9.1 (q), 20.1 (t), 26.7 (t), 51.6 (t), 57.3 (t), 60.0 (t), 73.6 (d), 75.8 (d), 128.0 (d), 129.6 (d), 129.6 (d), 141.8 (s). - **5:** ^1H nmr (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.3 Hz, 3 H), 1.35 (t, *J* = 7.2

Hz, 3 H), 2.13 (m, 1 H), 2.23-2.40 (m, 2 H), 2.82 (m, 1 H), 3.38-3.52 (m, 2 H), 3.71 (m, 2 H), 3.87 (m, 2 H), 5.46 (dd, J = 4.5, 9.1 Hz, 1 H), 7.54 (m, 2 H), 7.66 (m, 1 H), 8.03 (m, 2 H). - ^{13}C nmr (100 MHz, $CDCl_3$): δ = 8.3 (q), 9.1 (q), 20.3 (t), 26.9 (t), 50.0 (t), 54.6 (t), 60.2 (t), 71.7 (d), 129.0 (d), 129.6 (d), 133.3 (s), 135.5 (d), 193.8 (s). - MS (FAB); *m/z* (%): 232 (100) [M^+], 147 (18) [M^+-$CHN(CH_2CH_3)_2$], 95 (18), 73 (37), 55 (15).

The oxidative cyclization reaction of **1g** according to the general procedure yielded 53% of **3fa** and 20% of **5** as brown oils.

The oxidative cyclization reaction of **1f under N_2** led to a product mixture of **3fa** and **5** in a ratio of 34:1. Recrystallization from iPrOH/CH_2Cl_2 gave 103 mg (78%) of **3fa** as a yellow salt. mp 136°C. - Anal. Calcd. for $C_{15}H_{24}F_6NOP$ (379.32): C 47.50, H 6.38, N 3.96; Found: C 47.65, H 6.54, N 3.70.

2-(1-Acetylamino-1-methylethyl)-1,1-dibenzylpyrrolidinium hexafluorophosphate (3ha) and **1,1-Dibenzyl-2-(propen-2-yl)pyrrolidinium hexafluorophosphate (6)**: In this reaction, 2,6-di-*tert*-butylpyridine (2 equiv.) was used as base and was added at once before starting the reaction. **2a** (3 equiv.) was added in small portions at -20°C until the color of the reaction mixture turned to blue. After completion (tlc), acetone was added to dissolve the triarylamine and the homogeneous solution was stirred with K_2CO_3 (6 equiv.) for 15 min. The inorganic materials were filtered, the solvent was evaporated under reduced pressure, and the residue was dissolved in a minimum amount of acetone. This solution was added dropwise into a ether/hexane mixture (70 ml, 1:1). The precipitated product was filtered and purified by flash column chromatography (CH_2Cl_2/acetone 25:1 gradient to 1:1) followed by recrystallization from iPrOH/CH_2Cl_2. Yield: 46 mg (26%) of **3ha** and 50 mg (32%) of **6**. **3ha:** R_f : 0.25 (CH_2Cl_2/acetone 10:1). mp 145°C. - IR (KBr): 3417 (m, NH), 3033, 2995, 2927, 1683, 1655, 1648, 841, 558 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.63 (m, 1 H), 1.72 (s, 3 H), 1.91 (s, 3 H), 2.10 (s, 3 H), 2.21-2.51 (m, 3 H), 3.38 (m, 1 H), 3.76 (m, 1 H), 4.63 (d, J = 13.4 Hz, 1 H), 4.76 (dd, J = 8.3, 10.8 Hz, 1 H), 4.87 (d, J = 13.4 Hz, 1 H), 4.91 (d, J = 12.6 Hz, 1 H), 5.46 (d, J = 12.6 Hz, 1 H), 7.42-7.63 (m, 7 H), 7.76 (m, 3 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 20.4 (t), 24.4 (q), 25.0 (q), 26.0 (t), 30.9 (q), 56.9 (s), 60.3 (t), 62.0 (t), 63.4 (t), 78.3 (d), 129.0 (s), 129.5 (s), 130.0 (s), 130.1 (d), 131.2 (d), 131.5 (d), 134.5 (d), 134.5 (d), 172.1 (s). - MS (FAB); *m/z* (%): 351 (100) [M^+], 310 (17), 292 (48), 259 (5), 210 (20) [CH_2NBn_2], 181 (3), 160 (22), 112 (3), 91 (58), 77 (3), 58 (2) [$NHCOCH_3$]. - Anal. Calcd. for $C_{23}H_{31}F_6N_2OP$ (496.48): C 55.64, H 6.29, N 5.64; Found: C 55.45, H 6.11, N 5.00. **6:** R_f: 0.66 (CH_2Cl_2/acetone 10:1). mp 175°C. - IR (KBr): 3097, 2985, 1458, 1389, 1213, 876, 838, 759, 705 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.77 (m, 1 H), 2.08 (s, 3 H), 2.14 (m, 1 H), 2.26 (m, 1 H), 2.42 (m, 1 H), 3.43 (m, 1 H), 3.75 (m, 1 H), 4.48-4.61 (m, 4 H), 4.73 (d, J = 13.5 Hz, 1 H), 5.60 (s, 1 H), 5.61 (s, 1 H), 7.39 (m, 8 H), 7.64 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 21.7 (t), 22.0 (q), 26.9 (t), 58.8 (t), 62.8 (t), 63.3 (t), 78.1 (d), 126.8 (t), 128.9 (s), 129.4 (s), 130.1 (d), 130.1 (d), 131.4 (d), 131.4

(d), 134.1 (d), 134.2 (d), 137.0 (s). - MS (FAB); *m/z* (%): 292 (100) [M^+], 210 (5), 200 (10), 160 (11), 91 (30) [Bn], 77 (2) [Ph]. - Anal. Calcd. for $C_{21}H_{26}F_6NP$ (437.41): C 57.67, H 5.99, N 3.20; Found: C 57.36, H 6.13, N 2.79.

N,N'-Bis(5,5-diphenylpent-4-enyl)-N,N'-dimethylbiphenyl-4,4'-diamine (4): In this reaction, the color did not change to blue, but it changed between brown and green. Isolation by flash column chromatography (CH_2Cl_2/MeOH 1:0 gradient to 1:1) gave 52 mg (46%) of a brown oil. IR (Film): 3025, 2933, 2867, 1611, 1506, 1466, 1195 cm^{-1}. - ^1H nmr (400 MHz, $CDCl_3$): δ = 1.74 (m, 4 H), 2.16 (m, 4 H), 2.89 (s, 6 H), 3.29 (m, 4 H), 6.10 (t, *J* = 7.4 Hz, 2 H), 6.71 (d, *J* = 8.4 Hz, 4 H), 7.28 (m, 24 H). - ^{13}C nmr (100 MHz, $CDCl_3$): δ = 26.9 (t), 27.4 (t), 38.5 (q), 52.5 (t), 112.6 (d), 125.6 (d), 126.9 (d), 127.0 (d), 127.2 (d), 128.1 (d), 128.2 (d), 129.1 (d), 129.7 (s), 129.9 (d), 132.5 (d), 140.1 (s), 142.2 (s), 142.7 (s), 147.7 (s). - MS (FAB), *m/z* (%): 652 (100) [M^+], 459 (7) [M^+-Ph_2CCHCH_2], 445 (56) [M^+-$Ph_2CCH(CH_2)_2$], 431 (6) [M^+-$Ph_2CCH(CH_2)_3$], 251 (13), 223 (24), 193 (11), 165 (4), 115 (13), 91 (14), 77 (8) [Ph].

Oxidative Cyclization of 1a and 1f with 2a in Alcohols (General procedure): To a solution of 0.35 mmol **1a** or **1f** in dry MeOH or EtOH [50m*M*] under N_2 was added **2a** (1-1.5 equiv.) in small portions at -20°C until the reaction mixture became dark. K_2CO_3 (1 equiv.) was added and the color of the mixture turned to beige. Addition of **2a** (0.5-1.5 equiv.) in small portions was continued until the color of the reaction mixture turned to dark again, followed by addition 0.5 equiv. K_2CO_3. This addition cycle was repeated until the reaction was complete by tlc. (The oxidant was always added in small portions until the color of the reaction mixture changed to dark (total maximum amount: 3.0 equiv. **2a**. The amount of K_2CO_3 was always reduced to half the amount of the foregoing cycle). Acetone was added to dissolve the triarylamine. The inorganic salts were removed by filtration, the solvent was evaporated under reduced pressure, and the residue was dissolved in a minimum amount of acetone. This solution was added dropwise into an ether/hexane mixture (70 ml, 1:1) to precipitate the product which was filtered and purified by flash column chromatography and/or recrystallization.

1,1-Diethyl-2-(1-methoxydiphenylmethyl)pyrrolidinium hexafluorophosphate (3ka): Purification by flash column chromatography (CH_2Cl_2/acetone 20:1 gradient to 0:1) followed by recrystallization from iPrOH/CH_2Cl_2 gave 84 mg (51%) of a colorless salt. mp. 152°C. - IR (KBr): 3008, 2997, 2951, 1618, 1451, 836, 557 cm^{-1}. - ^1H nmr (400 MHz, acetone-d_6): δ = 1.21 (t, *J* = 7.2 Hz, 3 H), 1.56 (t, *J* = 7.1 Hz, 3 H), 2.03 (m, 1 H), 2.17 (m, 1 H), 2.51 (m, 2 H), 3.07 (s, 3 H), 3.17 (m, 2 H), 3.42 (m, 1 H), 3.71 (m, 3 H), 5.21 (t, *J* = 8.5 Hz, 1 H), 7.47 (m, 8 H), 7.64 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 9.1 (q), 9.3 (q), 19.9 (t), 26.3 (t), 53.4 (t), 53.8 (q), 57.1 (t), 60.3 (t), 78.7 (d), 87.0 (s), 129.4 (d), 129.4 (d), 129.5 (d), 129.5 (d), 129.7 (d), 130.4 (d), 138.0 (s), 140.6 (s). - MS

(FAB); *m/z* (%): 324 (100) [M^+], 176 (3), 98 (6), 77 (2). - Anal. Calcd. for $C_{22}H_{30}F_6NOP$ (469.45): C 56.27, H 6.44, N 2.98; Found: C 56.45, H 6.32, N 2.77.

1,1-Diethyl-2-(1-methoxybenzyl)pyrrolidinium hexafluorophosphate (3la): Purification by flash column chromatography (CH_2Cl_2/acetone 20:1 gradient to 0:1) gave 96 mg (70%) of a 1:1 diastereomeric mixture of a beige salt. ^{1}H nmr (200 MHz, acetone-d_6): δ = 1.51 (m, 12 H), 1.87-2.18 (m, 8 H), 3.31 (s, 3 H), 3.33 (s, 3 H), 3.50-4.02 (m, 14 H), 4.75 (d, *J* = 10.0 Hz, 1 H), 5.06 (s, 1 H), 7.47 (m, 10 H). - ^{13}C nmr (50 MHz, acetone-d_6): δ = 8.6 (q), 8.7 (q), 9.0 (q), 9.3 (q), 20.1 (t), 20.6 (t), 21.5 (t), 26.8 (t), 51.7 (t), 51.8 (t), 55.0 (t), 55.8 (q), 56.5 (q), 57.3 (t), 60.1 (t), 62.0 (t), 75.0 (d), 77.2 (d), 79.0 (d), 82.2 (d), 127.7 (d), 128.6 (d), 129.3 (d), 129.7 (d), 130.0 (d), 137.8 (s), 138.0 (s).

1,1-Diethyl-2-(1-ethoxydiphenylmethyl)pyrrolidinium hexafluorophosphate (3ma): Purification by recrystallization from iPrOH/CH_2Cl_2 gave 78 mg (46%) of a colorless salt. mp. 166°C. - IR (KBr): 2973, 2931, 2898, 1450, 1062, 874, 840, 739, 705, 558 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.24 (m, 6 H), 1.62 (t, *J* = 7.1 Hz, 3 H), 2.06 (m, 1 H), 2.18 (m, 1 H), 2.47 (m, 2 H), 2.89 (m, 1 H), 3.12 (m, 1 H), 3.21 (m, 1 H), 3.32 (m, 1 H), 3.43 (m, 1 H), 3.76 (m, 3 H), 5.27 (t, *J* = 8.6 Hz, 1 H), 7.41-7.64 (m, 10 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 9.1 (q), 9.4 (q), 15.1 (q), 19.7 (t), 26.0 (t), 53.4 (t), 57.0 (t), 59.9 (t), 61.9 (t), 78.7 (d), 86.8 (s), 129.4 (d), 129.4 (d), 129.5 (d), 129.5 (d), 129.8 (d), 130.4 (d), 137.9 (s), 140.8 (s). - MS (FAB); *m/z* (%): 338 (100) [M^+], 167 (2), 126 (2), 112 (9), 86 (16) [CH_2NEt_2], 77 (2). - Anal. Calcd. for $C_{23}H_{32}F_6NOP$ (483.48): C 57.14, H 6.67, N 2.90; Found: C 57.20, H 6.72, N 2.59.

2-(Chlorodiphenylmethyl)-1,1-diethylpyrrolidinium hexafluorophosphate (3na): To a mixture of **1a** (0.35 mmol), 10 equiv. of dried LiCl and dry acetonitrile [50 m*M*] was added **2a** (1-1.5 equiv.) in small portions at -20°C under N_2 until the reaction mixture became blue. K_2CO_3 (1 equiv.) was added and the color of the mixture turned to brown. Addition of **2a** (0.5-1.5 equiv.) in small portions was continued until the color of the reaction mixture turned to dark again, followed by addition 0.5 equiv. K_2CO_3. This addition cycle was repeated until the reaction was complete by tlc. (The oxidant was always added in small portions until the color of the reaction mixture changed to blue (total maximum amount: 3.0 equiv. **2a**. The amount of K_2CO_3 was always reduced to half the amount of the foregoing cycle). Acetone was added to dissolve the triarylamine. The inorganic salts were removed by filtration, the solvent was evaporated under reduced pressure and the residue was dissolved in a minimum amount of acetone. This solution was added dropwise into an ether/hexane mixture (70 ml, 1:1) to precipitate the product which was filtered and purified by recrystallization from iPrOH/CH_2Cl_2. Yield 84 mg (51%) of a yellow salt. mp 175°C. - IR (KBr): 3055, 2987, 2925, 1448, 857, 834, 707, 558 cm^{-1}. - ^{1}H nmr (400 MHz, acetone-d_6): δ = 1.16 (t, *J* = 7.1 Hz, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 2.27 (m, 2 H), 2.42 (m, 1 H), 2.65 (m, 1 H), 2.93 (m, 1 H), 3.26 (m, 1 H), 3.55 (m, 1 H), 3.66 (m, 1 H), 3.84 (m, 1 H), 4.03 (m, 1 H), 5.74 (dd, *J* =

5.0, 9.0 Hz, 1 H), 7.18 (m, 2 H), 7.31 (m, 4 H), 7.67 (m, 2 H), 7.75 (m, 2 H). - ^{13}C nmr (100 MHz, acetone-d_6): δ = 9.2 (q), 9.8 (q), 20.7 (t), 30.0 (t), 53.8 (t), 57.5 (t), 64.6 (t), 78.9 (d), 81.5 (s), 126.9 (d), 127.4 (d), 128.9 (d), 129.3 (d), 129.6 (d), 130.2 (d), 142.8 (s), 145.3 (s). - MS (FAB); *m/z* (%): 328 (100) [M^+], 292 (6) [M^+-Cl], 176 (5), 98 (7) , 86 (14) [CH_2NEt_2], 77 (4).

Oxidation of 1a with 2c: Under N_2, 0.35 mmol **1a** was dissolved in acetonitrile [50 m*M*] and 10 equiv. water. **2c** (3 equiv.) was added in small portions at -20°C. After completion (tlc), the solvent was evaporated under reduced pressure. The residue was diluted with CH_2Cl_2/acetone (6:1) and filtered through a pad of silica gel. The solvent was evaporated under reduced pressure and the solid was carefully washed with acetone. The yellow solution was added dropwise to ether to precipitate the product which was filtered and purified by recrystallization from iPrOH/CH_2Cl_2. Yield 49%.

References:

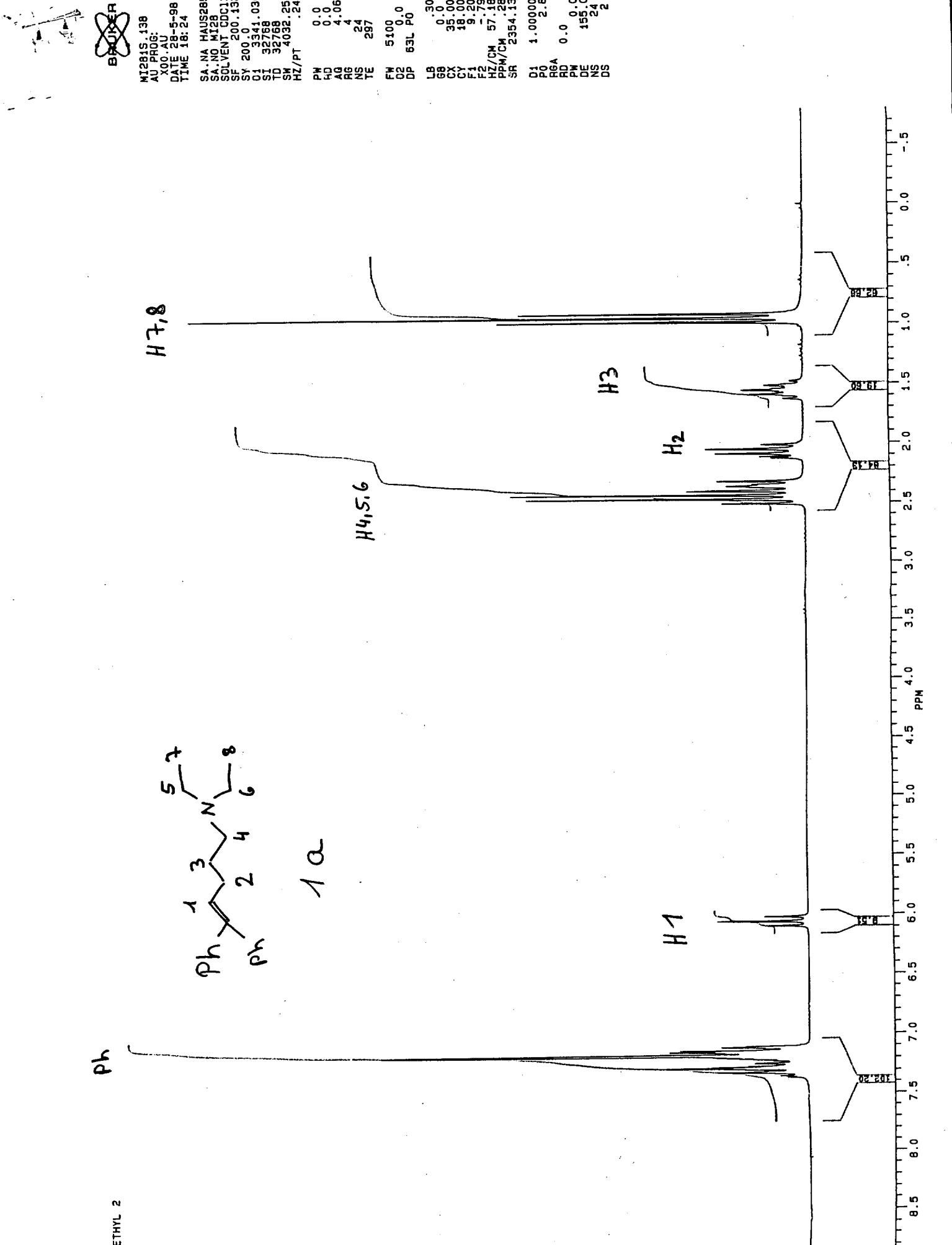
(1) Newcomb, M.; Horner, J. H.; Shakin, H. *Tetrahedron Lett.* **1993**, *34*, 5523-5526.

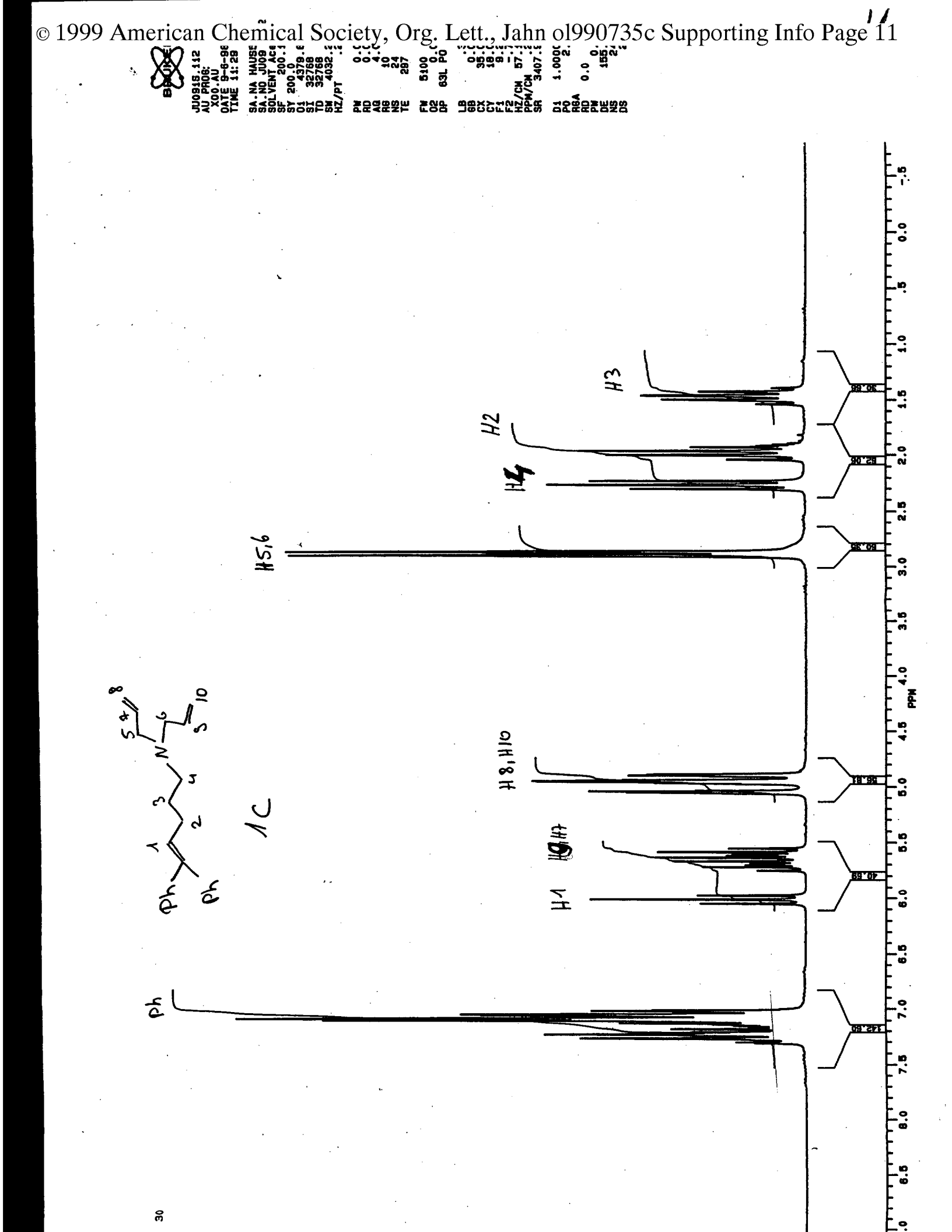
(2) Ding, M. W.; Shi, D. Q.; Xiao, W. J.; Huan, W. F. *Synth. Commun.* **1994**, *24*, 3235-3239

(3) Denmark, S. E.; Forbes, D. C.; Hays, D. S.; De Pue, J. S.; Wilde, R. G. *J. Org. Chem.* **1995**, *60*, 1391-1407.

(4) Biernacke, W.; Gdula, A. *Synthesis* **1979**, 37-38.

(5) Rodriguez, L. R.; Franke, A.; Wolf, H.; Wray, V. *Tetrahedron* **1984**, *40*, 3491-3498.

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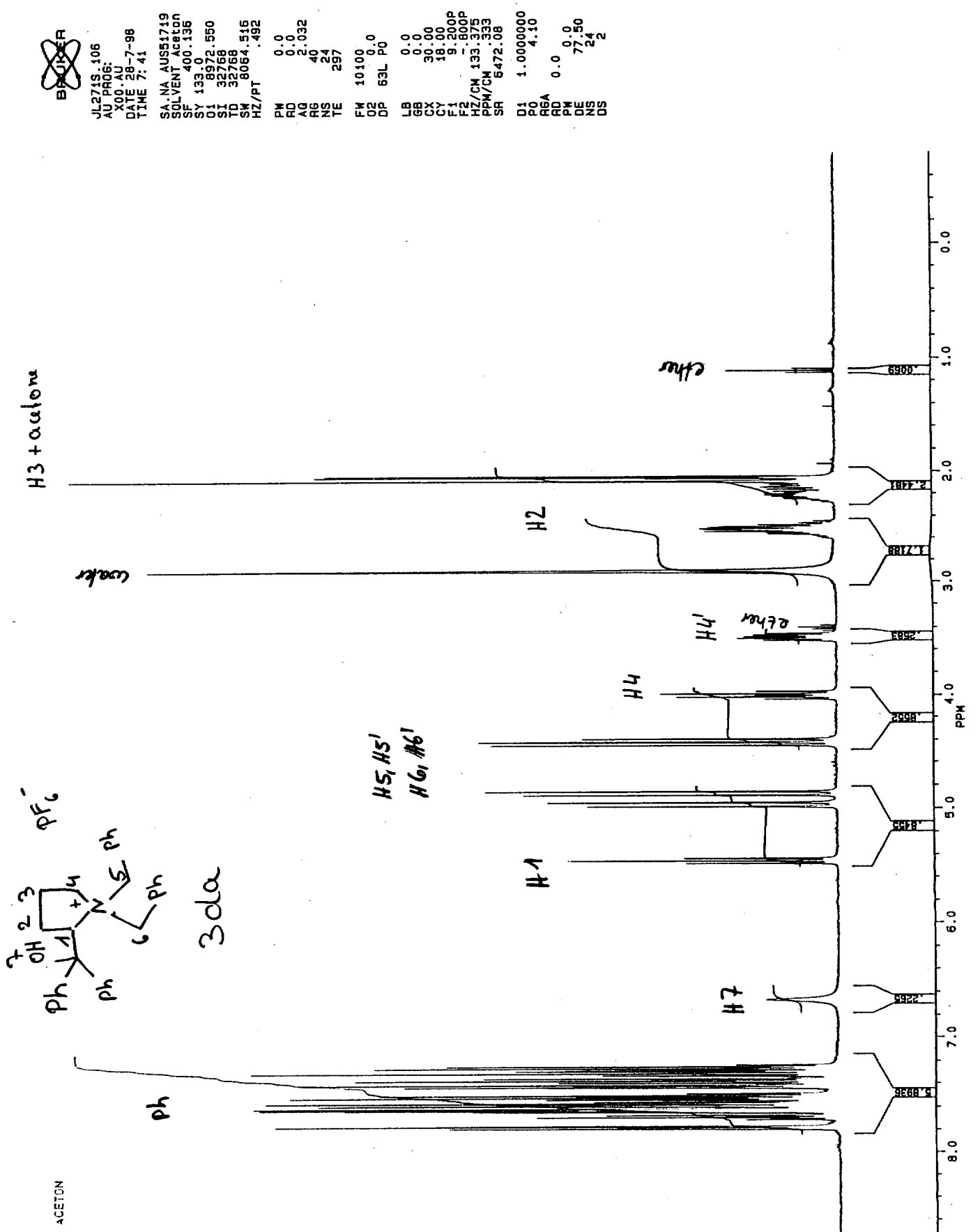
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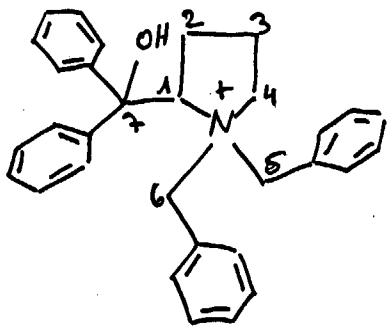

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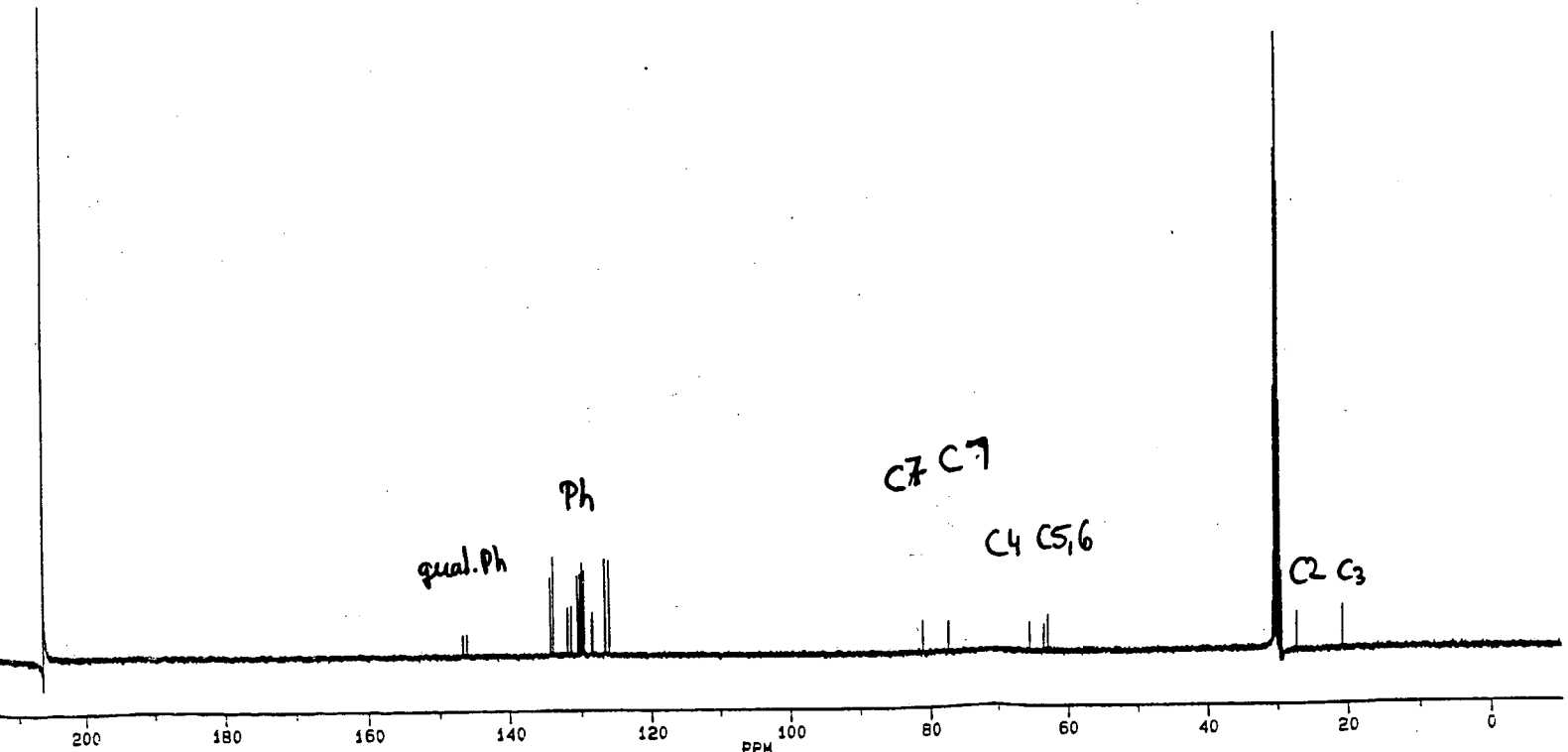

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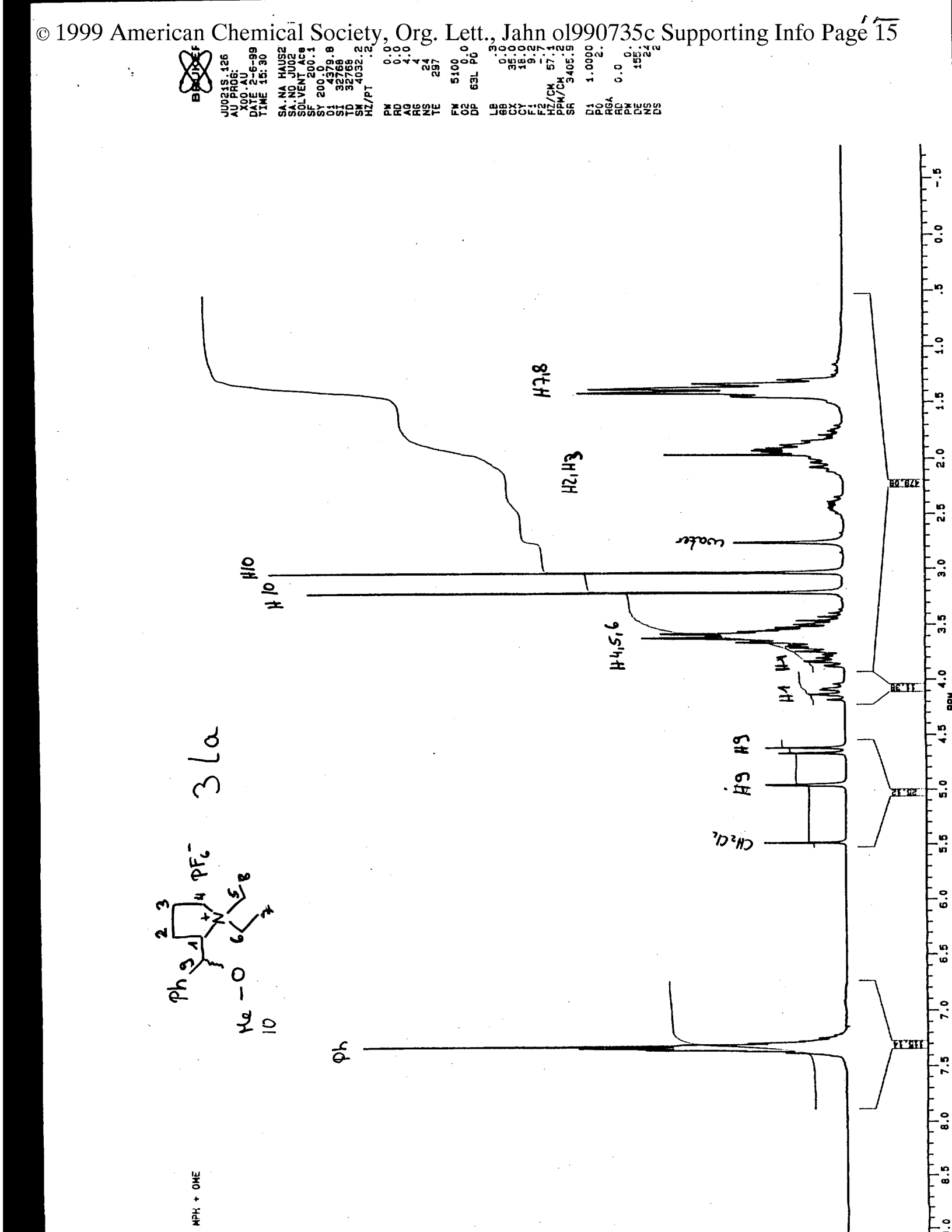

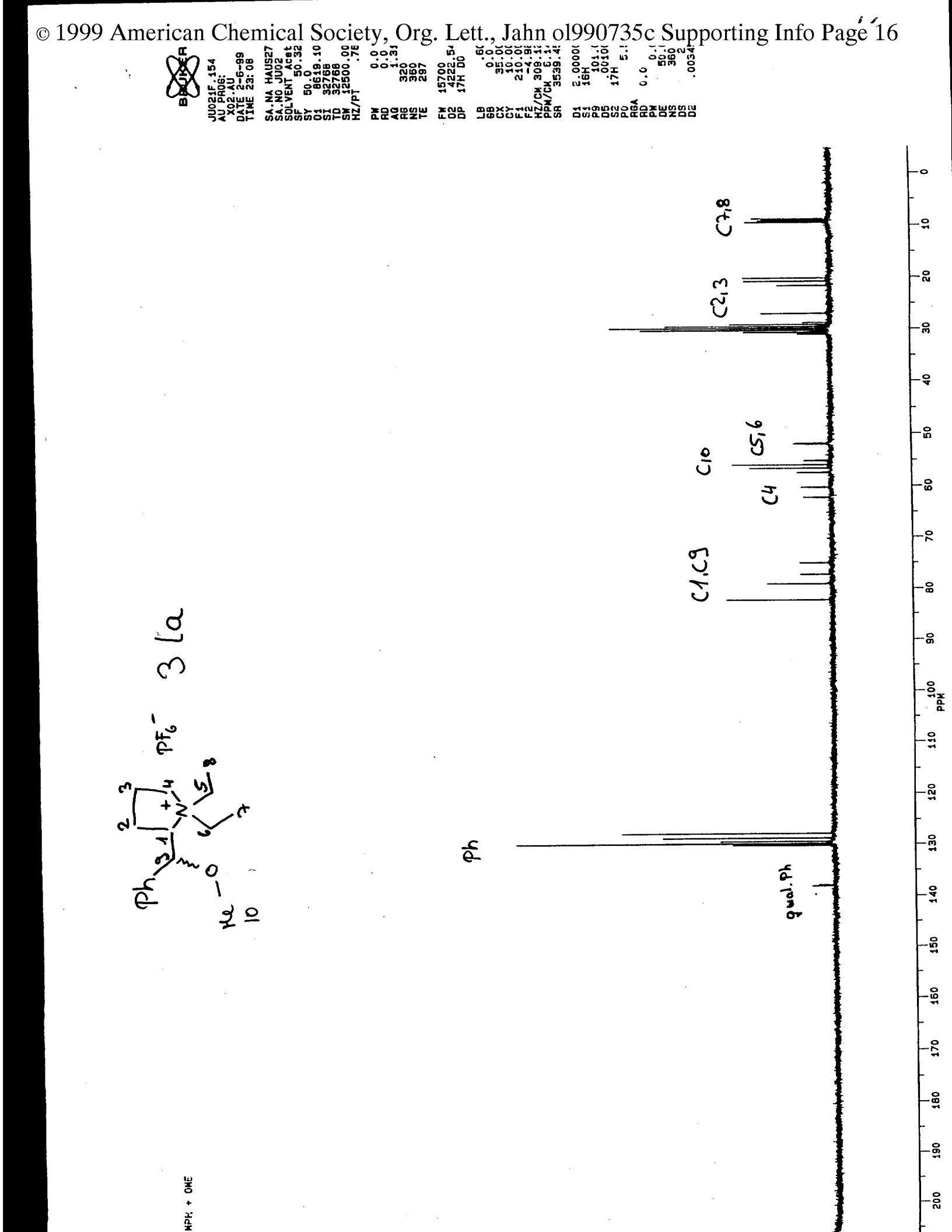

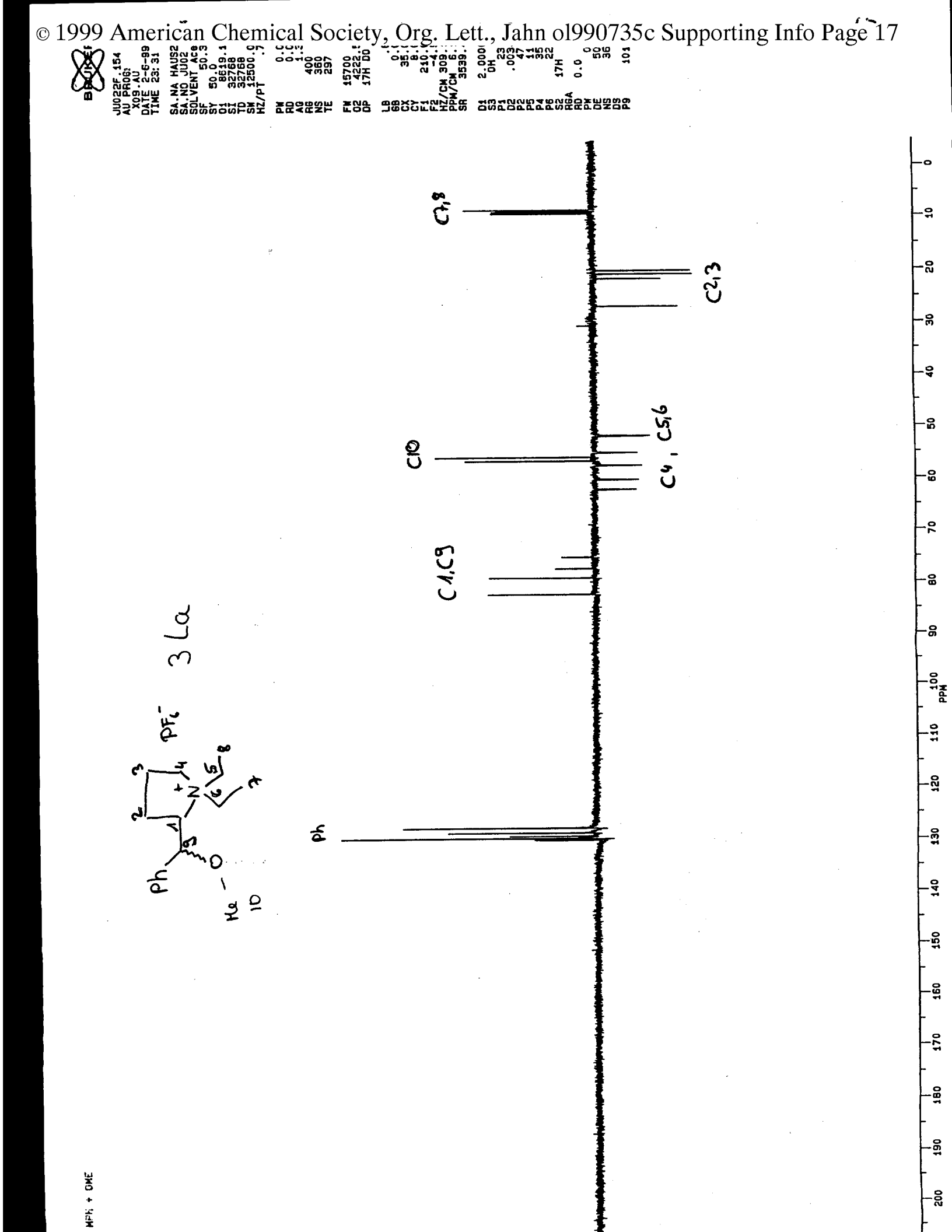

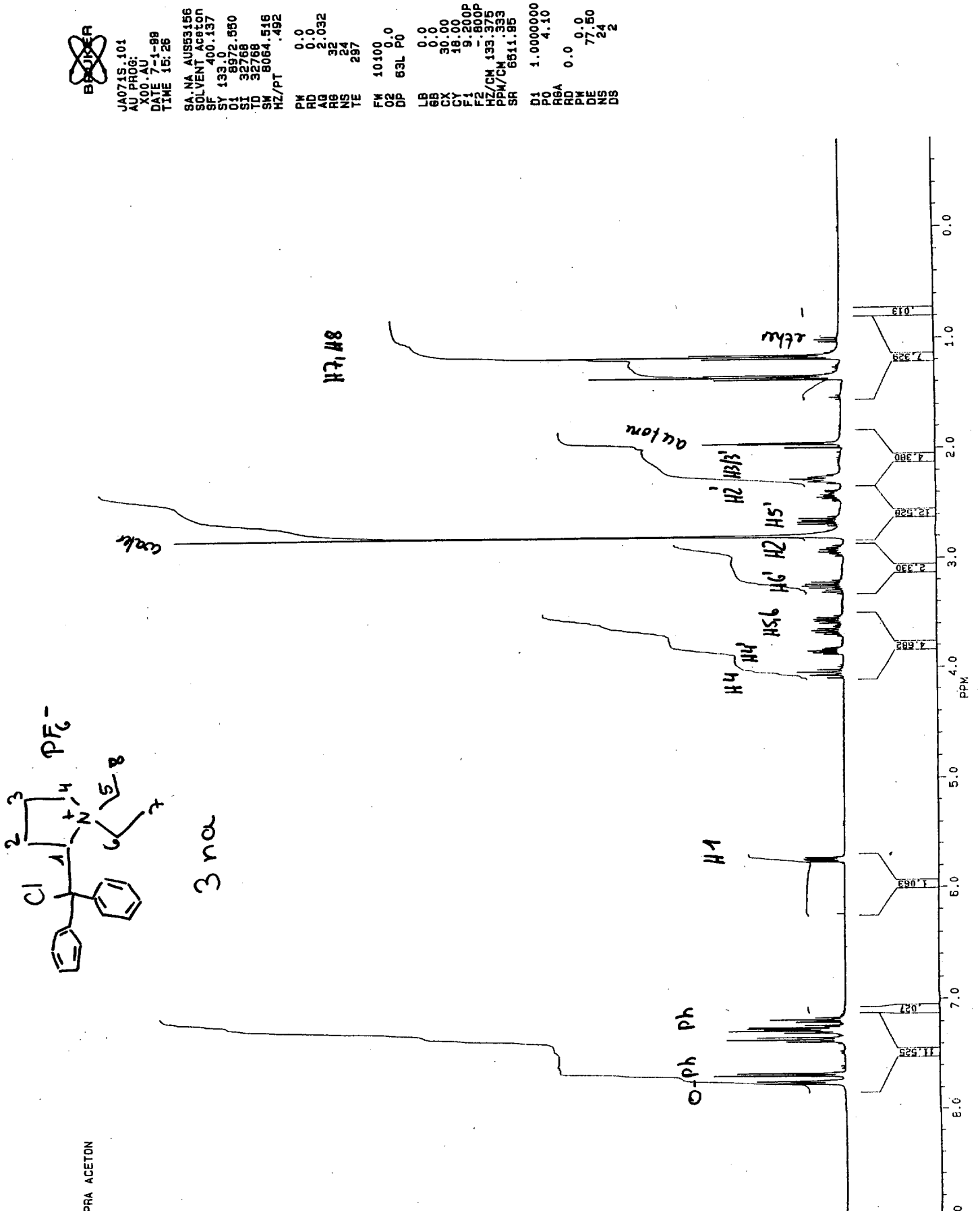

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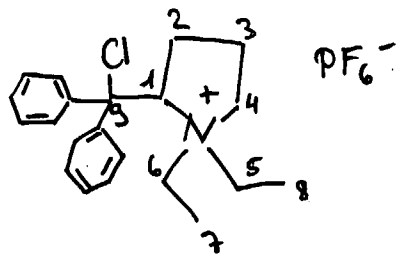

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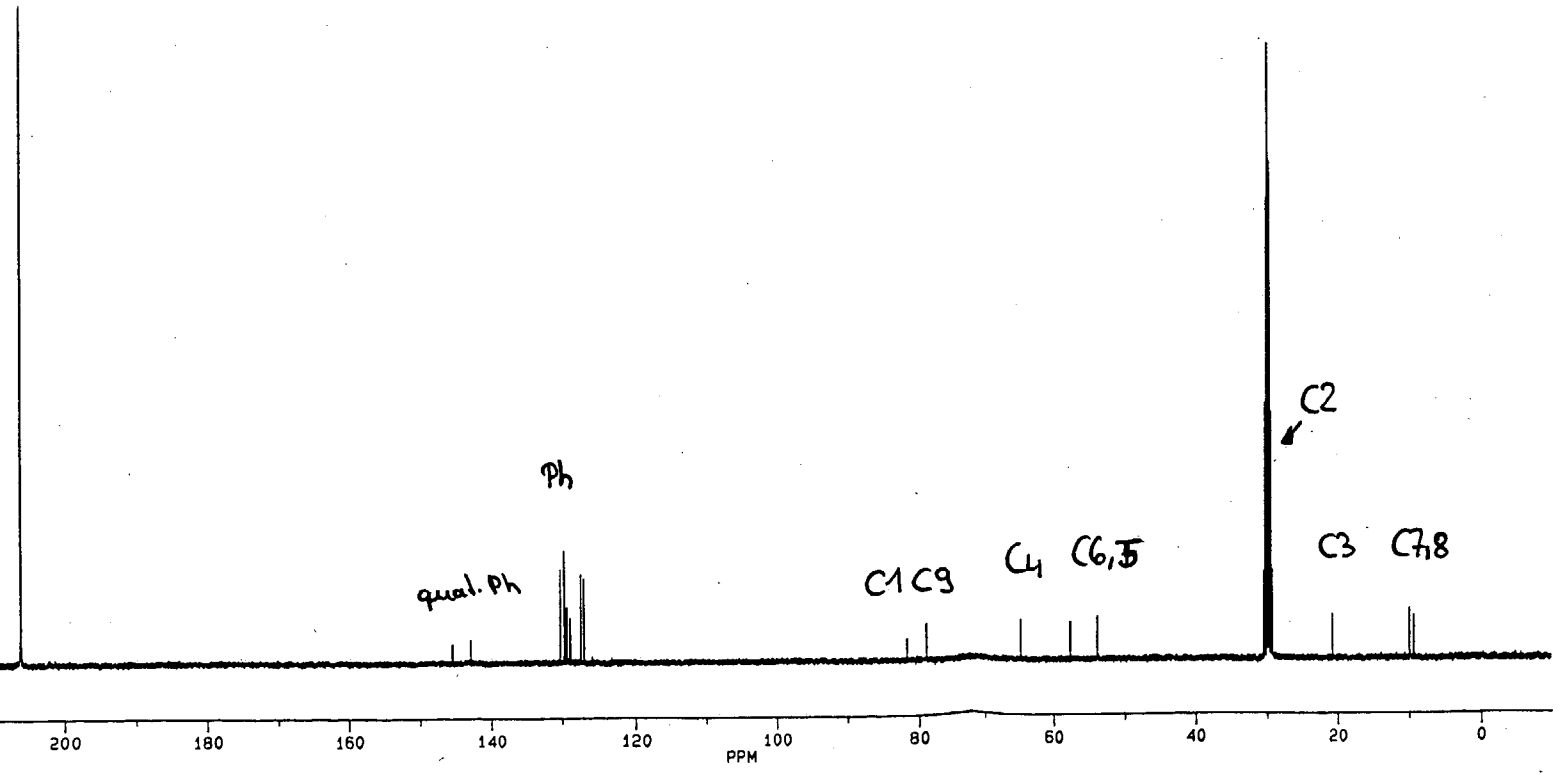

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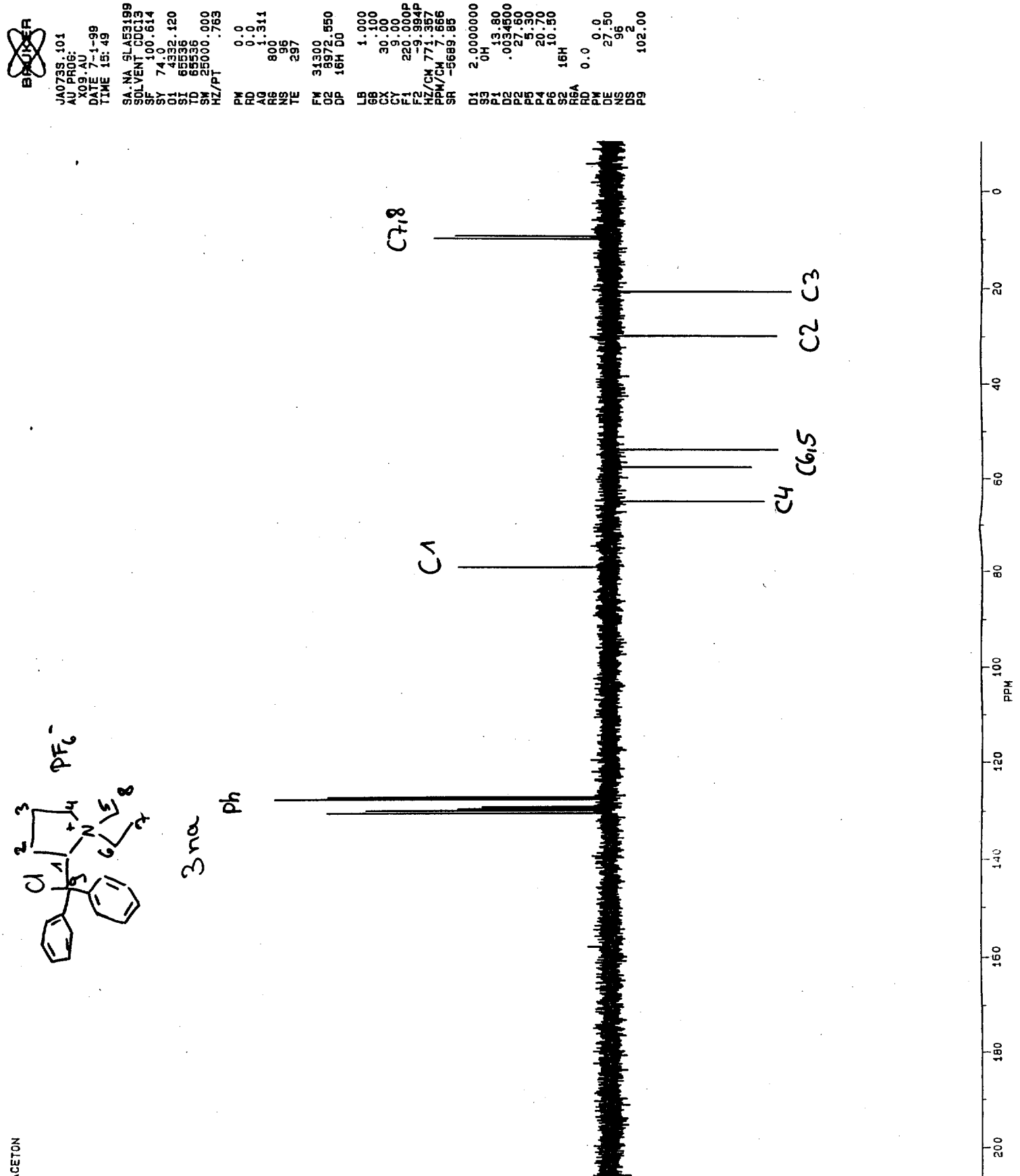

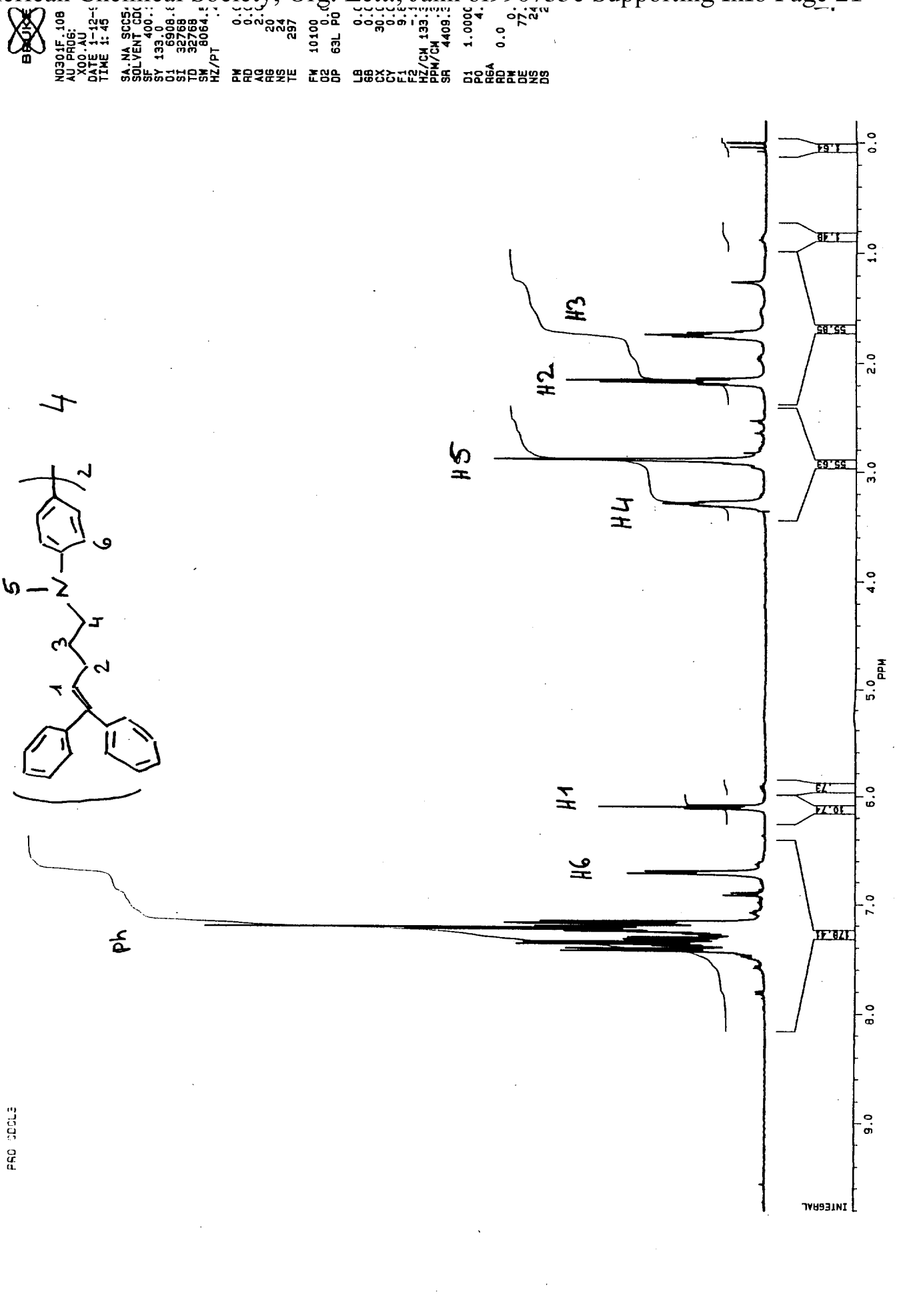

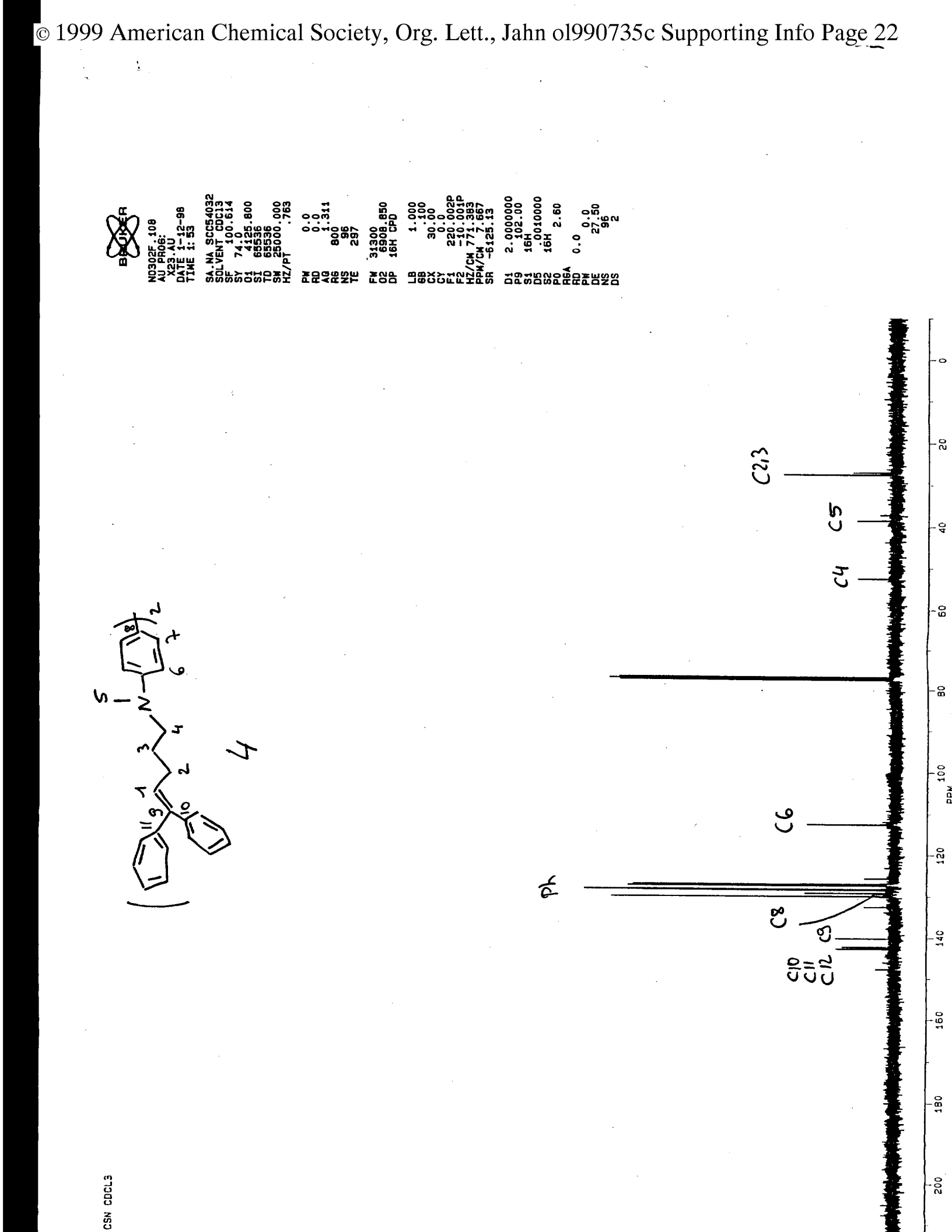

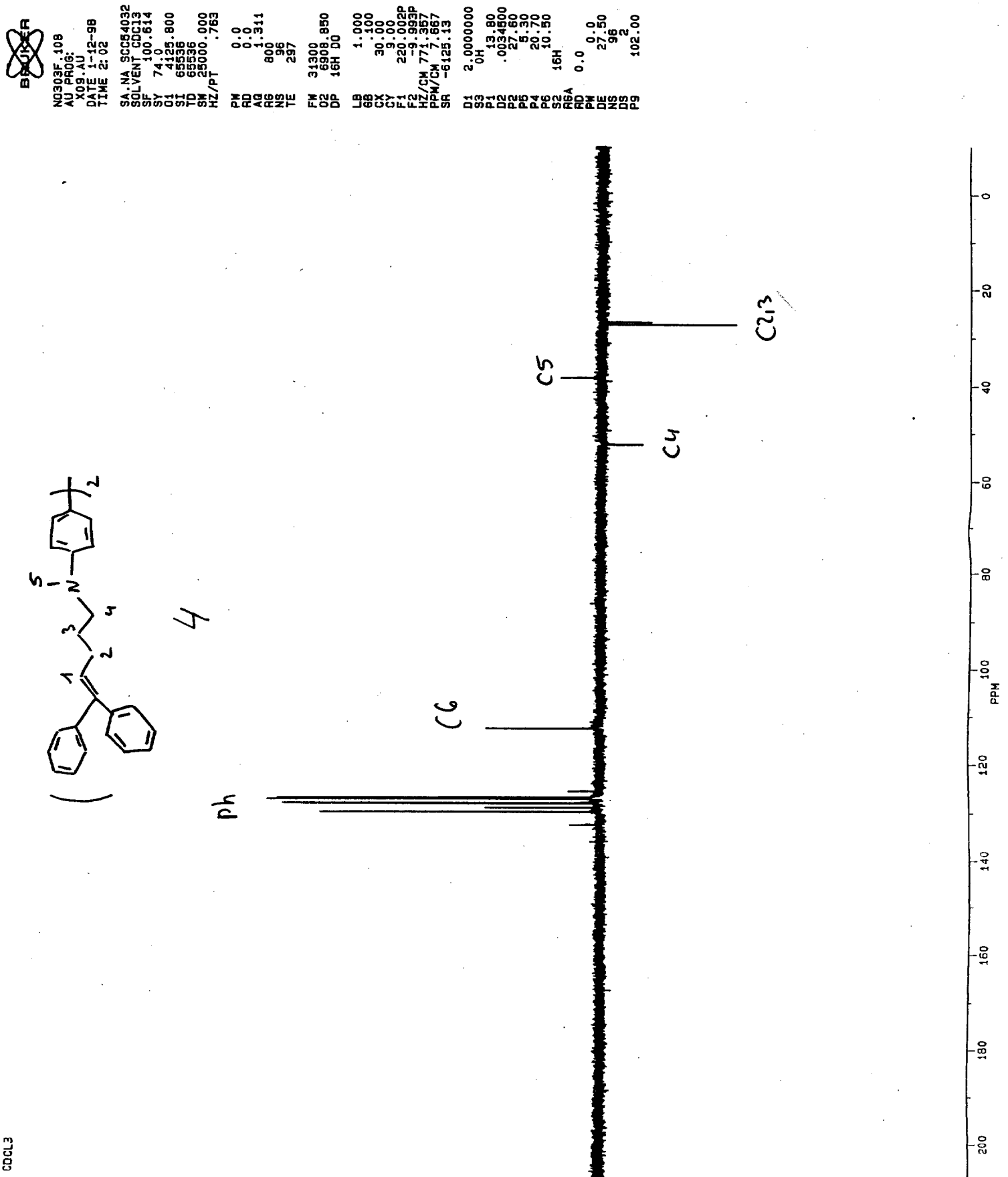
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