

Melting points were determined on a Fisher-Johns microscope melting point apparatus and are not corrected. ^1H NMR spectra were recorded at 300 MHz and are expressed as ppm downfield from tetramethylsilane as an internal standard.

2,2-Dimethylhex-4-ynylamine (17a). A solution of 1.50 g (10.8 mmol) of alkyne amide **16a** in 25 mL anhydrous dimethylether was added slowly to a slurry of 1.64 g (43.2 mmol) of LiAlH_4 in 75 mL of dimethylether. After addition was complete, the reaction was heated at reflux for a period of 4 h, cooled to RT, and carefully quenched by sequential addition of 2.5 mL of water, 2.5 mL of 5 N NaOH, and 10 mL of water. The mixture was stirred at RT until a precipitate formed, and then the ether layer was decanted. The precipitate was extracted with 3 x 50 mL of ether. The combined extracts and decanted ether were washed with brine, dried over anhydrous K_2CO_3 overnight, and concentrated under reduced pressure to afford 1.34 g (99%) of **17a** as a clear oil; IR (neat) 3387, 3310, 2959, 2921, 1584, 1471, 1364, 1321 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.91 (s, 6H), 1.78 (t, $J = 2.4$ Hz, 3H), 2.03 (d, $J = 2.5$ Hz, 2H), 2.51 (s, 2H); MS (EI) m/z (%) 126 ($\text{M}^+\text{+H}$, 38), 125 (M^+ , 5), 110 (100); HRMS (EI) Calcd for $\text{C}_8\text{H}_{15}\text{N}$: 125.1204. Found: 125.1204.

2,2-Dimethylpent-4-ynylamine (17b). This material was prepared in 99% yield from 1.00 g (8.0 mmol) of alkyne amide **16b** and 1.21 g (32 mmol) of LiAlH_4 in 100 mL of anhydrous ether, following an identical procedure to that described above for **17a**; IR (neat) 3304, 2960, 2871, 2115, 1675, 1604, 1472, 1367 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.95 (s, 6H), 2.00 (s, 1H), 2.15 (s, 2H), 2.60 (s, 2H).

3,3-Dimethylpent-4-ynylamine (17c). This material was prepared in 75% yield from 1.50 g (12 mmol) of alkyne amide **16c** and 1.80 g (48 mmol) of LiAlH_4 in 100 mL of anhydrous ether, following an identical procedure to that described above for **17a**; ^1H NMR (300 MHz, CDCl_3) δ 1.21 (s, 6H), 1.57 (t, $J = 9.0$ Hz, 2H), 2.09 (s, 1H), 2.86 (t, $J = 9.0$ Hz, 2H).

3,3-Dimethylhex-4-ynylamine (17d). This material was prepared in 91% yield from 432 mg (3.11 mmol) of alkyne amide **16d** and 708 mg (18.6 mmol) of LiAlH_4 in 100 mL of anhydrous ether, following an identical procedure to that described above for

17a; IR (neat) 3342, 2966, 2919, 1672, 1566, 1467, 1343 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.17 (s, 6H), 1.52 (t, $J = 9.0$ Hz, 2H), 1.78 (s, 3H), 2.85 (t, $J = 9.0$ Hz, 2H).

2-((4,4-Dimethylpyrrolidin-2-ylidene)ethyl)-3,3,5-trimethyl-1-pyrroline-5-carbonitrile (19a). A solution of 51.3 mg (0.180 mmol) of imidoyl triflate **18**,^{6a} 33.9 mg (0.270 mmol) of acetylenic amine **17a**, 62.0 mg (0.270 mmol) of triethylbenzylammonium chloride, 8.4 mg (0.036 mmol) of tri-2-furylphosphine, and 0.255 mL (1.85 mmol) of triethylamine in 5 mL of CH_3CN was degassed with argon for 5 min, and was then treated with 18.6 mg (0.018 mmol) of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ under an argon atmosphere. The reaction was then heated to 80 $^\circ\text{C}$, with vigorous stirring, for a period of 45 min, and then concentrated to dryness. The residue was diluted with 100 mL of CH_2Cl_2 , washed with sat'd NaHCO_3 and sat'd brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, $\text{EtOAc}:\text{hexane}:\text{Et}_3\text{N} = 10:90:1$, to 30: 90 :1) to give 32 mg (70%) of **19a** as a yellow solid, mp 108-9 $^\circ\text{C}$; R_f 0.39-0.28 (33% $\text{EtOAc}:\text{hexane}$); ^1H NMR (300 MHz, CDCl_3) δ 1.15 (s, 3H), 1.16 (s, 3H), 1.36 (s, 3H), 1.43 (s, 3H), 1.66 (s, 3H), 1.84 (s, 3H), 1.77/1.81/2.34/2.39 (AB, $J = 13.5$ Hz, 2H), 2.39/2.44/2.45/2.50 (AB, $J = 15.0$ Hz, 2H), 3.34 (s, 2H), 10.1 (br s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.9, 26.3, 28.0, 28.1, 28.2, 29.6, 36.7, 47.5, 51.0, 54.3, 61.9, 62.1, 87.2, 124.9, 164.1, 180.3; MS (EI) m/z (%) 259 (M^+ , 58), 258 (85), 244 (100); HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_3$: 259.2048. Found: 259.2046.

2-((4,4-Dimethylpyrrolidin-2-ylidene)methyl)-3,3,5-trimethyl-1-pyrroline-5-carbonitrile (19b). A solution of 52.0 mg (0.185 mmol) of imidoyl triflate **18**, 31.0 mg (0.277 mmol) of acetylenic amine **17b**, and 0.260 mL (1.85 mmol) of Et_3N in 3 mL of THF was degassed with argon for 5 min, and was then treated with a solution of 21.0 mg (0.018 mmol) of $\text{Pd}(\text{Ph}_3\text{P})_4$ in 2 mL of THF under an argon atmosphere. After stirring an additional 20 h at RT, the reaction mixture was diluted with 100 mL of CH_2Cl_2 , washed with sat'd NaHCO_3 and sat'd brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, $\text{EtOAc}:\text{hexane}:\text{Et}_3\text{N} = 20:100:1$) to give 36.0 mg (80%) of **19b** as a white crystal, mp 116-17 $^\circ\text{C}$; R_f 0.64 (33% $\text{EtOAc}:\text{hexane}$); IR (neat) 3248, 2955, 2872, 2226, 1619, 1525, 1307, 1184 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.16 (s, 6H), 1.18 (s, 3H), 1.27 (s, 3H), 1.66 (s, 3H), 1.68/1.72/2.33/2.37 (AB, $J = 13.0$ Hz,

2H), 2.41 (s, 2H), 3.31 (s, 2H), 4.48 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 27.3, 27.4, 27.6, 28.1, 29.6, 37.5, 47.3, 50.7, 51.3, 60.5, 64.4, 78.4, 125.0, 163.7, 182.9; MS (EI) m/z (%) 245 (M^+ , 30), 230 (100); Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_3$: C, 73.43; H, 9.45; N, 17.12. Found: C, 73.20; H, 9.52; N, 16.87.

3,3,5-Trimethyl-2-(pyrrolidin-2-ylidenemethyl)-1-pyrroline-5-carbonitrile (19e). This material was prepared in 85% yield from 78 mg (0.28 mmol) of imidoyl triflate **18** and 34 mg (0.41 mmol) of pent-4-ynylamine (**17e**)^a following an identical procedure to that described above for **19b**. Chromatography (silica gel, EtOAc:hexane: Et_3N = 20:100:1) gave 51 mg (85%) of **19e** as a white solid, mp 110-111 °C; R_f 0.41 (33% EtOAc/hexane); ^1H NMR (300 MHz, CDCl_3) δ 1.19 (s, 3H), 1.28 (s, 3H), 1.66 (s, 3H), 1.69/1.74/2.34/2.38 (AB, J = 13.2 Hz, 2H), 2.00 (quint., J = 7.3 Hz, 2H), 2.64 (t, J = 7.7 Hz, 2H), 3.59 (t, J = 6.9 Hz, 2H), 4.56 (s, 1H).

a: Fukuda, Y.; Matsubara, S.; Utimoro, K. *J. Org. Chem.* **1991**, *56*, 5812.

4,4,5-trimethyl-2-((trifluoromethyl)sulfonyloxy)-1-pyrroline-5-carbonitrile (20). A solution of 173 mg (1.14 mmol) of 2,3,3-trimethyl-5-oxopyrrolidine-2-carbonitrile,^{6a} 700 mg (3.41 mmol) of 2,6-di-*t*-butyl-4-methylpyridine, and 0.379 mL (2.28 mmol) of triflic anhydride in 5 mL of CH_2Cl_2 was stirred at 0 °C under nitrogen for 20 min. The reaction mixture was poured into 50 mL of a solvent combination consisting of hexane, EtOAc and Et_3N in a ratio of 75:25:1. After concentrating under reduced pressure, the residue was chromatographed on silica gel which had been pretreated with eluent (EtOAc:hexane: Et_3N = 10:90:1, to 25:75:1) to afford 197 mg (61%) of imidoyl triflate **20** as a pale yellow oil; R_f 0.67 (33% EtOAc/hexane); ^1H NMR (300 MHz, CDCl_3) δ 1.20 (s, 3H), 1.42 (s, 3H), 1.58 (s, 3H), 2.68/2.74/2.78/2.84 (AB, J = 17.3 Hz, 2H).

2-((4,4-Dimethylpyrrolidin-2-ylidene)ethyl)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile (21a). A solution of 90 mg (0.32 mmol) of imidoyl triflate **20**, 60 mg (0.48 mmol) of acetylenic amine **17a**, 111 mg (0.48 mmol) of triethylbenzylammonium chloride, 15 mg (0.0063 mmol) of tri-2-furylphosphine, and 0.46 mL (3.2 mmol) of triethylamine in 10 mL of CH_3CN was degassed with argon for 5 min, and was then treated with 29 mg (0.032 mmol) of $\text{Pd}_2(\text{dba})_3$ under an argon atmosphere. The reaction was then heated to 80 °C, with vigorous stirring, for a period of 1.5 h, and

then concentrated to dryness. The residue was diluted with 100 mL of CH₂Cl₂, washed with sat'd NaHCO₃ and sat'd brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel) to give 43 mg (52%) of **21a** (EtOAc:hexane:Et₃N = 20:100:1) as a yellow solid, and 31 mg (37%) of byproduct **22a** (EtOAc:hexane:Et₃N = 30:90:1).

21a: mp 86-7 °C; R_f 0.23 (25% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.06 (s, 3H), 1.17 (s, 3H), 1.18 (s, 3H), 1.33 (s, 3H), 1.51 (s, 3H), 1.74 (s, 3H), 2.43 (s, 2H), 2.52/2.57/2.63/2.68 (AB, *J* = 16.2 Hz, 2H), 3.30/3.33/3.34/3.37 (AB, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 15.6, 22.5, 23.2, 26.1, 27.8 (two signals), 37.0, 43.3, 46.5, 50.3, 61.2, 73.2, 88.0, 123.0, 160.8, 175.6; MS (EI) *m/z* (%) 259 (M⁺, 21), 258 (M⁺-H, 100); HRMS (EI) Calcd for C₁₆H₂₄N₃ (M-H): 258.1970. Found: 258.1966.

2-((3,3-Dimethylpyrrolidin-2-ylidene)methyl)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile (21c). A solution of 270 mg (0.950 mmol) of imidoyl triflate **20**, 127 mg (1.14 mmol) of acetylenic amine **17c**, and 1.23 mL (9.50 mmol) of Et₃N in 20 mL of THF was degassed with argon for 5 min, and was then treated with a solution of 109 mg (0.095 mmol) of Pd(Ph₃P)₄ in 5 mL of THF under an argon atmosphere. After stirring an additional 16 h at RT, the reaction mixture was diluted with 150 mL of CH₂Cl₂, washed with sat'd NaHCO₃ and sat'd brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexane:Et₃N = 10:100:1, to 50:50:1) to give 72 mg (31%) of **21c** as a yellow solid and 146 mg (62%) of byproduct **22c** as a yellow oil.

21c: mp 89-90 °C; R_f 0.51 (25% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 3H), 1.21 (s, 3H), 1.22 (s, 3H), 1.33 (s, 3H), 1.52 (s, 3H), 1.85 (t, *J* = 6.6 Hz, 2H), 2.44/2.50/2.61/2.66 (AB, *J* = 16.2 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 4.50 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 22.4, 23.1, 25.8, 27.1, 27.2, 38.6, 43.4, 43.8, 44.6, 52.0, 73.7, 79.1, 123.0, 170.4, 176.0; MS (EI) *m/z* (%) 245 (M⁺, 51), 230 (100); HRMS (EI) Calcd for C₁₅H₂₃N₃: 245.1892. Found: 245.1892.

22c: R_f 0.10 (25% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.03 (s, 3H), 1.26 (s, 6H), 1.32 (s, 3H), 1.49 (s, 3H), 1.69 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 1H), 2.22/2.228/2.55/2.61 (AB, *J* = 18.0 Hz, 2H), 3.47 (br m, 2H), 4.59 (br s, 1H).

2-((3,3-Dimethylpyrrolidin-2-ylidene)ethyl)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile (21d). A stirring solution of 25 mg (0.086 mmol) of

imidoyl chloride **27d**^{6b} in 3 mL of THF was cooled to -78 °C under nitrogen, and was then treated with 0.10 mL (0.10 mmol) of 1.0 M lithium triethylboronhydride (superhydride) in THF. After stirring an additional 1.5 h at -78 °C, the solution was quenched with sat'd NaHCO₃ at RT for 10 min. The reaction mixture was then extracted with 2 x 30 mL of CH₂Cl₂. The combined organic phases were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexane:Et₃N = 25:75:1) to give 12 mg (53%) of **21d** as a pale yellow oil; R_f 0.39 (25% EtOAc/hexane); ¹H-NMR (300 MHz, CDCl₃) δ 1.06 (s, 3H), 1.34 (s, 6H), 1.37 (s, 3H), 1.53 (s, 3H), 1.86 (s, 3H), 1.89 (t d, *J* = 6.9 Hz, *J* = 3.0 Hz, 2H), 2.56/2.61/2.67/2.72 (AB, *J* = 16.2 Hz, 2H), 3.48 (t, *J* = 6.9 Hz, 2H). MS (EI) *m/z* (%) 259 (M⁺, 21), 258 (100); HRMS (EI) Calcd for C₁₆H₂₄N₃ (M-H): 258.1970. Found: 258.1973.

2-((3,3-Dimethylhex-4-ynyl)amino)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile (22d). A solution of 31 mg (0.11 mmol) of imidoyl triflate **20**, 20 mg (0.16 mmol) of acetylenic amine **17d**, 37 mg (0.16 mmol) of triethylbenzylammonium chloride, and 0.15 mL (1.1 mmol) of triethylamine in 4 mL of CH₃CN was heated to 80 °C, with vigorous stirring, for a period of 12 h. The reaction mixture was then concentrated to dryness. The residue was diluted with 100 mL of CH₂Cl₂, washed with sat'd NaHCO₃ and sat'd brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was then purified by flash chromatography (silica gel, EtOAc:hexane:Et₃N = 30:90:1) to give 20 mg (70%) of **22d** as a yellow oil; R_f 0.12 (28% EtOAc/hexane); ¹H-NMR (300 MHz, CDCl₃) δ 1.02 (s, 3H), 1.19 (s, 6H), 1.31 (s, 3H), 1.48 (s, 3H), 1.62 (t, *J* = 7.5 Hz, 2H), 1.78 (s, 3H), 2.21/2.26/2.55/2.60 (AB, *J* = 15.0 Hz, 2H), 3.41 (br m, 2H), 4.70 (br s, 1H); MS (EI) *m/z* (%) 244 (M⁺-CH₃, 22), 217 (M⁺-CH₃-HCN, 80).

2-((3,3-Dimethyl-2-methylthio(1-pyrrolin-5-ylidene))methyl)-3,3,5-trimethyl-1-pyrroline-5-carbonitrile (24). A solution of 400 mg (1.54 mmol) of semicorrin **23**^{6a} in 50 mL of THF was treated with 412 mg (0.93 mmol) of P₄S₁₀, and the resulting suspension was heated at 75 °C for 12 hr. The reaction was then diluted with 100 mL of CH₂Cl₂, washed with sat'd NaHCO₃ and sat'd brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexane = 25:75) to give 332 mg (78%) of

thiolactam as a yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.25 (s, 3H), 1.32 (s, 3H), 1.38 (s, 3H), 1.40 (s, 3H), 1.76 (s, 3H), 1.79/1.83/2.44/2.49 (AB, $J = 13.5$ Hz, 2H), 2.88 (s, 2H), 5.13 (s, 1H).

A stirring solution of 96 mg (0.35 mmol) of thiolactam and 0.108 mL (1.75 mmol) of methyl iodide in 16 mL of THF was treated with 0.261 mL (1.75 mmol) at RT under nitrogen for a period of 16 h. The resulting white precipitate was then filtered, and the filtrate was diluted with 100 mL of EtOAc, washed with sat'd NaHCO_3 and sat'd brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel (EtOAc:hexane: $\text{Et}_3\text{N} = 20:100:1$) to afford 87 mg (87%) of thioiminoester **24** as a pale yellow solid, mp 106-8 °C; R_f 0.23 (25% EtOAc/hexane); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.26 (s, 3H), 1.31 (s, 9H), 1.71 (s, 3H), 1.78/1.82/2.41/2.45 (AB, $J = 13.2$ Hz, 2H), 2.58 (s, 3H), 3.00/3.06/3.10/3.16 (AB d, $J = 19.2$ Hz, $J = 2.4$ Hz, 2H), 6.11 (t, $J = 2.4$ Hz, 1H). MS (EI) m/z (%) 289 (M^+ , 40), 274 (100); HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{23}\text{N}_3\text{S}$: 289.1612. Found: 289.1613.

2-((2-((2-((3,3-Dimethylpyrrolidin-2-ylidene)methyl)-4,4-dimethyl(1-pyrrolin-5-ylidene))methylthio)-4,4-dimethyl(1-pyrrolin-5-ylidene))ethyl)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile (30). A solution of 23 mg (0.093 mmol) of reduced semicorrin **21c** in 0.5 mL of anhydrous *t*-BuOH was treated with 0.14 mL (0.14 mmol) of 1.0 M *t*-BuOK/*t*-BuOH under nitrogen with stirring. The reaction was then heated at 50 °C for 10 min, cooled to RT, and concentrated under reduced pressure. The residue was taken up in ether, washed with sat'd brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. Flash chromatography (silica gel, EtOAc:hexane: $\text{Et}_3\text{N} = 10:90:1$, to 25:75:1) then gave 12 mg (59%) of **29** as a pale yellow oil, which was used immediately due to its instability; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.21 (s, 3H), 1.23 (s, 3H), 1.29 (s, 6H), 1.84 (t, $J = 6.9$ Hz, 2H), 2.59 (s, 2H), 3.60 (t, $J = 6.6$ Hz, 2H), 4.21 (s, 1H), 4.64 (s, 1H), 4.71 (s, 1H).

A solution of 14.0 mg (0.0494 mmol) of thiolactam **28^{6b}** and 9.8 mg (0.0450 mmol) of enamine **29** in 3 mL of anhydrous CH_3CN was treated with 10.0 mg (0.0450 mmol) of *N*-iodosuccinimide, followed by 0.027 mL (0.18 mmol) of 1,8-diazabicyclo-[5,4,0]undec-7-ene at RT under argon (vigorous stirring). After stirring an additional 4 hr at RT, the resulting dark brown solution was concentrated to dryness under reduced pressure. The residue was then dissolved in 60 mL of CH_2Cl_2 , washed with sat'd brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. Flash

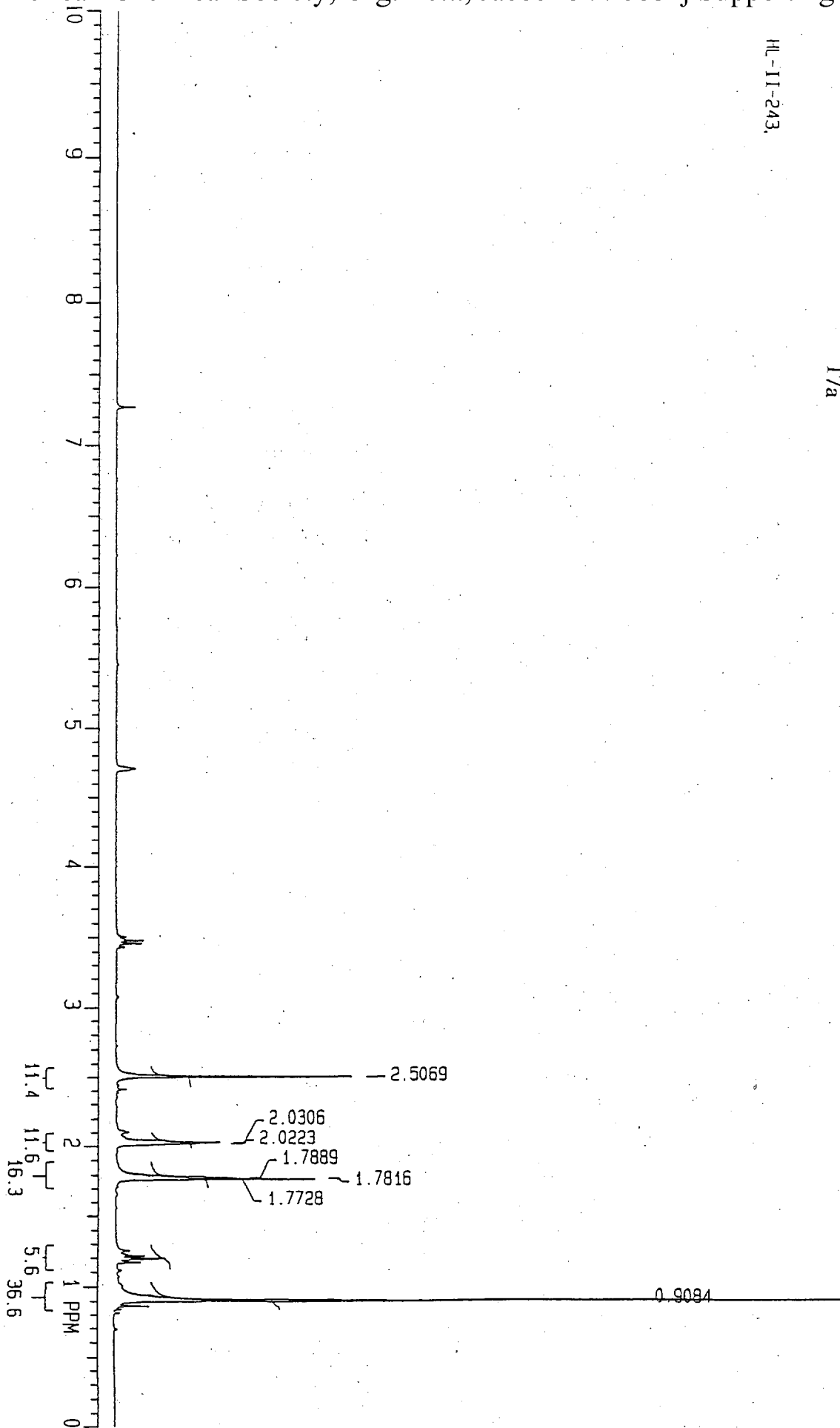
chromatography (silica gel, EtOAc:hexane:Et₃N = 10:90:1, to 25:75:1) then gave 10.1 mg (48%) of vinyl sulfide **30** as a yellow oil; *R_f* 0.56 (25% EtOAc/hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 3H), 1.24 (s, 6H), 1.27 (s, 3H), 1.29 (s, 3H), 1.30 (s, 3H), 1.42 (s, 3H), 1.43 (s, 3H), 1.54 (s, 3H), 1.90 (t, *J* = 6.9 Hz, 2H), 2.14 (s, 3H), 2.68 (s, 2H), 2.77 (s, 2H), 3.28 (s, 2H), 3.65 (t, *J* = 6.9 Hz, 2H), 4.73 (s, 1H), 5.85 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 14.7, 21.7, 23.0, 26.6, 26.9, 27.3, 27.4, 29.5, 38.5, 41.1, 43.9, 44.0, 44.4, 45.4, 52.1, 55.3, 55.4, 73.2, 81.0, 92.2, 117.7, 121.9, 168.0, 168.4, 172.6, 175.5, 176.1, 180.2; MS (EI) *m/z* (%) 505 (M⁺, 4); HRMS (EI) Calcd for C₃₀H₄₃N₅S: 505.3239. Found: 505.3246.

2-((2-((2-((3,3-Dimethylpyrrolidin-2-ylidene)methyl)-4,4-dimethyl(1-pyrrolin-5-ylidene))methyl)-4,4-dimethyl(1-pyrrolin-5-ylidene))ethyl)-4,4,5-trimethyl-1-pyrroline-5-carbonitrile cadmium chloride (31). A solution of 10.1 mg (0.0198 mmol) of vinyl sulfide **30**, 26.5 mg (0.099 mmol) of triphenylphosphine, and 17 mg (0.20 mmol) of sodium bicarbonate in 3 mL of CH₃CN was degassed with argon, and was treated with vigorous stirring, and protection from light, with 73 mg (0.40 mmol) of CdCl₂.^{6b} The reaction was then stirred at RT for 24 h under argon, and the resulting solution was concentrated to dryness under reduced pressure. The residue was dissolved in 60 mL of CH₂Cl₂ and washed thoroughly with three portions of sat'd brine. The aqueous phase was back extracted with 3 x 10 mL of CH₂Cl₂. The combined organic extracts were concentrated under reduced pressure, and the dark residue was purified by PTLC (silica gel, EtOAc:hexane = 1:1) to afford 6.8 mg (53%) of **31** as a dark red solid (two tautomers with a ratio of 1:0.6), mp 235-36 °C. *R_f* 0.22 (50% EtOAc/hexane); UV-Vis (in MeOH) (rel.int.) λ_{max} 274 (56), 330 (100), 516 (49); ¹H NMR (300 MHz, CDCl₃) δ 0.92 (s, 4.8 H), 1.19 (s, 1.8H), 1.20 (s, 3H), 1.23 (s, 7.2H), 1.27 (s, 3H), 1.29 (s, 9H), 1.40 (s, 3H), 1.42 (s, 1.8H), 1.45 (app s, 4.8H), 1.52 (s, 3H), 1.67 (s, 1.8H), 1.81 (m, 3.2H), 1.98 (s, 1.8H), 2.02 (s, 3H), 2.45-3.06 (m, 9.6H), 3.94 (m, 0.6H), 4.24 (m, 2.6H), 4.91 (s, 1H), 4.93 (s, 0.6H), 5.02 (s, 1H), 5.12 (s, 0.6H); MS (EI) *m/z* (%) 474 (M⁺-CdCl+2H, 100), 472 (M⁺-CdCl, 3); HRMS (EI) Calcd for C₃₀H₄₄N₅ (M-CdCl+2H): 474.3597. Found: 474.3595

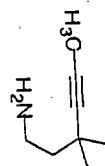


17a

HL-11-243

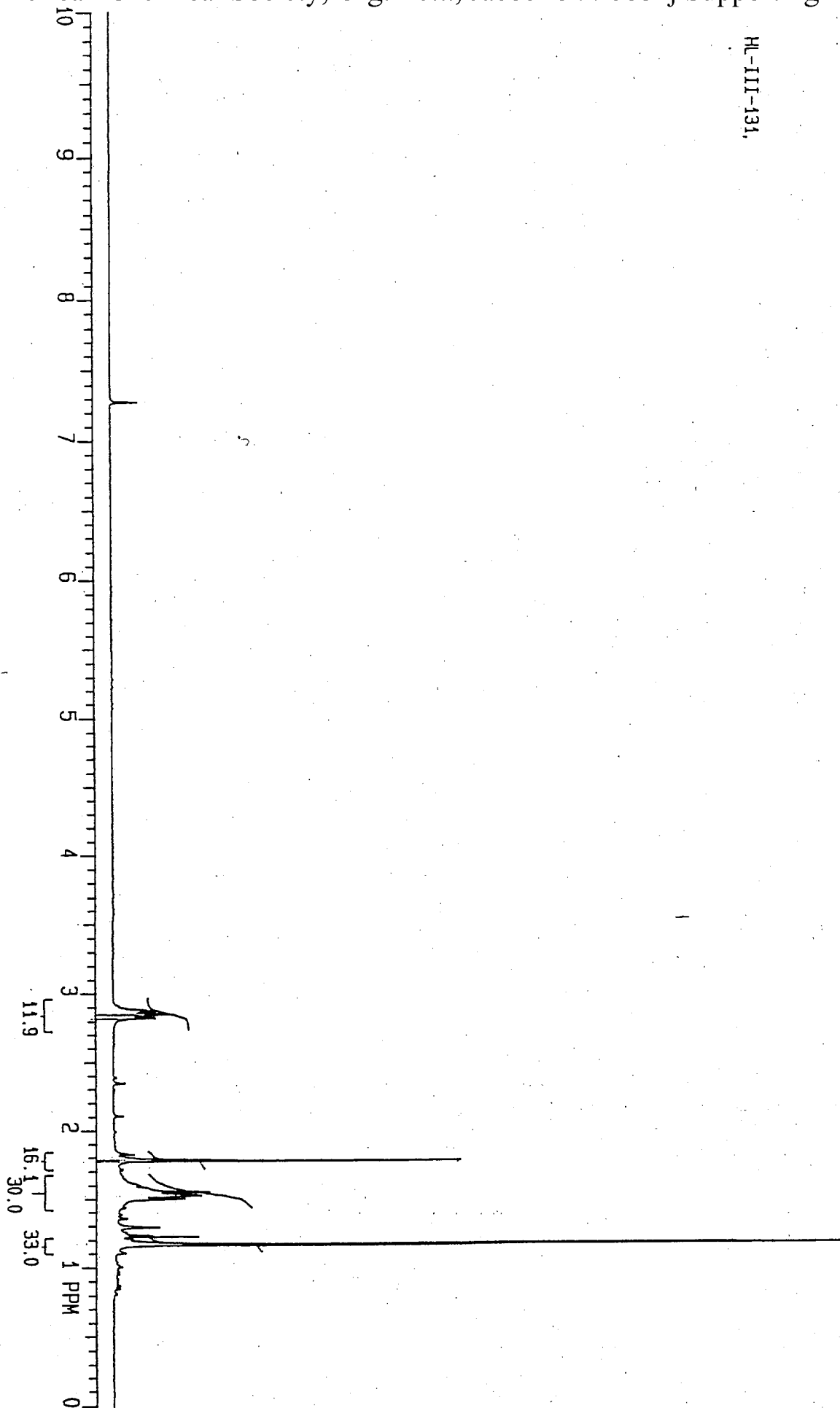


S8



17d

HL-III-131.



S9

h1-1v-224, HNMR Before, J13NMR, 3/15/93

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solvent CDCl3 dn H1

11e exp dpwr 26

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dn H1 dnm c

2.504 dmf n

28544 homo n

5699.6 dseq undefined

3200 dres undefined

16 PROCESsing

59 ml/11e

7.0 pproc fl

1.000 fn not used

077.5 math f

32 werr

32 wexd

lock n wds

aln not used

FLAGS nml

1 n

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DISPLAY

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3348.5

124

0

250

13.39

586.88

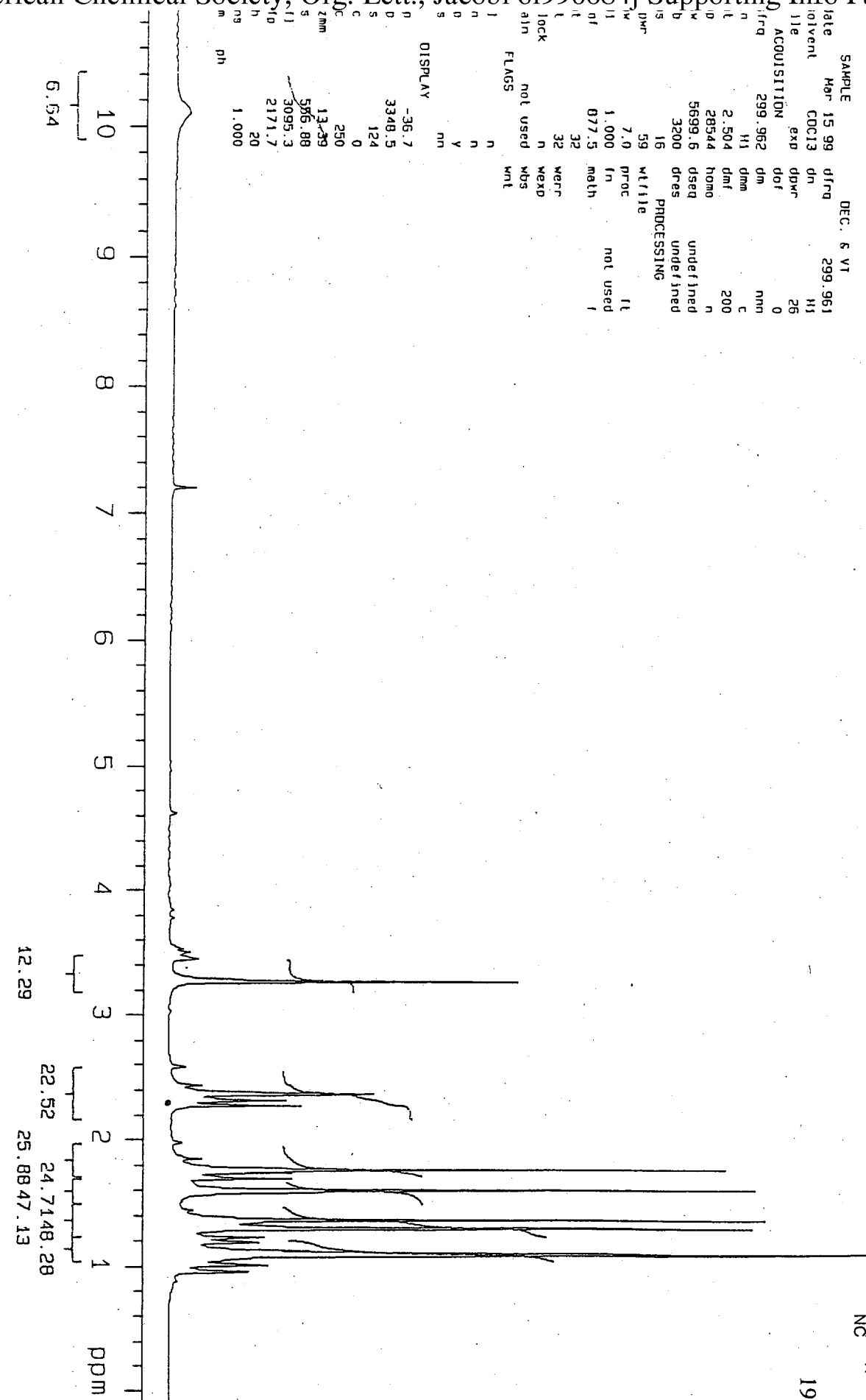
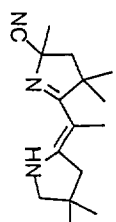
3095.3

2171.7

20

1.000

ph



S 10

6.54

12.29

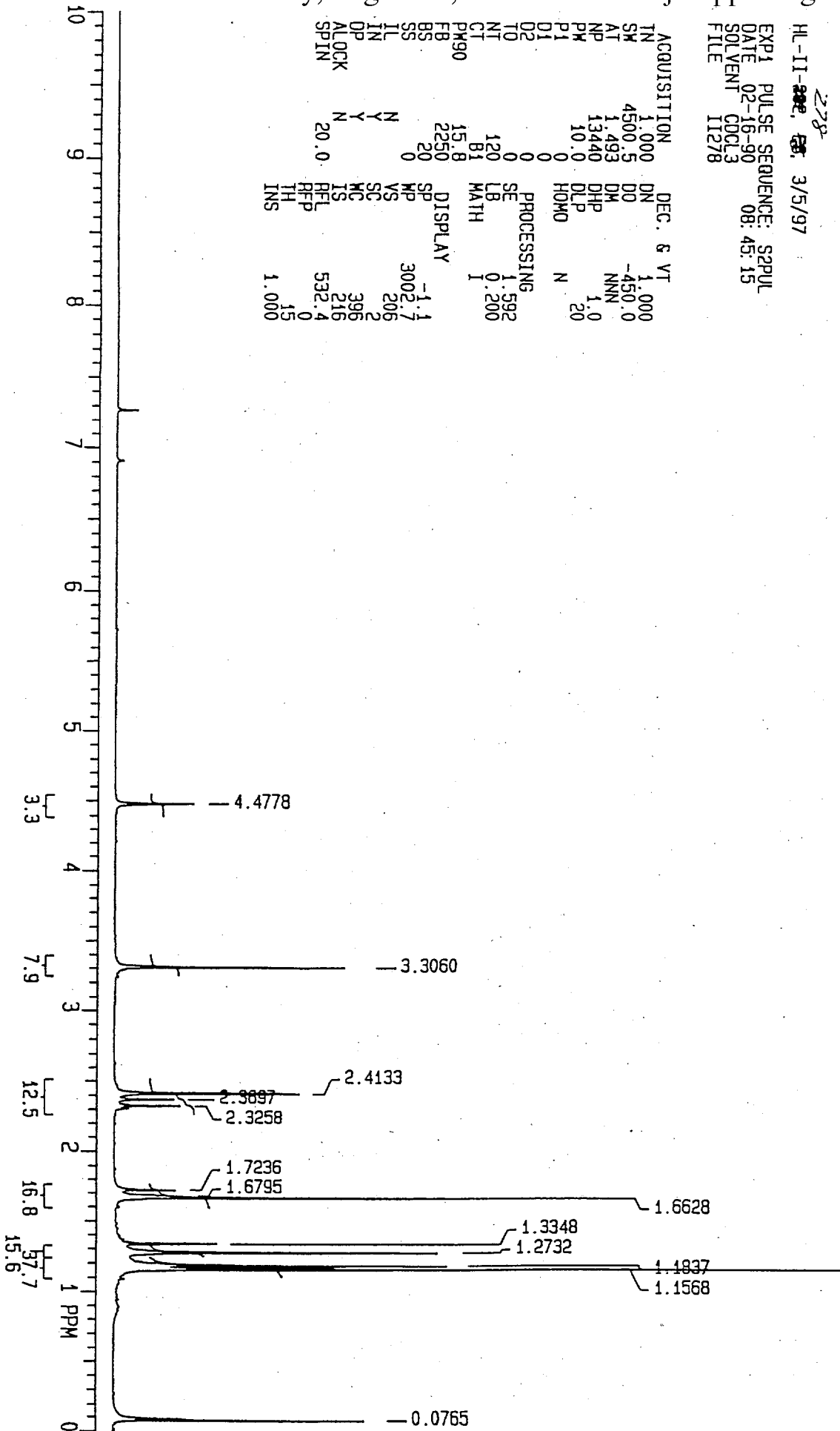
22.52 24.71 48.28

25.88 47.13

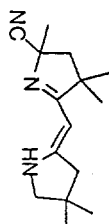
ppm

HL-II-~~808~~ ²⁷⁸ ~~83~~ 3/5/97
 EXP1 PUL SE SEQUENCE: S2PUL
 DATE 02-16-90 08:45:15
 SOLVENT CDCl3
 FILE I1278

ACQUISITION	DEC. & VT
TN 1.000	DN 1.000
SM 4500.5	DO -450.0
AT 1.493	DM NNN
NP 13440	DHP 1.0
PM 10.0	DLP 20
P1 0	HOMO N
D1 0	
D2 0	
TO 0	PROCESSING
NT 0	SE 1.592
CT 120	LB 0.200
PK90 15.8	MATH I
FB 2250	
BS 20	DISPLAY
SS 0	SP -1.1
IL N	MP 3002.7
LN Y	VS 206
IN Y	SC 2
DP Y	MC 396
ALOCK N	IS 216
SPIN 20.0	RFL 532.4
	RFP 0
	TH 15
	INS 1.000

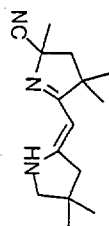
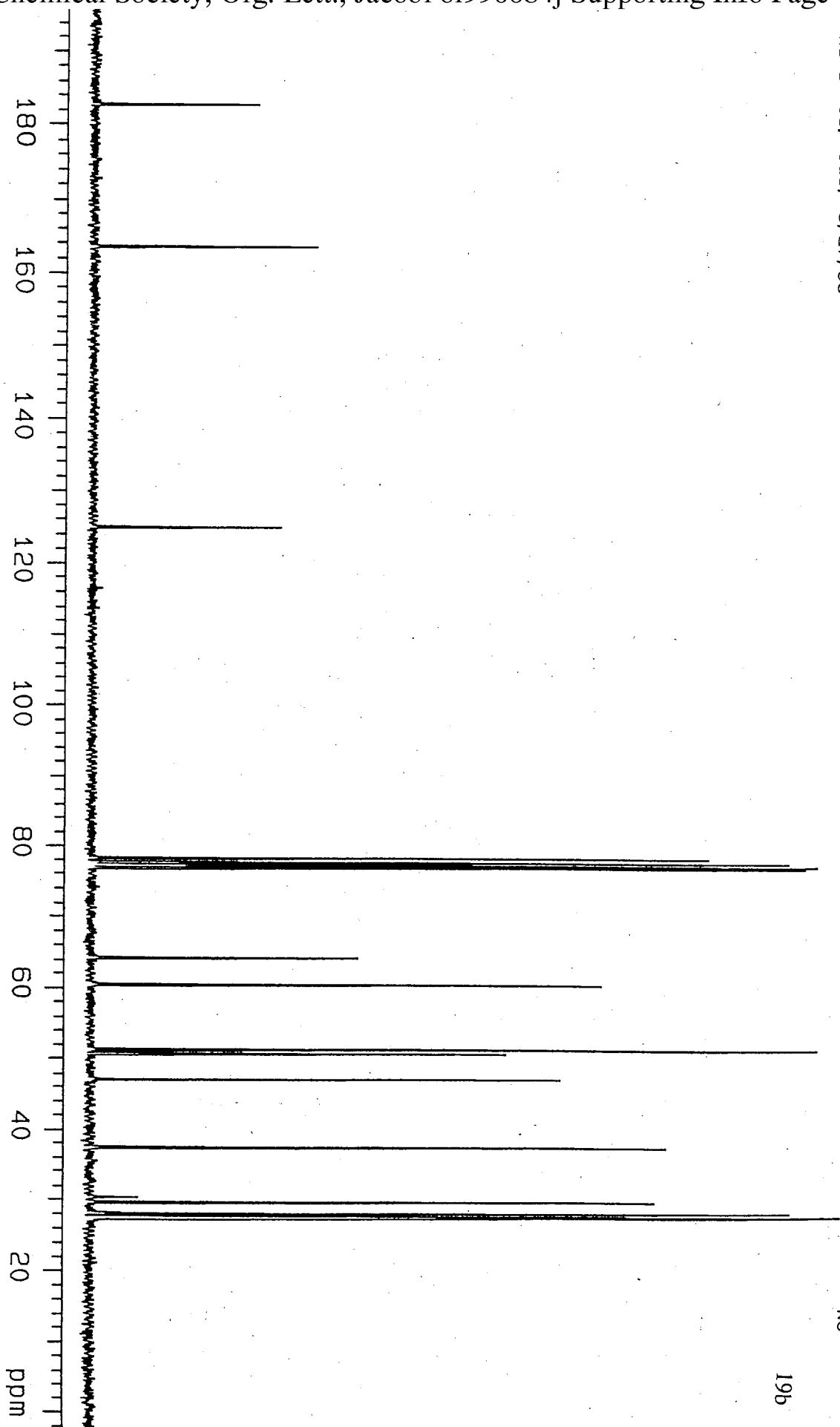


S 12

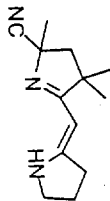


19b

h1-1v-91, c13, 8/27/98



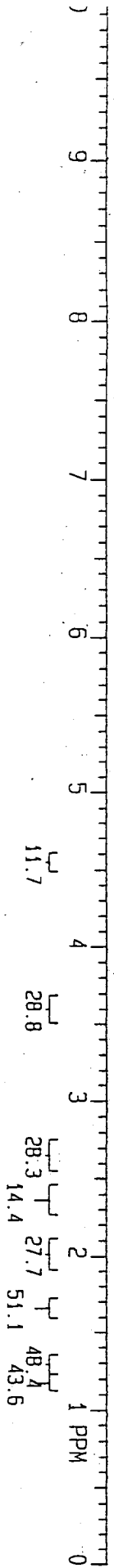
S 13



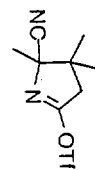
19e

HL-11-247, F1, 1/20/97
 EXP-11-247-SEQUENCE 1/20/97PUL
 DATE: 01-05-90 09:13:21
 SOLVENT: CDCL3
 FILE: H

ACQUISITION		DEC. & VI	
TN	1.000	DN	1.000
SW	4500.5	DD	-450.0
AT	1.493	DM	NNN
NP	13440	DHP	1.0
PM	10.0	DLP	1.20
P1	0	HOMO	N
D1	0		
D2	0		
IO	0		
NT	120	SE	1.592
NI	120	LB	0.200
CT	120	MATH	I
PM90	15.8		
FB	2250		
BS	20		
SS	0		
IL	N	DISPLAY	-1.1
IN	Y	SP	3002.7
DP	Y	VS	206
ALOCK	Y	SC	2
SPIN	N	WC	396
		IS	766
		RFL	532.4
		RFP	0
		TH	17
		INS	1.000

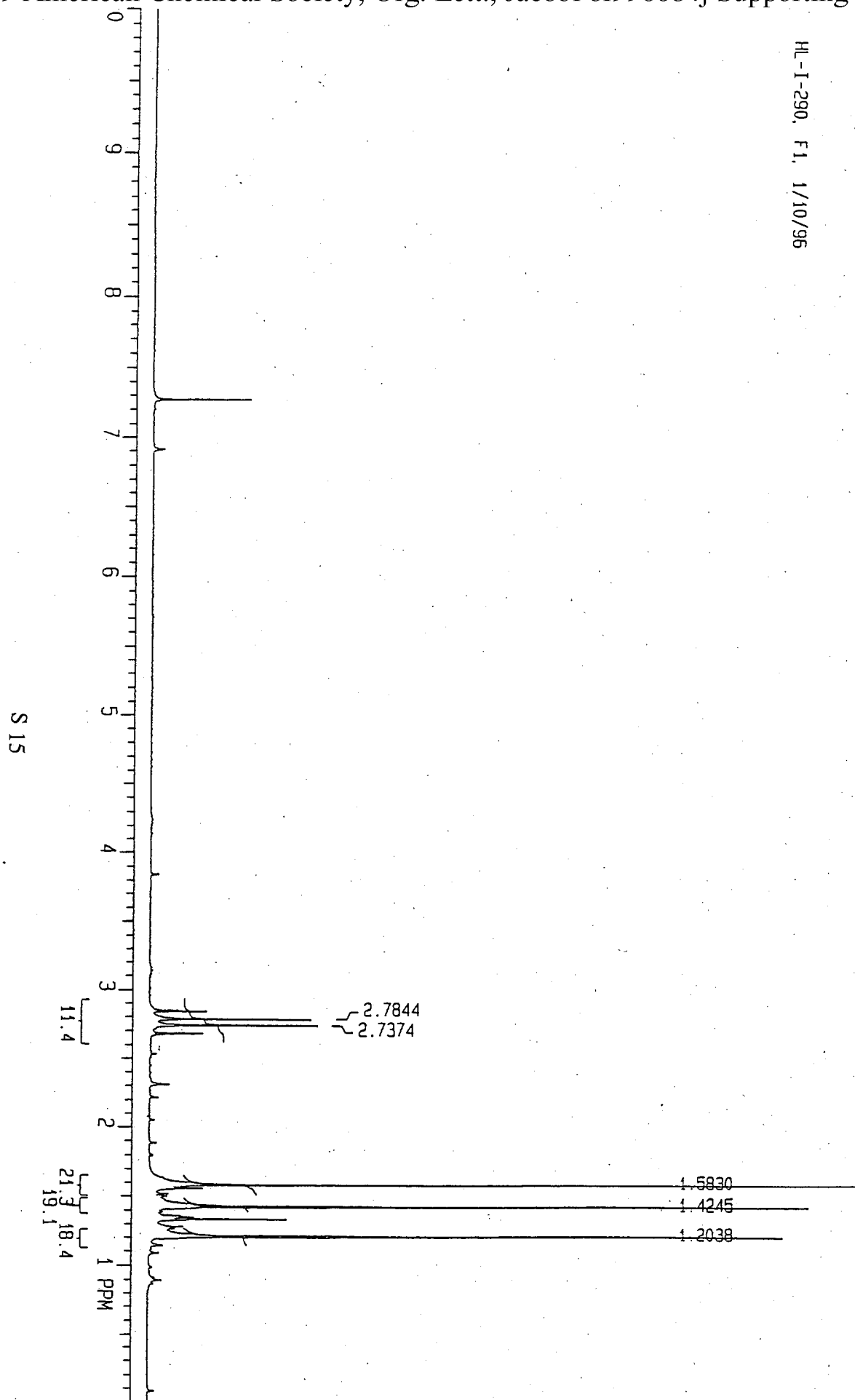


S 14



20

HL-I-290, F1, 1/10/96



h1-1v-208, HNMR, before, C13NMR, 12/9/90

exp1 pulse sequence: std1h

SAMPLE Dec 9 90 DEC. 6 VT

date Dec 9 90 d1r4 299.961

solvent CDCl3 dn H1

file /data2/dba-dpwr 26

01/HL/h1-1v-208.HNMR.dof 0

n_before_C13NMR.f1-dm nnn

ACQUISITION d dmm c

slrq 299.961 dmf 200

ln H1 homo n

at 2.504 dseq underfined

mp 20032 dres underfined

sv 4000.0 wflie PROCESSING

lb 2200 proc fl

lbwr 16 fn not used f

dv 7.0 math

d1 1.000 werr

tof 0 wekd

nt 32 wds

ct 32 wnt

ajlock n

gain not used

11 n

in n

dp y

hs nn

DISPLAY -13.1

sd 3027.0

vs 124

sc 0

kc 250

12mm 12.11

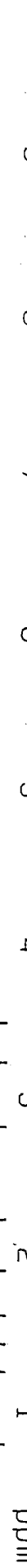
15 556.88

-f1 3095.3

-f0 2171.7

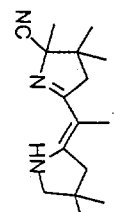
ln 20

im 1.000



12.76
31.42
20.4525.69
24.10 76.42

S 16



21a

h1-iv-94, 8/31/99

ex01 pulse sequence: sld1h

SAMPLE DEC. & VT

date Aug 31 98 dfrq 299.961

solvent COCl3 dn H1

file /data2/oa/dmr 26

11 //IL/h1-iv-98_type.dof 0

_cyanomline.fid dm nnn

ACQUISITION dmm c

strq 299.961 dmf 200

tn H1 homo n

at 2.504 dseq undefined

no 20032 dres undefined

sw 4000.0 PROCESsing

fb 2200 wlfll

l6 proc ll

lpm 59 tn not used

pw 7.0 math ?

d1 1.000

tof 0 veqr

nt 32 wexp

ct 32 vbs

ajack n nnt

gain not used

flags not used

l1 n

ln n

dp y

hs nn

DISPLAY

-5.3

3011.7

142

0

250

12.05

870.12

3095.3

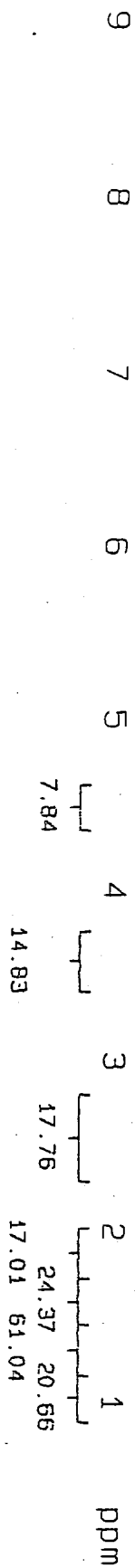
2171.7

20

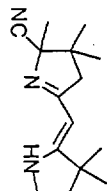
1.000

nm

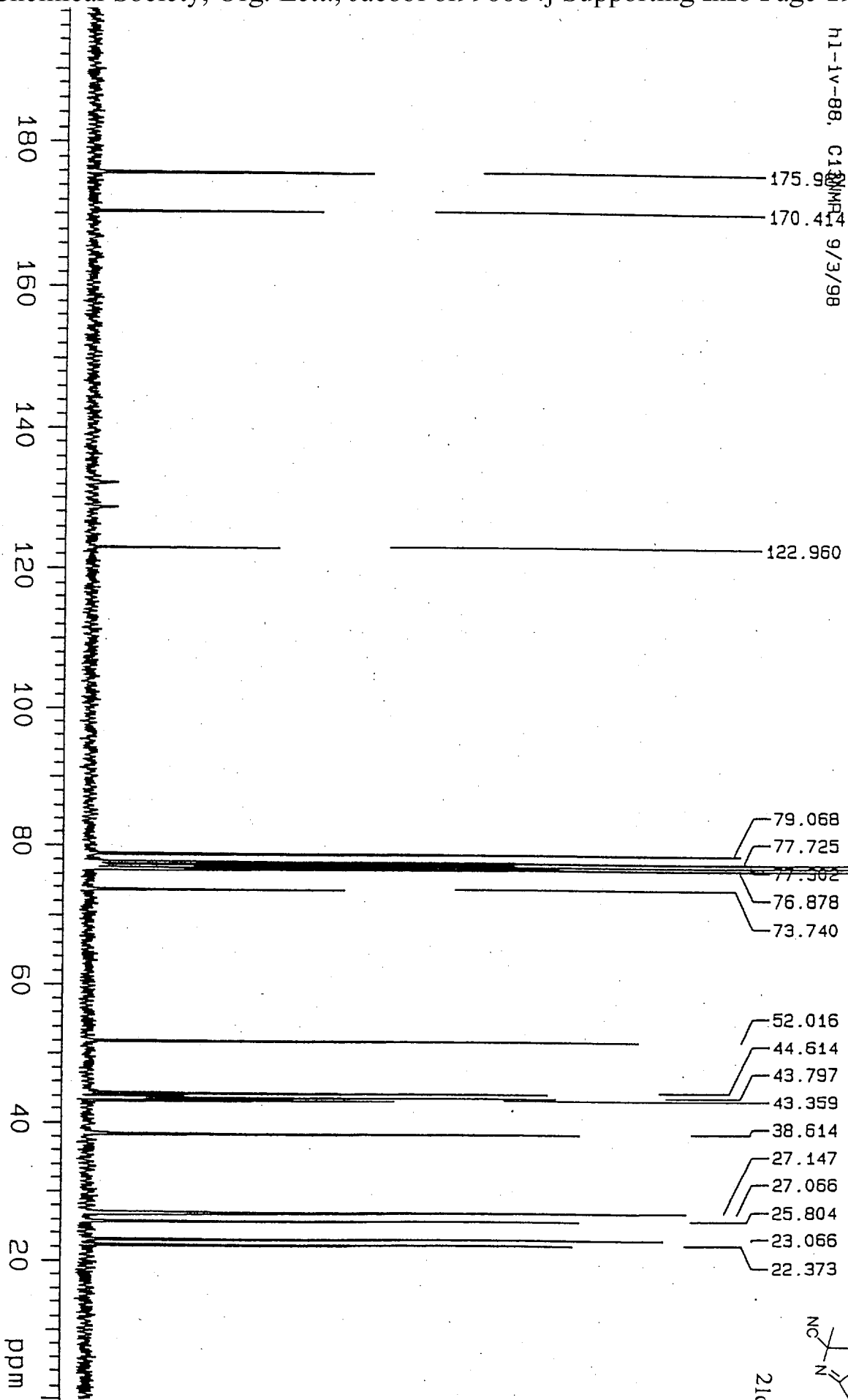
ph



S 18

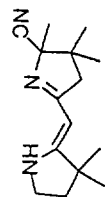


21c



S 19

21c



hl-1v-75, f2, 6/12/99

2xp01 pulse sequence: sldjh

SAMPLE Jun 12 98 dfrc DEC. 6 VI

299.961

solvent CDC13 dn H1 26

file /data2/ra_ dpr 0

20032 dres undefined

4000.0 wtfile PROCESSING

2500 mtfile

16 proc ft

59 fn not used

7.0 math

1.000

0 kern

60 wexp

60 nbs

lock n mtl

ain not used

1 n

1 n

1 n

1 y

1 n

1 n

1 n

1 n

1 n

1 n

1 n

1 n

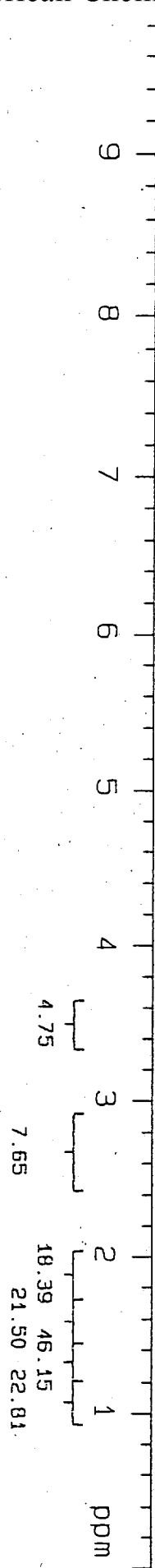
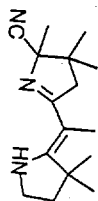
1 n

1 n

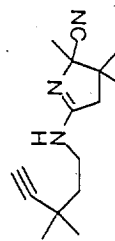
1 n

1 n

21d

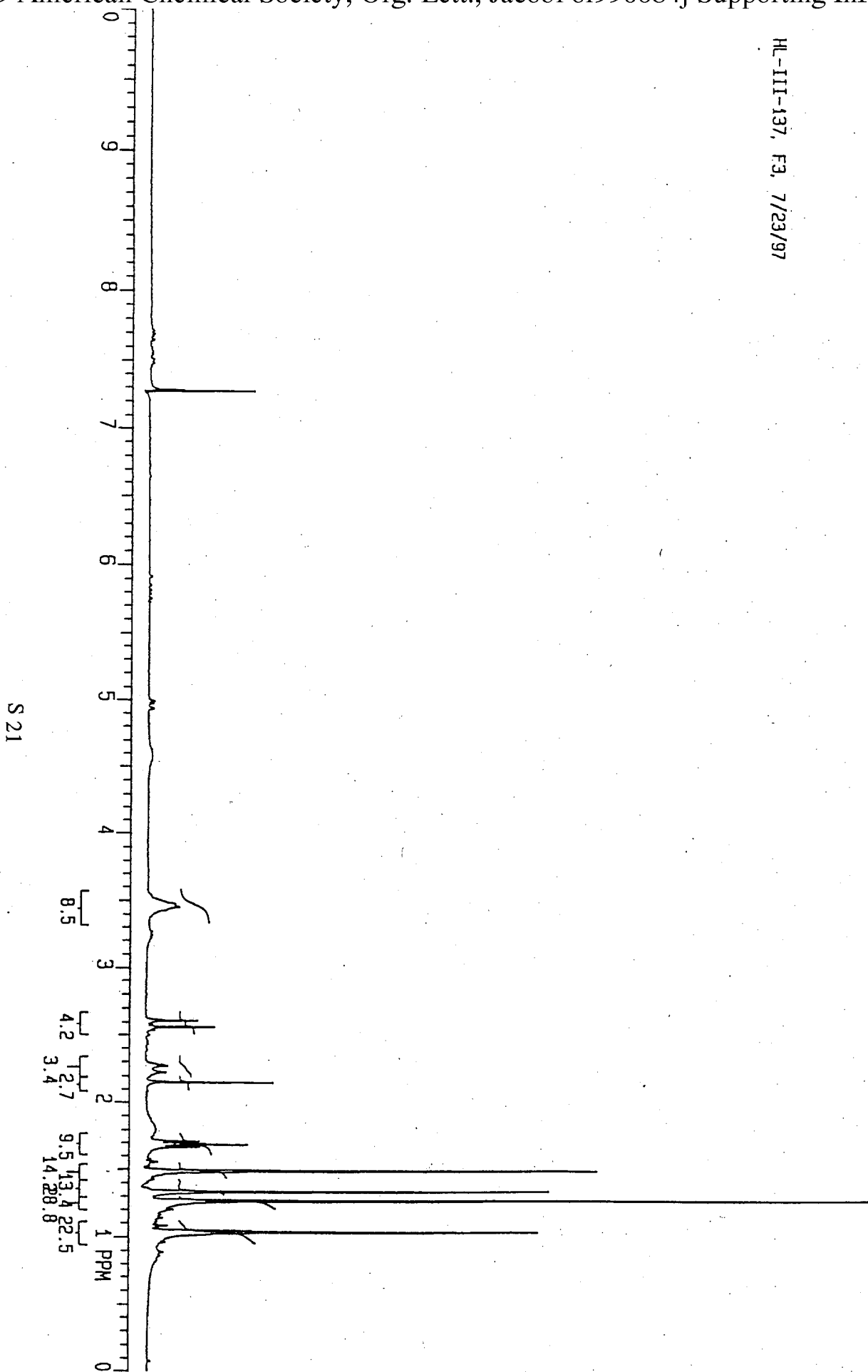


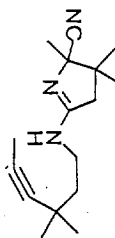
S 20



22c

HL-III-137, F3, 7/23/97

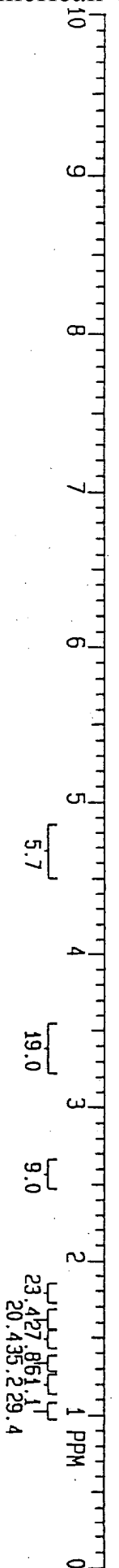




22d

HL-III-139, 7/28/97
 EXP4 PULSE SEQUENCE: S2PUL
 DATE 02-24-97 20:02:46
 SOLVENT CDCL3
 FILE H

ACQUISITION		DEC. & VT	
TN	1.000	DN	1.000
SM	4500.5	DD	-450.0
AT	1.493	DM	NNN
NP	13440	DHP	1.0
PM	10.0	DLP	20
P1	0	HOMO	N
D1	0		
D2	0		
TO	0		
NT	120	SE	1.592
CT	116	LB	0.200
PK90	19.5	MATH	I
FB	2250		
BS	20		
SS	0		
IL	N	DISPLAY	-1.1
IN	Y	SP	3002.7
DP	Y	VS	209
ALOCK	N	SC	2
SPIN	20.0	MC	396
		IS	787
		RFL	532.4
		RFP	0
		TH	10
		INS	1.000



S 22

h1-111-283, lower_part, 2/25/99

exp1 pulse sequence: st01h

SAMPLE Mar 4 90 dfrq DEC: 6 VT 299.961

solvent COCl3 dn H1

file /data2/pa-dpwr 26

0/HL/h1-111-283.10 dof 0

mer_part.110 dm nnn

ACQUISITION dmm c

299.961 dmf 200

h1 homo n

2.504 dseq undefined

20032 dres undefined

4000.0 PROCESSING

2200 mfile

16 dproc ft

59 fn not used

5.0 math f

1.000

0 werr

30 wexd

30 wds

n mlt

not used

FLAGS

1 n

1 n

1 n

1 y

1 nn

DISPLAY

-13.1

3019.2

124

0

250

12.08

556.88

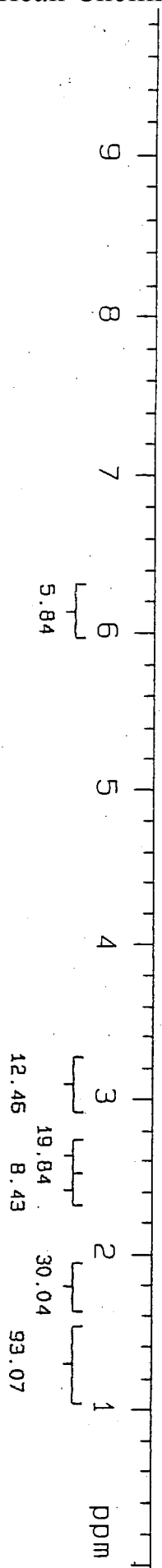
3095.3

2171.7

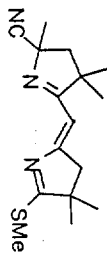
20

1.000

ph



S 23

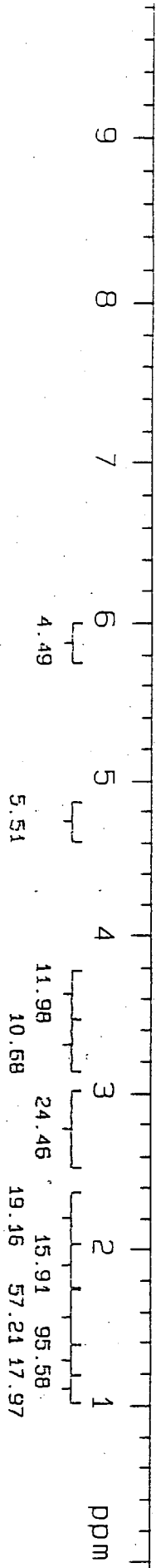


-1v-157, rd-check, 3/16/99

001 pulse sequence: stdjh

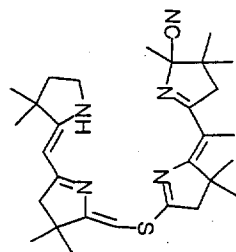
SAMPLE Mar 16 99 dfrq 299.961
 ivent COC13 dn H1
 le exp dpr H1
 ACQUISITION dot 26
 299.961 dm 0
 H1 dmm nnn
 2.504 dmf c
 20032 homo n
 4000.0 dseq undefined
 2200 dres undefined
 16 PROCESSING
 59 m/llle ll
 7.0 proc not used
 1.000 fn f
 0 math
 120 merr
 120 n mexd
 ock n nbs
 in not used
 FLAGS nll

DISPLAY
 -20.9
 3027.0
 124
 0
 250
 12.11
 838.97
 3095.3
 2171.7
 20
 1.000
 ph

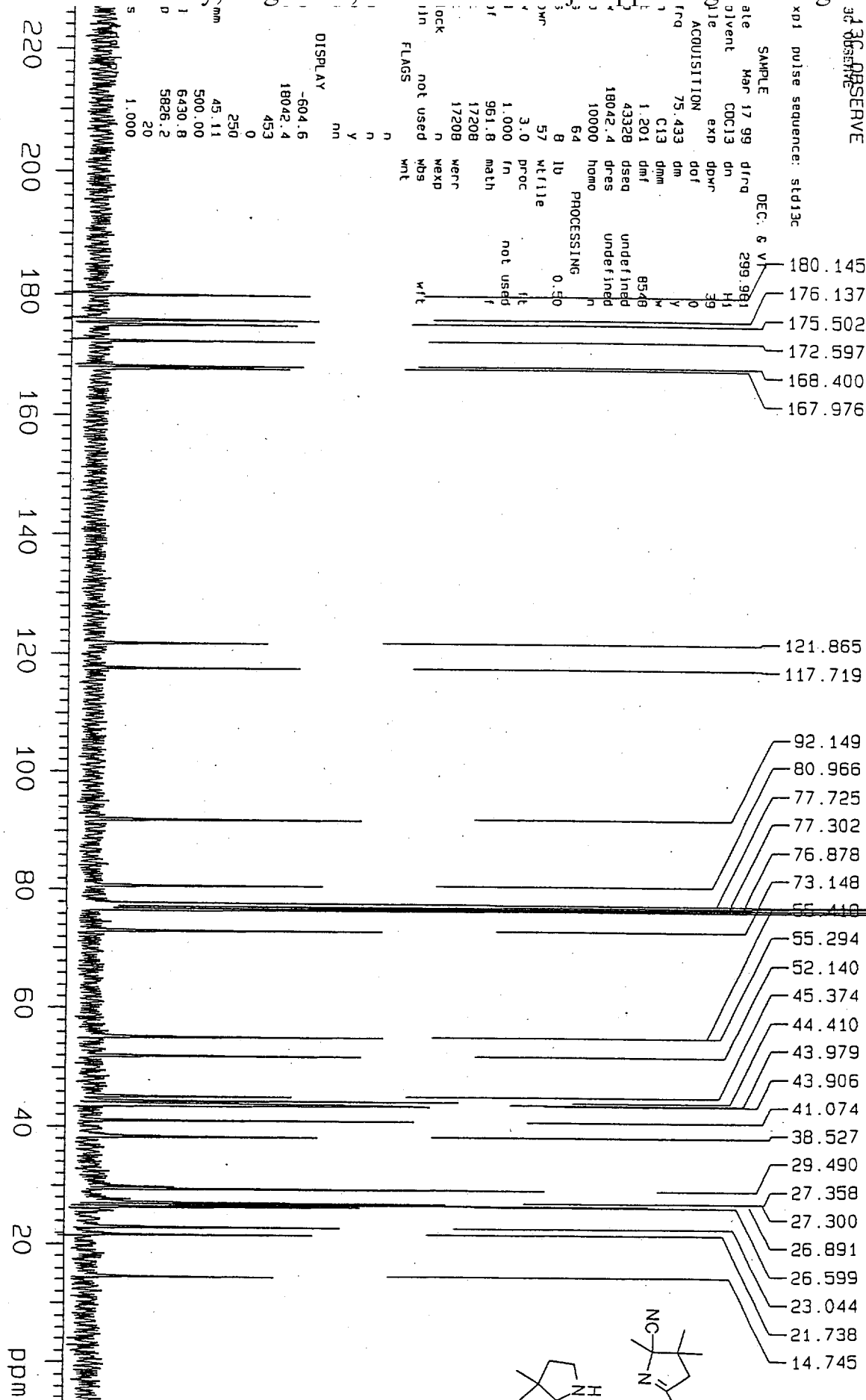


S 24

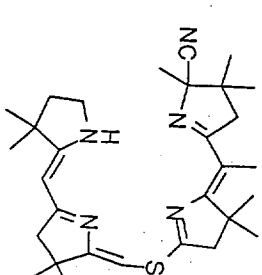
30



13C NMR SPECTRUM



XP1 pulse sequence: std13c
 SAMPLE Mar 17 99
 solvent CDCl3
 ACQUISITION exp 75.433
 C13 1.201
 43328 dseq
 18042.4 dres
 10000 homo
 64
 57 wt11e
 3.0 proc
 1.000 fn
 961.8 math
 17208
 17208
 lock n
 11n not used
 FLAGS n n n y
 DISPLAY -604.6
 18042.4
 453
 0
 250
 45.11
 500.00
 6430.8
 5826.2
 20
 1.000



S 25

h1-1v-197, 11/17/98

exp1 pulse sequence: sld1h

SAMPLE Nov 17 98 dfrc DEC: 6 VI 299.961

solvent CDCl3 dn III

file /data2/pa_dpr 26

g/hl/h1-1v-197.hnm dof 0

R.11d dm nnn

ACQUISITION dmm c

dfrc 299.961 dmf 200

h1 homo n

2.504 dseq undefined

20032 dres undefined

4000.0 PROCESsing

2200 Mfile

16 proc ft

59 fn not used

7.0 math f

1.000

0 werr

240 wexp

240 wds

n wlt

not used

FLAGS

1 n

2 n

3 y

4 nn

DISPLAY

-13.1

3011.7

376

0

250

12.05

717.84

3095.3

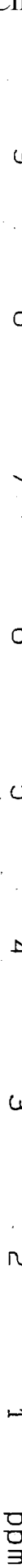
2171.7

20

1.000

ph

m



3.97

3.93

10.81

10.91

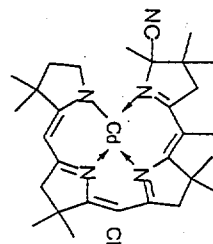
38.33

21.69

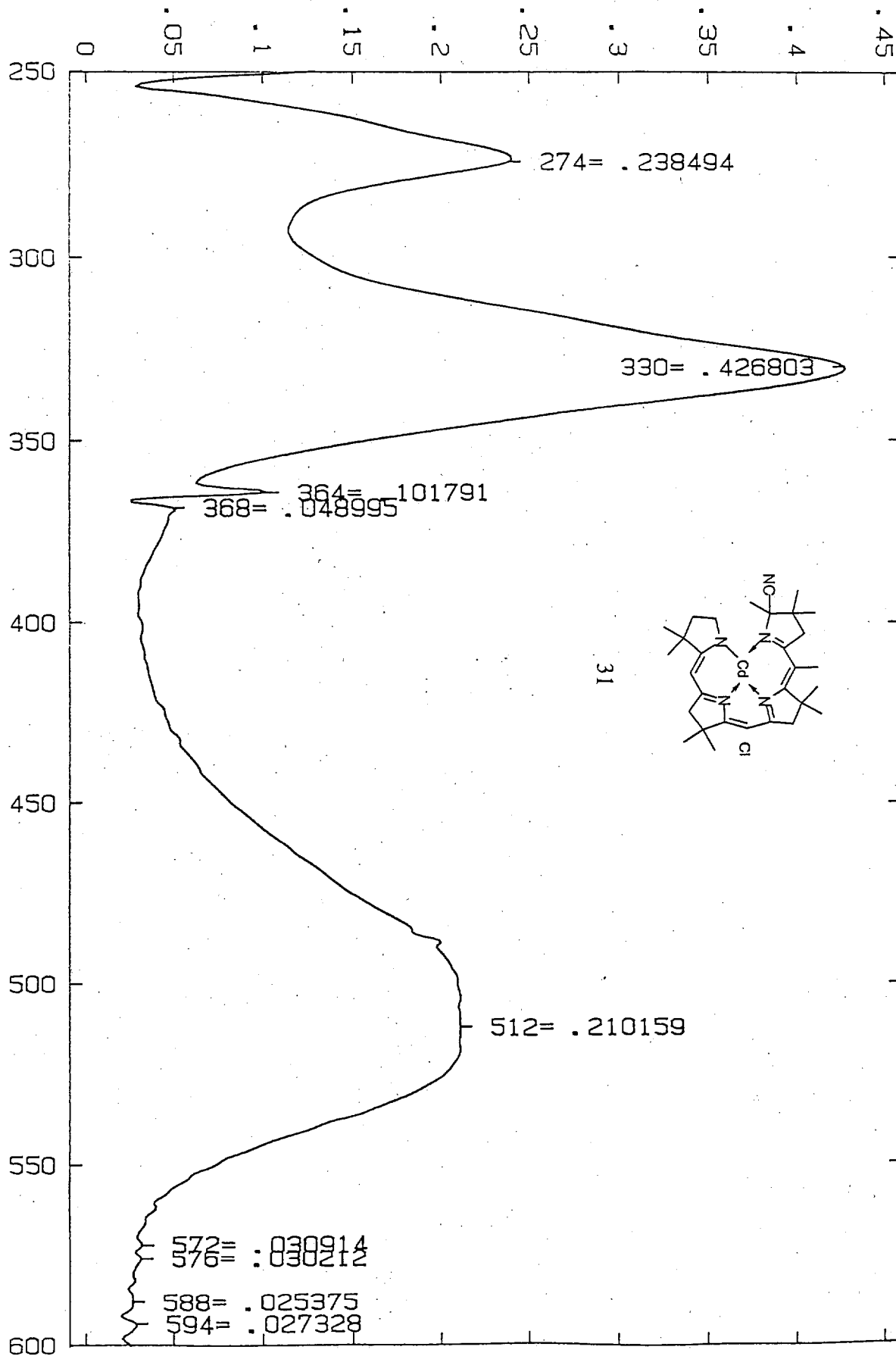
81.75

S 26

31



ABSORBANCE



11/17/98
Moores reference, samp in MeOH
S27
WAVELENGTH (nm)

