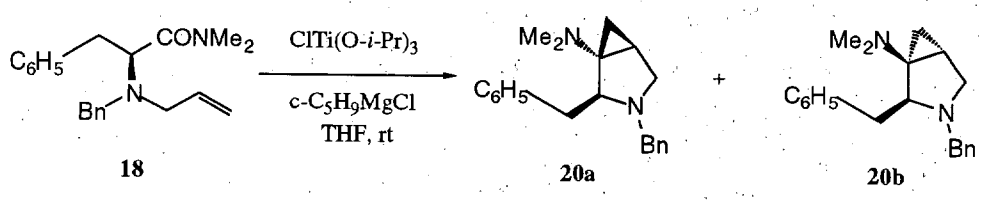
SUPPORTING INFORMATION

General

All solvents were reagent grade and were distilled before use. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Reagent cyclopentyl magnesium chloride was purchased from Aldrich. Proton magnetic resonance spectra (^{1}H NMR) and carbon magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker AMX-500 spectrometer. Chemical shifts are in parts per million (ppm) relative to the solvent as the internal reference. Infrared spectra were obtained on a Perkin-Elmer Model 281-B spectrometer. Absorptions were reported in wavenumber (cm^{-1}). Optical rotations (in degrees) were measured with a Perkin-Elmer Model 241 polarimeter. Flash column chromatography was carried out on E. Merck silica gel 60 (240-400 mesh) using the solvent systems listed under individual experiments.

Representative Procedure for the Intramolecular Aminocyclopropanation



18 **20a** **20b**

To a solution of 2-(allylbenzylamino)-*N,N*-dimethyl-3-phenyl-propionamide (**18**, 50mg, 0.155 mmol) in 1.55 mL anhydrous THF was added $ClTi(O\text{-}i\text{-}Pr)_3$ (0.155 mL of 1.0 M solution in hexanes, 1.0 equiv), cyclopentyl magnesium chloride (0.349 mL of 2.0 M solution in diethyl ether, 4.5 equiv) was added dropwise at room temperature over a period of 1 h. The reaction mixture was stirred for an additional 2 h, poured into ice water (5 mL), and stirred for 30 min. THF was evaporated under reduced pressure and 10 mL Et_2O was added to the residue. The organic layer was separated, and the aqueous layer was extracted with ether (3x10 mL). The combined extracts were washed with aqueous $NaHCO_3$ (10 mL), followed by brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent, followed by silica gel column chromatography (acetone-hexanes, 10:90) of the residue afforded 28 mg (60% yield) of **20a** as a light yellow solid, and 11mg (23%) of **20b** as a light yellow oil.

(1R,2S,6S)-2,3-Dibenzyl-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**20a**)

- Mp: 32.8-33.8 °C; R_f 0.2 (ethyl acetate:petroleum ether, 20:80); $[\alpha]_D^{20}$ +18.4 (c=1.0, $CHCl_3$); ^{1}H NMR (500MHz, $CDCl_3$) δ 7.14-7.32 (m, 10H), 3.81 (d, 1H, J = 13.3 Hz), 3.18 (m, 1H), 3.14-3.19 (dd, 1H, J = 4.2 Hz, 13.7 Hz), 3.02 (d, 1H, J = 13.3 Hz), 2.86 (dd, 1H, J = 13.7 Hz, 4.8 Hz), 2.72 (d, 1H, J = 9.0 Hz), 2.38 (s, 6H), 2.30 (dd, 1H, J = 3.9 Hz, 9.0Hz), 1.24 (m, 1H), 0.89 (dd, 1H, J = 4.5 Hz), 0.59 (dd, 1H, J = 4.5 Hz, 8.7Hz); ^{13}C NMR (500MHz, $CDCl_3$) δ 140.4, 139.8, 129.6, 128.4, 128.0, 128.0, 126.6, 125.8, 62.9, 58.3, 55.4, 54.6, 42.2, 38.7, 21.7, 14.5; IR (neat): 3026, 2926.7, 2817.4, 2776.9, 1602.1, 1494.0, 1452.2, 1376.8, 1351.6, 737.2, 697.1 cm^{-1}; HRMS calcd for MH^+ $C_{21}H_{27}N_2$, 307.2174; found, 307.2160.

(1S,2S,6R)-2,3-Dibenzyl-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**20b**)

- R_f 0.2 (ethyl acetate:petroleum ether, 5:95); $[\alpha]_D^{20}$ -48.0 (c=1.0, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$) δ 7.07-7.23 (m, 10H), 3.68 (d, 1H, J = 13.8 Hz), 3.55 (d, 1H, J = 13.8 Hz), 3.42 (dd, 1H, J = 4.7 Hz, 6.4 Hz), 3.10 (dd, 1H, J = 13.8 Hz, 4.5 Hz), 2.79 (dd, 1H, J = 3.2 Hz, 9.3 Hz), 2.73 (dd, 1H, J = 6.4 Hz, 13.8Hz), 2.51 (d, 1H, J = 9.3 Hz), 2.12 (s, 6H), 1.55-1.58 (m, 1H), 0.72 (dd, 1H, J = 4.2 Hz, 8.5 Hz), 0.63 (dd, 1H, J = 4.0 Hz); ^{13}C NMR (500MHz, $CDCl_3$) δ 142.5, 140.5, 129.6, 128.2, 127.9, 127.8, 126.4, 125.0, 68.0, 57.0, 55.8, 51.9, 42.1, 34.5, 22.8, 8.45; IR (neat): 3025.2, 2936.1, 2817.4, 2774.8, 1602.1, 1493.4, 1452.7, 1348.6, 730.7, 697.3 cm^{-1}; HRMS calcd for MH^+ $C_{21}H_{27}N_2$, 307.2174; found, 307.2160.

(1R,2S,6S)-3-Benzyl-2-(4-hydroxybenzyl)-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**22a**)

- Mp: 143-144 °C; R_f 0.35 (acetone:hexanes, 30:70); $[\alpha]_D^{20}$ +14.4 (c=1.0, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$) δ 7.15-7.29 (m, 7H), 6.70 (d, 2H, J = 8.1 Hz), 5.88 (br, s, 1H), 3.84 (d, 1H, J = 13.3 Hz), 3.16 (m, 1H), 3.02-3.10 (m, 2H), 2.81 (d, 1H, J = 10.5 Hz), 2.72 (d, 1H, J = 8.4 Hz), 2.38 (s, 6H), 2.31 (m, 1H), 1.28 (m, 1H), 0.89 (m, 1H), 0.62 (d, 1H, J = 3.0 Hz); ^{13}C NMR (500MHz, $CDCl_3$) δ 154.0, 139.5, 132.1, 130.6, 128.5, 128.1, 126.6, 115.2, 62.8, 58.3, 55.4, 54.5, 42.3, 37.7, 21.9, 14.5; IR (neat): 3300 (br), 2930.5, 2785.1, 1612.6, 1514.3, 1453.5, 1240.1, 1170.0, 827.1, 751.7, 699.2 cm^{-1}; HRMS calcd for MH^+ $C_{21}H_{27}N_2O$, 323.2123; found, 323.2111.

(1S,2S,6R)-3-Benzyl-2-(4-hydroxybenzyl)-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**22b**)

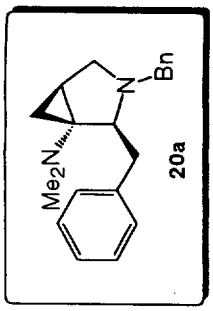
- R_f 0.55 (acetone:hexanes, 30:70); $[\alpha]_D^{20}$ -34.2 (c=1.0, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$) δ 7.08-7.24 (m, 7H), 6.67 (d, 2H, J = 8.4 Hz), 4.91 (br, s, 1H), 3.68 (d, 1H, J = 13.8 Hz), 3.56 (d, 1H, J = 13.8 Hz), 3.35 (m, 1H), 3.01 (dd, 1H, J = 13.7 Hz, 3.6 Hz), 2.79 (dd, 1H, J = 6.9 Hz, 8.7 Hz), 2.68 (dd, 1H, J = 6.1 Hz, 13.6 Hz), 2.49 (d, 1H, J = 9.4 Hz), 2.13 (s, 6H), 1.56 (m, 1H), 0.74 (dd, 1H, J = 3.6 Hz, 7.7Hz), 0.59 (m, 1H); ^{13}C NMR (500MHz, $CDCl_3$) δ 153.2, 140.5, 134.4, 130.7, 128.2, 128.0, 126.4, 114.7, 68.2, 57.3, 55.8, 52.0, 42.0, 33.8, 22.9, 8.73; IR (neat): 3318.8 (br), 2934.8, 2817.8, 2776.1, 1612.3, 1513.5, 1453.3, 1352.2, 1243.2, 1170.4, 828.5, 740.0, 698.4 cm^{-1}; HRMS calcd for MH^+ $C_{21}H_{27}N_2O$, 323.2123; found, 323.2118.

(1R,2S,6S)-3-Benzyl-2-(1*H*-indol-3-ylmethyl)-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**27a**)

- R_f 0.35 (acetone:hexanes, 30:70); $[\alpha]_D^{20}$ -9.8 (c=1.0, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$) δ 7.97 (br, s, 1H), 7.72 (d, 1H, J = 7.7 Hz), 7.30 (d, 1H, J = 7.8 Hz), 7.10-7.23 (m, 7H), 7.05 (d, 1H, J = 1.9 Hz), 3.80 (d, 1H, J = 13.3 Hz), 3.36 (dd, 1H, J = 4.1 Hz, 6.1 Hz), 3.30 (dd, 1H, J = 4.0 Hz, 15.3 Hz), 2.98-3.03 (m, 2H), 2.77 (d, 1H, J = 9.0 Hz), 2.42 (s, 6H), 2.33 (dd, 1H, J = 3.9 Hz, 9.0Hz), 1.30 (m, 1H), 1.09 (dd, 1H, J = 4.3 Hz), 0.65 (dd, 1H, J = 4.4 Hz, 8.6Hz); ^{13}C NMR (500MHz, $CDCl_3$) δ 140.0, 136.3, 128.4, 127.9, 127.9, 126.5, 122.1, 121.8, 119.3, 119.1, 114.8, 111.0, 61.2, 58.8, 56.0, 54.9, 42.2, 28.9, 22.4, 14.5; IR (neat): 3420.3, 3058.2, 2922.9, 2783.6, 1619.7, 1493.8, 1477.5, 1453.8, 1353.2, 738.7, 699.2 cm^{-1}; HRMS calcd for M^+ $C_{23}H_{27}N_3$, 345.2205; found, 345.2203.

(1S,2S,6R)-3-Benzyl-2-(1*H*-indol-3-ylmethyl)-3-aza-bicyclo[3.1.0]hex-1-yl-dimethyl amine (**27b**)

- R_f 0.55 (acetone:hexanes, 30:70); $[\alpha]_D^{20}$ -30.3 (c=1.0, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$) δ 7.81 (br, s, 1H), 7.60 (d, 1H, *J* = 7.8 Hz), 7.28 (d, 1H, *J* = 8.0 Hz), 7.06-7.21 (m, 7H), 6.92 (d, 1H, *J* = 1.7 Hz), 3.73 (d, 1H, *J* = 14.0 Hz), 3.56 (d, 1H, *J* = 14.0 Hz), 3.51 (dd, 1H, *J* = 4.0 Hz, 6.9 Hz), 3.29 (dd, 1H, *J* = 3.9 Hz, 14.8 Hz), 2.91 (dd, 1H, *J* = 3.2 Hz, 9.3 Hz), 2.84 (dd, 1H, *J* = 7.0 Hz, 14.8 Hz), 2.50 (d, 1H, *J* = 9.3 Hz), 2.21 (s, 6H), 1.61 (m, 1H), 0.77 (dd, 1H, *J* = 4.2 Hz, 8.5 Hz), 0.62 (dd, 1H, *J* = 4.0 Hz); ^{13}C NMR (500MHz, $CDCl_3$) δ 140.9, 136.1, 128.1, 128.0, 127.9, 126.3, 122.5, 121.4, 119.2, 118.8, 115.9, 110.9, 67.2, 57.2, 55.9, 52.2, 42.4, 23.8, 23.0, 9.34; IR (neat): 3421.1, 3057.1, 2935.8, 2817.0, 2774.6, 1617.9, 1492.5, 1454.1, 1351.1, 738.1, 698.0 cm^{-1}; HRMS calcd for MH^+ $C_{23}H_{28}N_3$, 346.2283; found, 346.2273.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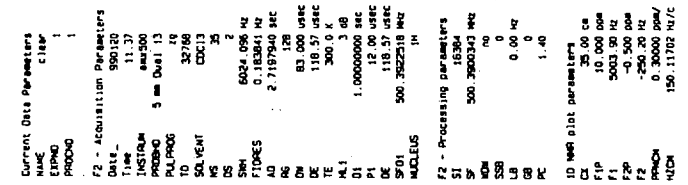
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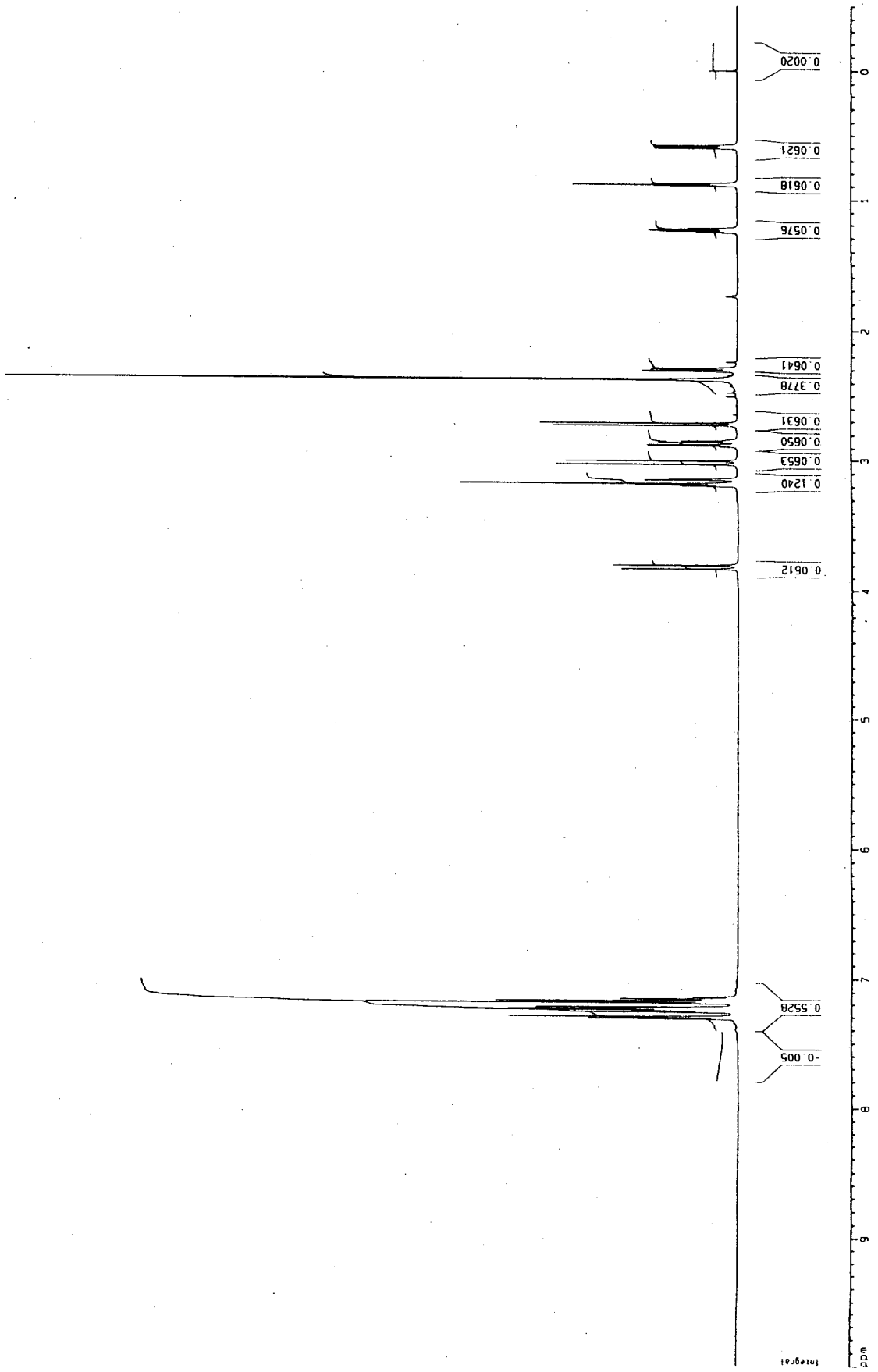
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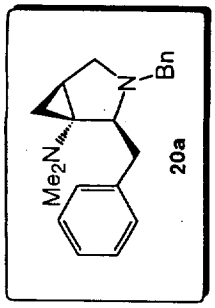

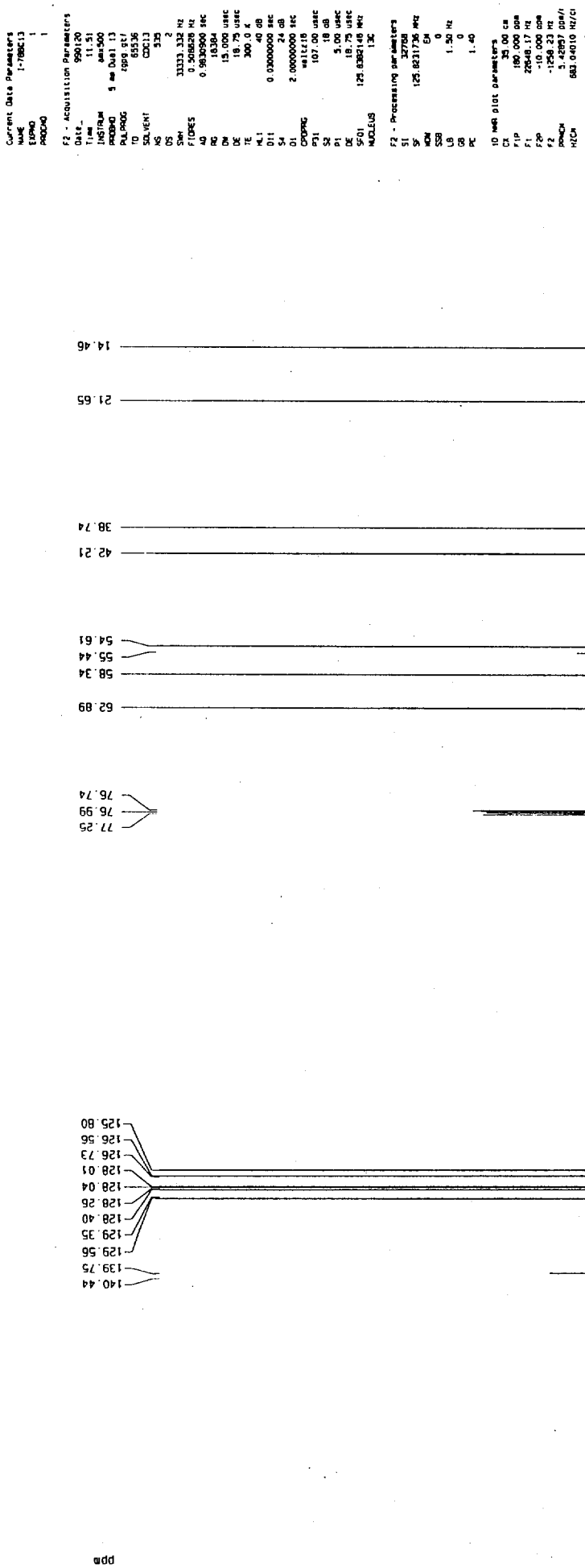

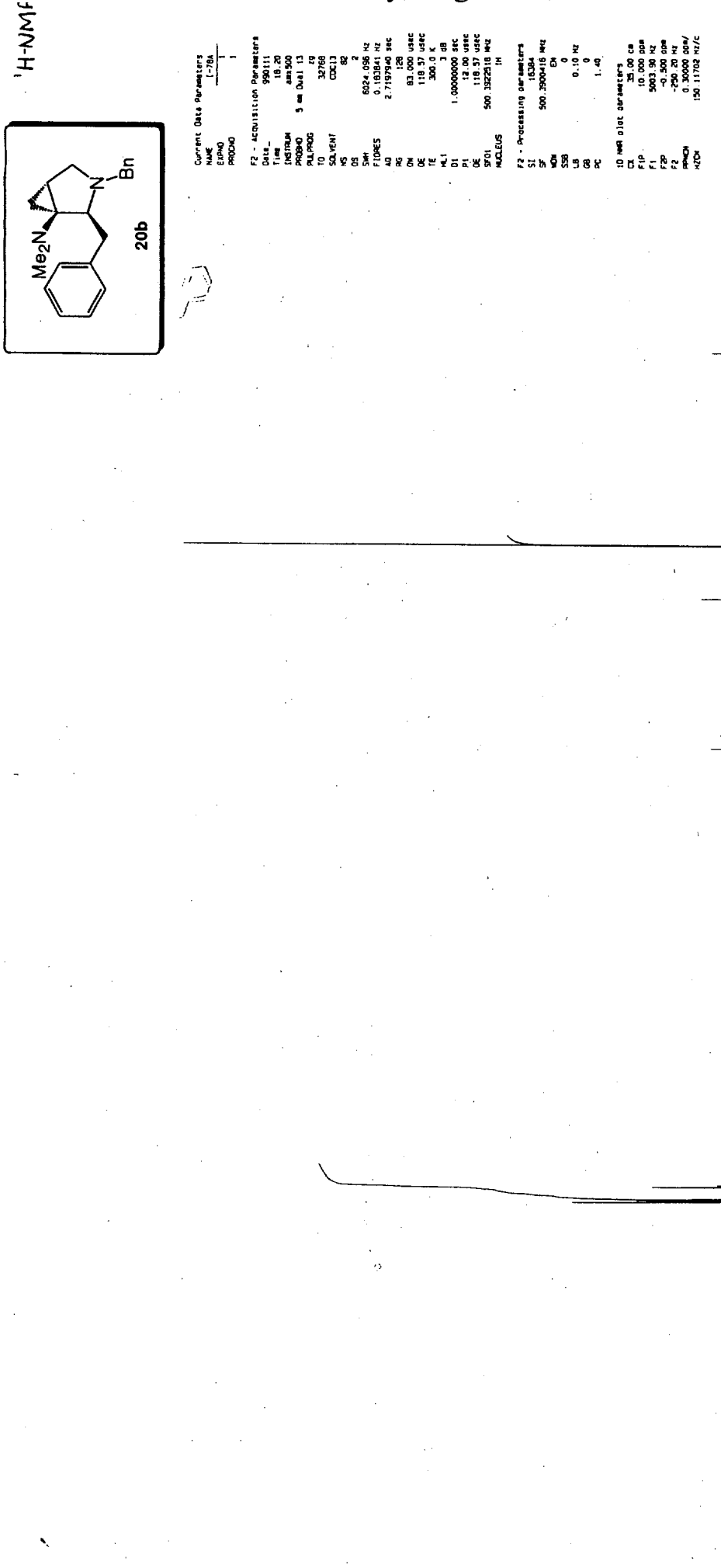

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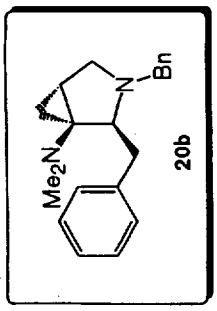

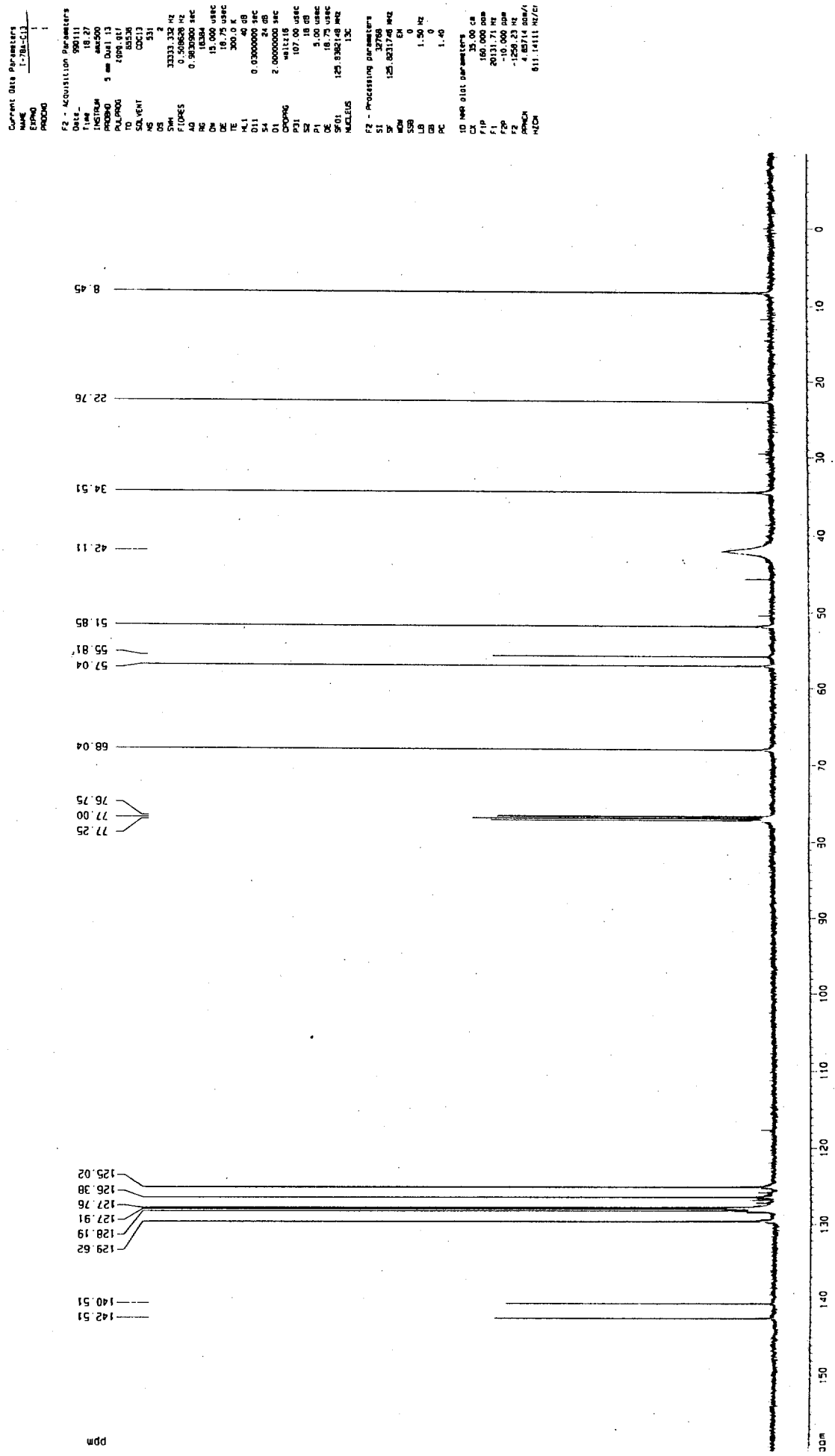

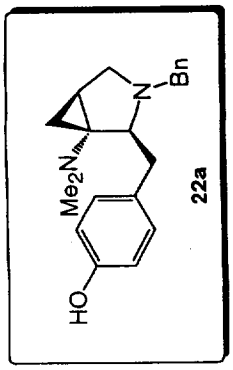

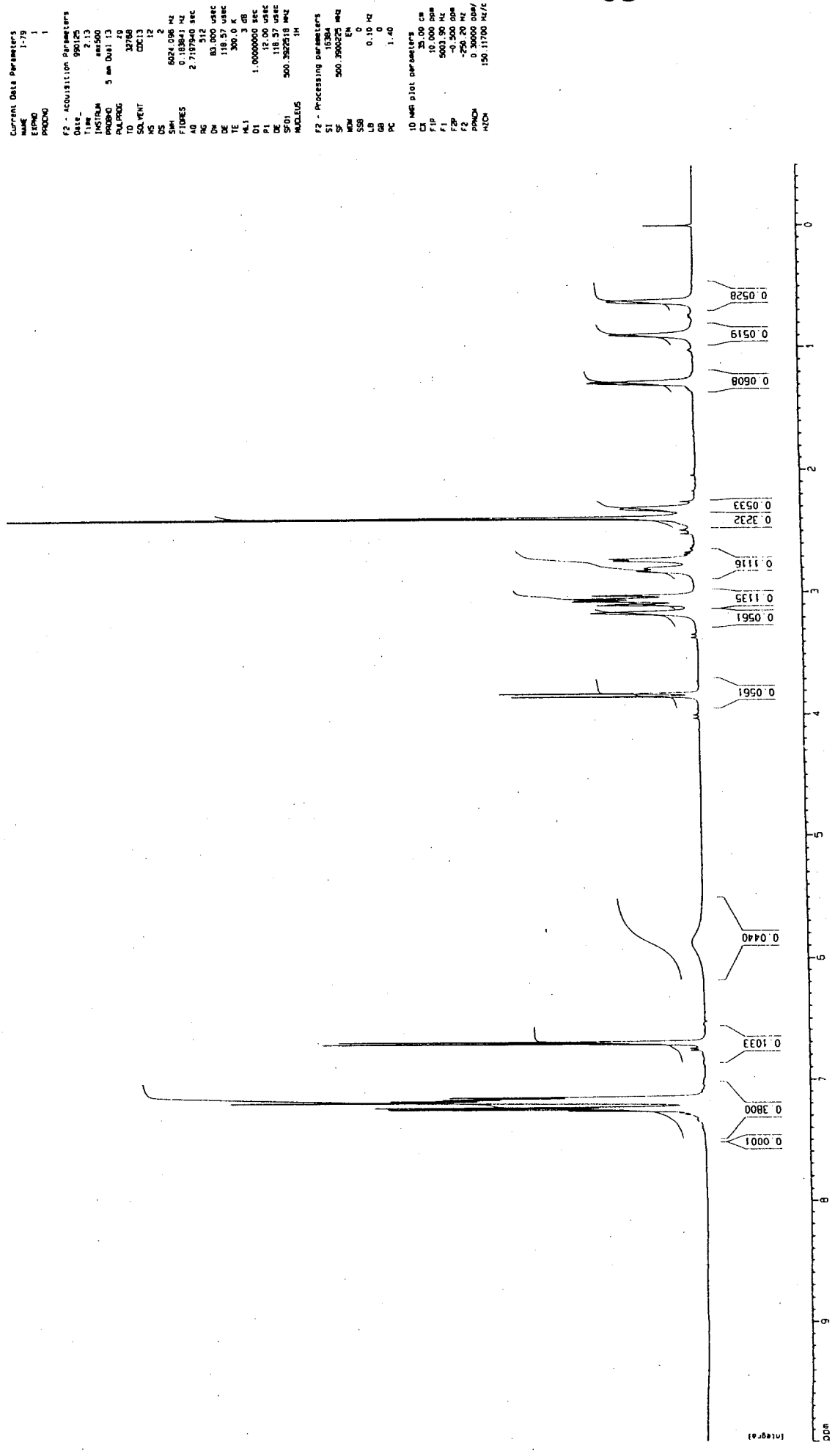

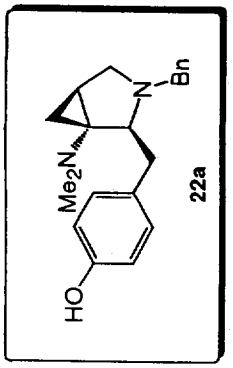

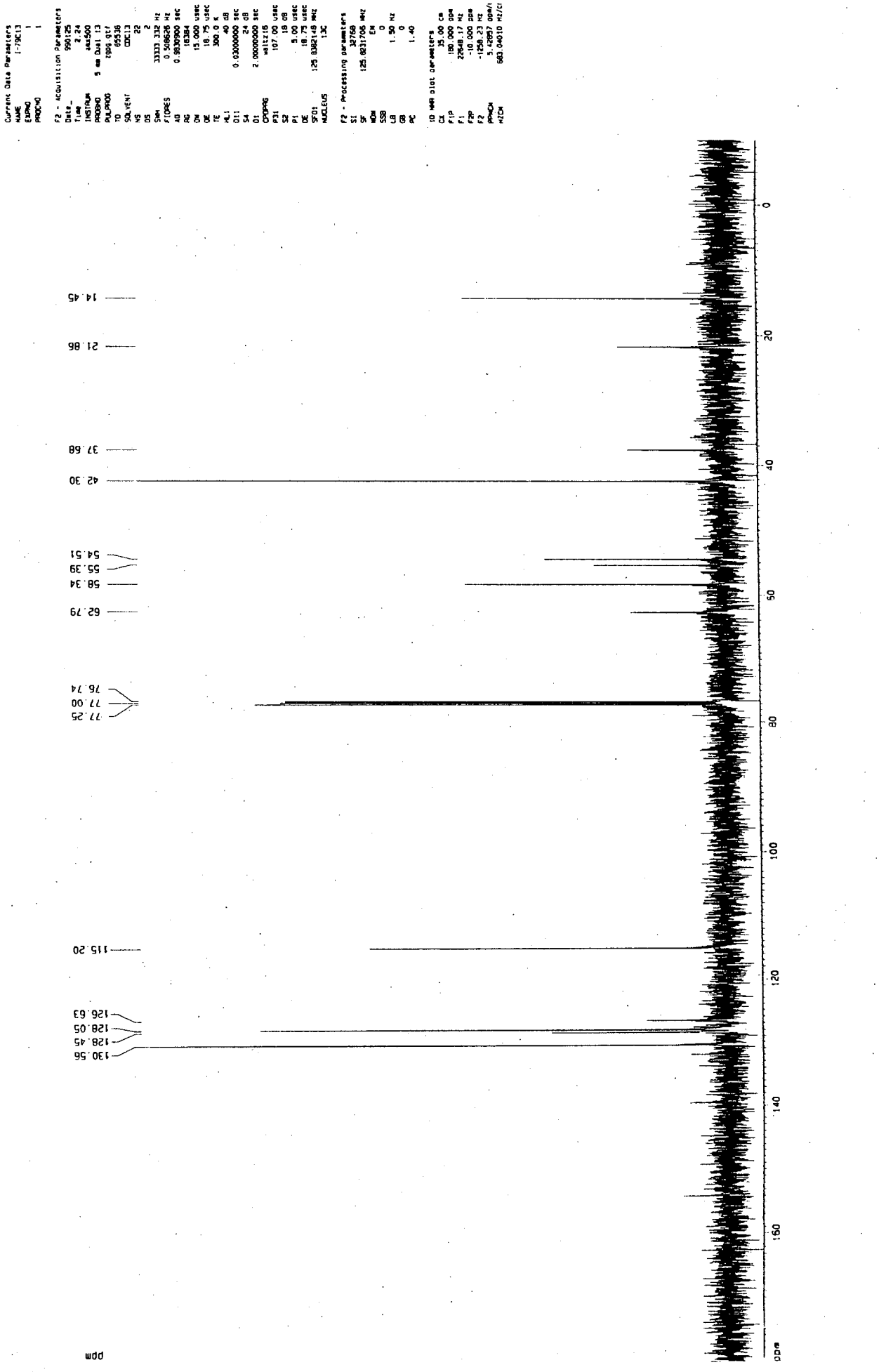

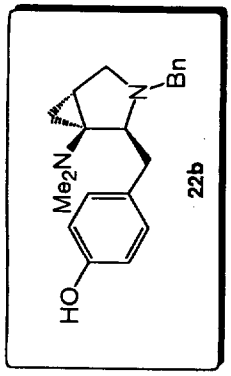

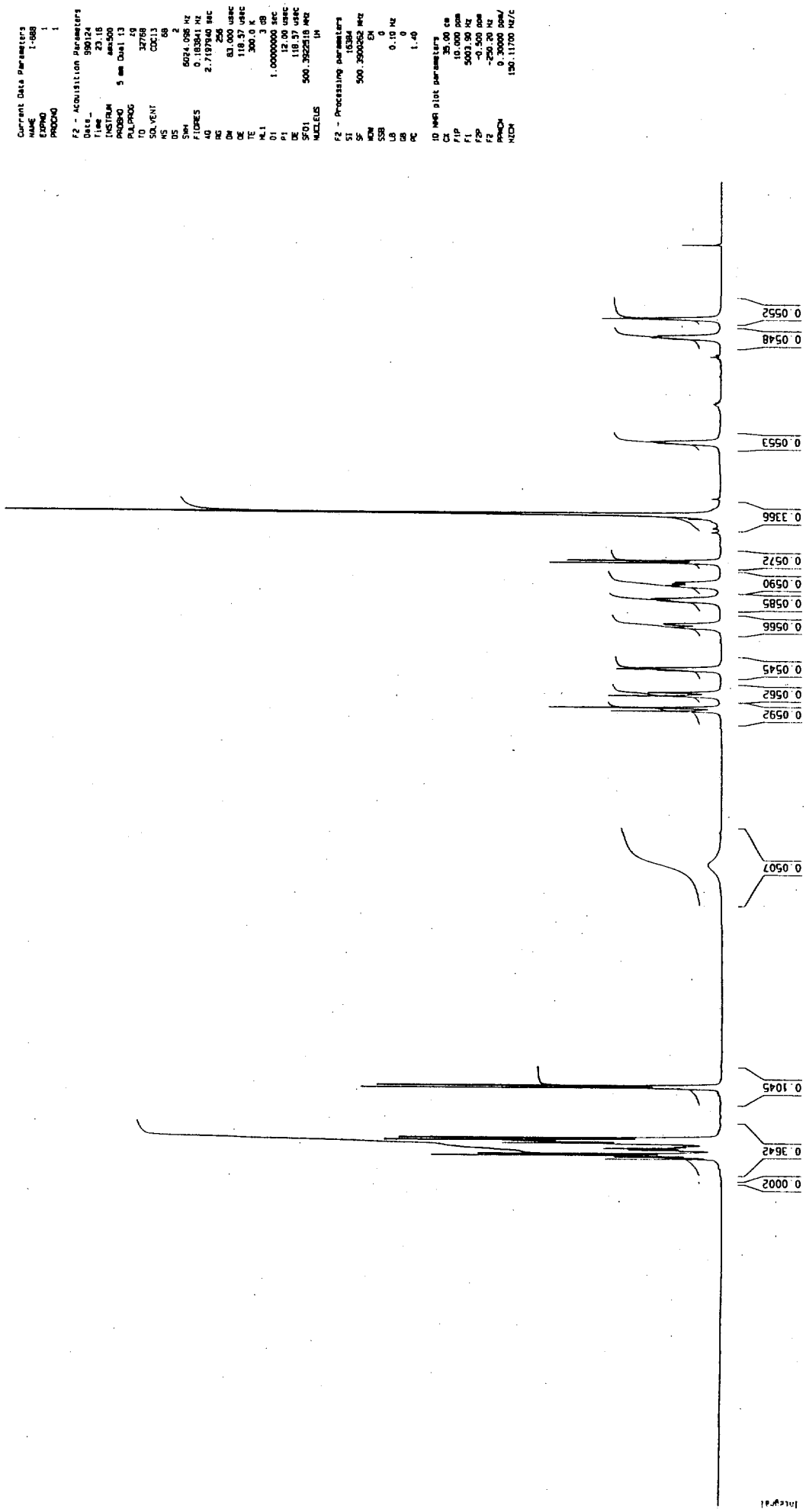

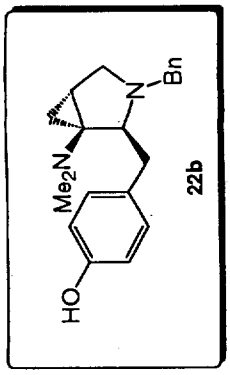

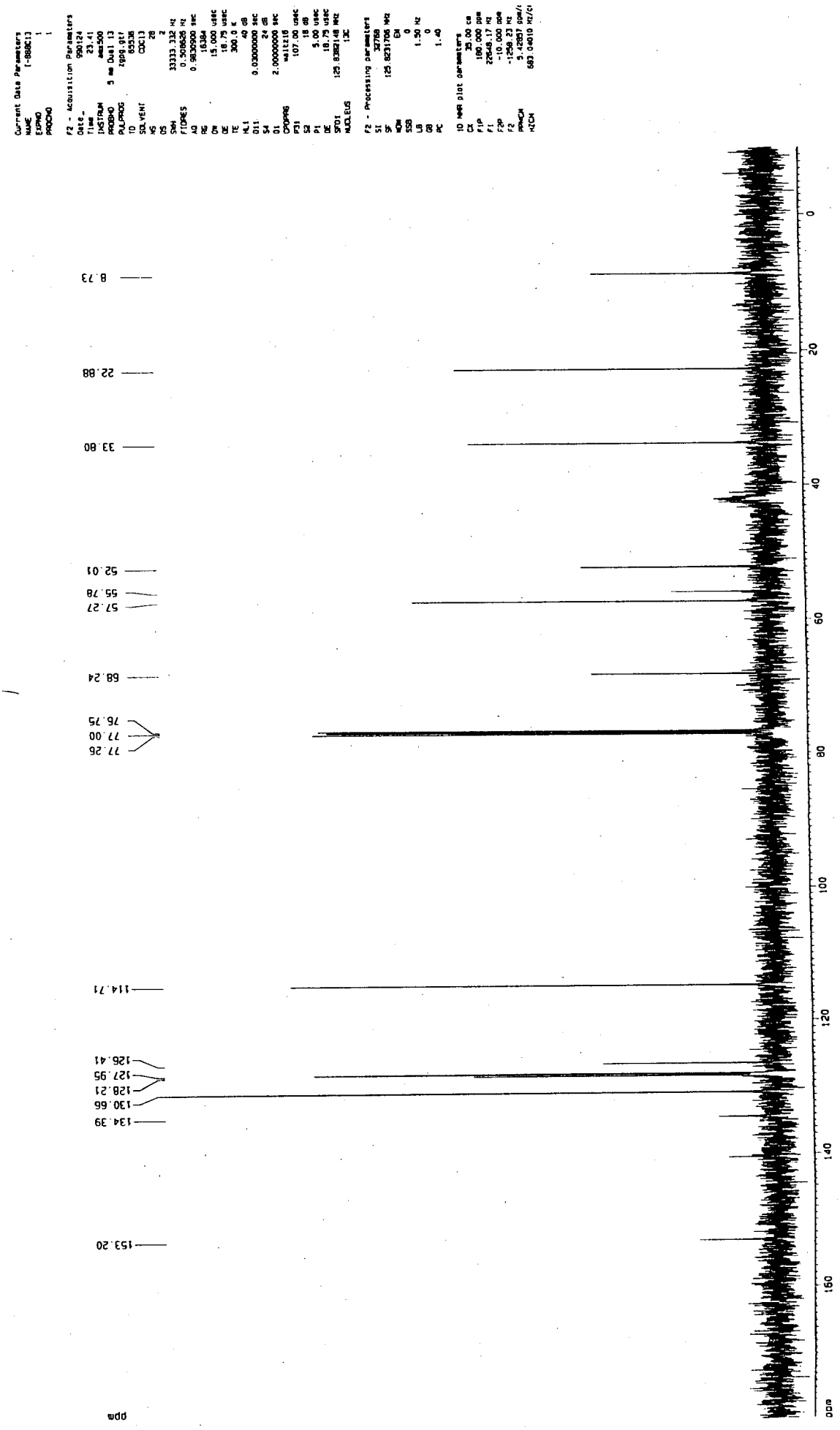

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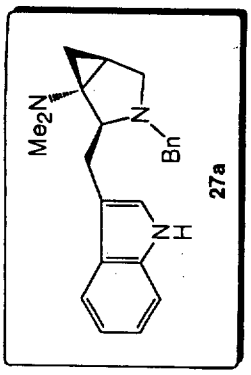

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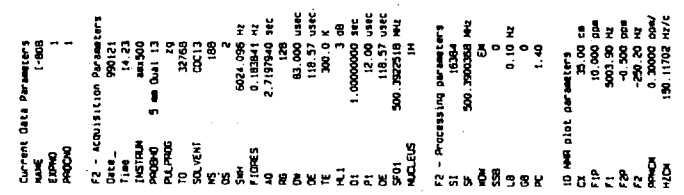

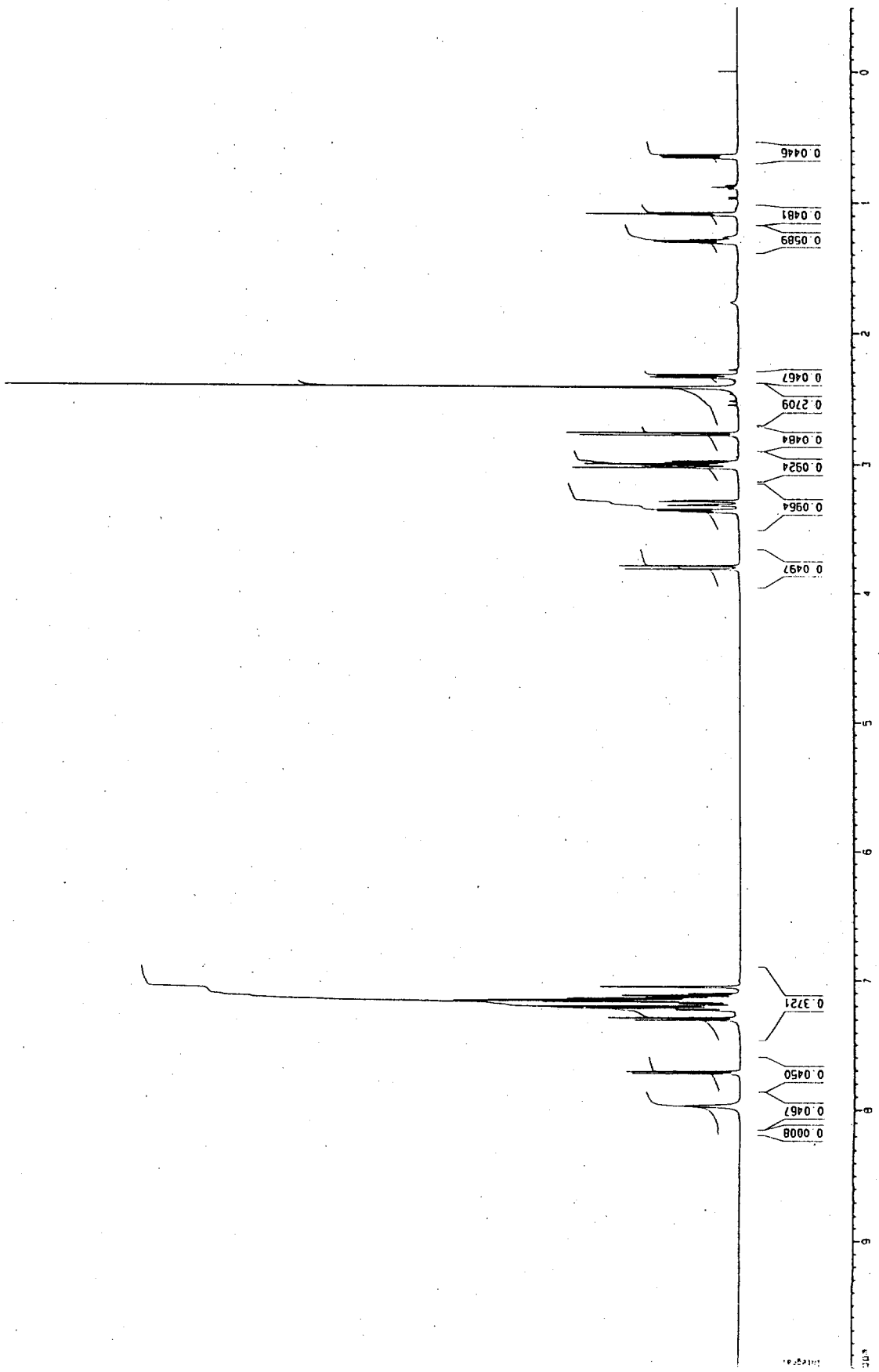

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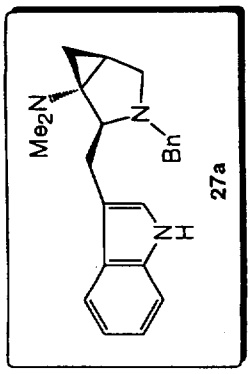

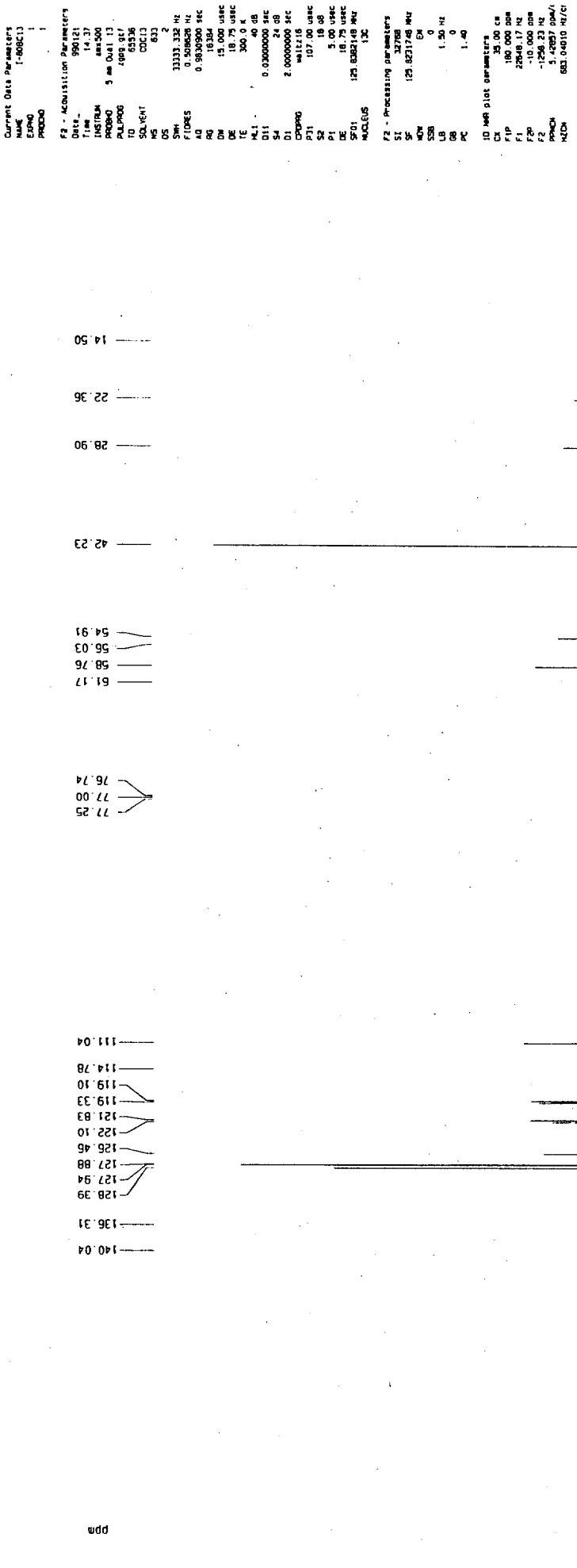

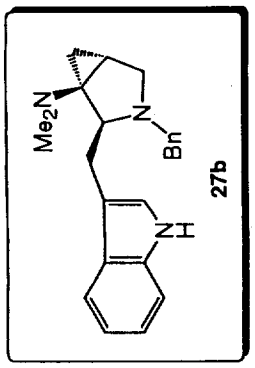

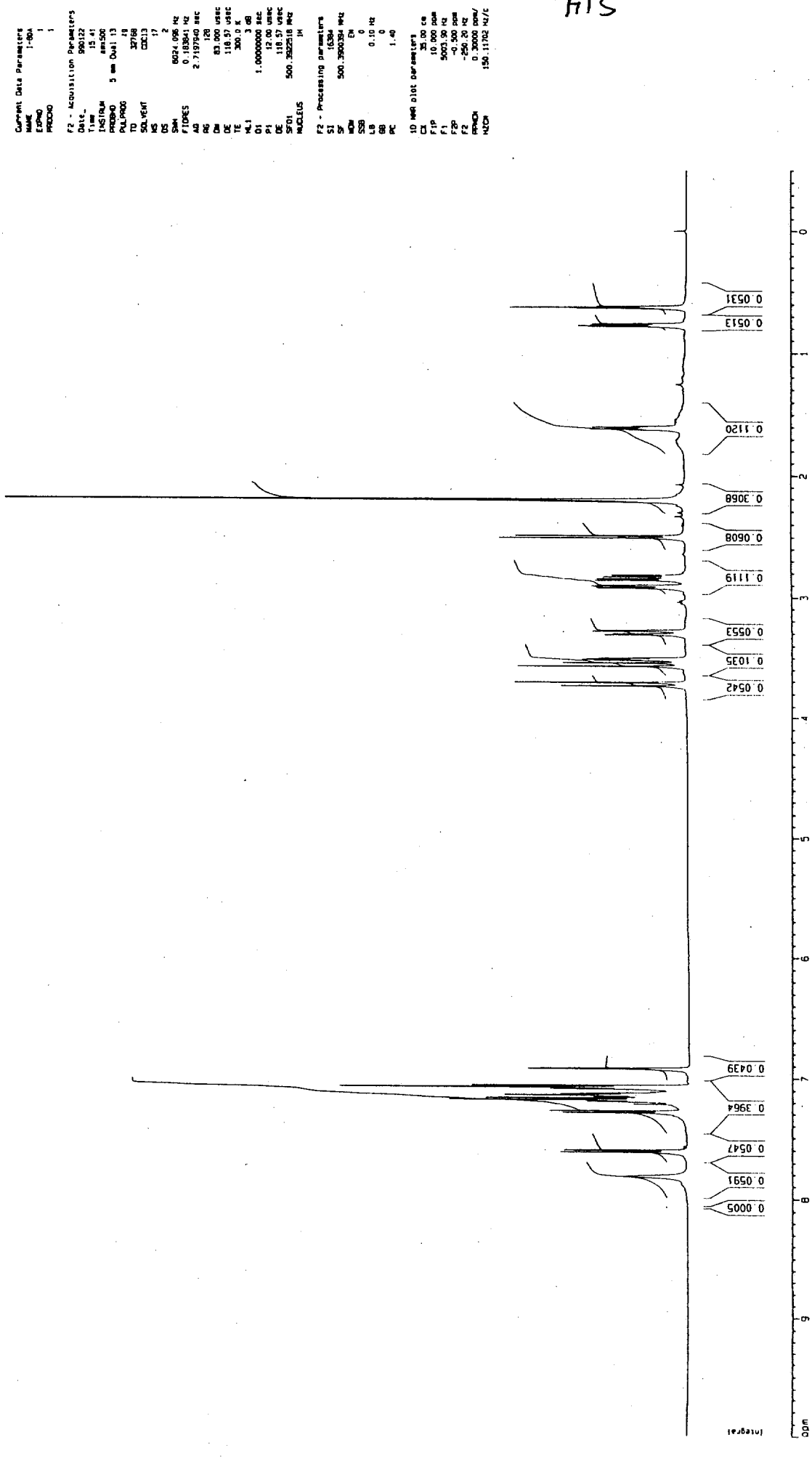

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