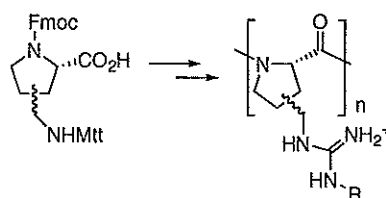


Supplementary Material for

Strategies for the Solid-Phase Diversification Poly-L-Proline Type II Peptide Mimic Scaffolds and Peptide Scaffolds Through Guanidinylation

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Graphical abstract:



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Experimentals and Characterization Data for Compounds **15**, **17**, **18a-p**,
44-62, **68**, **69**

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Supporting Spectra

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Unless otherwise specified, all reagents were purchased from commercial sources and were used without further purification. THF was distilled over potassium metal, and Dichloromethane was distilled over calcium hydride. All reactions were carried out under N₂ atmosphere. Flash chromatography was carried out on 230-400 mesh silica gel. Melting points were uncorrected.

2,2,5,7,8-Pentamethylchroman-6-sulfonamide (15). 2,2,5,7,8-Pentamethylchroman-6-sulfonyl chloride (5.0 g, 0.017 mol) was dissolved in CH₂Cl₂ (75 mL) in a 250 mL round bottom flask. The resulting solution was brought to 0 °C in an ice bath and ammonia was bubbled through for 20 min. At the end of this time, it was noted that a white solid had precipitated out of the solution. This slurry was introduced to a 500 mL separatory funnel containing 150 mL EtOAc and 150 mL H₂O. After repeated shaking, the organic layer was separated, dried over MgSO₄, and concentrated affording the sulfonamide **15** (4.67 g, 100%) as a colorless solid that was used without further need for purification: mp 157-159 °C; ¹H NMR (500 MHz, acetone d₆) δ 6.20 (br. s, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.54 (s, 3H), 2.52 (s, 3H), 2.11 (s, 3H), 1.84 (t, *J* = 6.5 Hz, 2H), 1.31 (s, 6H); ¹³C NMR (125 MHz, acetone d₆) 154.4, 135.9, 135.6, 134.3, 124.4, 119.0, 74.5, 33.2, 26.8, 21.8, 18.6, 17.5, 12.1 ppm; IR (film) 3287 cm⁻¹ (NH); MS (CI) *m/z* 284 (MH). Anal. Calcd. for C₁₄H₂₁NO₃S: C, 59.34; H, 7.47; N, 4.94. Found: C, 59.40; H, 7.66; N, 5.00.

2,2,5,7,8-Pentamethylchroman-6-sulfonyl-isothiocyanate (17). 2,2,5,7,8-Pentamethylchroman-6-sulfonamide **3.16** (4.67 g, 0.017 mol), KOH (2.00 g, 0.036 mol), and a magnetic stirring bar were placed in a 250 mL round bottom flask were heated at reflux for 24 h in 4:1 (v/v) benzene/CS₂ (100 mL) under Dean Stark conditions. At the end of this time, most of the residual solvent was distilled away and the mixture was redistilled two times with additional benzene (2 × 50 mL) in order to remove any residual CS₂. The resulting yellow slurry was cooled to 0 °C in an ice bath and phosgene (20% in toluene; 15 mL, 2 eq) was added dropwise over 30 min. The mixture was allowed to reach room temperature overnight, at which time nitrogen was bubbled through for 20 min in order to remove remaining phosgene. The solvent was removed *in vacuo* and the residue was taken up and triturated in 100 mL hexane. Filtration of the solids and concentration of the supernatant *in vacuo* afforded **17** (4.15 g, 75%) as a light yellow gum that was used without further purification: ¹H NMR (500 MHz, CDCl₃) δ 2.67 (t, *J* = 6.8 Hz, 2H), 2.59 (s, 3H), 2.57 (s, 3H), 2.14 (s, 3H), 1.85 (t, *J* = 6.8 Hz, 2H), 1.34 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) 156.3, 154.9, 137.31, 137.27, 129.4, 125.2, 118.8, 74.8,

32.5, 26.8, 21.4, 18.4, 17.4, 12.2 ppm; IR (film) 1898 cm^{-1} ; MS (CI) m/z 205, 267, 326 (MH). Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}_2$: C, 55.36; H, 5.88; N, 4.30. Found: C, 55.30; H, 6.01; N, 4.12.

General Procedure for the Preparation of N-Pmc-N'-substituted Thioureas 18a-p from thiocyanate 17. A solution of isothiocyanate **17** (0.50 g, 1.5 mmol in 15 mL CH_2Cl_2) in a 100 mL round bottom flask was cooled to 0 °C and the primary amine (1.05 eq) was added dropwise as a solution in CH_2Cl_2 (10 mL). After 15 min (overnight for **18e**), the solvent was removed *in vacuo* to yield crude product, which was purified by flash chromatography on silica gel using 20% EtOAc/Hex as eluent (except for **18k** thiourea which was purified by way of trituration in 1:1 CH_2Cl_2 /Hexanes and filtered).

N-Pmc-N'-cyclohexyl-thiourea (18a). (0.61 g, 94%) isolated as a colorless friable foam: mp 72-76 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.06 (br. s, 1H), 7.67 (d, $J = 7.3$ Hz, 1H), 3.97-4.07 (m, 1H), 2.65 (t, $J = 6.8$ Hz, 2H), 2.59 (s, 3H), 2.57 (s, 3H), 2.12 (s, 3H), 1.83 (t, $J = 6.8$ Hz, 2H), 1.76-1.79 (m, 2H), 1.54-1.56 (m, 3H), 1.29-1.32 (m, 8H), 1.17-1.23 (m, 1H), 1.05-1.12 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) 176.6, 155.7, 136.9, 136.8, 127.4, 125.3, 118.9, 74.5, 54.0, 32.4, 31.4, 26.6, 25.3, 24.1, 21.3, 18.3, 17.3, 12.1 ppm; IR 3335 cm^{-1} (film) 3335 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z 205, 425 (MH). Anal. Calcd. for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_3\text{S}_2$: C, 59.40; H, 7.60; N, 6.60. Found: C, 59.50; H, 7.73; N, 6.46.

N-Pmc-N'-cyclopropyl-thiourea (18b). (0.58 g, 99%) isolated as a colorless friable foam: mp 142-143 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.40 (br. s, 1H), 7.79 (br. s, 1H), 2.90-2.93 (m, 1H), 2.65 (t, $J = 6.8$ Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.13 (s, 3H), 1.84 (t, $J = 6.8$ Hz, 2H), 1.33 (s, 6H); 0.75-0.78 (m, 2H), 0.30 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) 179.9, 155.7, 136.9, 136.8, 127.3, 125.3, 118.9, 74.5, 32.4, 27.7, 26.6, 21.3, 18.2, 17.2, 12.1, 7.2 ppm; IR (film) 3333 cm^{-1} , 1138 cm^{-1} ; MS (CI) m/z 204, 267, 383 (MH). Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_3\text{S}_2$: C, 56.51; H, 6.85; N, 7.32. Found: C, 56.78; H, 6.92; N, 7.29.

N-Pmc-N'-(p-toluidyl)-thiourea (18c). (0.59 g, 88%) isolated as a colorless friable foam: mp 63-66 °C; ^1H NMR (500 MHz, CDCl_3) δ 9.37 (br. s, 1H), 8.67 (br. s, 1H), 7.08-7.14 (m, 4H), 2.58-2.64 (m, 8H), 2.30 (s, 3H), 2.12 (s, 3H), 1.81 (t, $J = 6.8$ Hz, 2H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 177.5, 155.8, 136.9, 136.8, 136.7, 134.8, 129.3, 127.3, 125.3, 124.4, 118.9, 74.5, 38.4, 32.3, 26.6, 21.2, 20.9, 18.2, 17.2, 12.1 ppm; IR (film) 3301 cm^{-1} , 1122 cm^{-1} ; MS (CI) m/z 433 (MH). Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3\text{S}_2$: C, 61.08; H, 6.52; N, 6.48. Found: C, 61.17; H, 6.79; N, 6.38.

N-Pmc-N'-heptyl-thiourea (18d). (0.64 g, 95%) isolated as a transparent gum: ^1H NMR (500 MHz, CDCl_3) δ 8.57 (br. s, 1H), 7.81-7.82 (m, 1H), 3.45-3.48 (m, 2H), 2.65 (t, J = 6.8 Hz, 2H), 2.58 (s, 3H), 2.57 (s, 3H), 2.12 (s, 3H), 1.83 (t, J = 6.8 Hz, 2H), 1.37-1.47 (m, 2H), 1.32 (s, 6H), 1.12-1.31 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) 178.0, 155.6, 136.7, 136.6, 127.5, 125.1, 118.8, 74.4, 45.6, 32.3, 31.4, 28.7, 28.1, 26.5, 26.3, 22.4, 21.2, 18.1, 17.2, 13.9, 12.0 ppm; IR (film) 3336 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z 204, 267, 441 (MH). HRMS Calcd. for $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_3\text{S}_2$: 441.2245. Found: 441.2269 $[\text{M}+\text{H}]^+$.

N-Pmc-N'-(*o*-methoxyphenyl)-thiourea (18e). (0.56 g, 81%) isolated as a colorless friable foam: mp 76-78 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 9.94 (br. s, 1H), 8.36 (d, J = 7.9 Hz, 1H), 8.04 (br. s, 1H), 7.12-7.16 (m, 1H), 6.84-6.93 (m, 2H), 3.84 (s, 3H), 2.56-2.76 (m, 8H), 2.12 (s, 3H), 1.82 (t, J = 6.8 Hz, 2H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 175.4, 155.7, 150.4, 136.8, 136.7, 127.7, 127.0, 126.4, 125.2, 122.7, 120.1, 118.8, 110.6, 74.4, 55.8, 32.4, 26.6, 21.3, 18.1, 17.1, 12.1 ppm; IR (film) 3272 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z , 205, 267, 449 (MH). HRMS Calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$: 449.1569. Found: 449.1577 $[\text{M}+\text{H}]^+$.

N-Pmc-N'-(2-adamantyl)-thiourea (18f). (0.70g, 96%) isolated as a colorless friable foam: mp 83-90 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.59 (br. s, 1H), 8.08 (d, J = 7.3 Hz, 1H), 4.21 (m, 1H), 2.54-2.71 (m, 8H), 2.10 (s, 3H), 1.69-1.89 (m, 10H), 1.50-1.58 (m, 2H), 1.38-1.45 (m, 2H), 1.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 176.4, 155.5, 136.7, 136.6, 127.7, 125.2, 118.8, 74.4, 59.4, 37.2, 36.6, 32.4, 31.7, 30.8, 26.9, 26.8, 26.5, 21.1, 18.3, 17.2, 11.8 ppm; IR (film) 3341 cm^{-1} , 1122 cm^{-1} ; MS (CI) m/z 477 (MH). HRMS Calcd. for $\text{C}_{25}\text{H}_{36}\text{N}_2\text{O}_3\text{S}_2$: 477.2245. Found: 477.2240 $[\text{M}+\text{H}]^+$.

N-Pmc-N'-allyl-thiourea (18g). (0.58 g, 99%) isolated as a colorless friable foam: mp 112-116 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.59 (br. s, 1H), 7.90 (br. s, 1H), 5.65-5.72 (m, 1H), 5.08 (d, J = 10.4 Hz, 1H), 4.98 (d, J = 14.5 Hz, 1H), 4.15 (dd, J = 4.3 Hz, J = 1.0 Hz, 2H), 2.66 (t, J = 6.8 Hz, 2H), 2.59 (s, 3H), 2.58 (s, 3H), 2.14 (s, 3H), 1.85 (t, J = 6.8 Hz, 2H), 1.34 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 178.3, 155.7, 136.8, 136.7, 131.7, 127.3, 125.3, 118.9, 117.1, 74.5, 47.7, 32.4, 26.6, 21.2, 18.2, 17.2, 12.0 ppm; IR (film) 3341 cm^{-1} , 1146 cm^{-1} ; MS (CI) m/z 204, 267, 383 (MH). Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_3\text{S}_2$: C, 56.51; H, 6.85; N, 7.32. Found: C, 56.93; H, 6.95; N, 7.20.

N-Pmc-N'-(1-adamantyl)-thiourea (18h). (0.43 g, 58%) isolated as a colorless crystalline solid: mp 158-160 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.00 (br. s, 1H), 7.41

(br. s, 1H), 2.66 (t, $J = 6.2$ Hz, 2H), 2.60 (s, 6H), 2.14 (s, 3H), 2.00 (br. s, 3H), 1.90 (s, 6H), 1.84 (t, $J = 6.6$ Hz, 2H), 1.59 (dd, $J = 11.7$ Hz, $J = 27.8$ Hz, 6H), 1.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 175.2, 155.5, 137.2, 136.8, 127.4, 125.0, 118.8, 74.4, 55.0, 40.1, 36.1, 32.4, 29.3, 26.6, 21.2, 18.4, 17.2, 12.0 ppm; IR (film) 3332 cm^{-1} , 1558 cm^{-1} ; MS (CI) m/z 477 (MH). Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3\text{S}_2$: C, 62.99; H, 7.61; N, 5.88. Found: C, 63.12; H, 7.72; N, 5.78.

N-Pmc-N'-benzyl-thiourea (18i). (0.65 g, 100%) isolated as a colorless friable foam: mp $60\text{--}66\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.31 (br. s, 1H), 7.96 (br. s, 1H), 7.21–7.27 (m, 3H), 6.94–6.96 (m, 2H), 4.67 (d, $J = 5.3$ Hz, 2H), 2.61 (t, $J = 6.8$ Hz, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 2.10 (s, 3H), 1.84 (t, $J = 6.8$ Hz, 2H), 1.35 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 178.2, 155.8, 136.9, 136.7, 135.9, 128.7, 127.8, 127.4, 125.5, 119.0, 74.6, 49.8, 32.5, 26.7, 21.3, 18.2, 17.2, 12.2 ppm; IR (film) 3336 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z 205, 267, 433 (MH). Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3\text{S}_2$: C, 61.08; H, 6.52; N, 6.48. Found: C, 61.38; H, 6.64; N, 6.37.

N-Pmc-N'-[(*tert*)-butoxycarbonyl]-methyl-thiourea (18j). (0.60 g, 86%) isolated as a colorless friable foam: mp $62\text{--}70\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.29 (br. s, 1H), 8.22 (br. s, 1H), 4.11 (d, $J = 4.3$ Hz, 2H), 2.66 (t, $J = 6.8$ Hz, 2H), 2.61 (s, 3H), 2.60 (s, 3H), 2.12 (s, 3H), 1.83 (t, $J = 6.8$ Hz, 2H), 1.46 (s, 9H), 1.33 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 177.8, 167.1, 155.8, 137.1, 137.0, 127.5, 125.4, 119.0, 82.9, 74.5, 48.3, 32.5, 28.0, 26.7, 21.4, 18.2, 17.3, 12.2 ppm; IR (film) 3319 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z 205, 401, 457 (MH). Anal. Calcd. for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{O}_5\text{S}_2$: C, 55.24; H, 7.06; N, 6.13. Found: C, 55.44; H, 7.05; N, 6.06.

N-Pmc-N'-(4-methylpyridyl)-thiourea (18k). (0.46 g, 69%) isolated as an amorphous colorless solid: mp $170\text{--}172\text{ }^\circ\text{C}$ (d); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.52 (t, $J = 5.4$ Hz, 1H), 8.38 (d, $J = 5.4$ Hz, 2H), 6.90 (d, $J = 4.9$ Hz, 2H), 4.72 (d, $J = 5.5$ Hz, 2H), 2.60 (t, $J = 6.3$ Hz, 2H), 2.52 (s, 6H), 2.07 (s, 3H), 1.79 (t, $J = 6.6$ Hz, 2H), 1.29 (s, 6H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) 179.3, 154.5, 149.2 (br.), 148.6 (br.), 147.1, 136.8, 136.5, 128.5, 123.6, 121.6, 118.5, 74.2, 46.2, 41.9 (br.), 31.8, 26.4, 20.7, 17.8, 16.9, 11.9 ppm; IR (KBr pellet) 3328 cm^{-1} , 1141 cm^{-1} ; MS (CI) m/z 204, 434 (MH). Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3\text{S}_2$: C, 58.17; H, 6.28; N, 9.69. Found: C, 57.92; H, 6.20; N, 9.73.

N-Pmc-N'-(3-methylpyridyl)-thiourea (18l). (0.66 g, 100%) isolated as a colorless friable foam: mp $90\text{--}98\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 9.99 (br. s, 1H), 8.58 (d, $J = 4.7$ Hz, 1H), 8.52 (s, 1H), 8.26 (t, $J = 5.1$ Hz, 1H), 7.35 (d, $J = 7.7$ Hz, 1H), 7.21 (m, 1H),

4.78 (d, $J = 5.5$ Hz, 2H),), 2.60 (t, $J = 6.5$ Hz, 2H), 2.52 (s, 3H), 2.50 (s, 3H), 2.09 (s, 3H), 1.82 (t, $J = 6.7$ Hz, 2H), 1.33 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 179.4, 155.5, 147.3, 136.8, 136.3, 133.1, 127.6, 125.1, 123.7, 118.8, 74.4, 46.1, 32.4, 26.6, 21.2, 18.0, 17.1, 12.0 ppm; IR (film) 3333 cm^{-1} , 1123 cm^{-1} ; MS (CI) m/z 204, 434 (MH). HRMS Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3\text{S}_2$: 434.1572. Found: 434.1564 $[\text{M}+\text{H}]^+$.

N-Pmc-N'-(2-methylpyridyl)-thiourea (18m). (0.39 g, 58%) isolated as a colorless friable foam: mp 51-54 °C; ^1H NMR (500 MHz, CDCl_3) δ 9.01 (br. s, 1H), 8.52 (d, $J = 3.7$ Hz, 1H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.19 (t, $J = 6.1$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 4.77 (d, $J = 3.6$ Hz, 2H), 2.52-2.75 (m, 8H), 2.08 (s, 3 H), 1.78 (t, $J = 6.5$ Hz, 2H), 1.28 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 177.7, 155.5, 154.3, 148.7, 136.9, 136.6, 127.5, 125.0, 122.4, 121.3, 118.7, 74.3, 50.3, 32.4, 26.6, 21.2, 18.1, 17.2, 12.1 ppm; IR (film) 3276 cm^{-1} , 1532 cm^{-1} ; MS (APCI) m/z 434 (MH). Anal Calcd for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3\text{S}_2$: C, 58.17; H, 6.28; N, 9.69. Found: C, 58.45; H, 6.38; N, 9.50.

N-Pmc-N'-(2-hydroxyethyl)-thiourea (18n). (0.52 g, 88 %) isolated as a colorless gum: ^1H NMR (500 MHz, CDCl_3) δ 8.98 (br. s, 1H), 8.16 (br. s, 1H), 3.64 (s, 4H), 2.65 (t, $J = 6.1$ Hz, 2H), 2.58 (s, 3H), 2.56 (s, 3H), 2.12 (s, 3H), 1.82 (t, $J = 6.5$ Hz, 2H), 1.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 178.5, 155.6, 137.0, 136.9, 127.1, 125.0, 118.8, 74.4, 60.3, 60.1, 47.6, 32.2, 26.5, 21.2, 18.0, 17.1, 14.0, 12.0 ppm; IR (film) 3331 cm^{-1} , 1547 cm^{-1} ; MS (MALDI) m/z 388 (MH). Anal. Calcd. for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2$: C, 52.82; H, 6.78; N, 7.25. Found: C, 52.97; H, 6.95; N, 7.22.

N-Pmc-N'-formyl-thiourea (18o). (0.50 g, 95%) isolated as a colorless friable foam: mp 58-63 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.75 (br. s, 1H), 7.62 (br. s, 1H), 6.96 (br. s, 1H), 2.68 (t, $J = 6.3$ Hz, 2H), 2.59 (s, 3H), 2.57 (s, 3H), 2.15 (s, 3H), 1.86 (t, $J = 6.5$ Hz, 2H), 1.36 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 180.4, 156.0, 136.9, 127.3, 125.4, 119.0, 74.6, 32.4, 26.7, 21.3, 18.2, 17.3, 12.2 ppm; IR (film) 1612 cm^{-1} , 1550 cm^{-1} , 1151 cm^{-1} ; MS (APCI) m/z 344 (MH). HRMS Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3\text{S}_2$: 342.1072. Found: 349.1232 $[\text{M}+\text{Li}]^+$.

N-Pmc-N'-(tert-butoxycarbonyl)amino-thiourea (18p). (0.57 g, 83%) isolated as a colorless friable foam: mp 84-87 °C; ^1H NMR (500 MHz, CDCl_3) δ 9.06 (br. s, 1H), 7.15 (br. s, 1H), 2.65 (t, $J = 6.3$ Hz, 2H), 2.58 (s, 3H), 2.57 (s, 3H), 2.12 (s, 3H), 1.82 (t, $J = 6.5$ Hz, 2H), 1.44 (s, 9H), 1.32 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 155.9, 153.9, 137.4, 137.1, 127.1, 125.2, 118.8, 82.6, 74.5, 32.4, 28.0, 26.7, 21.3, 18.1, 17.3, 12.1 ppm; IR

(film) 3228 cm^{-1} , 1150 cm^{-1} ; MS (MALDI) m/z 400 (M-*t*Bu). Anal. Calcd. for $\text{C}_{20}\text{H}_{31}\text{N}_3\text{O}_5\text{S}_2$: 52.49; H, 6.83; N, 9.18. Found: C, 52.72; H, 6.95; N, 9.15.

(44). (9.3 mg, 38%) ^1H NMR (500 MHz, CD_3OD) δ 4.60 (br s, 1H), 4.36-4.43 (m, 2H), 3.46-4.62 (m, 2H), 3.36 (m, 1H), 2.89 (m, 1H), 2.53 (m, 1H), 2.17 (m, 1H), 1.84 (m, 1H), 1.35-1.48 (m, 7H), 0.87 (m, 1H), 0.68 (m, 1H); MS (ESI) m/z 381 (MH); HRMS Calcd. for $\text{C}_{17}\text{H}_{29}\text{N}_6\text{O}_4$: 381.2250. Found: 381.2250 $[\text{M}+\text{H}]^+$.

(45). (17.9 mg, 72%) ^1H NMR (500 MHz, CD_3OD) δ 4.57 (br s, 1H), 4.33-4.44 (m, 2H), 4.01 (s, 1H), 3.48-3.59 (m, 2H), 3.34 (m, 1H), 2.98 (m, 1H), 2.16 (m, 1H), 1.85 (m, 1H), 1.36-1.48 (m, 7H); MS (ESI) m/z 399 (MH); HRMS Calcd. for $\text{C}_{16}\text{H}_{27}\text{N}_6\text{O}_6$: 399.1992. Found: 399.2004 $[\text{M}+\text{H}]^+$.

(46). (17.5 mg, 66%) ^1H NMR (500 MHz, CD_3OD) δ 4.57 (br. s, 1H), 4.33-4.43 (m, 2H), 4.47-4.61 (m, 2H), 3.33 (m, 1H), 3.17 (t, $J = 7.3$ Hz, 2H), 2.92 (m, 1H), 2.16 (m, 1H), 1.85 (m, 1H), 1.54-1.63 (m, 2H), 1.38-1.48 (m, 7H), 1.22-1.38 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 3H); MS (ESI) m/z 439 (MH); HRMS Calcd. for $\text{C}_{21}\text{H}_{39}\text{N}_6\text{O}_4$: 439.3033. Found: 439.3034 $[\text{M}+\text{H}]^+$.

(47). (21.2 mg, 76%) ^1H NMR (500 MHz, CD_3OD) δ 4.64 (br s, 1H), 4.40-4.51 (m, 2H), 3.77 (s, 1H), 3.55-3.68 (m, 2H), 3.37 (m, 1H), 3.11 (m, 1H), 2.23 (m, 1H), 2.07-2.16 (m, 2H), 1.87-2.03 (m, 9H), 1.85 (s, 2H), 1.67-1.77 (m, 2H), 1.43-1.58 (m, 7H); MS (ESI) m/z 476 (MH); HRMS Calcd. for $\text{C}_{24}\text{H}_{39}\text{N}_6\text{O}_4$: 475.3033. Found: 475.3033 $[\text{M}+\text{H}]^+$.

(48). (24.0 mg, 78%) ^1H NMR (500 MHz, CD_3OD) δ 8.78 (br. s, 1H), 8.71 (d, $J = 4.7$ Hz, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 7.89 (m, 1H), 4.66 (s, 2H), 4.47 (br. s, 1H), 4.34-4.41 (m, 2H), 3.45 (m, 2H), 3.28 (m, 1H), 3.12 (m, 1H), 2.13 (m, 1H), 1.87 (m, 1H), 1.36-1.46 (m, 6H), 1.33 (m, 1H); MS (ESI) m/z 432 (MH); HRMS Calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_7\text{O}_4$: 432.2359. Found: 432.2368 $[\text{M}+\text{H}]^+$.

(49). (14.9 mg, 49%) ^1H NMR (500 MHz, CD_3OD) δ 8.72 (d, $J = 6.3$ Hz, 2H), 7.90 (d, $J = 6.0$ Hz, 2H), 4.74 (s, 2H), 4.52 (s, 1H), 4.32-4.40 (m, 2H), 3.45-3.60 (m, 2H), 3.33 (m, 1H), 3.06 (m, 1H), 2.15 (m, 1H), 1.86 (m, 1H), 1.34-1.43 (m, 7H); MS (ESI) m/z 434 (MH); HRMS Calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_7\text{O}_4$: 432.2359. Found: 432.2357 $[\text{M}+\text{H}]^+$.

(50). (8.5 mg, 34%) ^1H NMR (500 MHz, CD_3OD) δ 5.89 (m, 1H), 5.31 (d, $J = 16.1$ Hz, 1H), 5.23 (d, $J = 10.4$ Hz, 1H), 4.60 (br. s, 1H), 4.36-4.42 (m, 2H), 3.87 (d, $J = 5.0$ Hz, 2H), 3.49-3.60 (m, 2H), 3.37 (m, 1H), 2.93 (m, 1H), 2.19 (m, 1H), 1.84 (m, 1H), 1.38-

1.46 (m, 7H); MS (ESI) m/z 381 (MH); HRMS Calcd. for $C_{17}H_{29}N_6O_4$: 381.2250. Found: 381.2246 [M+H]⁺.

(51). (17.9 mg, 68%) ¹H NMR (500 MHz, CD₃OD) δ 7.27-7.40 (m, 5H), 4.59 (br. s, 1H), 4.44 (s, 2H), 4.35-4.43 (m, 2H), 4.46-4.60 (m, 2H), 3.34 (m, 1H), 2.97 (m, 1H), 2.16 (m, 1H), 1.82 (m, 1H), 1.36-1.50 (m, 7H); MS (ESI) m/z 431 (MH); HRMS Calcd. for $C_{21}H_{31}N_6O_4$: 431.2407. Found: 431.2421 [M+H]⁺.

(52). (21.8 mg, 80%) ¹H NMR (500 MHz, CD₃OD) δ 7.38 (m, 1H), 7.26 (m, 1H), 7.15 (m, 1H), 7.03 (m, 1H), 4.61 (br. s, 1H), 4.35-4.44 (m, 2H), 3.88 (s, 3H), 3.50-3.63 (m, 2H), 3.40 (m, 1H), 3.11 (m, 1H), 2.20 (m, 1H), 1.90 (m, 1H), 1.39-1.52 (m, 7H); MS (ESI) m/z 447 (MH); HRMS Calcd. for $C_{21}H_{31}N_6O_5$: 447.2356. Found: 447.2350 [M+H]⁺.

(53). (13.8 mg, 53%) ¹H NMR (500 MHz, CD₃OD) δ 7.33 (d, J = 5.6 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 4.59 (br. s, 1H), 4.32-4.40 (m, 2H), 3.49-3.59 (m, 2H), 3.40 (m, 1H), 3.00 (3, 1H), 2.33 (s, 3H), 2.19 (m, 1H), 1.86 (m, 1H), 1.33-1.48 (m, 7H); MS (ESI) m/z 432 (MH); HRMS Calcd. for $C_{21}H_{31}N_6O_4$: 431.2407. Found: 431.2407 [M+H]⁺.

(54). (18.3 mg, 69%) ¹H NMR (500 MHz, CD₃OD) δ 7.39 (dd, apparent t, J = 6.9 Hz, 1H), 7.26 (d, J = 6.3 Hz, 1H), 7.15 (m, 1H), 7.03 (dd, apparent t, J = 7.7 Hz, 1H), 4.58 (t, J = 6.7 Hz, 1H), 4.32-4.42 (m, 2H), 3.89 (s, 3H), 3.60 (m, 1H), 3.40-3.50 (m, 2H), 3.28 (m, 1H), 2.73 (m, 1H), 2.31-2.43 (m, 2H), 1.38-1.49 (m, 6H); MS (ESI) m/z 435 (MH); HRMS Calcd. for $C_{20}H_{31}N_6O_5$: 435.2356. Found: 435.2350 [M+H]⁺.

(55). (16.1 mg, 65%) ¹H NMR (500 MHz, CD₃OD) δ 4.57 (t, J = 7.0 Hz, 1H), 4.32-4.50 (m, 2H), 4.03 (s, 2H), 3.57 (m, 1H), 3.37-4.42 (m, 2H), 3.28 (m, 1H), 2.70 (m, 1H), 2.31-2.38 (m, 2H), 1.38-1.47 (m, 6H); MS (ESI) m/z 387 (MH); HRMS Calcd. for $C_{15}H_{27}N_6O_6$: 387.1992. Found: 387.1980 [M+H]⁺.

(56). (16.3 mg, 65%) ¹H NMR (500 MHz, CD₃OD) δ 4.70 (t, J = 8.2 Hz, 1H), 4.31-4.45 (m, 3H), 3.55 (m, 1H), 3.39 (m, 1H), 3.14 (t, J = 5.9 Hz, 1H), 2.57 (m, 1H), 2.33 (m, 1H), 1.88-1.97 (m, 2H), 1.73-1.85 (m, 3H), 1.60-1.72 (m, 2H), 1.28-1.48 (m, 8H), 1.22 (m, 1H); MS (ESI) m/z 398 (MH); HRMS Calcd. for $C_{18}H_{33}N_6O_4$: 397.2563. Found: 397.2558 [M+H]⁺.

(57). (22.3 mg, 73%) ¹H NMR (500 MHz, CD₃OD) δ 8.66 (br. s, 1H), 8.58 (br. s, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.61 (m, 1H), 4.68 (t, J = 7.8 Hz, 1H), 4.59 (s, 2H), 4.31-4.46 (m, 3H), 3.63 (m, 1H), 3.51 (m, 1H), 2.56 (m, 1H), 2.45 (m, 1H), 1.35-1.46 (m, 6H); MS (ESI) m/z 407 (MH); HRMS Calcd. for $C_{18}H_{28}N_7O_4$: 406.2203. Found: 406.2200 [M+H]⁺.

(58). (15.1 mg, 61%) ^1H NMR (500 MHz, CD_3OD) δ 4.39 (q, $J = 7.2$ Hz, 1H), 4.32 (q, $J = 7.8$ Hz, 1H), 3.99 (d, $J = 7.8$ Hz, 1H), 3.47 (m, 1H), 3.28-3.39 (m, 3H), 2.50 (m, 1H), 2.36 (m, 1H), 2.25 (m, 1H), 2.07 (m, 1H), 1.74-1.84 (m, 2H), 1.43 (d, $J = 7.2$ Hz, 3H), 1.40 (d, $J = 7.3$ Hz, 3H), 0.84 (m, 2H), 0.63 (m, 2H); MS (ESI) m/z 383 (MH).

(59). (15.6 mg, 64%) ^1H NMR (500 MHz, CD_3OD) δ 5.81-5.90 (m, 1H), 5.26 (d, $J = 15.6$ Hz, 1H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.39 (q, $J = 7.2$ Hz, 1H), 4.32 (q, $J = 7.3$ Hz, 1H), 3.98 (d, $J = 7.8$ Hz, 1H), 3.84 (s, 1H), 3.47 (m, 1H), 3.34 (m, 1H), 2.35 (m, 1H), 2.25 (m, 1H), 2.10 (m, 1H), 1.79 (m, 1H), 1.41-1.46 (q, $J = 7.2$ Hz, 3H), 1.35-1.41 (q, $J = 7.3$ Hz, 3H); MS (ESI) m/z 383 (MH).

(60). (27.1 mg, 90%) ^1H NMR (500 MHz, CD_3OD) δ 8.68 (d, $J = 6.1$ Hz, 2H), 8.36 (d, $J = 7.1$ Hz, 2H), 4.69 (s, 2H), 4.40 (q, $J = 7.2$ Hz, 1H), 4.29 (q, $J = 7.3$ Hz, 1H), 3.95 (m, 1H), 3.26-3.34 (m, 2H), 1.91-2.01 (m, 2H), 1.77 (m, 1H), 1.71 (m, 1H), 1.35-1.46 (m, 6H); MS (ESI) m/z 408 (MH); HRMS Calcd. for $\text{C}_{18}\text{H}_{30}\text{N}_7\text{O}_4$: 408.2359. Found: 408.2345 $[\text{M}+\text{H}]^+$.

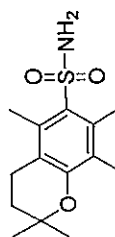
(61). (16.9 mg, 68%) ^1H NMR (500 MHz, CD_3OD) δ 7.25-7.40 (m, 5H), 4.36-4.48 (m, 3H), 4.32 (q, $J = 7.3$ Hz, 1H), 3.97 (t, $J = 6.1$ Hz, 1H), 3.26 (t, $J = 6.6$ Hz, 1H), 1.92-2.03 (m, 2H), 1.77 (m, 1H), 1.71 (m, 1H), 1.33-1.46 (m, 6H); MS (ESI) m/z 407 (MH); HRMS Calcd. for $\text{C}_{19}\text{H}_{31}\text{N}_6\text{O}_4$: 407.2407. Found: 407.2396 $[\text{M}+\text{H}]^+$.

(62). (18.3 mg, 68%) ^1H NMR (500 MHz, CD_3OD) δ 4.47 (q, $J = 7.2$ Hz, 1H), 4.41 (q, $J = 7.3$ Hz, 1H), 4.08 (m, 1H), 3.75 (s, 1H), 3.33 (t, $J = 6.6$ Hz, 2H), 1.66-2.12 (m, 18H), 1.42-1.52 (m, 6H); MS (ESI) m/z 451 (MH); HRMS Calcd. for $\text{C}_{22}\text{H}_{39}\text{N}_6\text{O}_4$: 451.3033. Found: 451.3029 $[\text{M}+\text{H}]^+$.

2-(Pmc)-amino-3,4-dihydro-oxazole (67). (0.48 g, 91%) isolated as a colorless friable foam: mp 60-63 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.70 (br. s), 4.47 (t, $J = 8.1$ Hz, 2H), 3.78 (t, $J = 8.2$ Hz, 2H), 2.63 (t, $J = 6.4$ Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H), 2.11 (s, 3H), 1.80 (t, $J = 6.6$ Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) 161.3, 154.0, 135.8, 135.4, 131.8, 124.0, 117.9, 73.6, 66.4, 42.5, 32.7, 26.6, 21.3, 18.3, 17.2, 11.9 ppm; IR (film) 3390, 1635 cm^{-1} ; MS (CI) m/z 353 (MH). Anal Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$: C, 57.93; H, 6.86; N, 7.95. Found: C, 57.75; H, 6.88; N, 7.90.

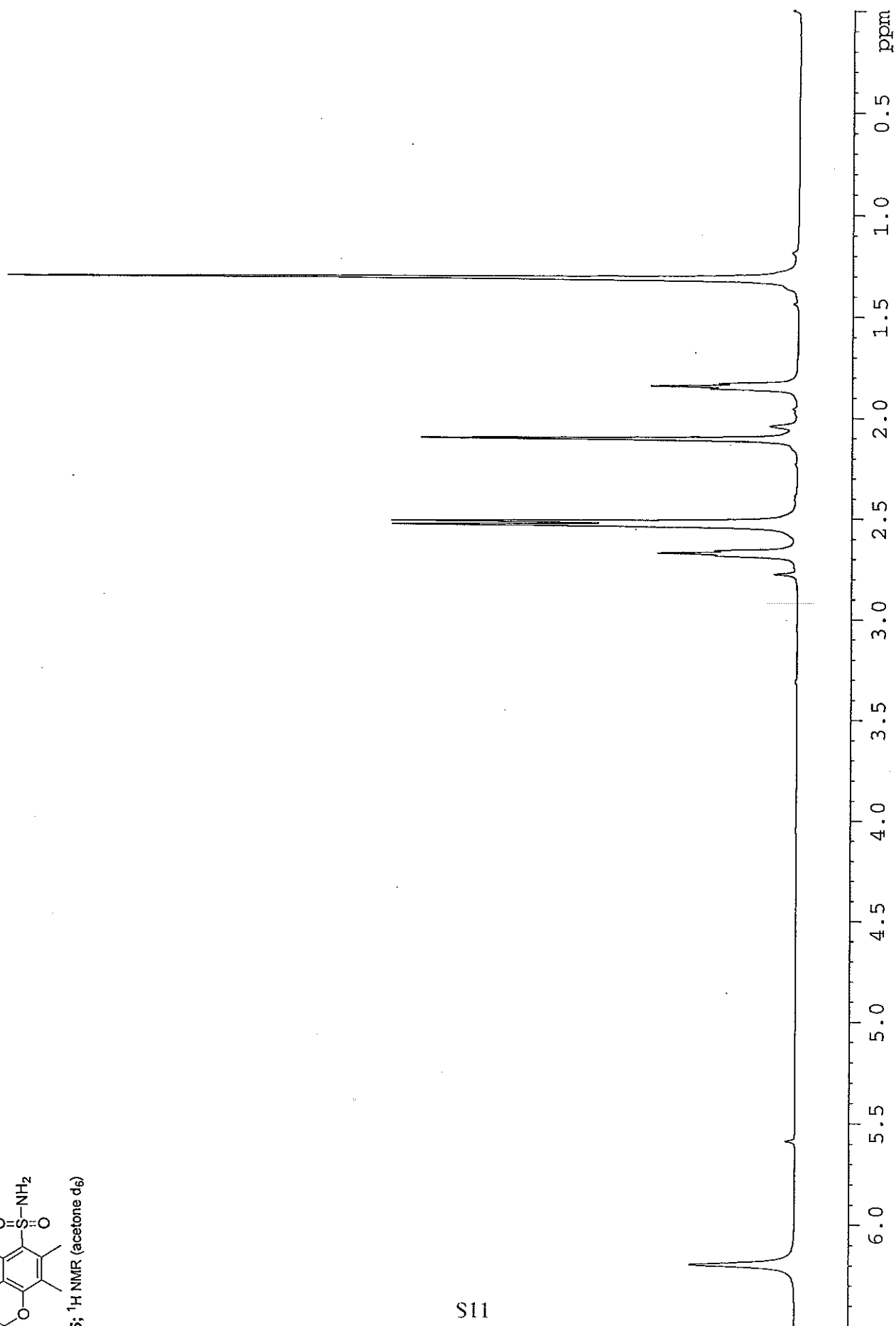
3-(Pmc)-amino-2,4-diaza-indene (68). (0.56 g, 93%) isolated as a light yellow friable foam: mp 70-73 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 9.3$ Hz, 1H), 6.80 (s, 1H), 6.54 (t, $J = 6.4$ Hz, 1H), 6.26 (t, $J = 6.6$ Hz, 1H), 2.59-2.78 (m, 8H), 2.11 (s, 3H), 1.79 (t, $J = 6.5$ Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3)

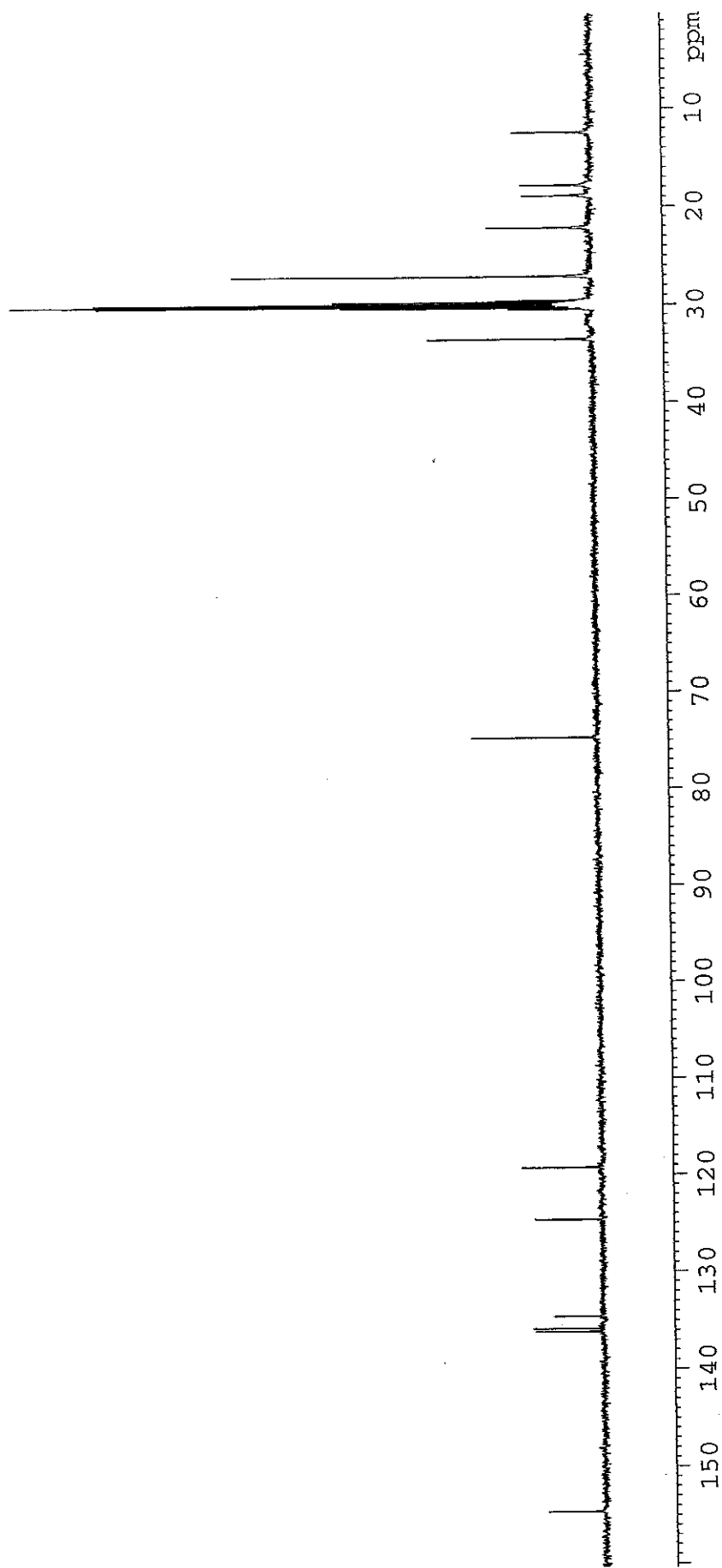
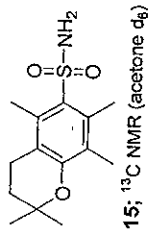
153.4, 139.9, 135.5, 134.8, 134.1, 123.9, 122.1, 121.1, 117.8, 117.5, 111.2, 100.2, 73.5, 32.8, 26.7, 21.4, 18.7, 17.6, 12.0 ppm; IR (film) 3294, 1599 cm^{-1} ; MS (CI) m/z 135 (M-Pmc).

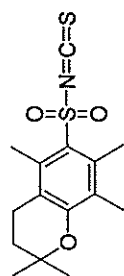


15; ^1H NMR (acetone d_6)

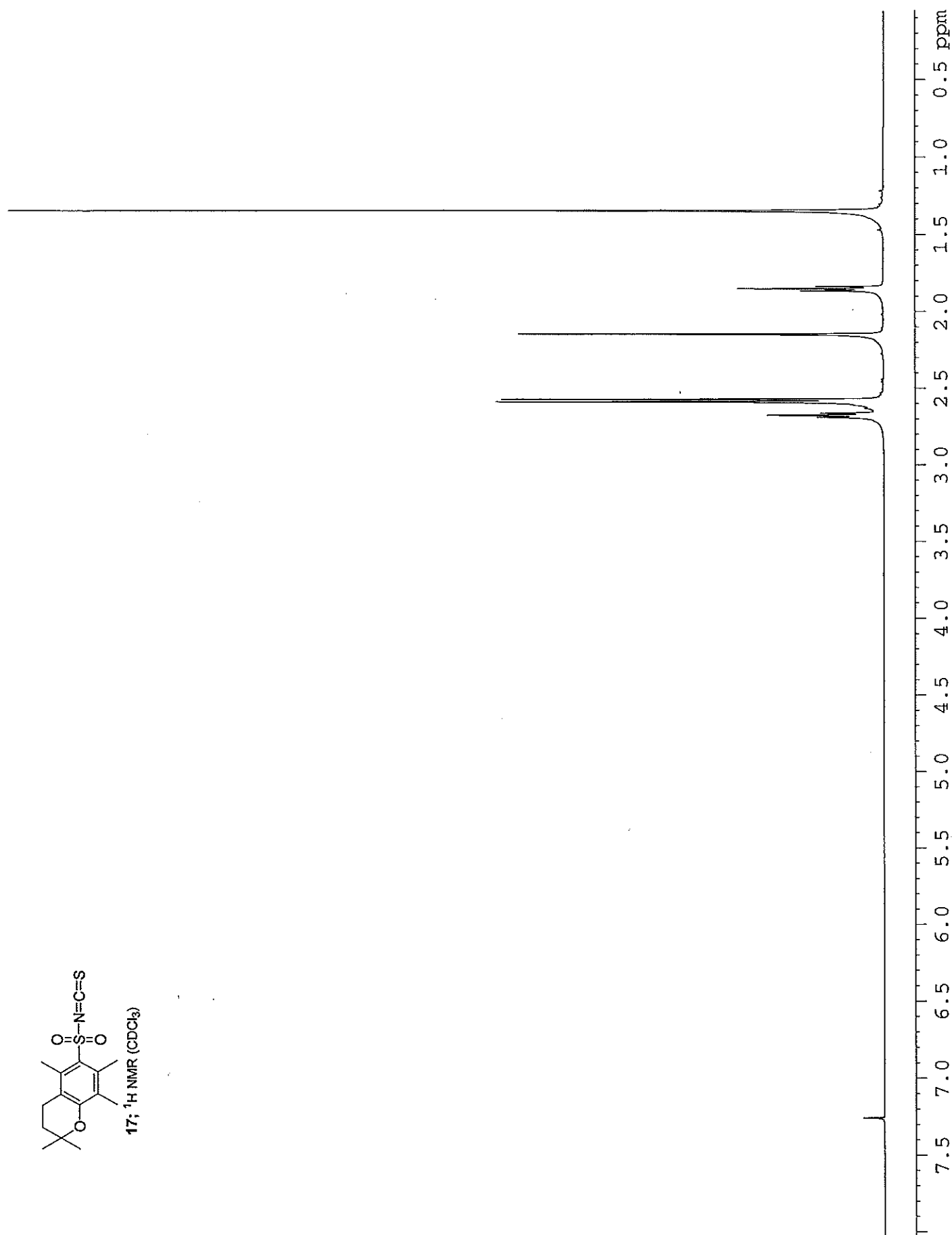
S11

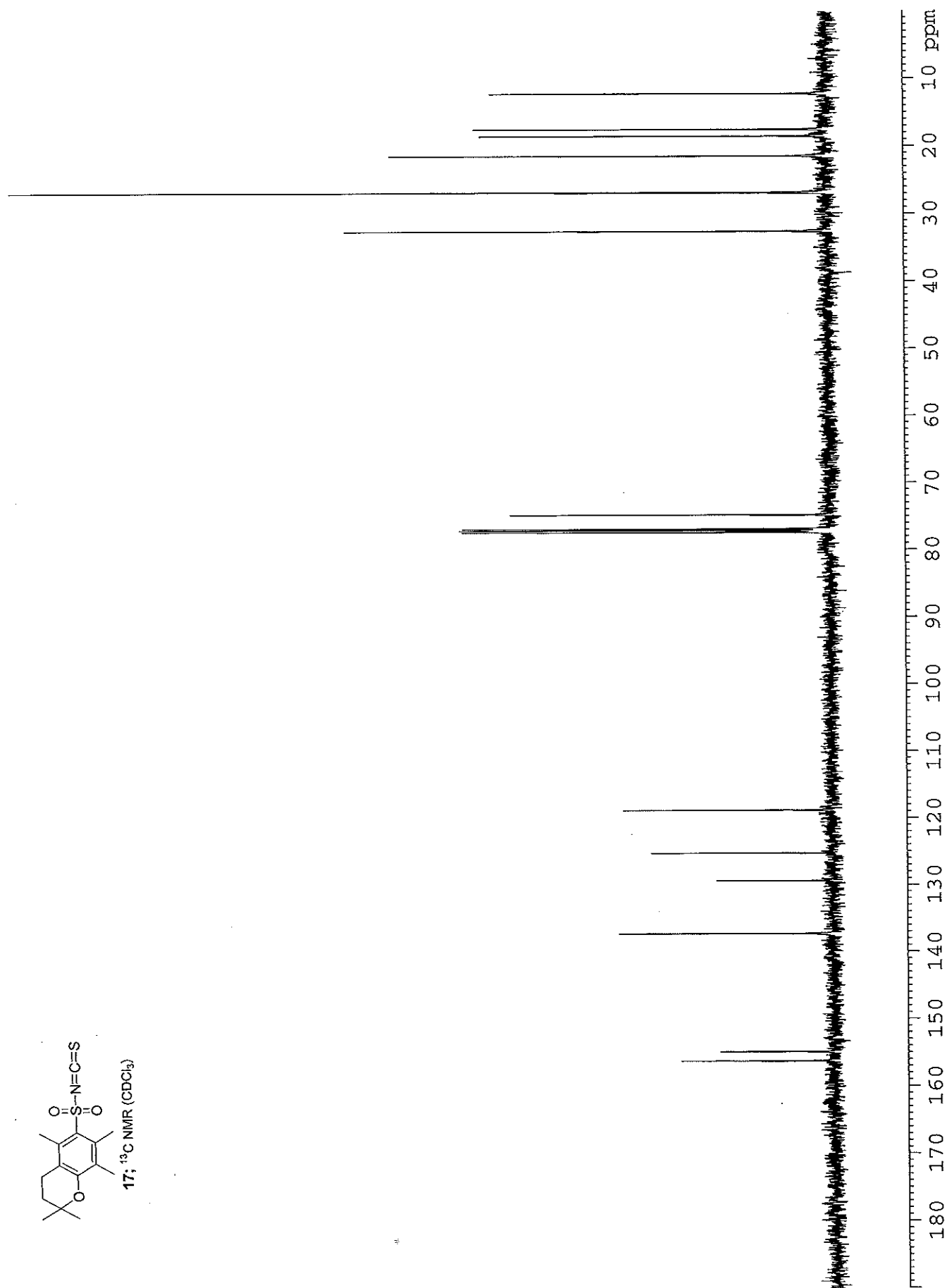
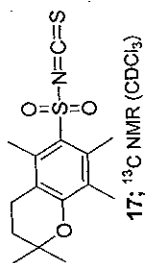


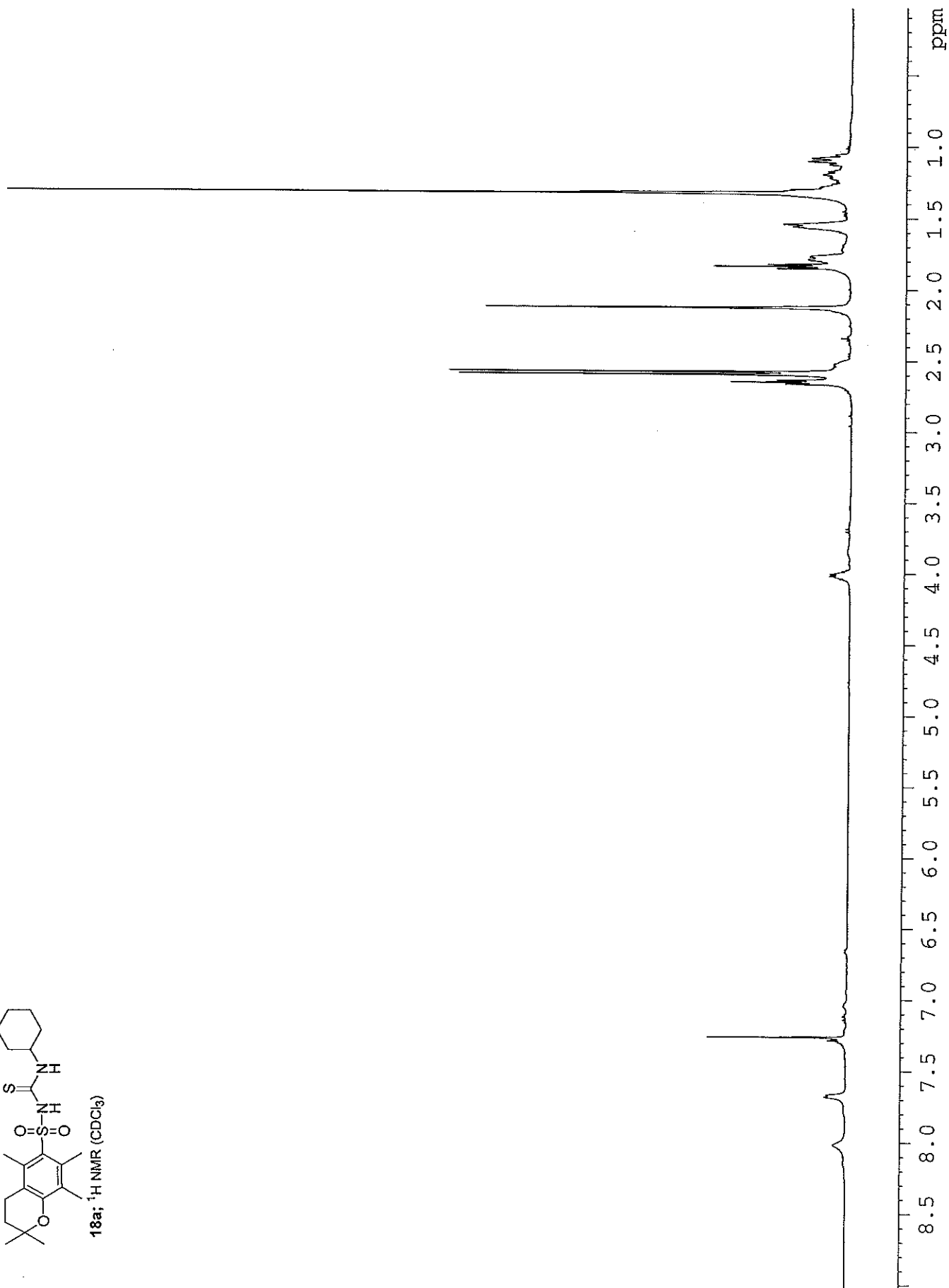
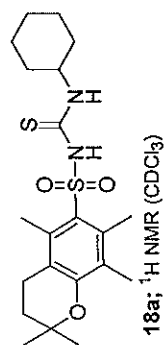


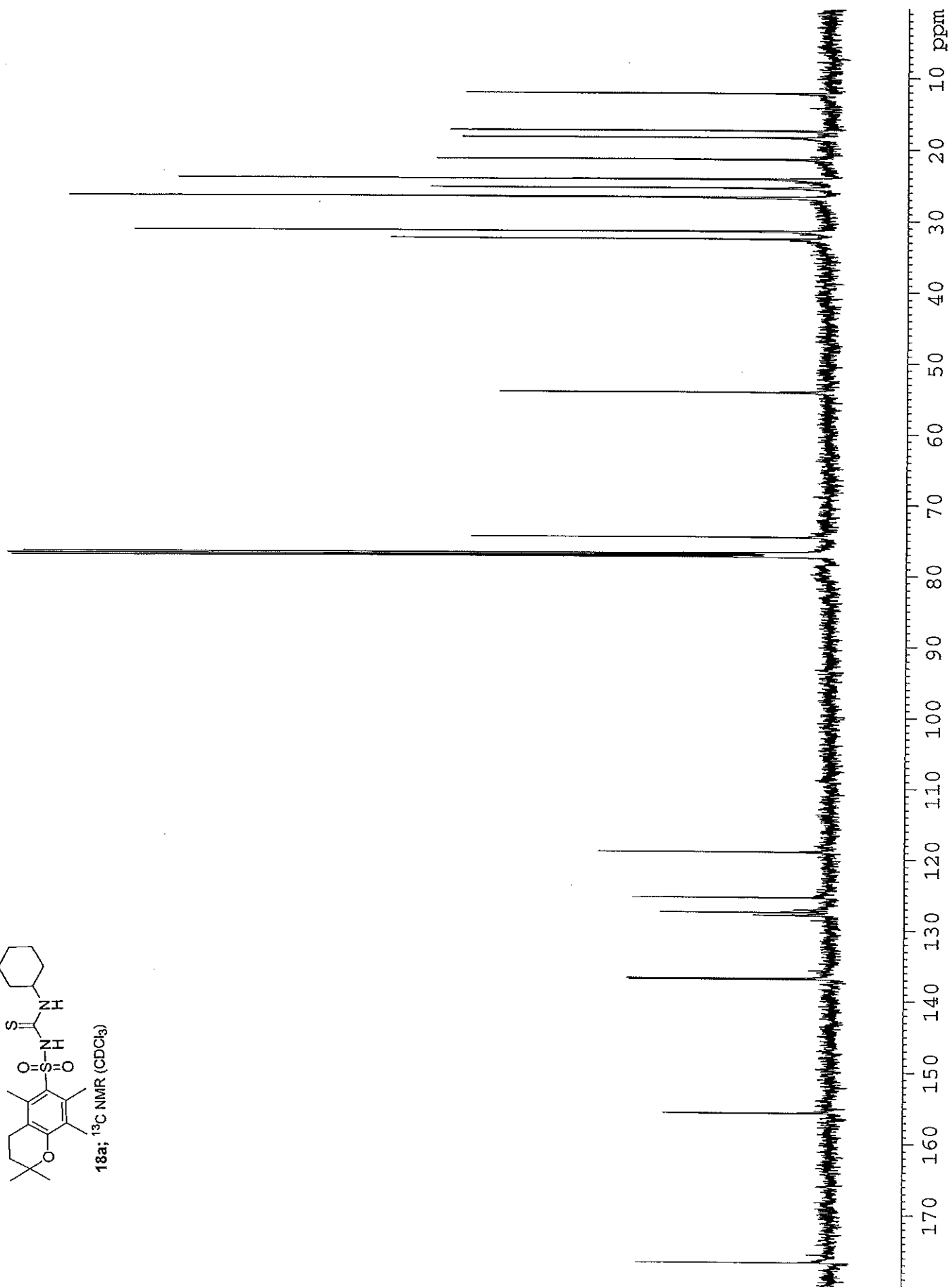
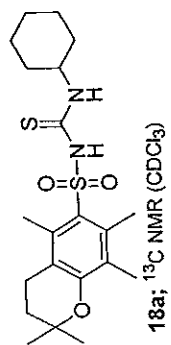


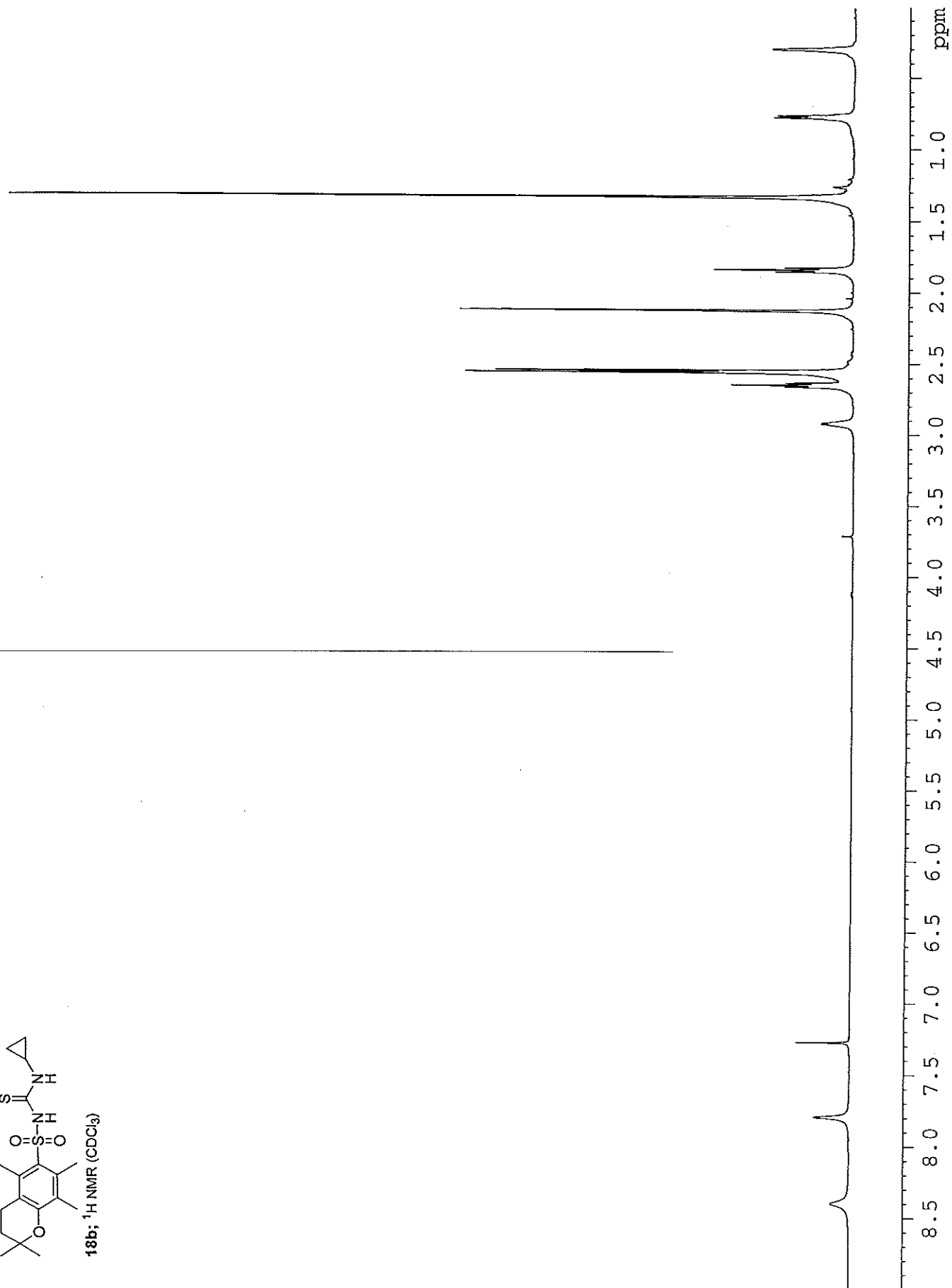
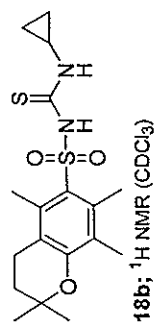
17; ^1H NMR (CDCl_3)

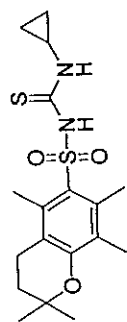




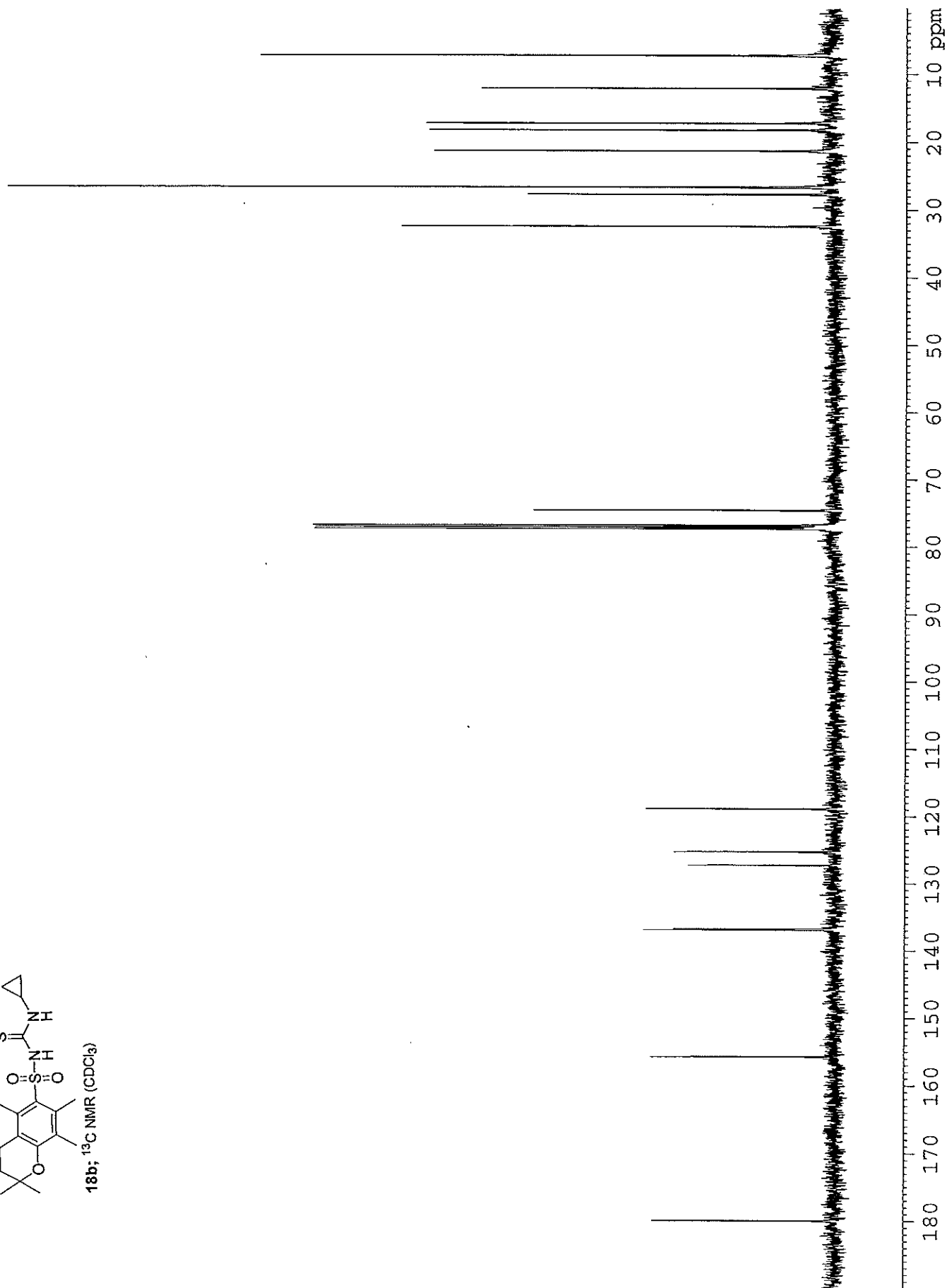


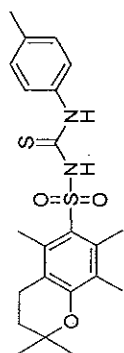




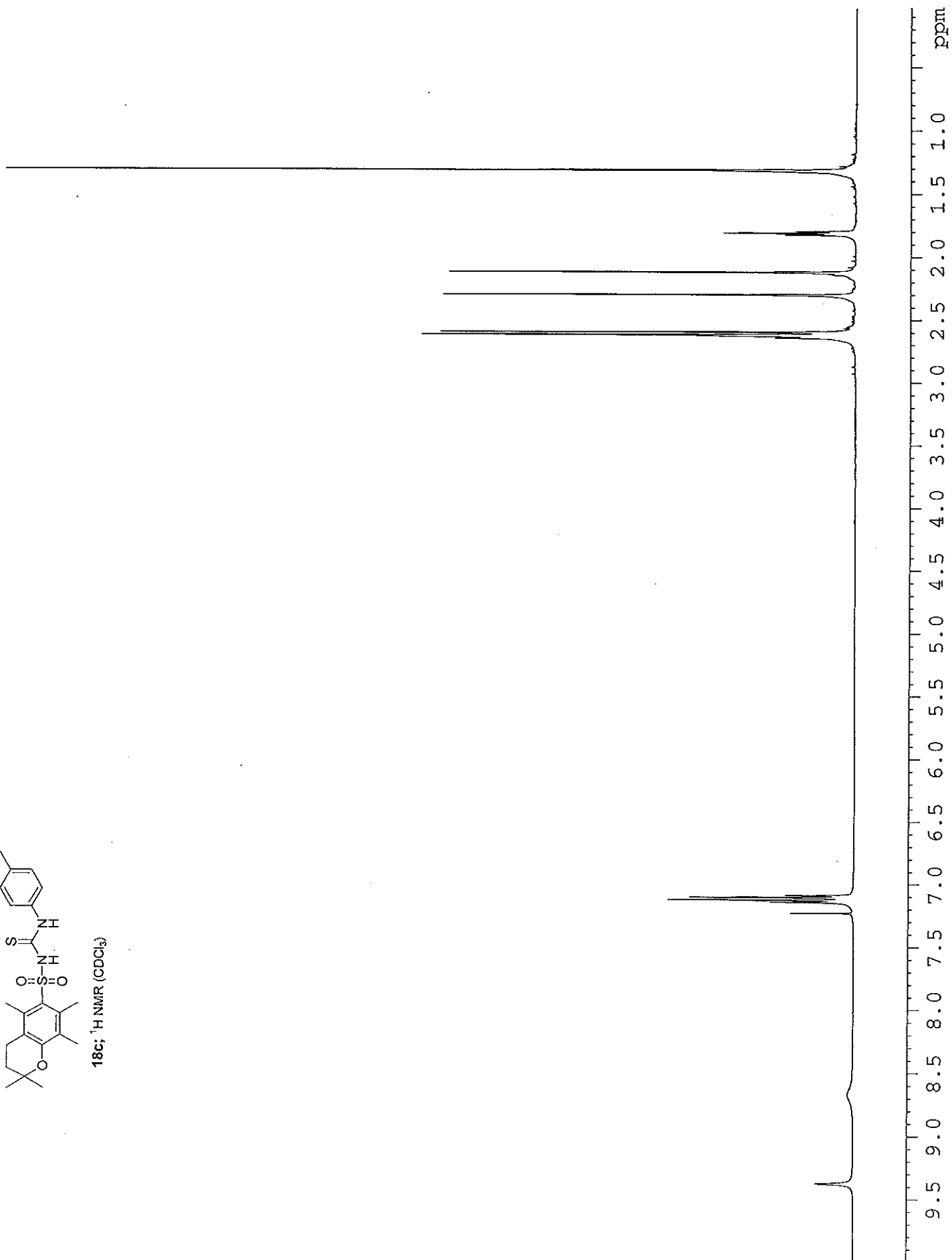


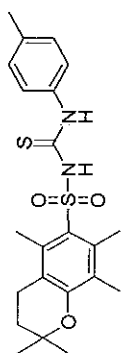
18b; ^{13}C NMR (CDCl_3)



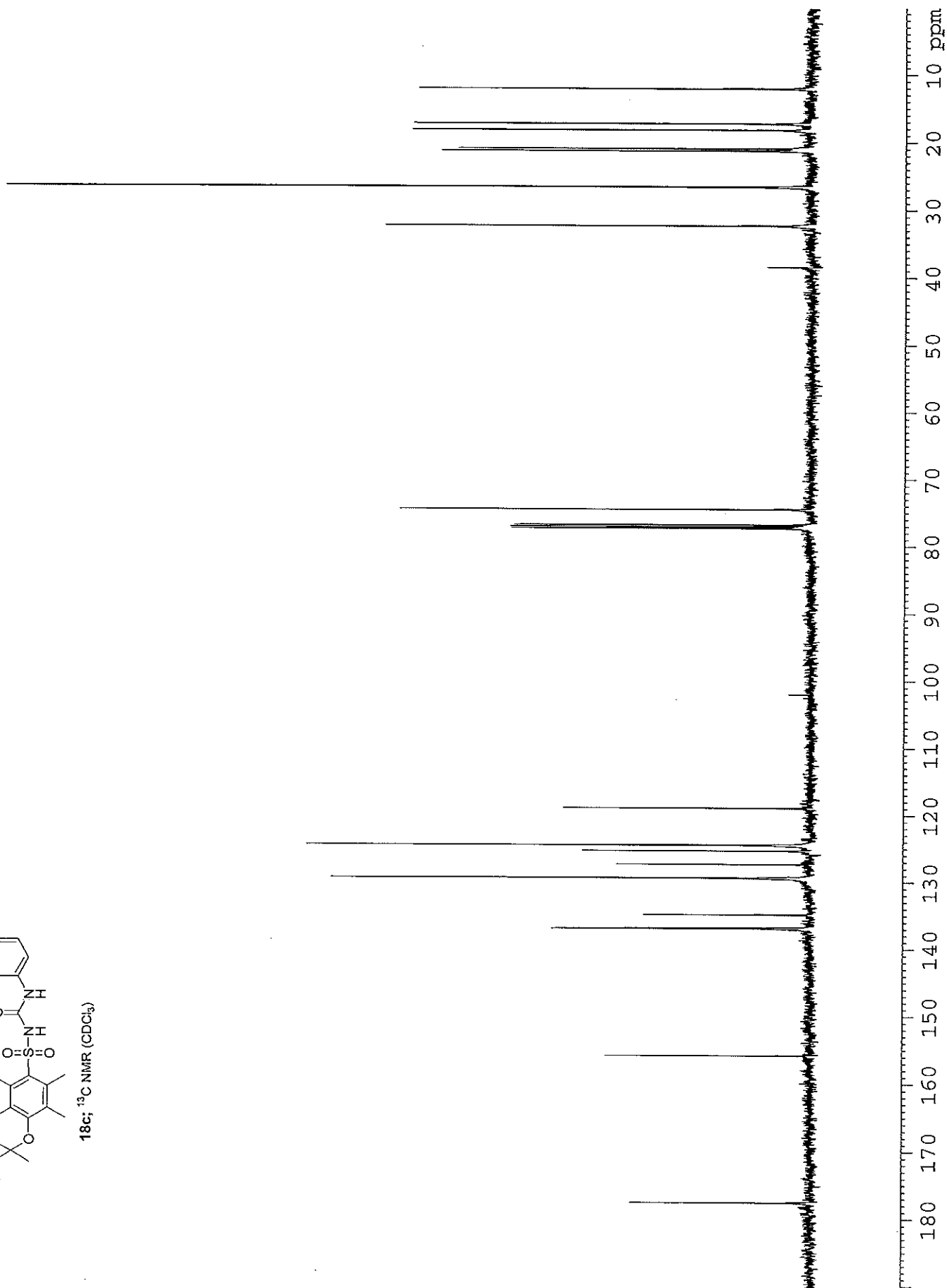


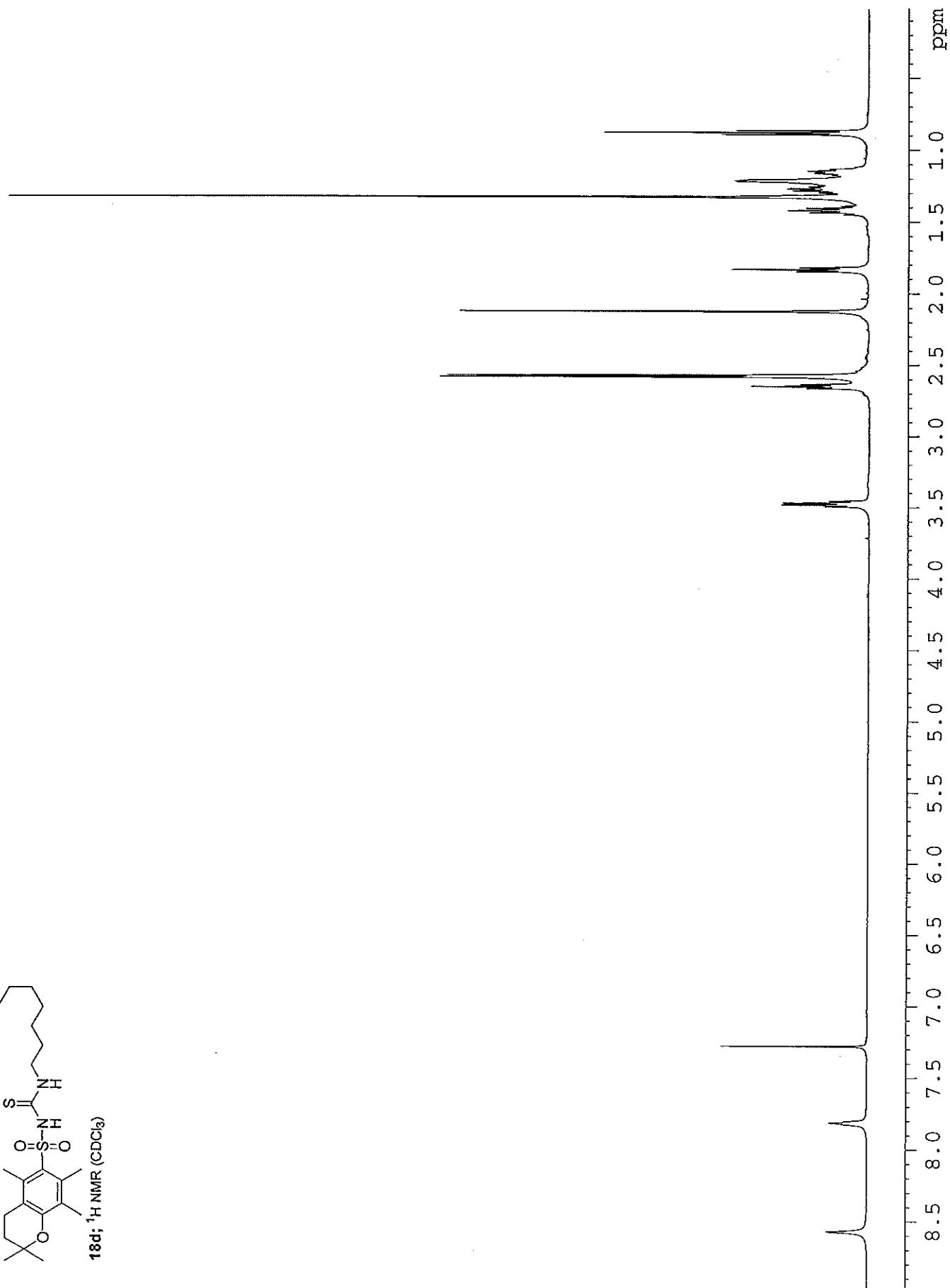
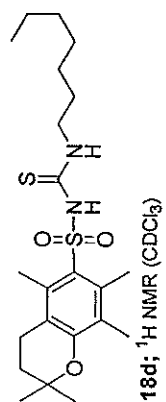
18c; ^1H NMR (CDCl_3)

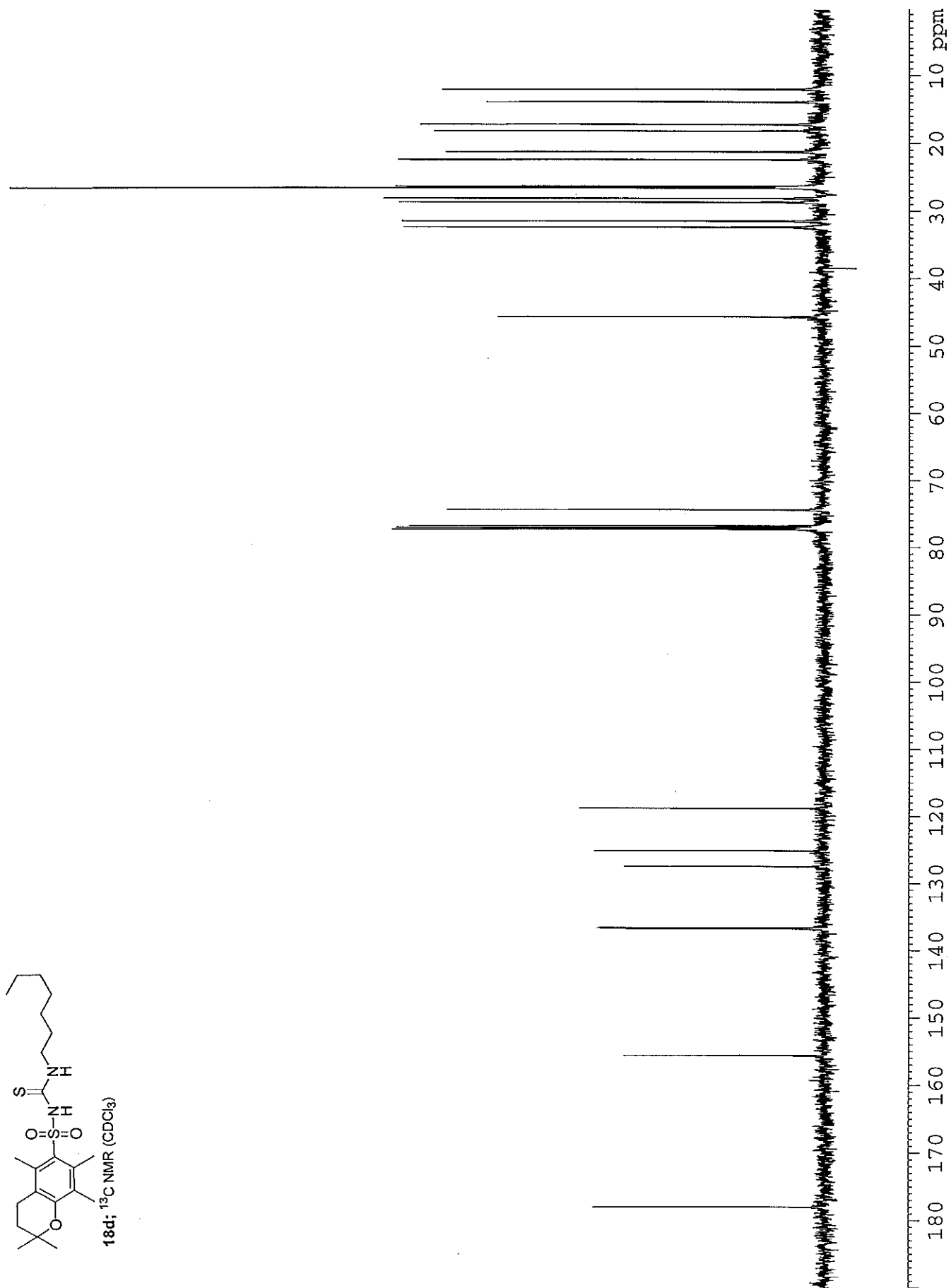
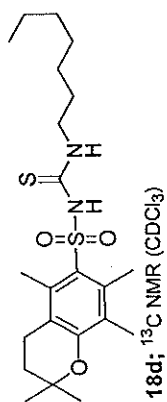


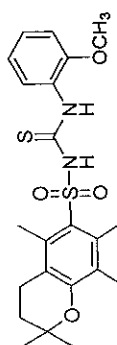


18c; ^{13}C NMR (CDCl_3)

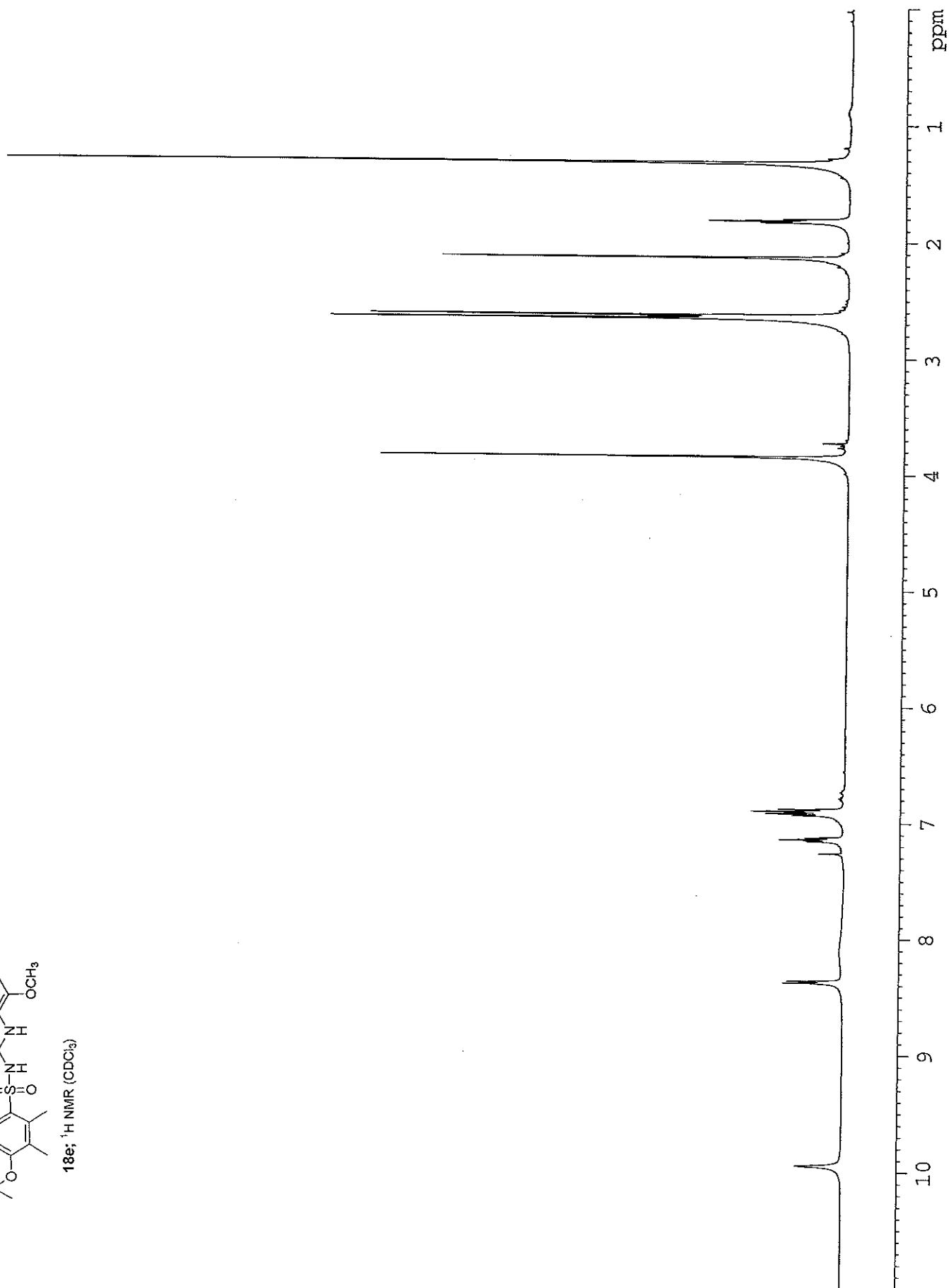


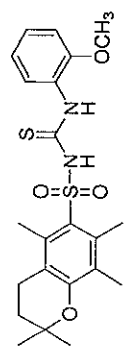




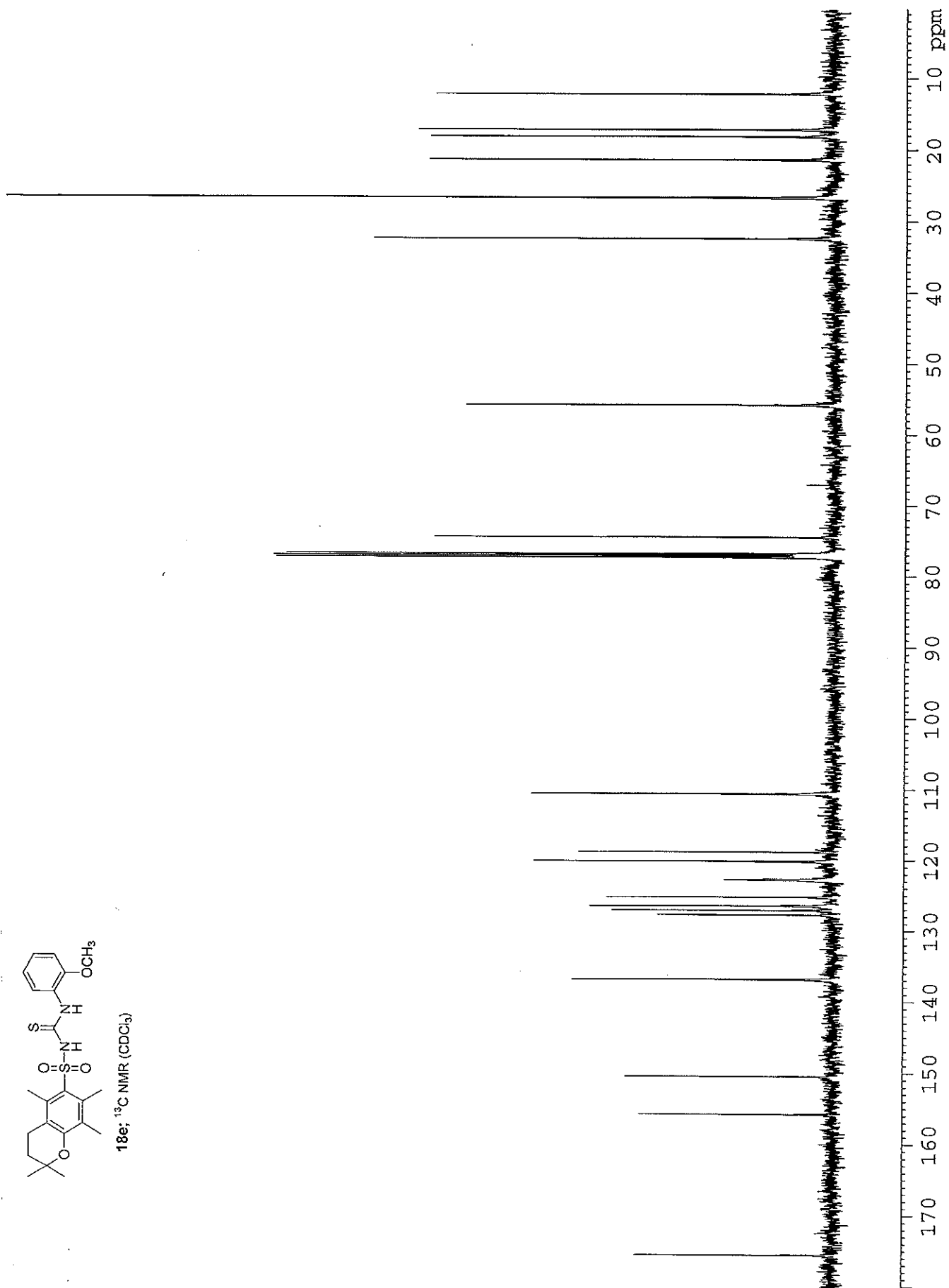


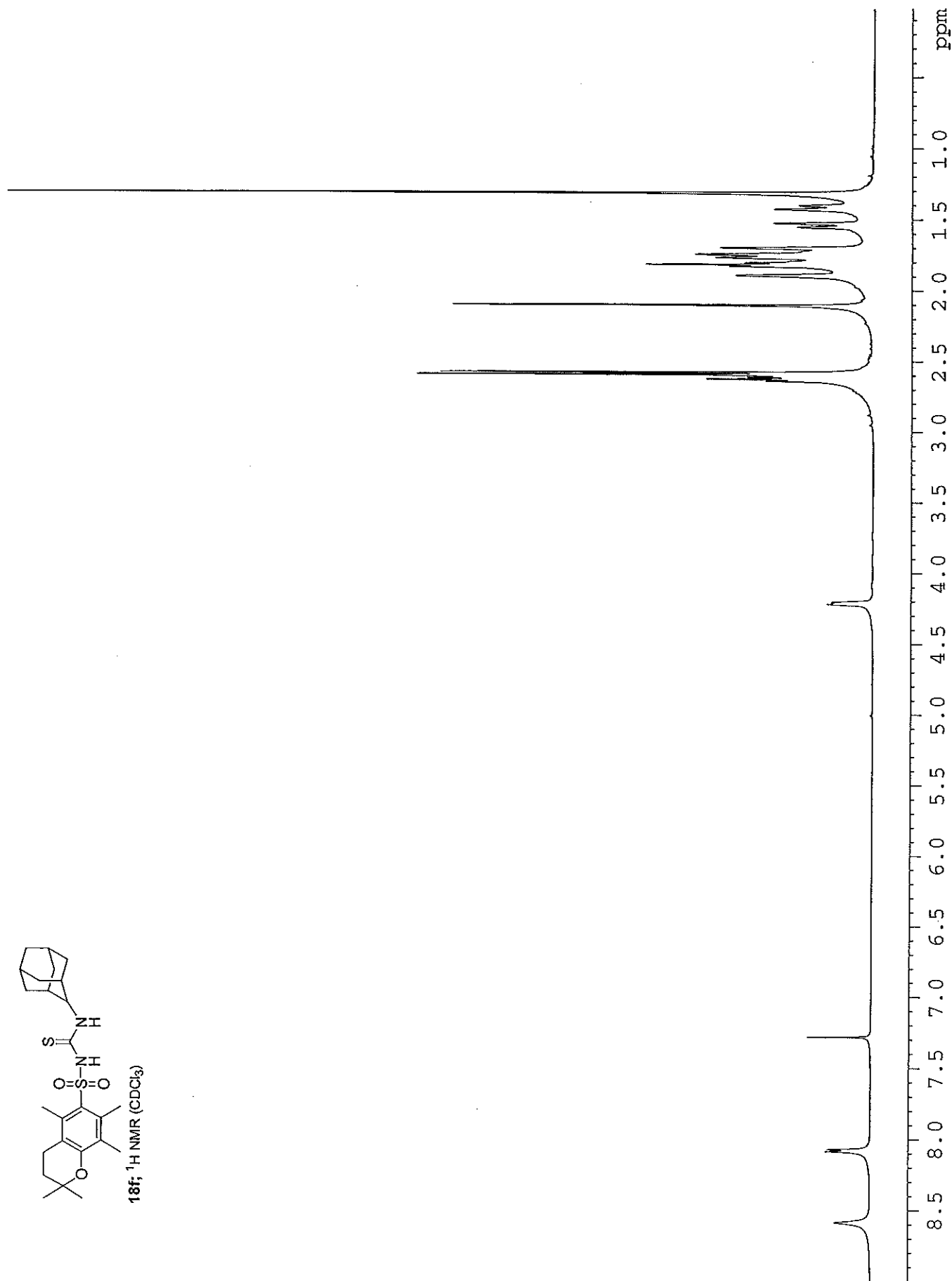
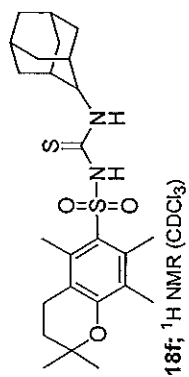
18e; ^1H NMR (CDCl_3)

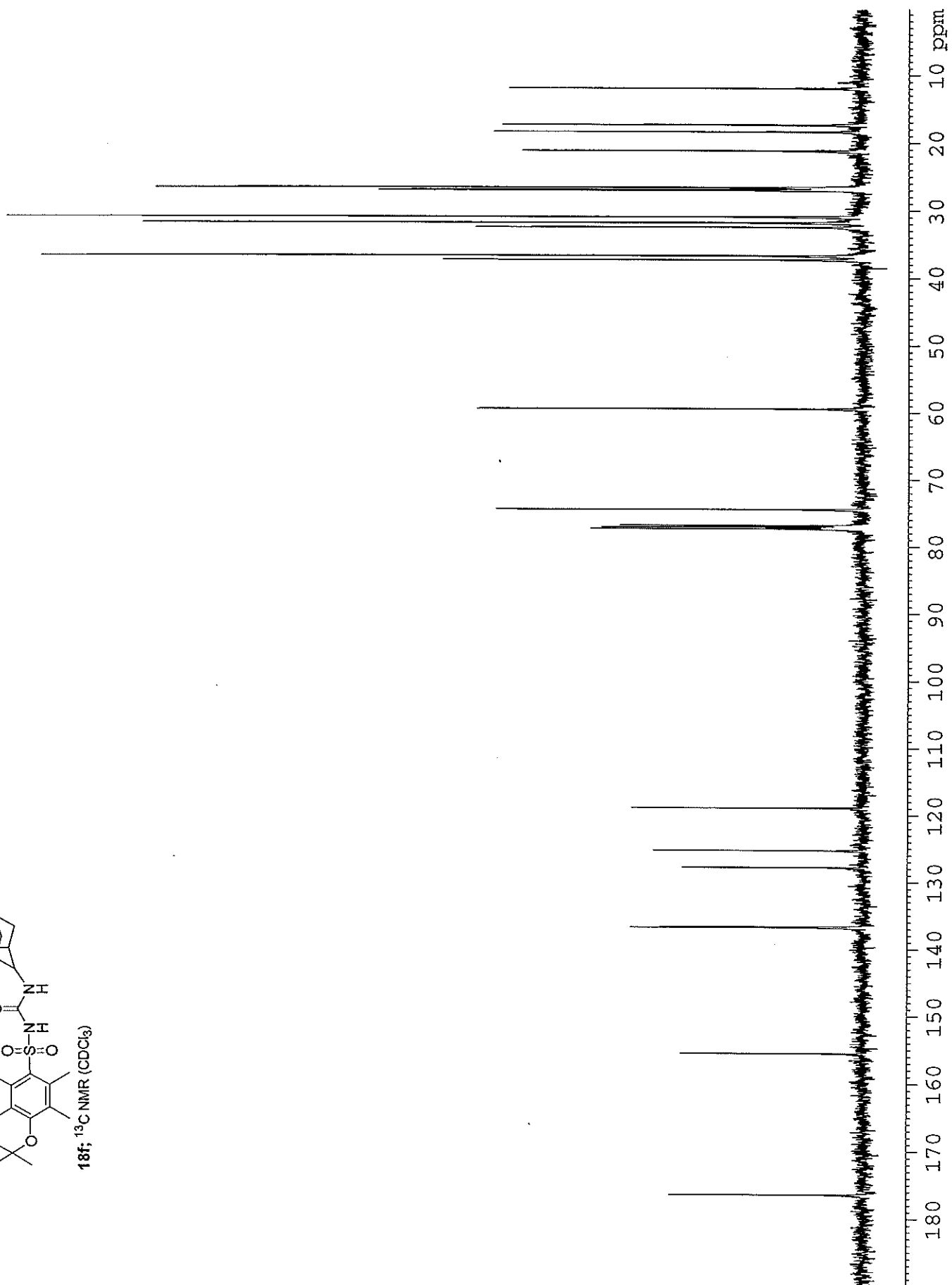
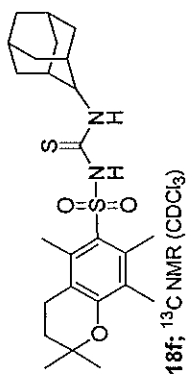


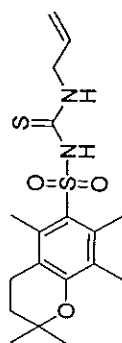


18e; ^{13}C NMR (CDCl_3)

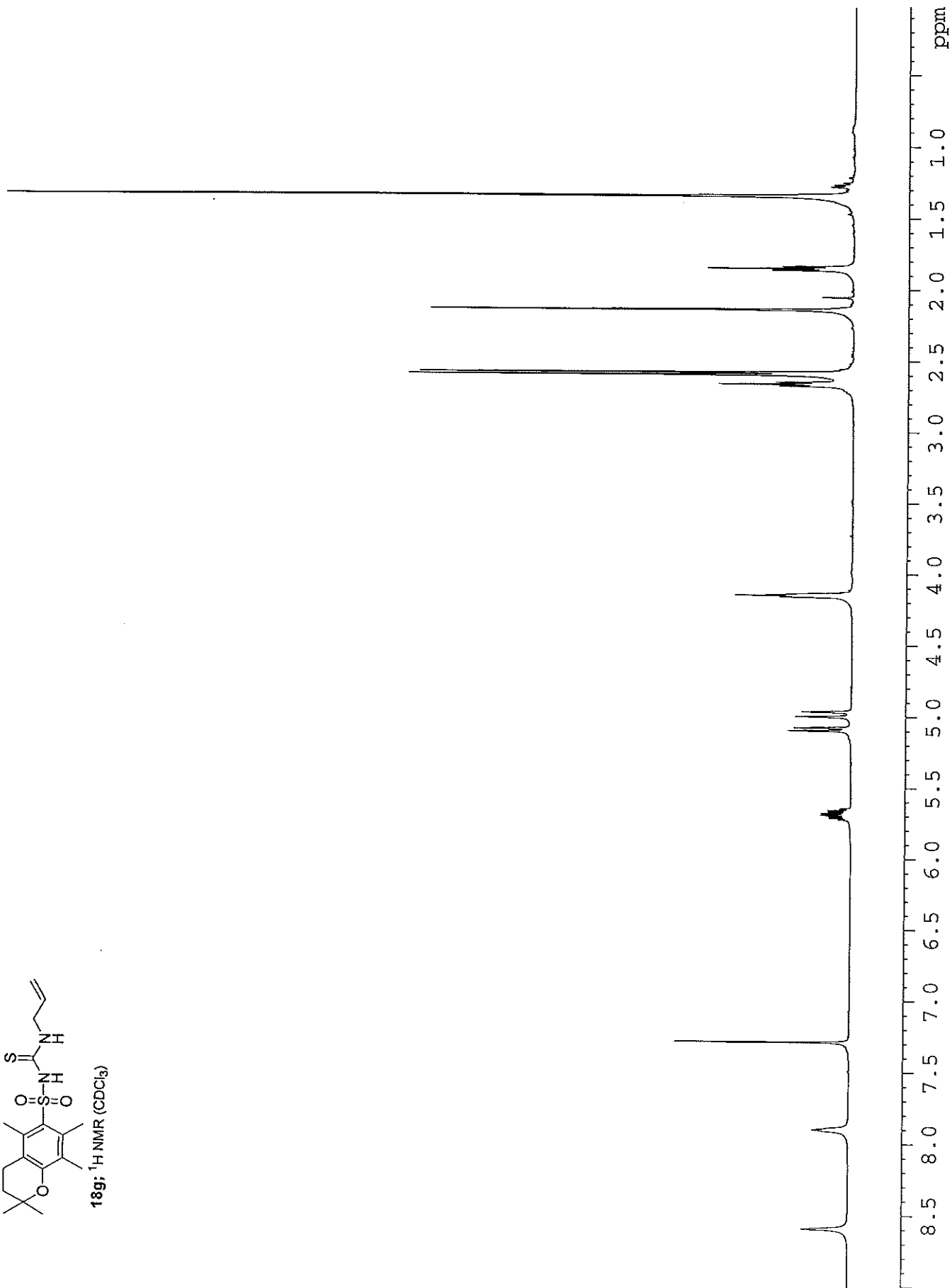


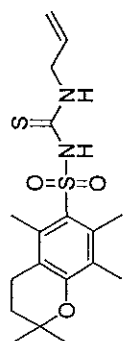




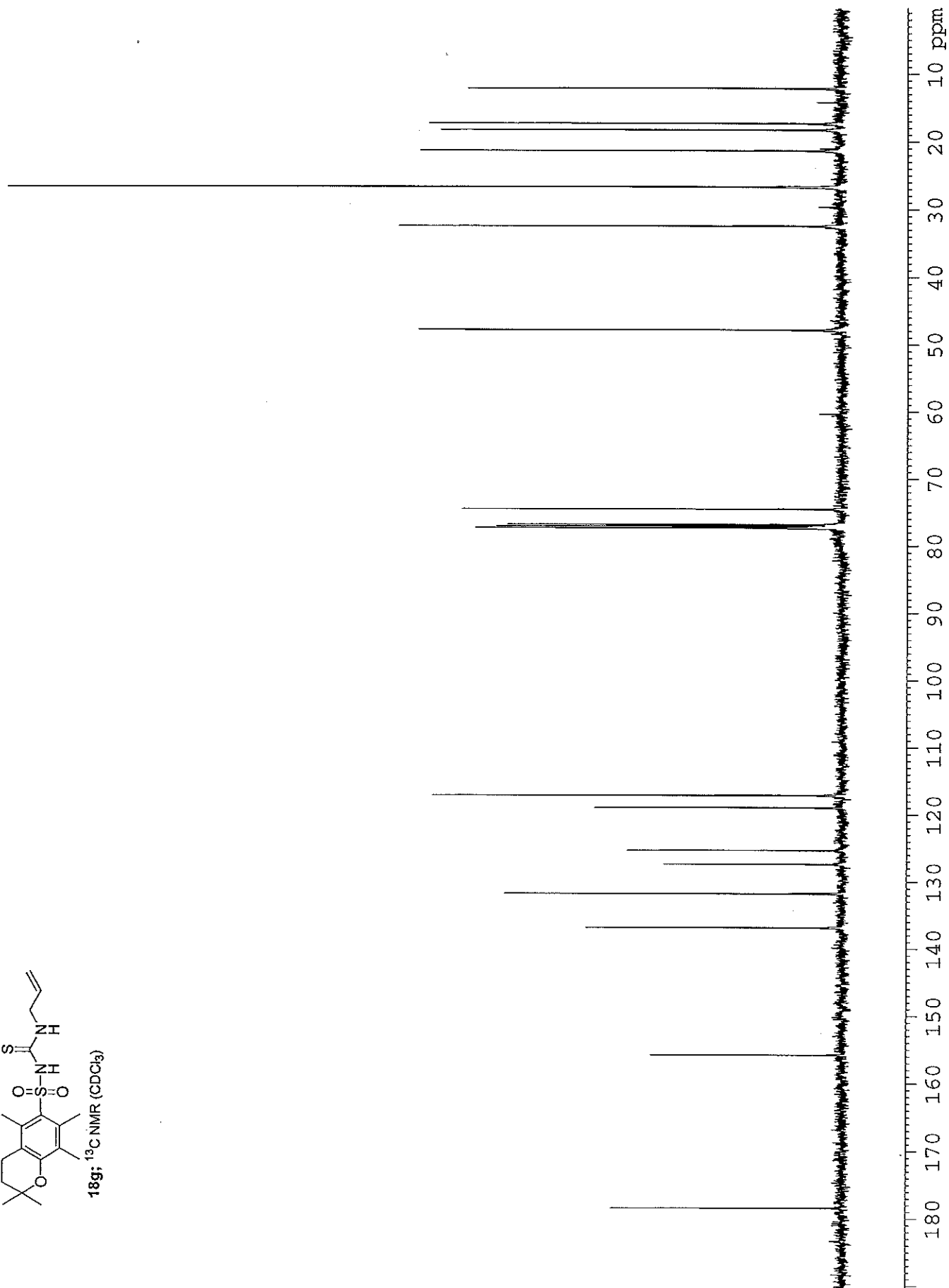


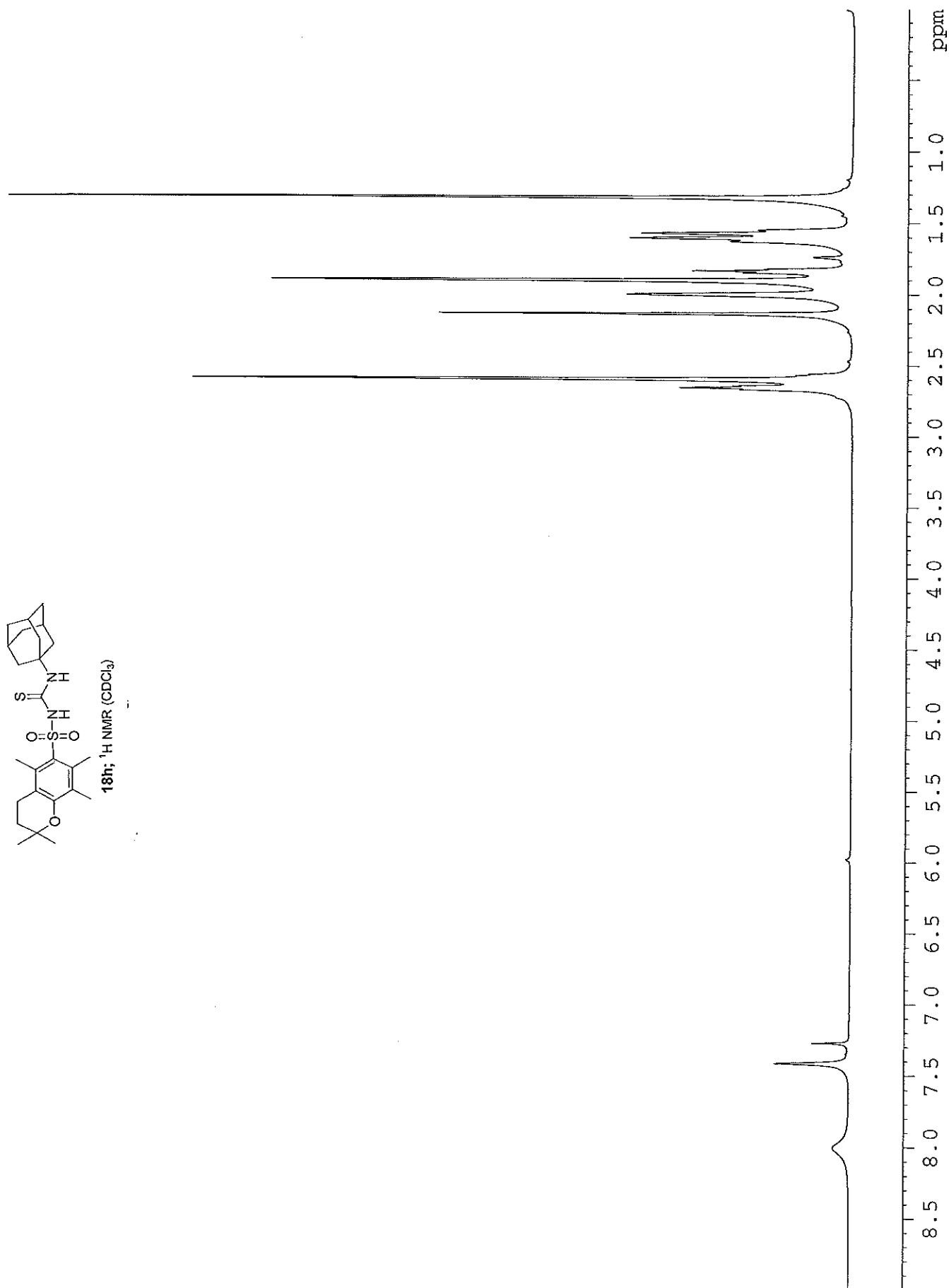
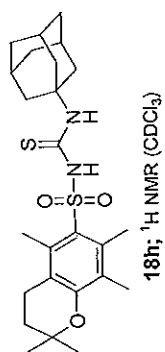
18g; ^1H NMR (CDCl_3)

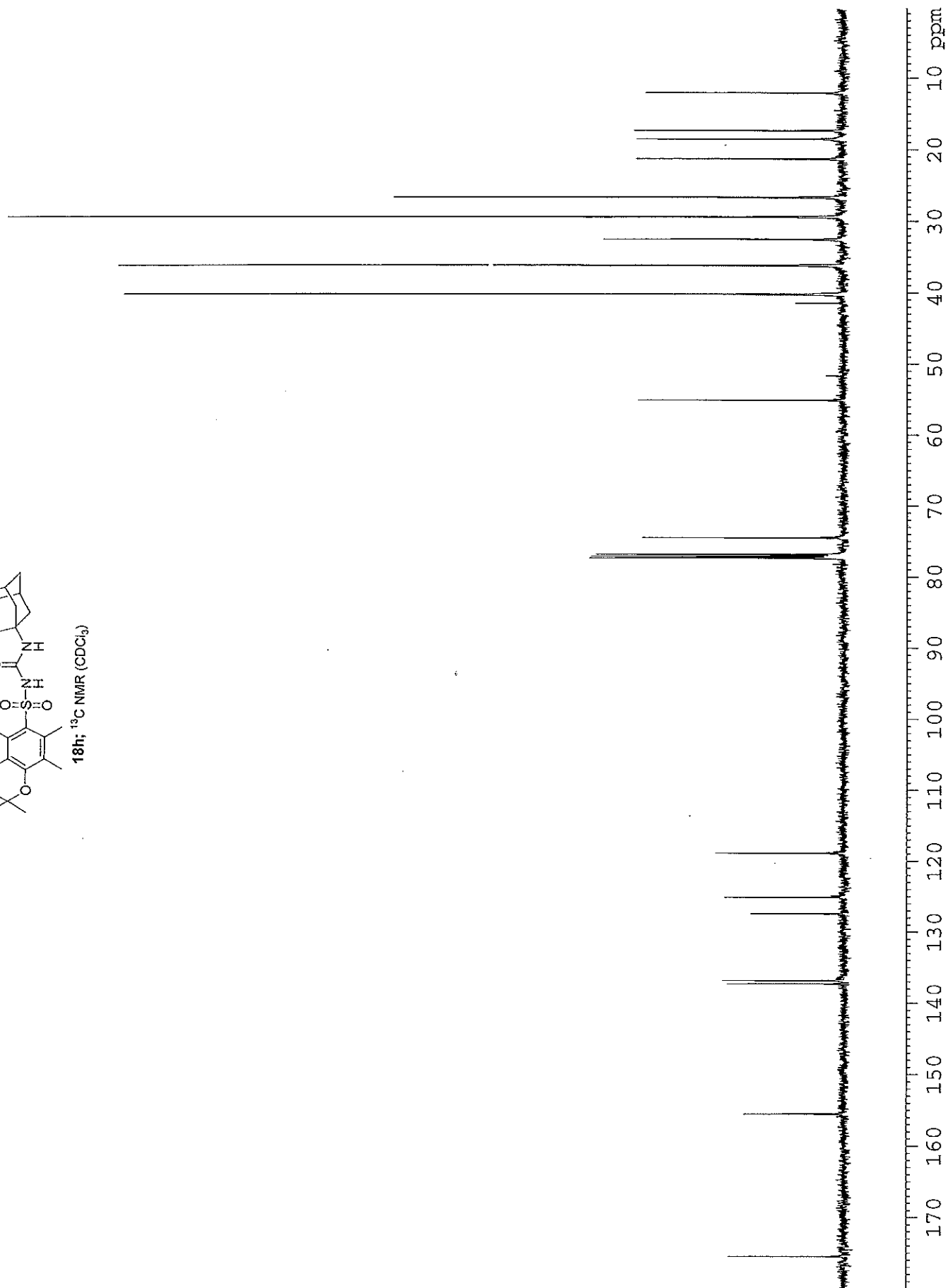
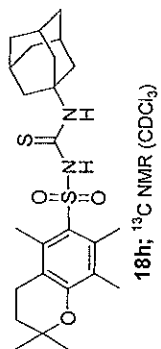


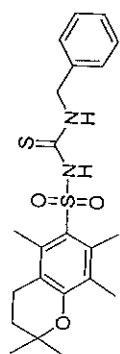


18g; ^{13}C NMR (CDCl_3)

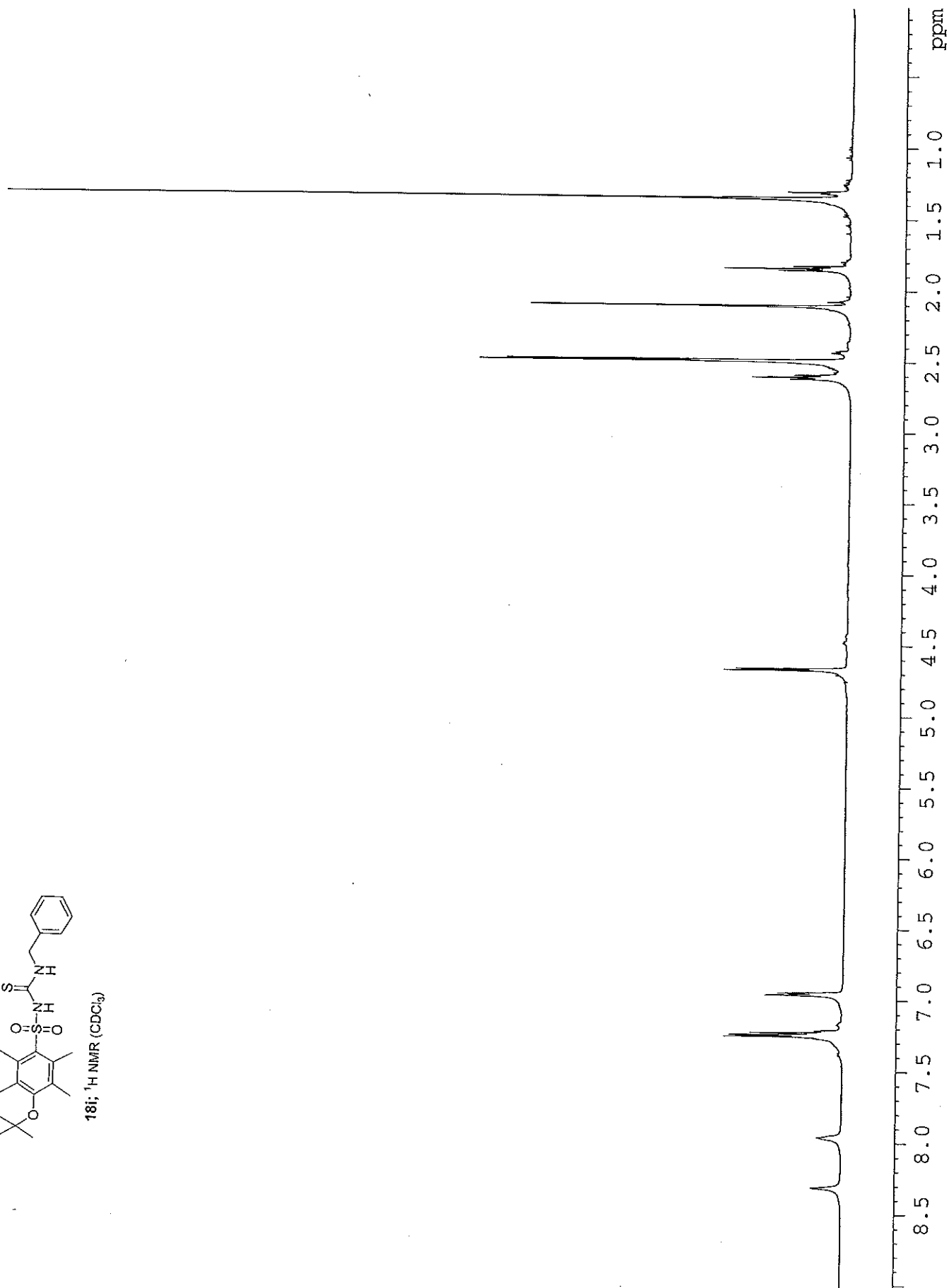


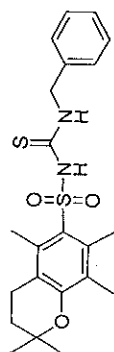




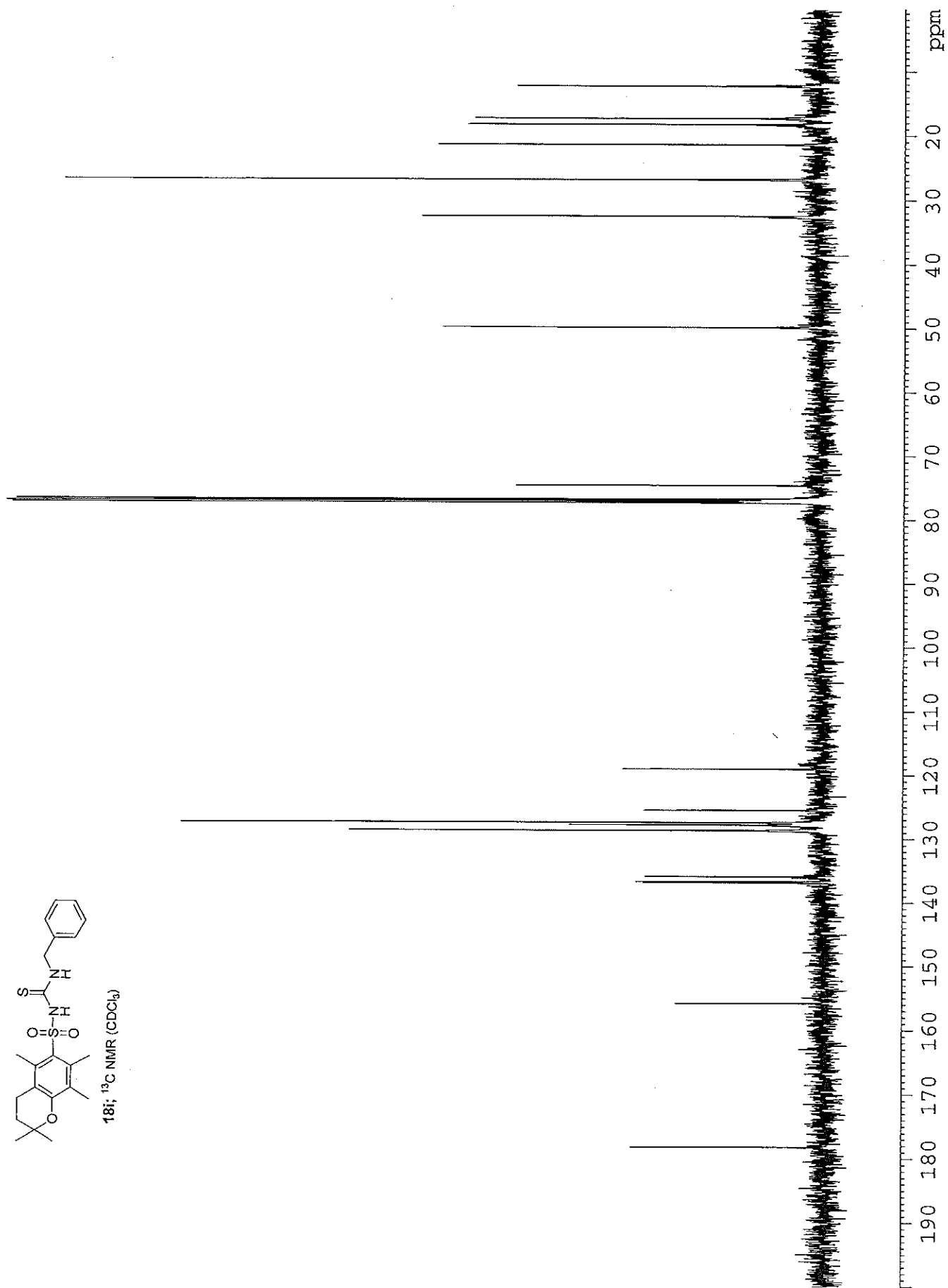


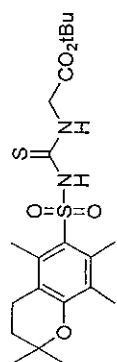
18i; ^1H NMR (CDCl_3)



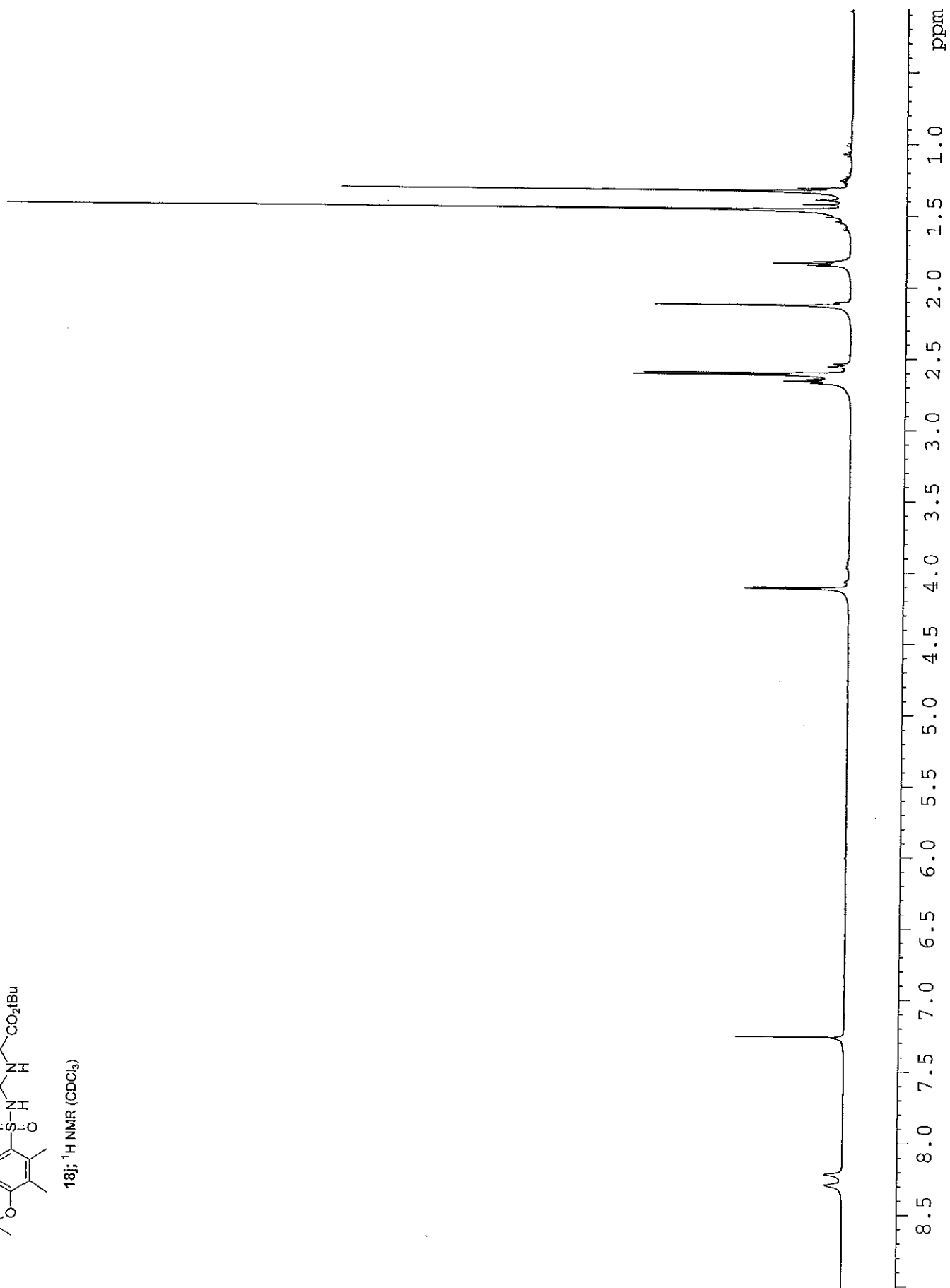


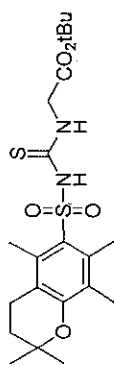
18i; ^{13}C NMR (CDCl_3)



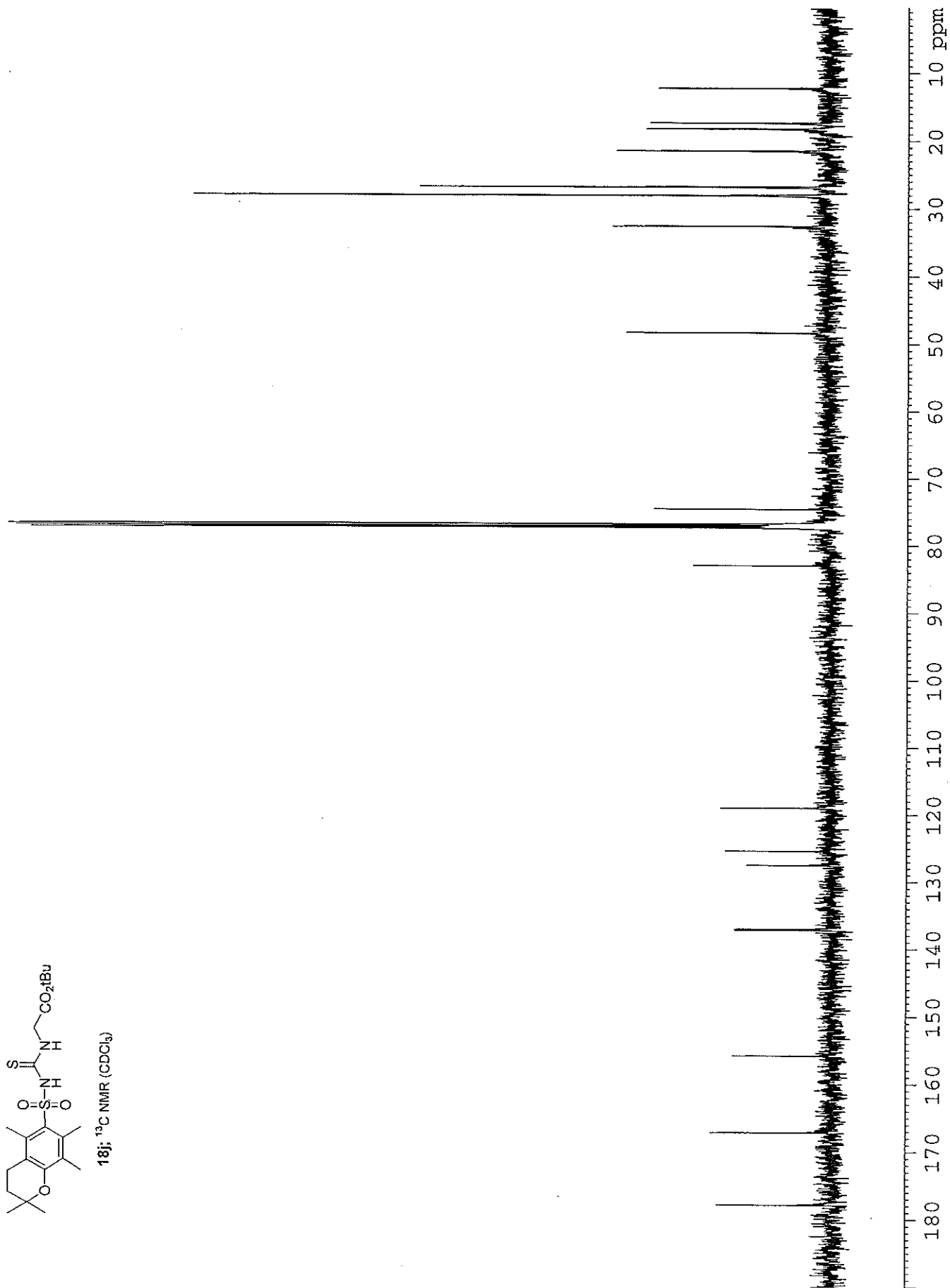


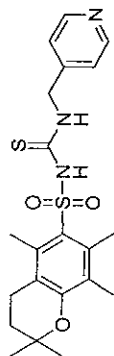
18j; ^1H NMR (CDCl_3)



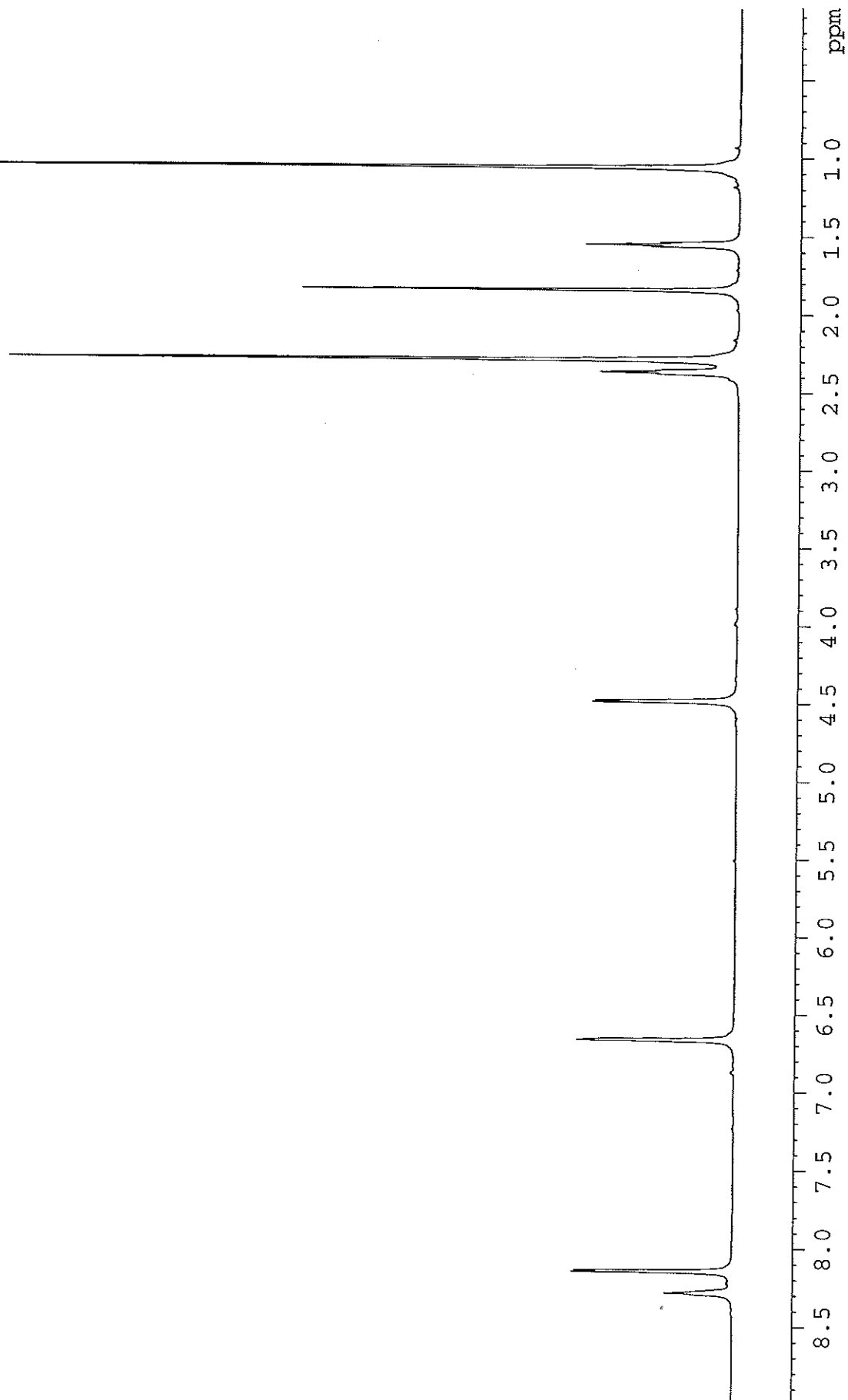


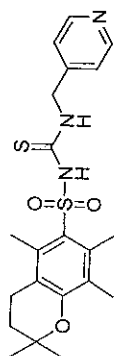
18j: ^{13}C NMR (CDCl_3)



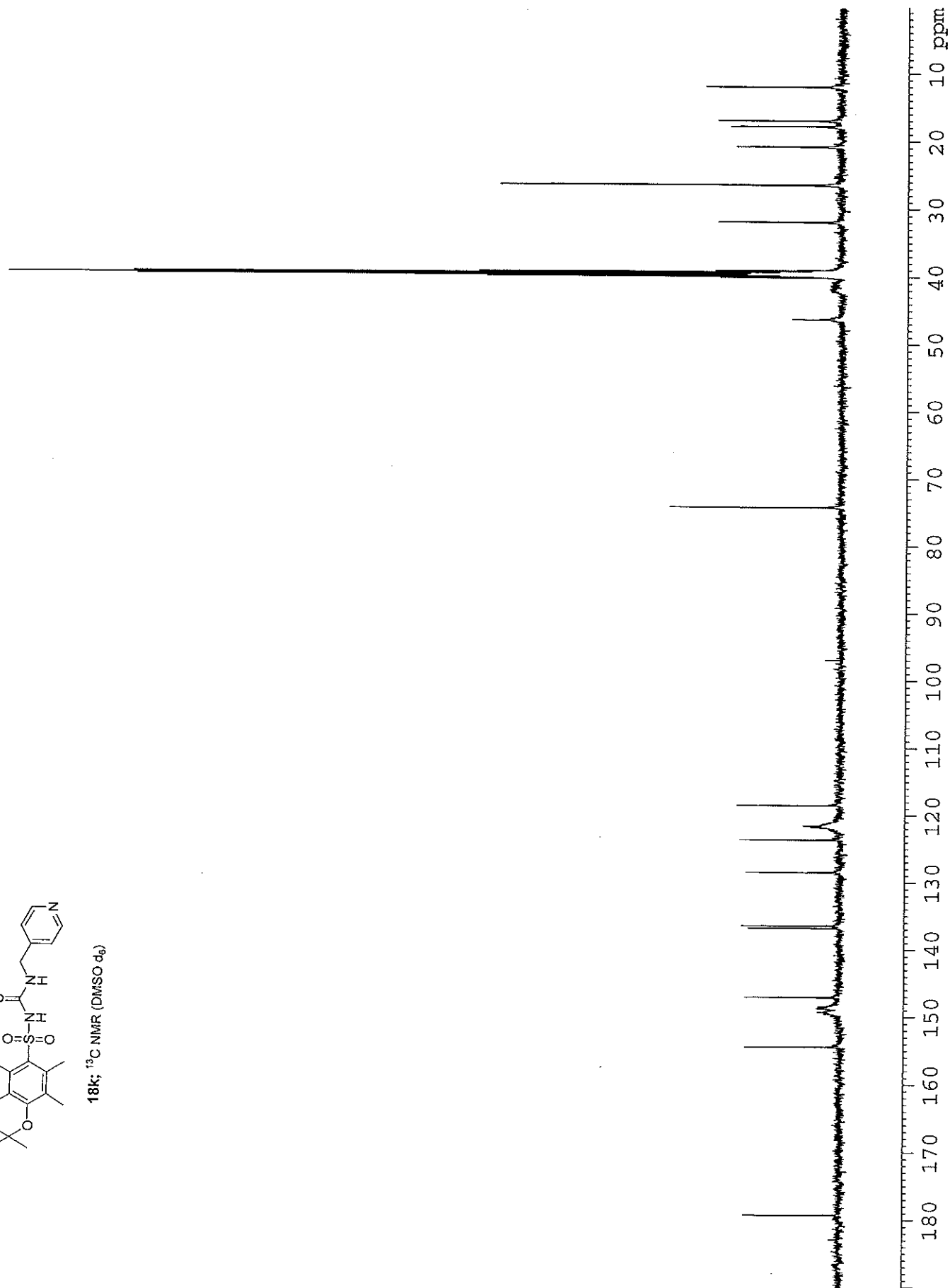


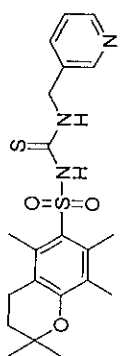
18k; ^1H NMR (DMSO d_6)



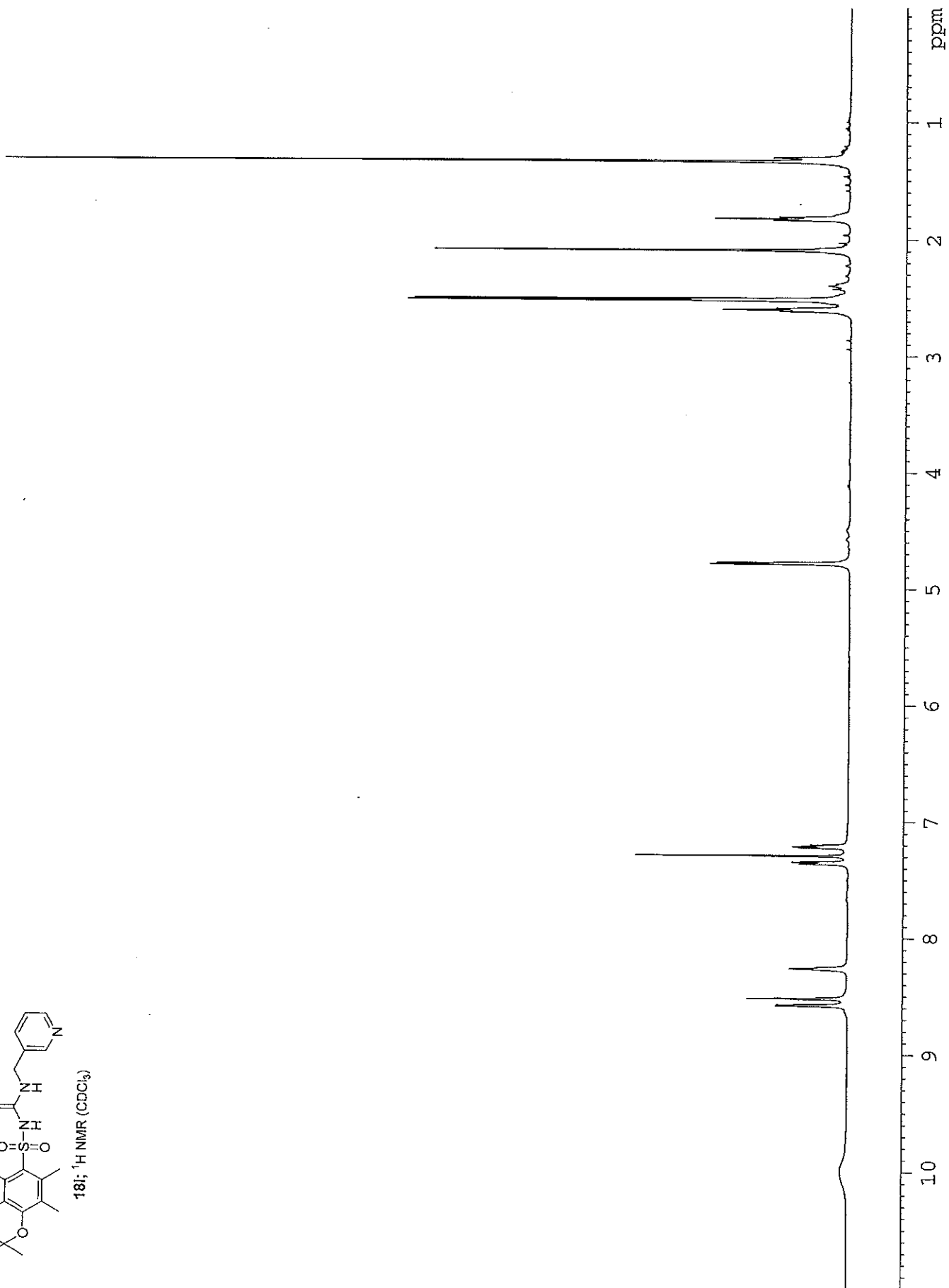


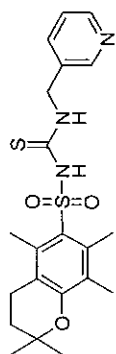
18k; ^{13}C NMR (DMSO d_6)



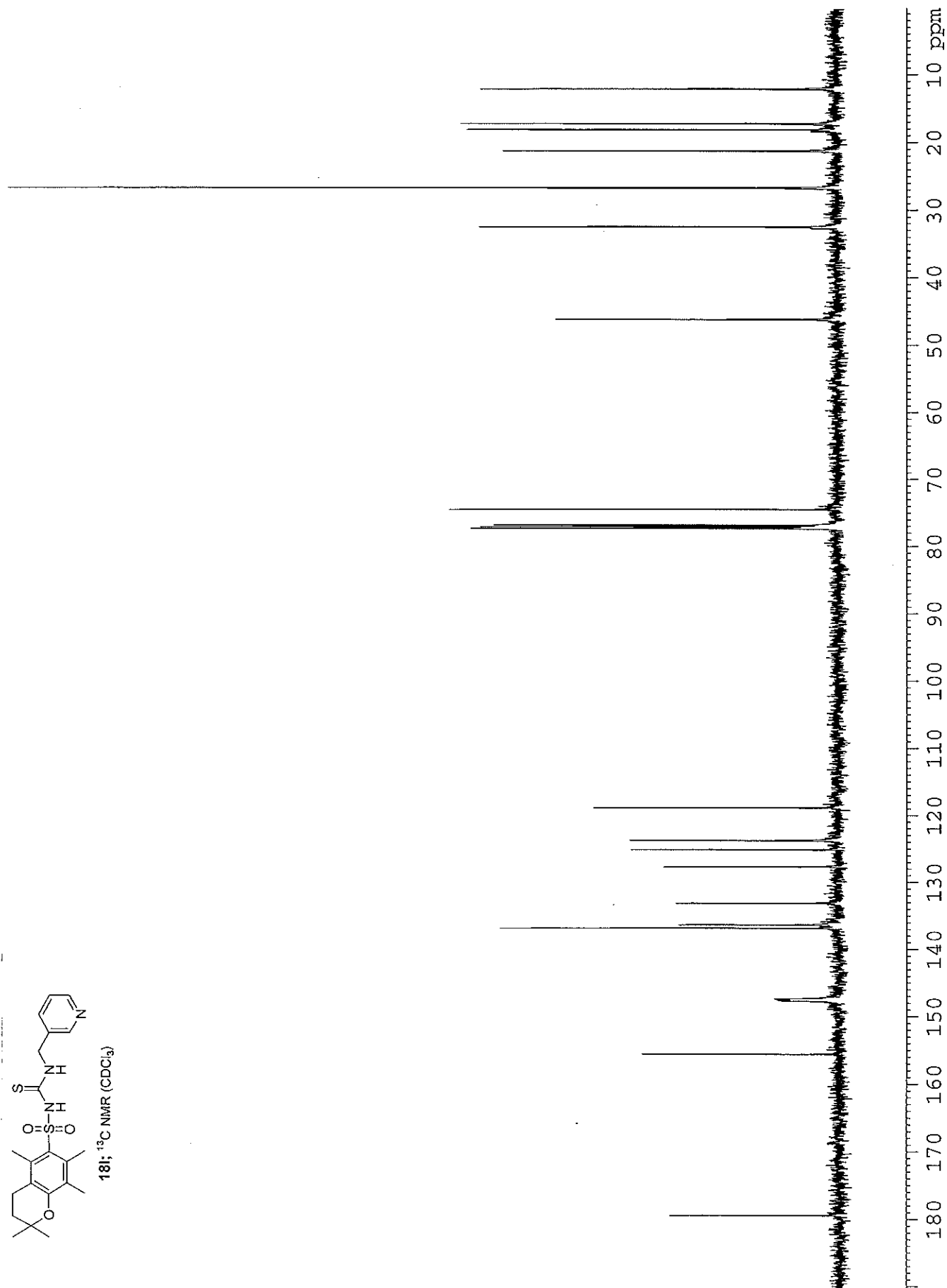


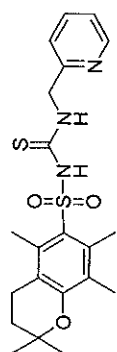
18i; ^1H NMR (CDCl_3)



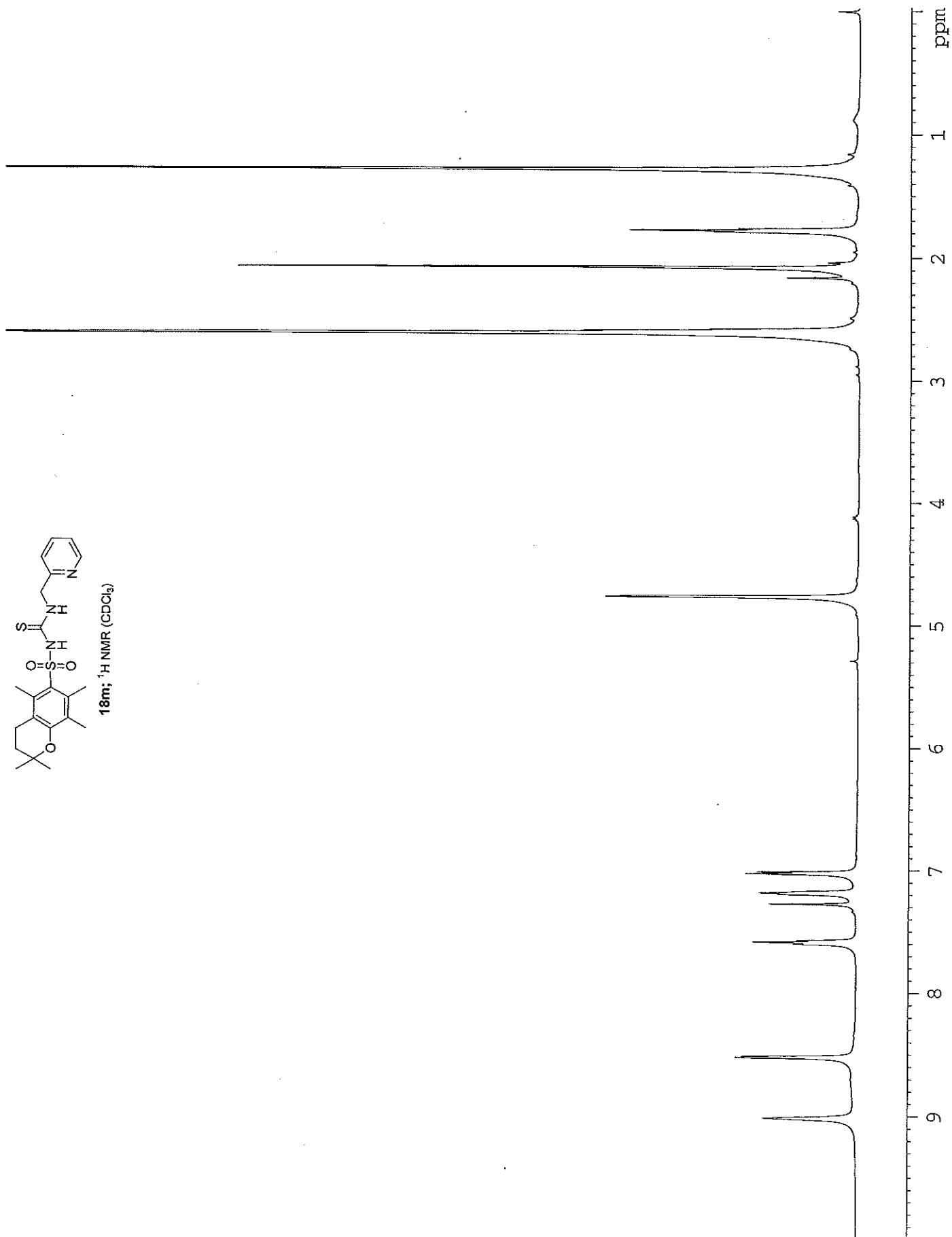


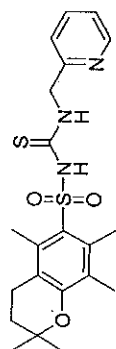
18l; ^{13}C NMR (CDCl_3)



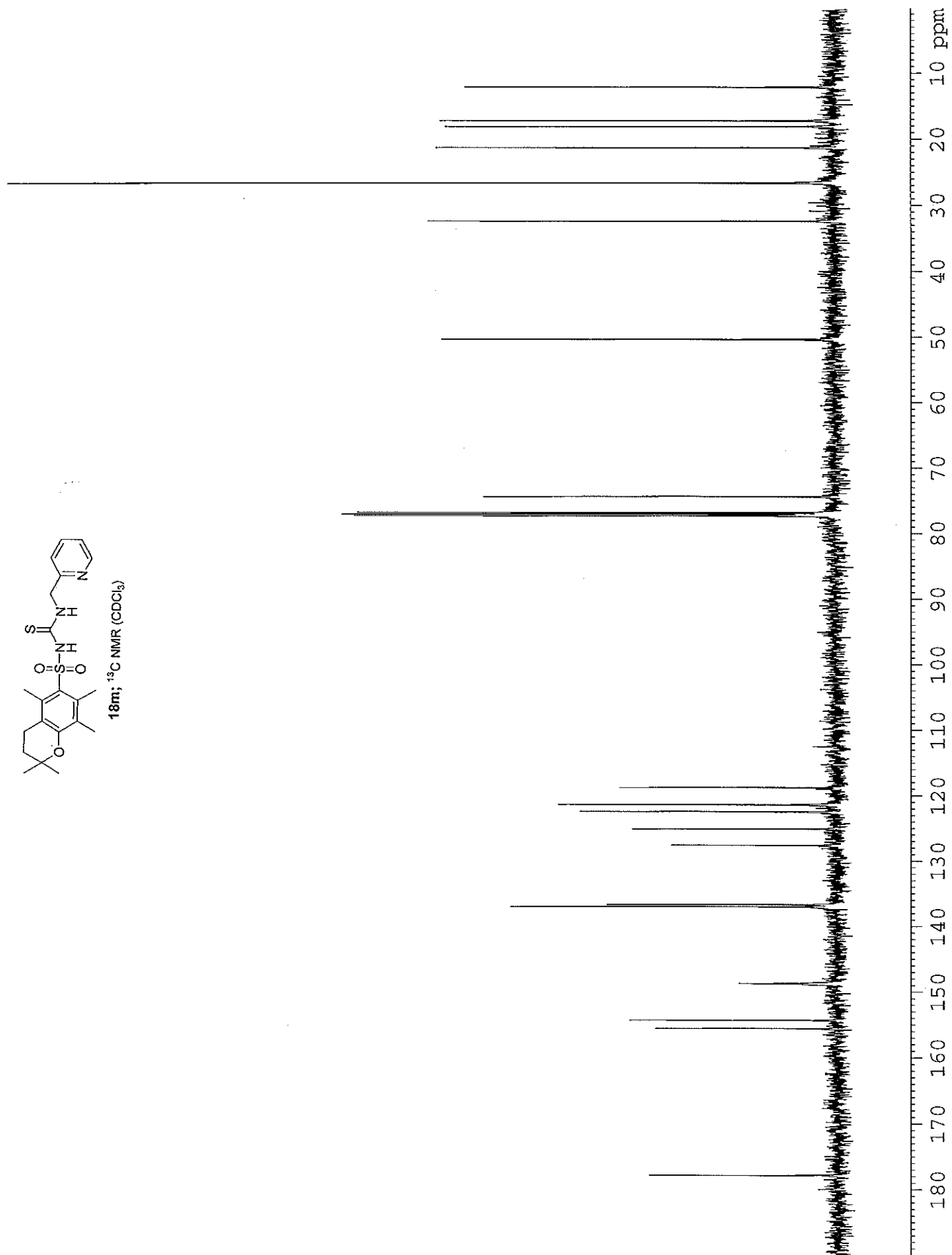


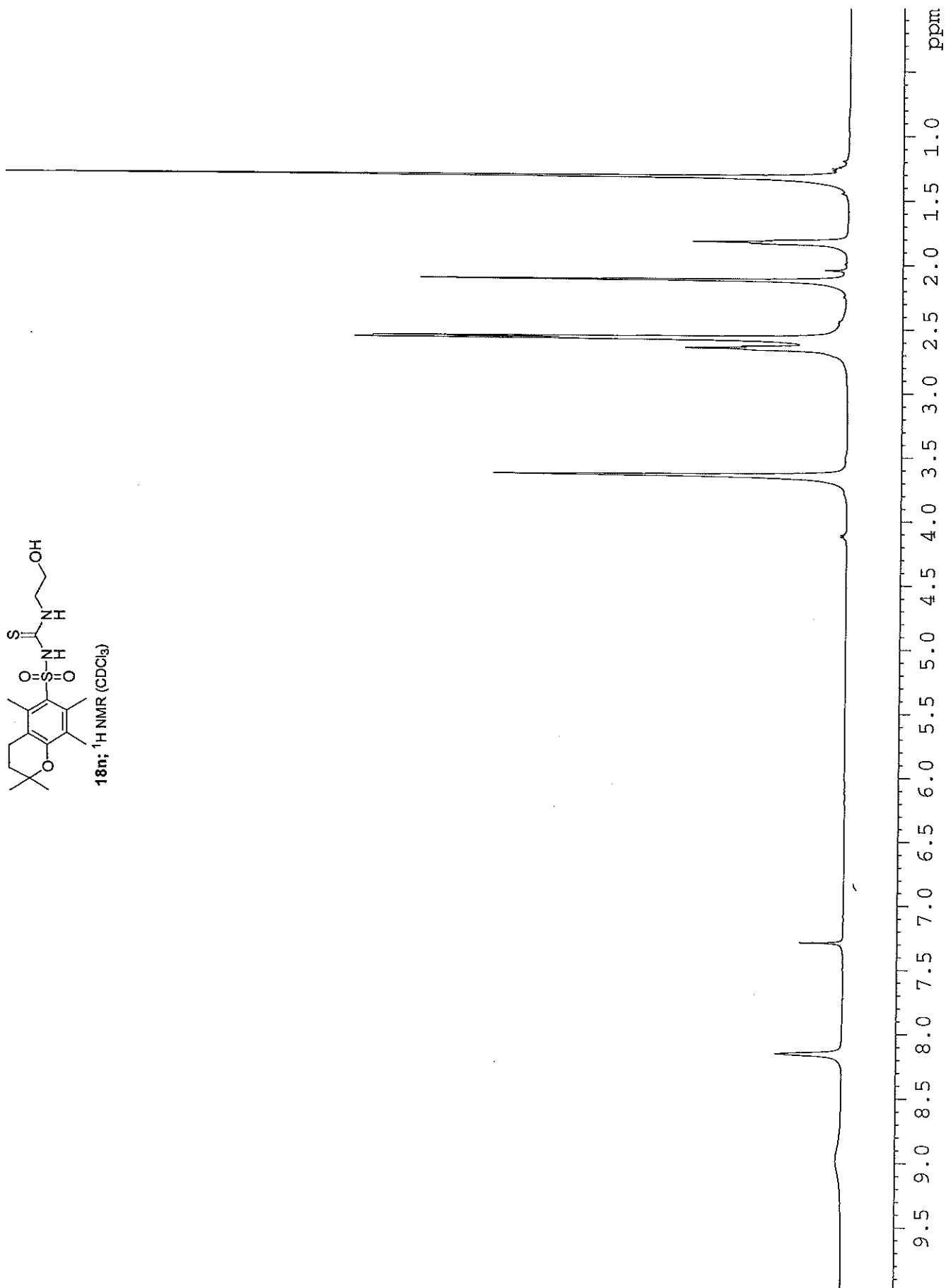
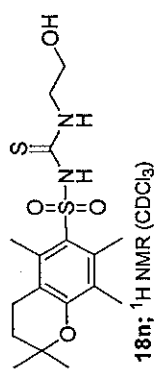
18m; ^1H NMR (CDCl_3)

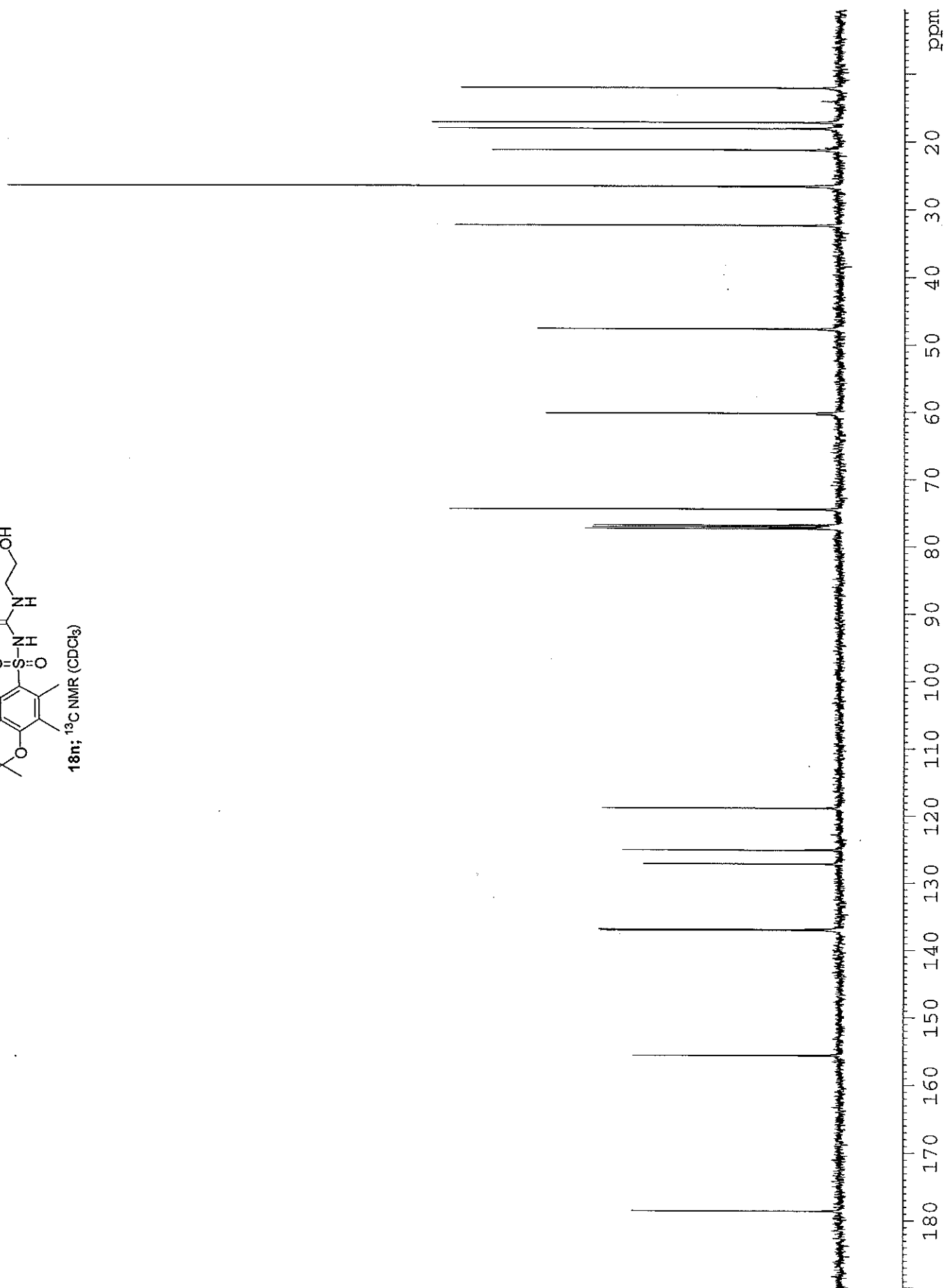
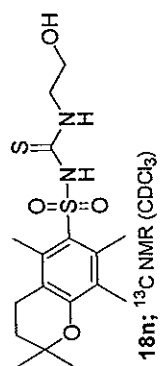


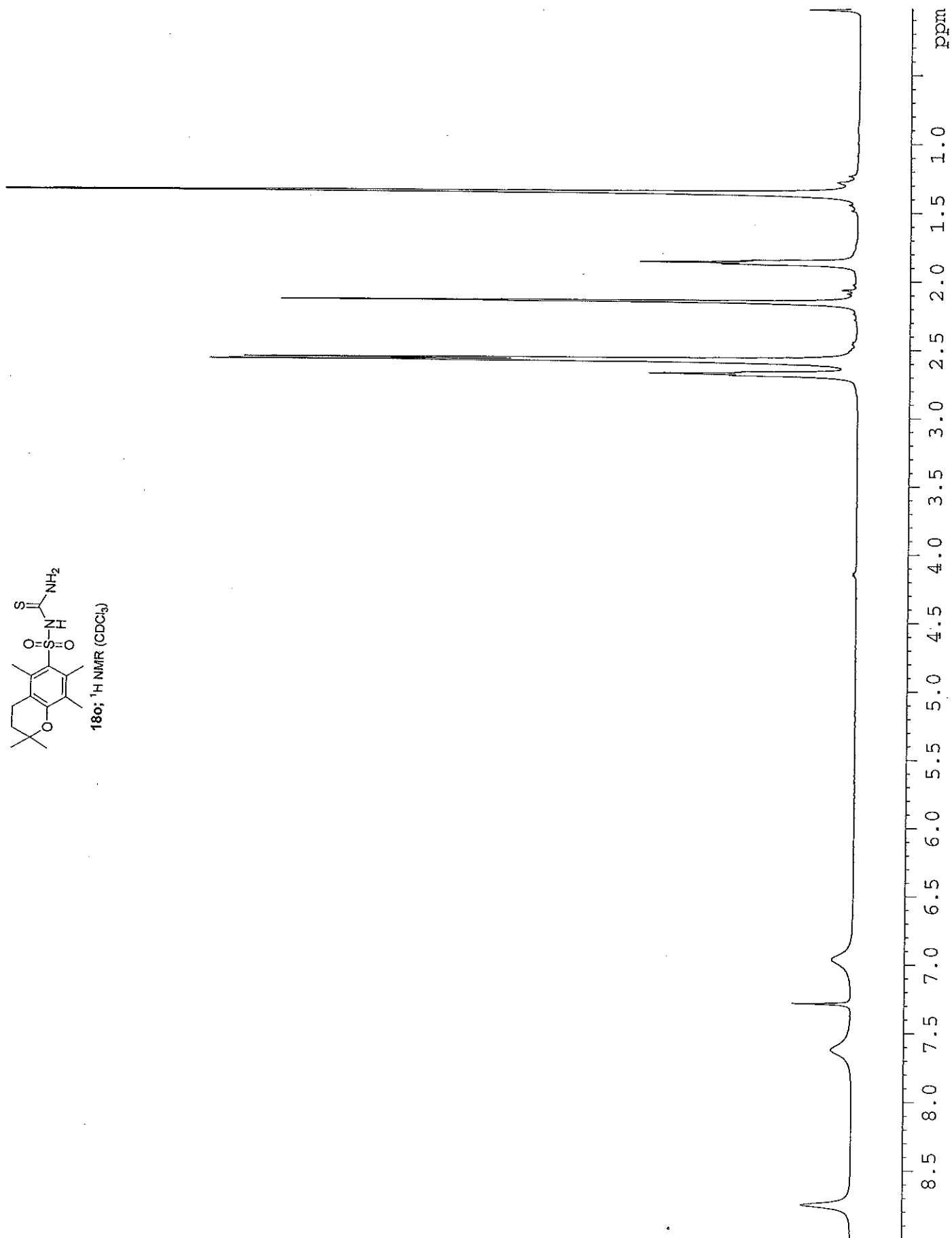
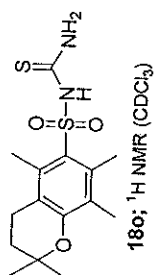


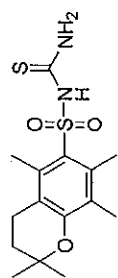
18m; ^{13}C NMR (CDCl_3)



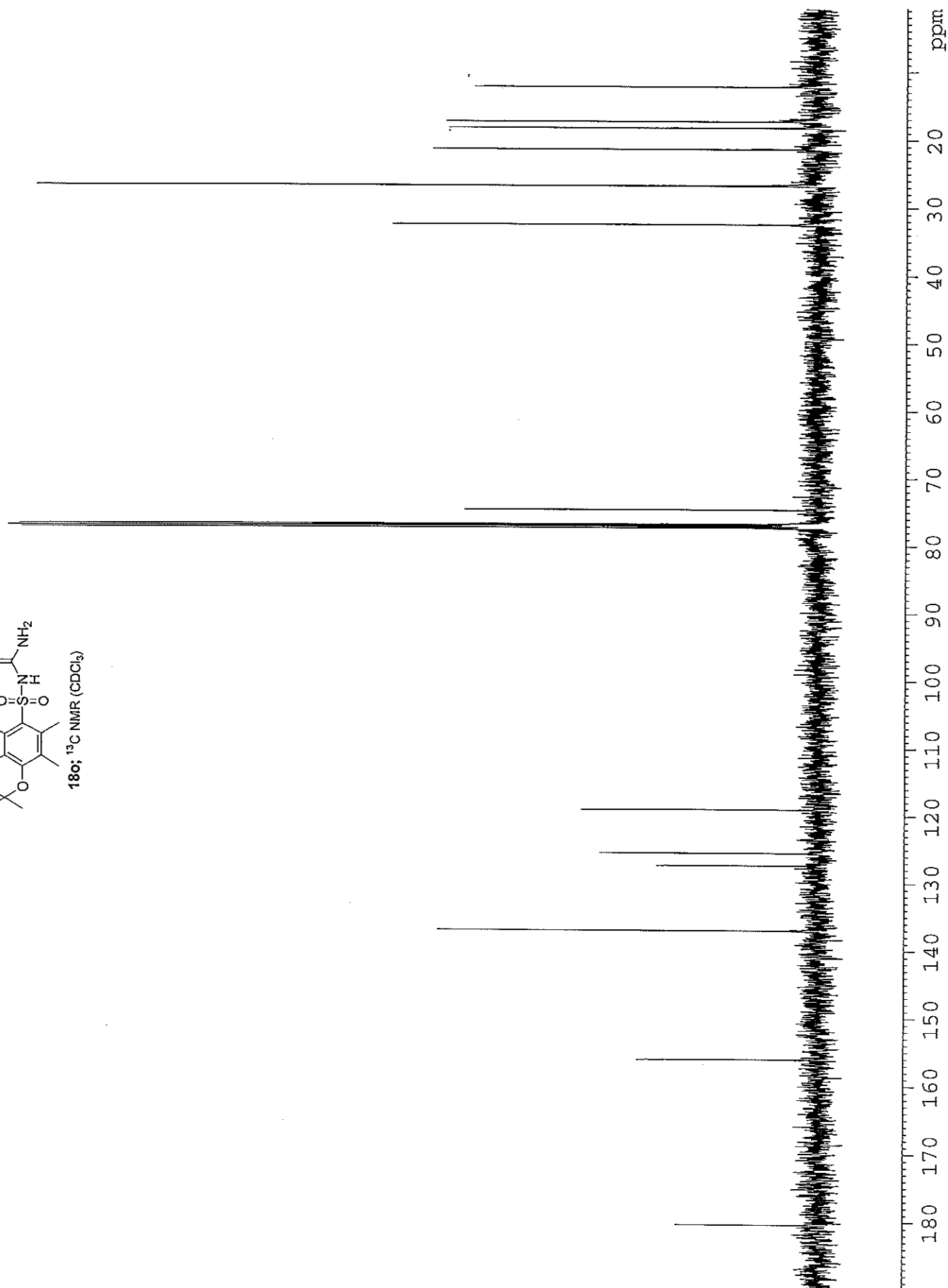


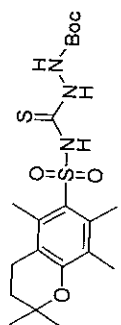




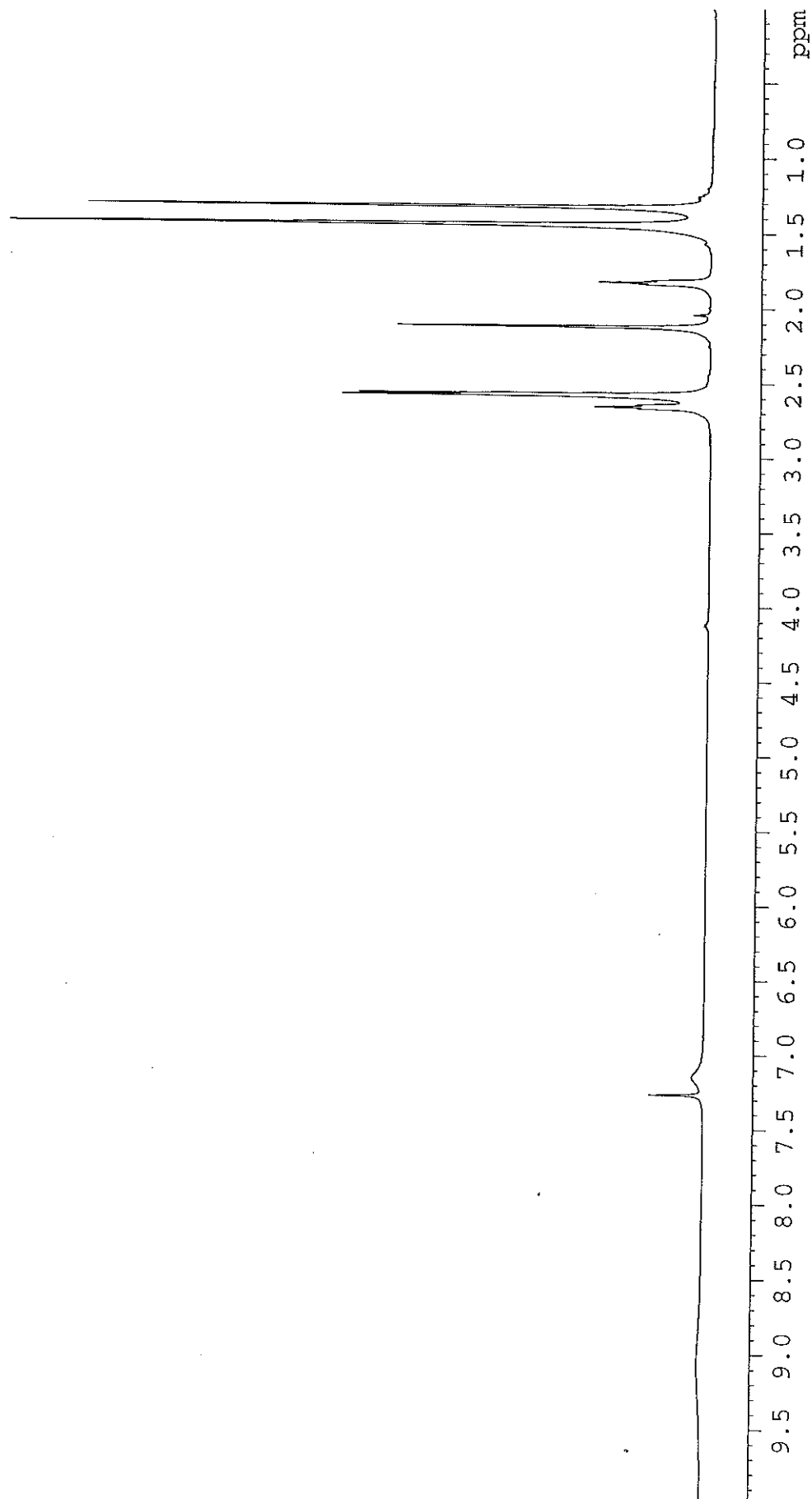


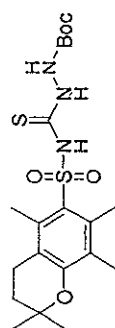
18o; ^{13}C NMR (CDCl_3)



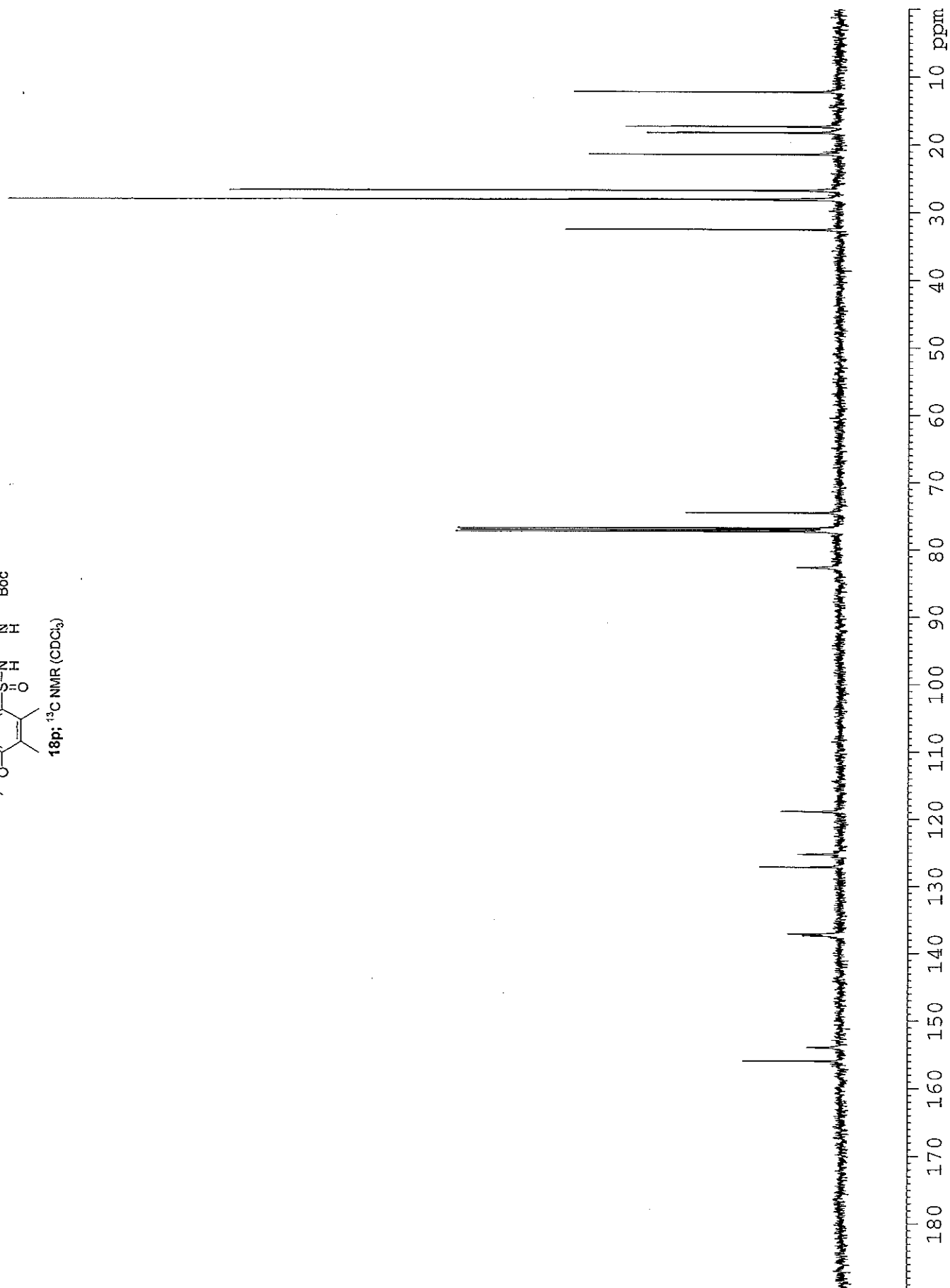


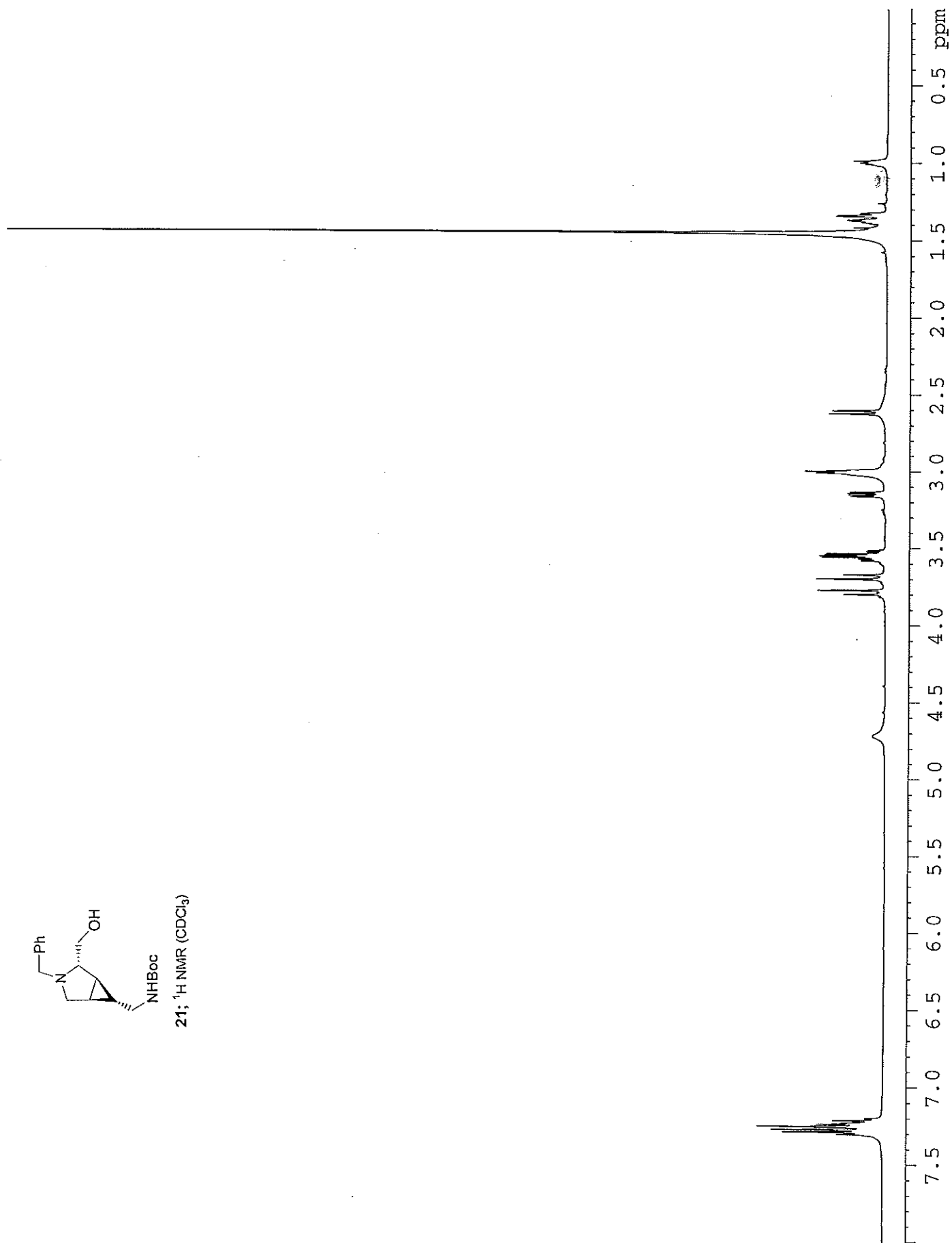
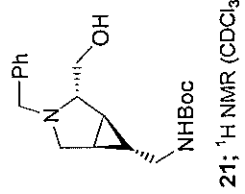
18p; ^1H NMR (CDCl_3)

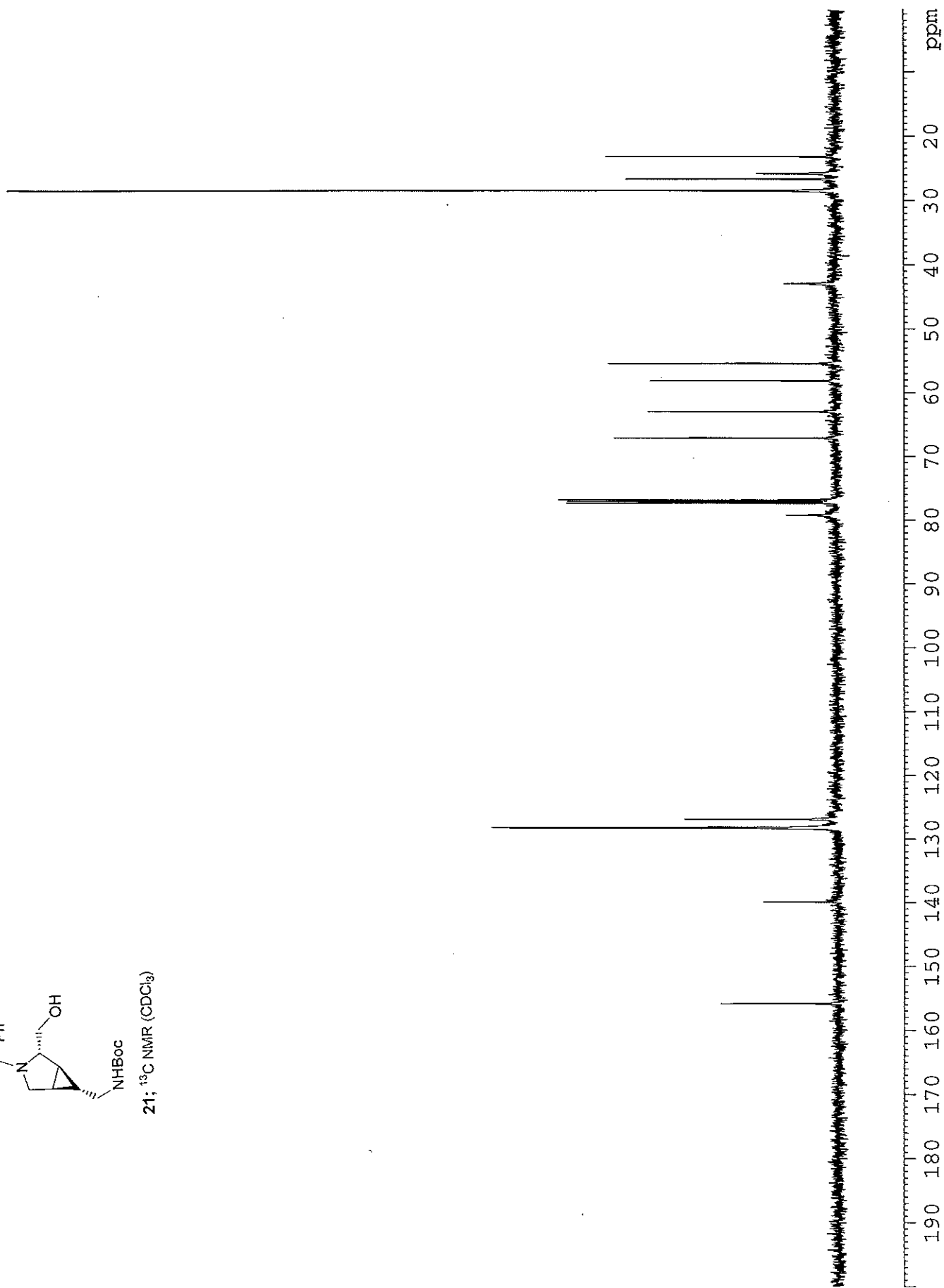
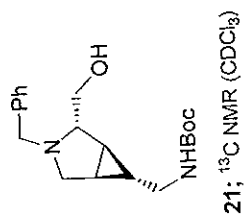


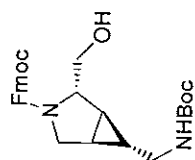


18p; ^{13}C NMR (CDCl_3)

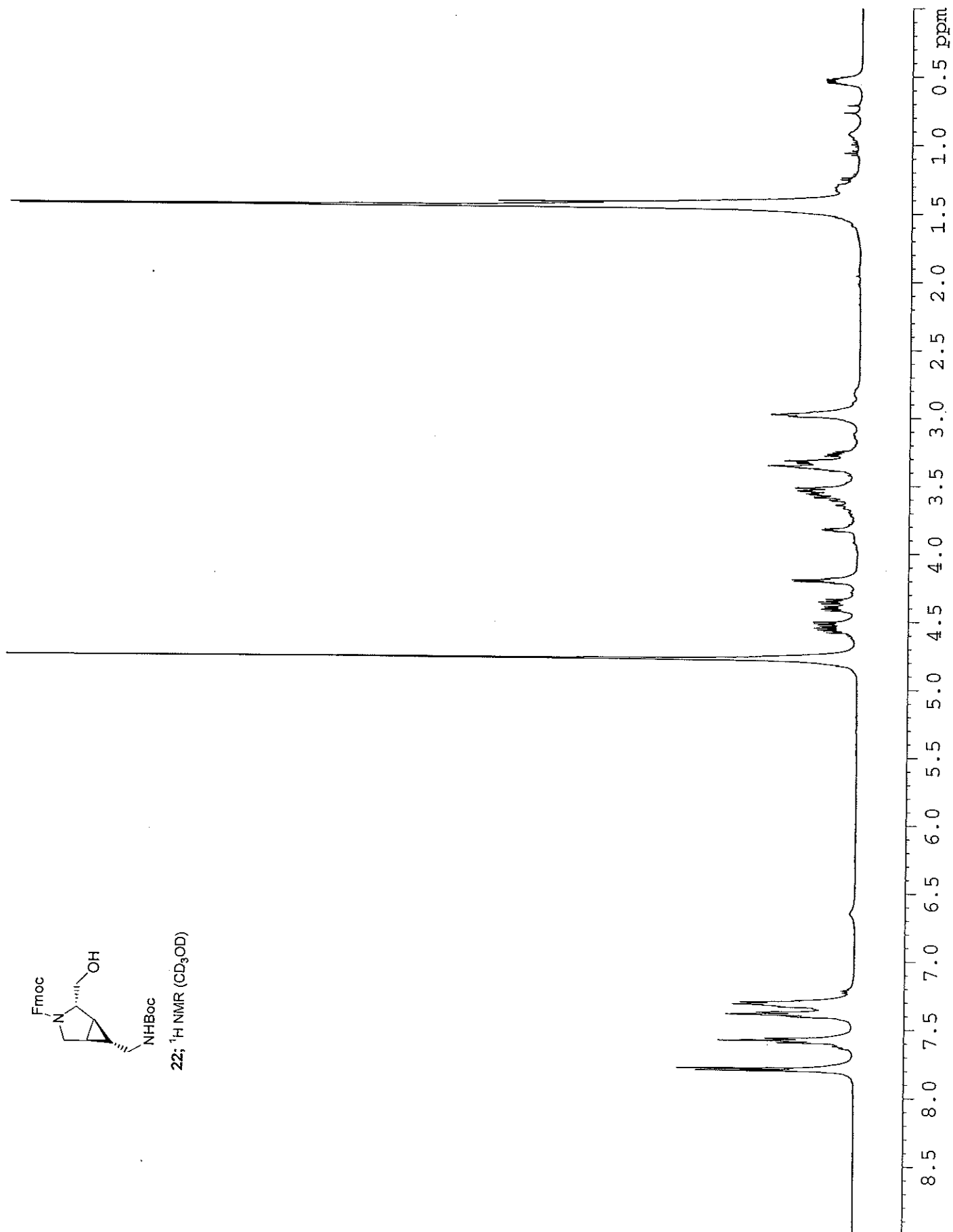


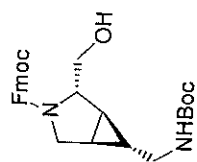




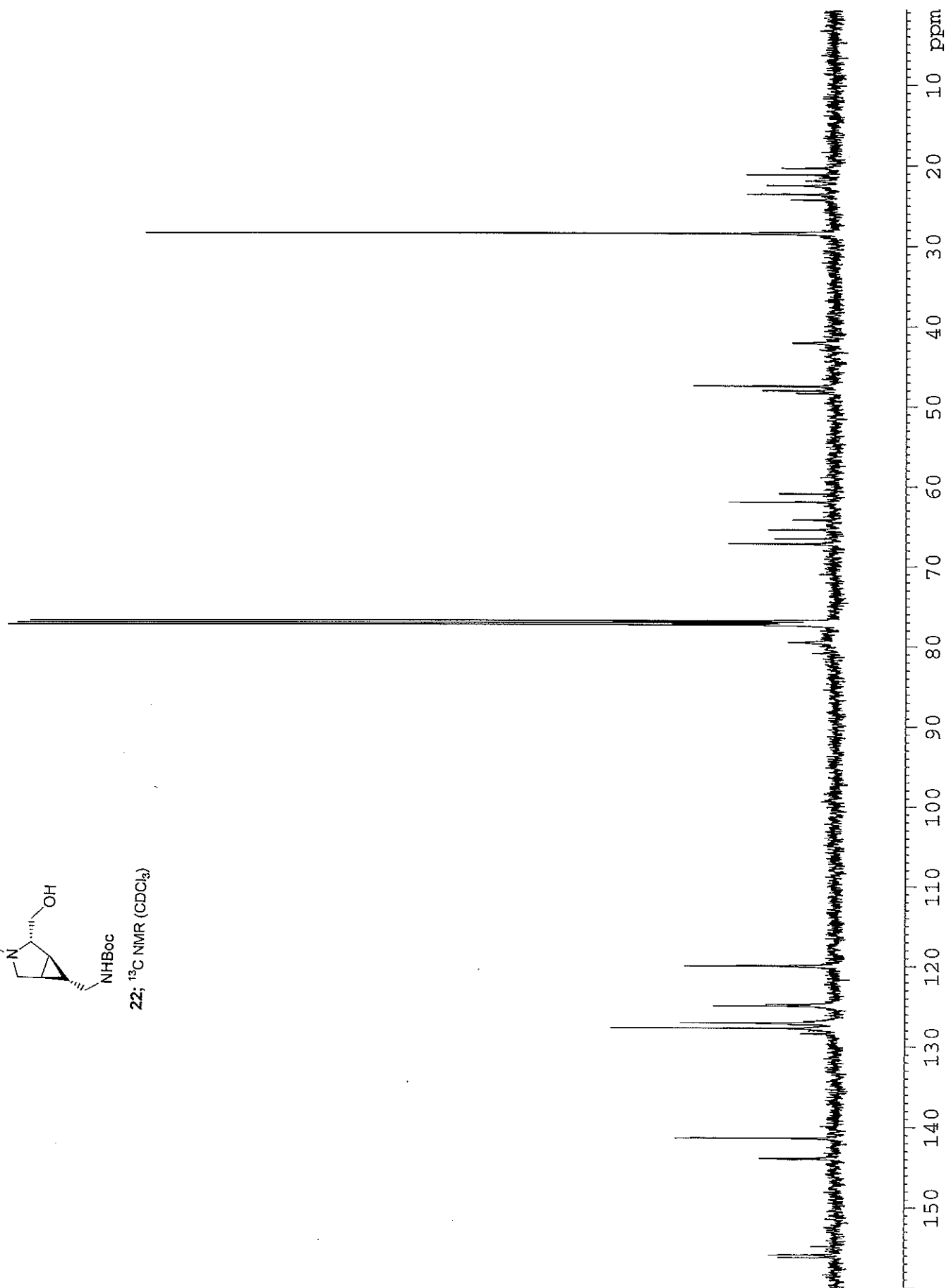


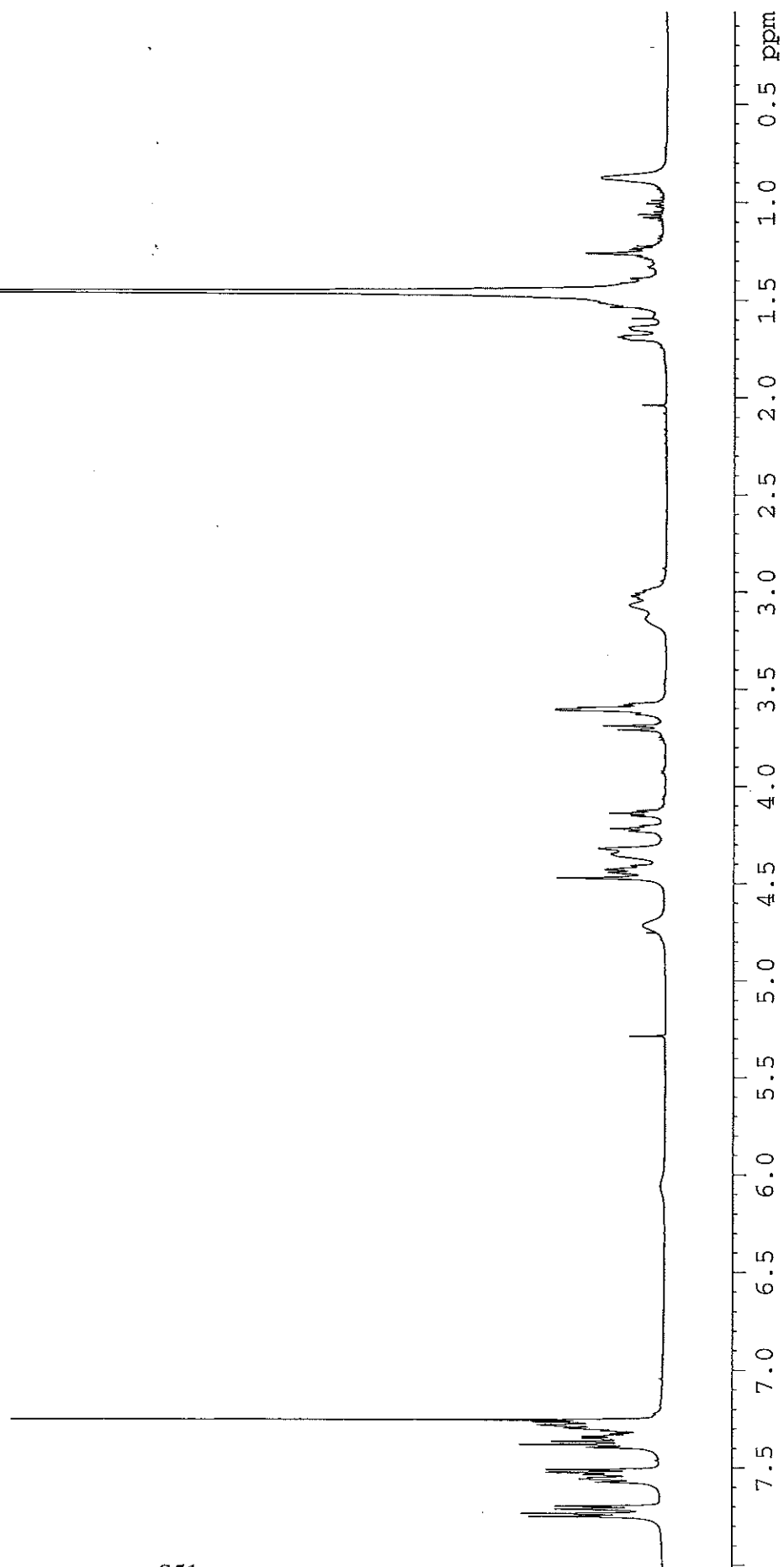
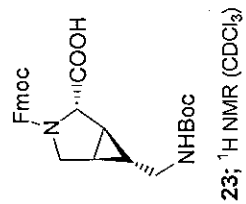
22; ^1H NMR (CD_3OD)

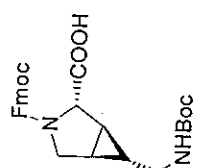




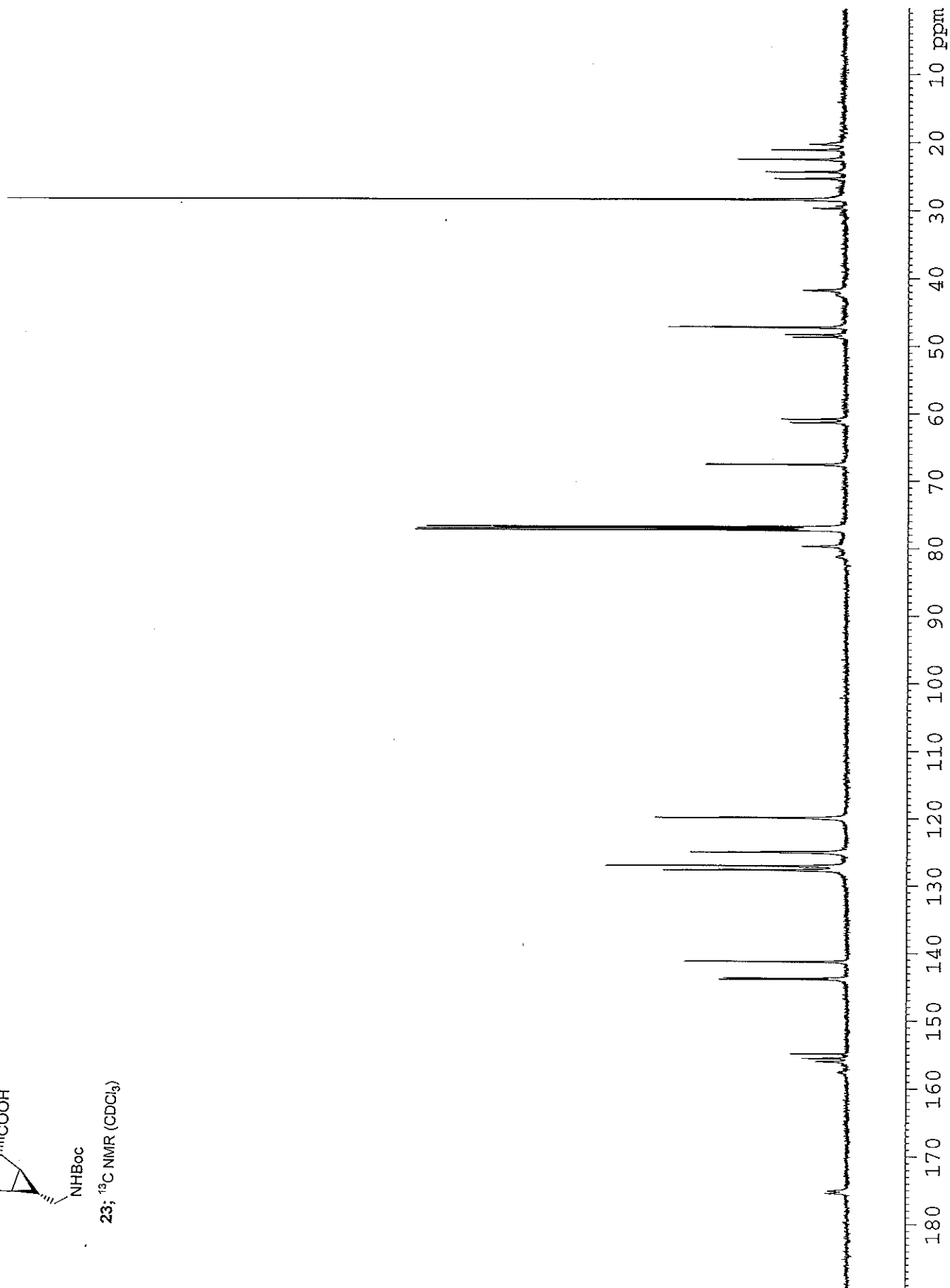
22; ^{13}C NMR (CDCl_3)

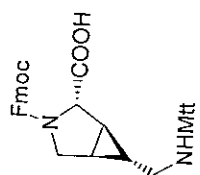




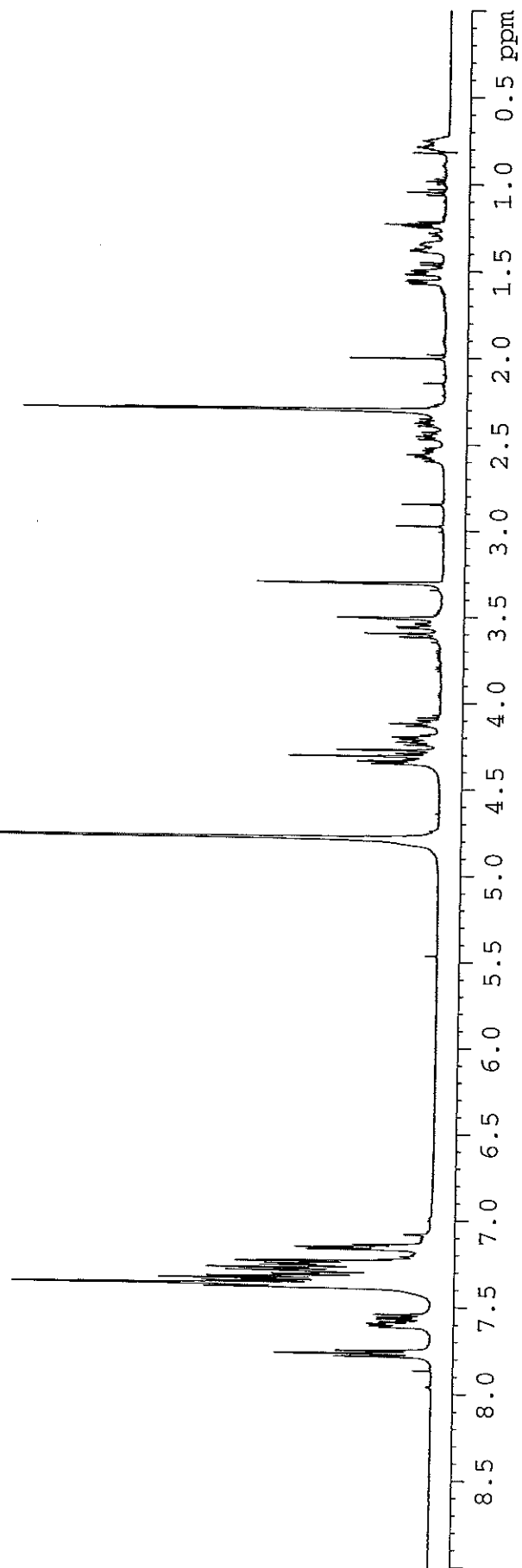


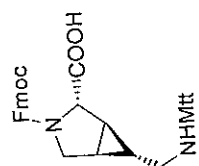
23; ^{13}C NMR (CDCl_3)



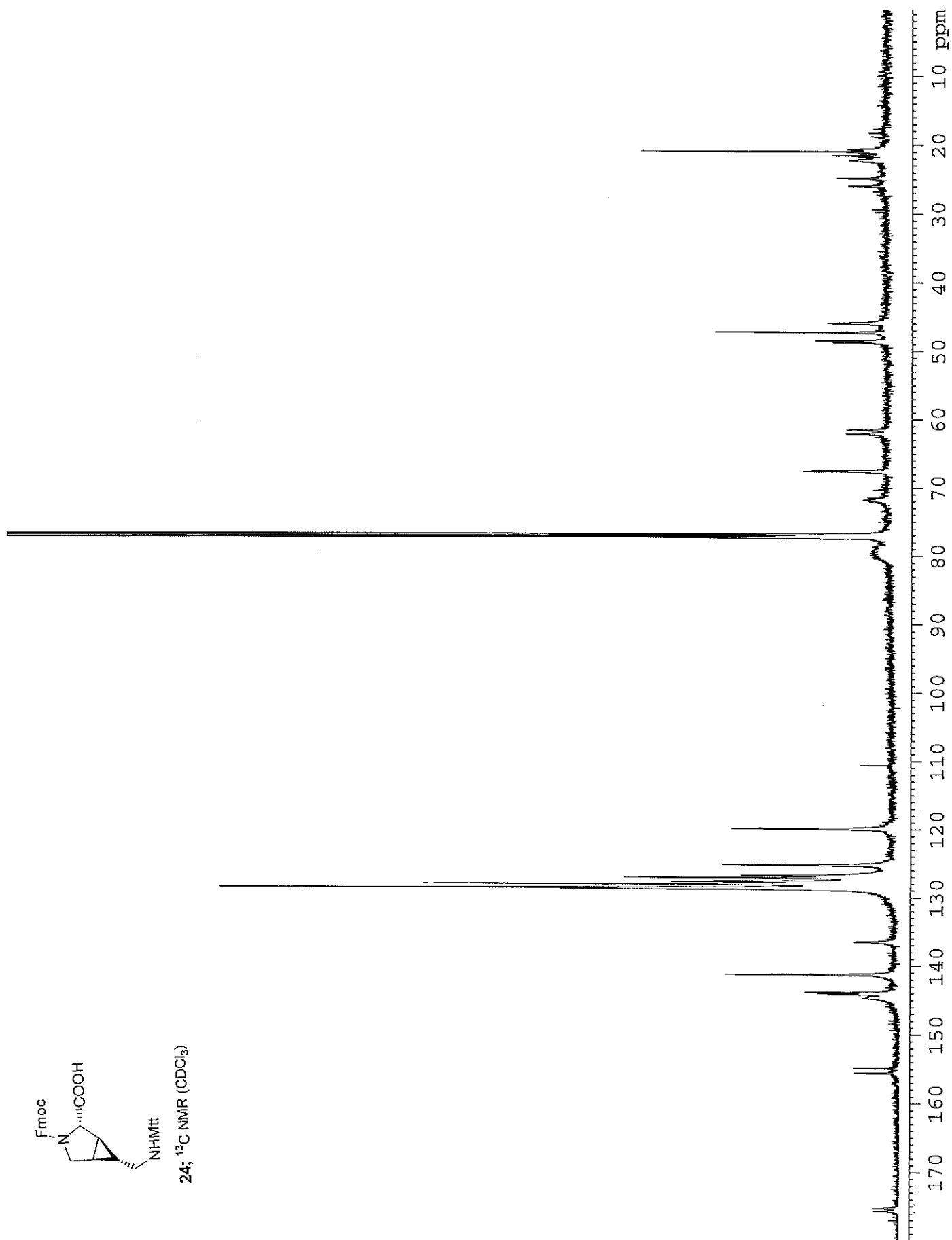


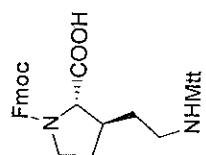
24; ^1H NMR (CD_3OD)



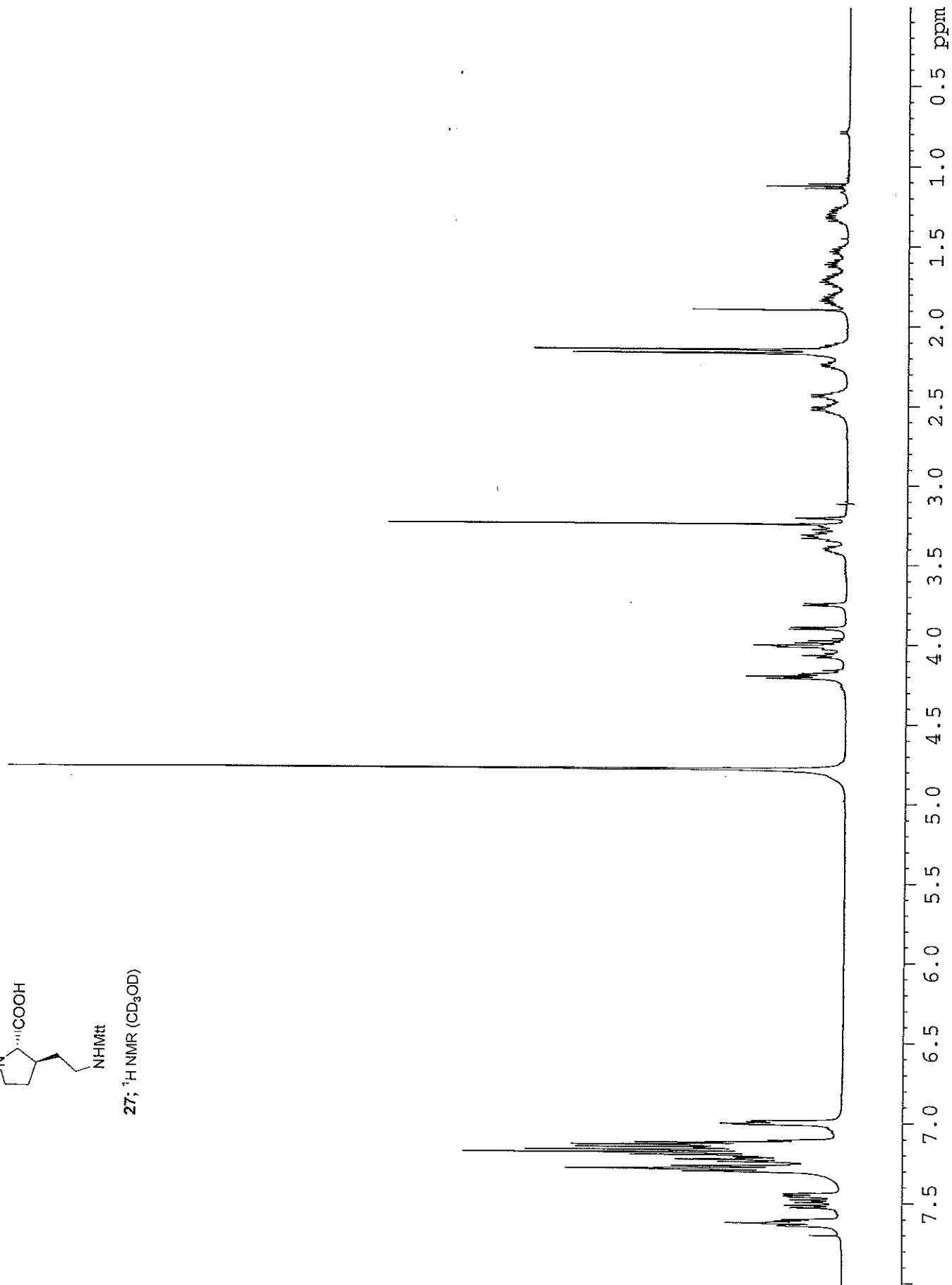


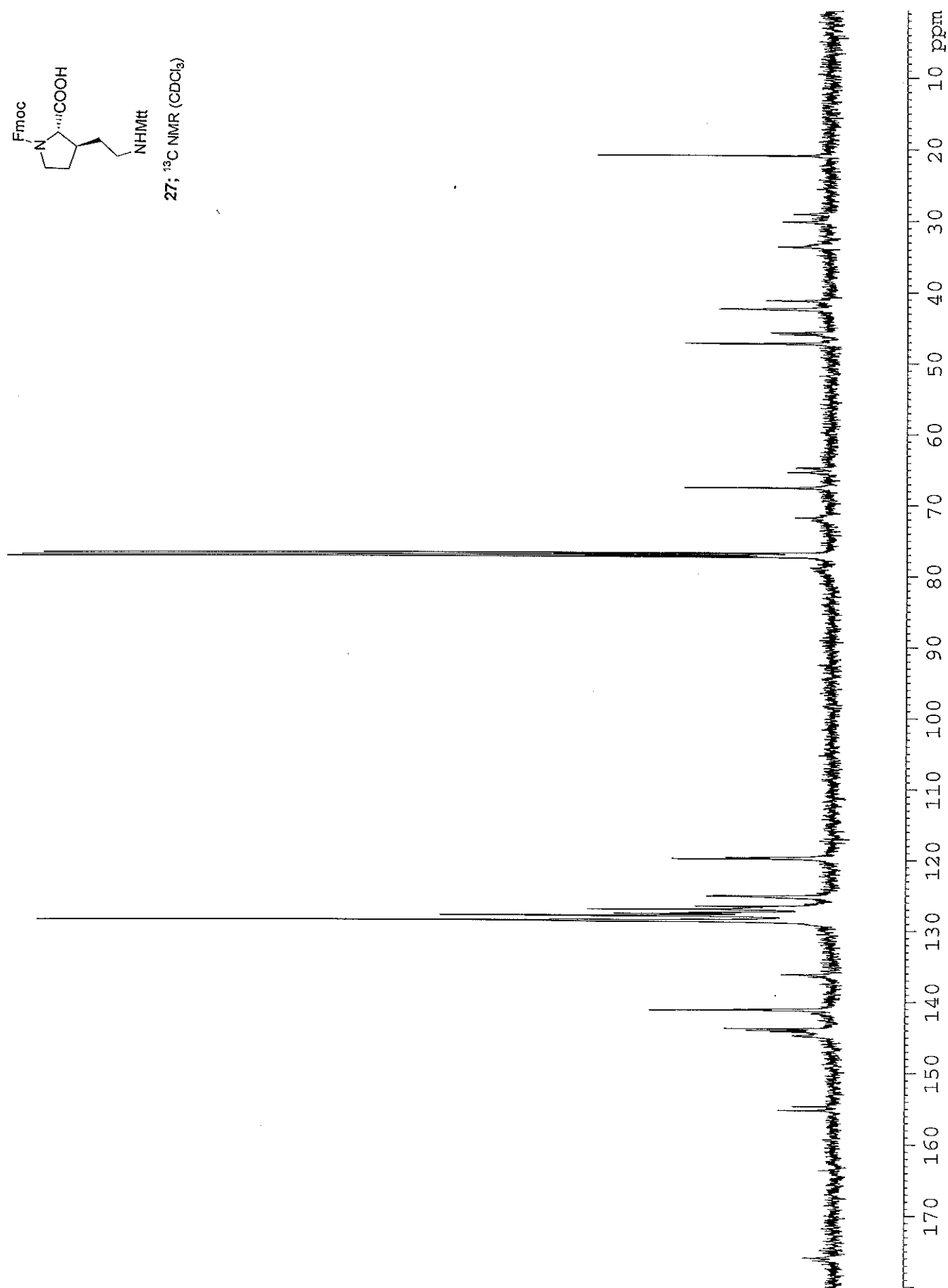
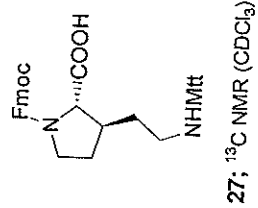
24; ^{13}C NMR (CDCl_3)



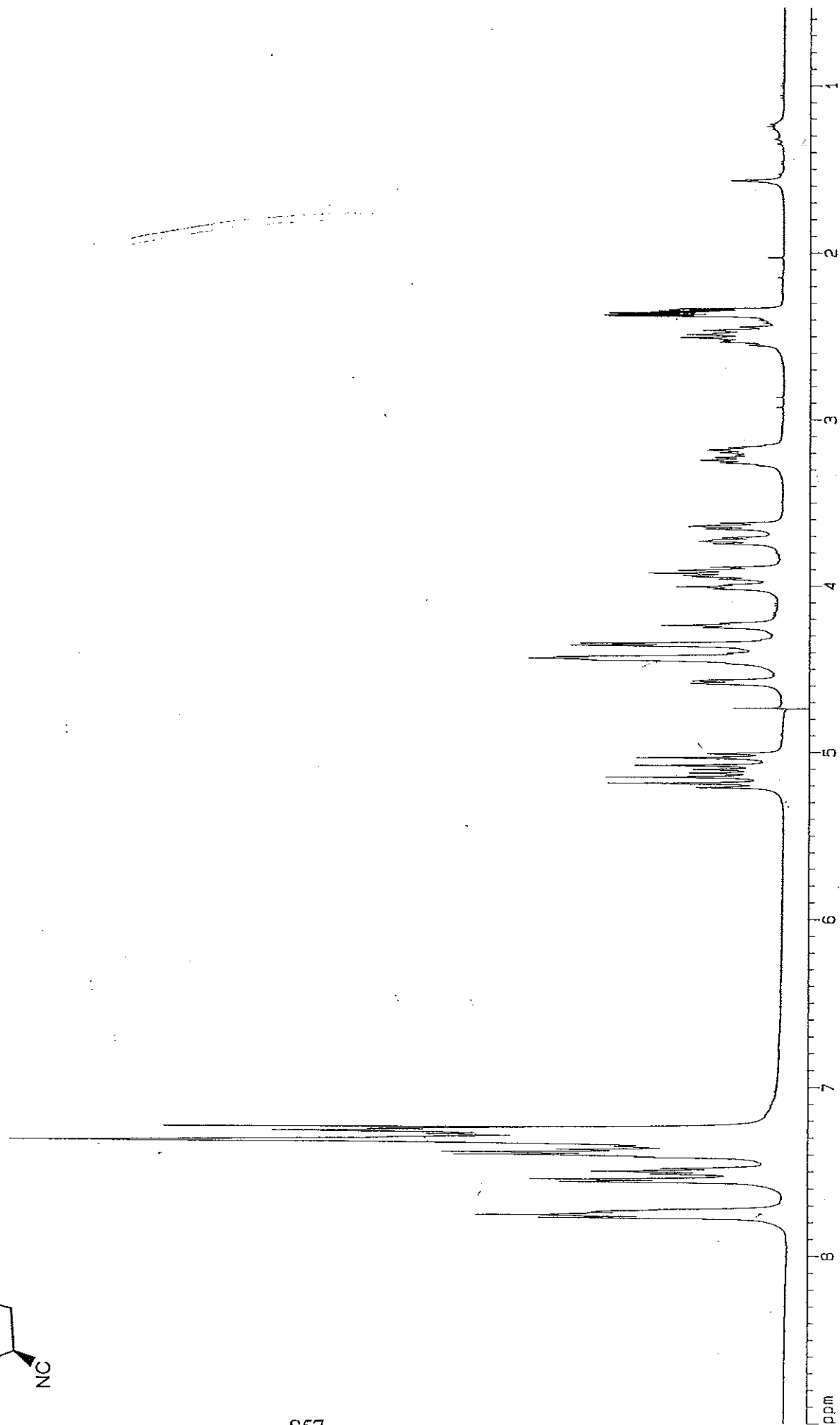
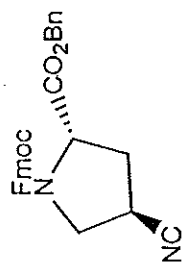


27; ^1H NMR (CD_3OD)

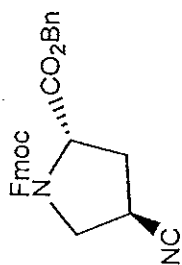




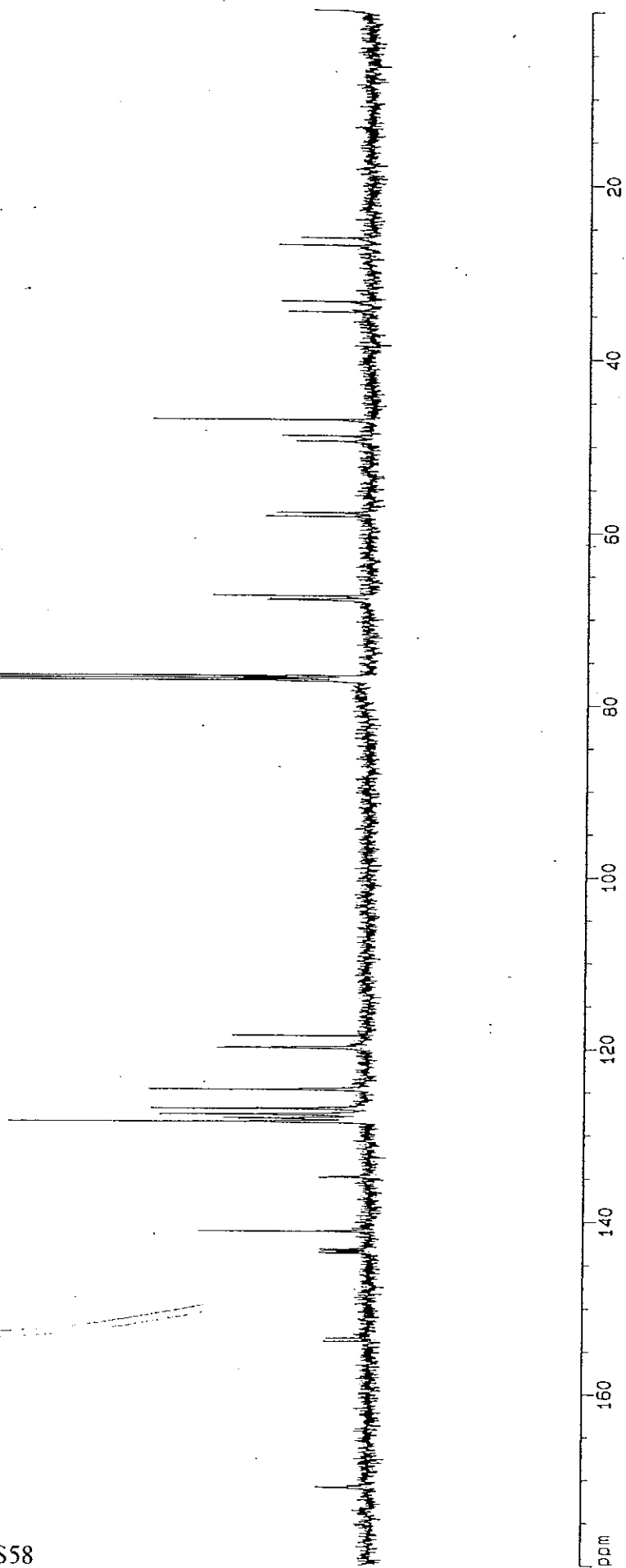
29, ^1H NMR, CDCl_3



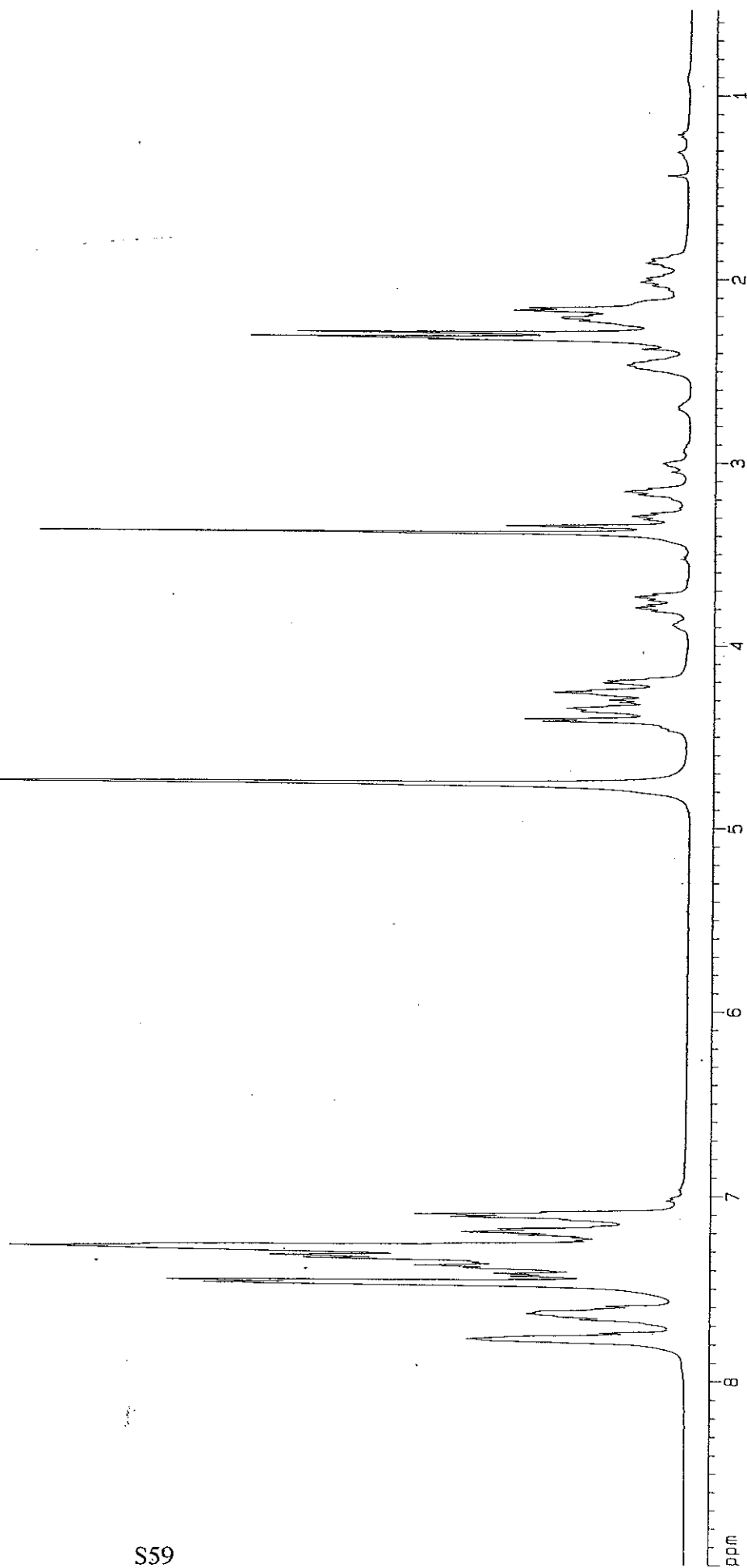
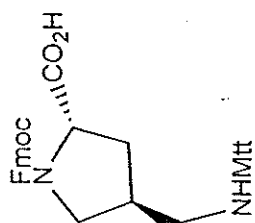
29, ^{13}C NMR, CDCl_3



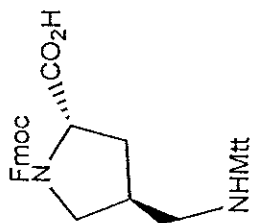
S58



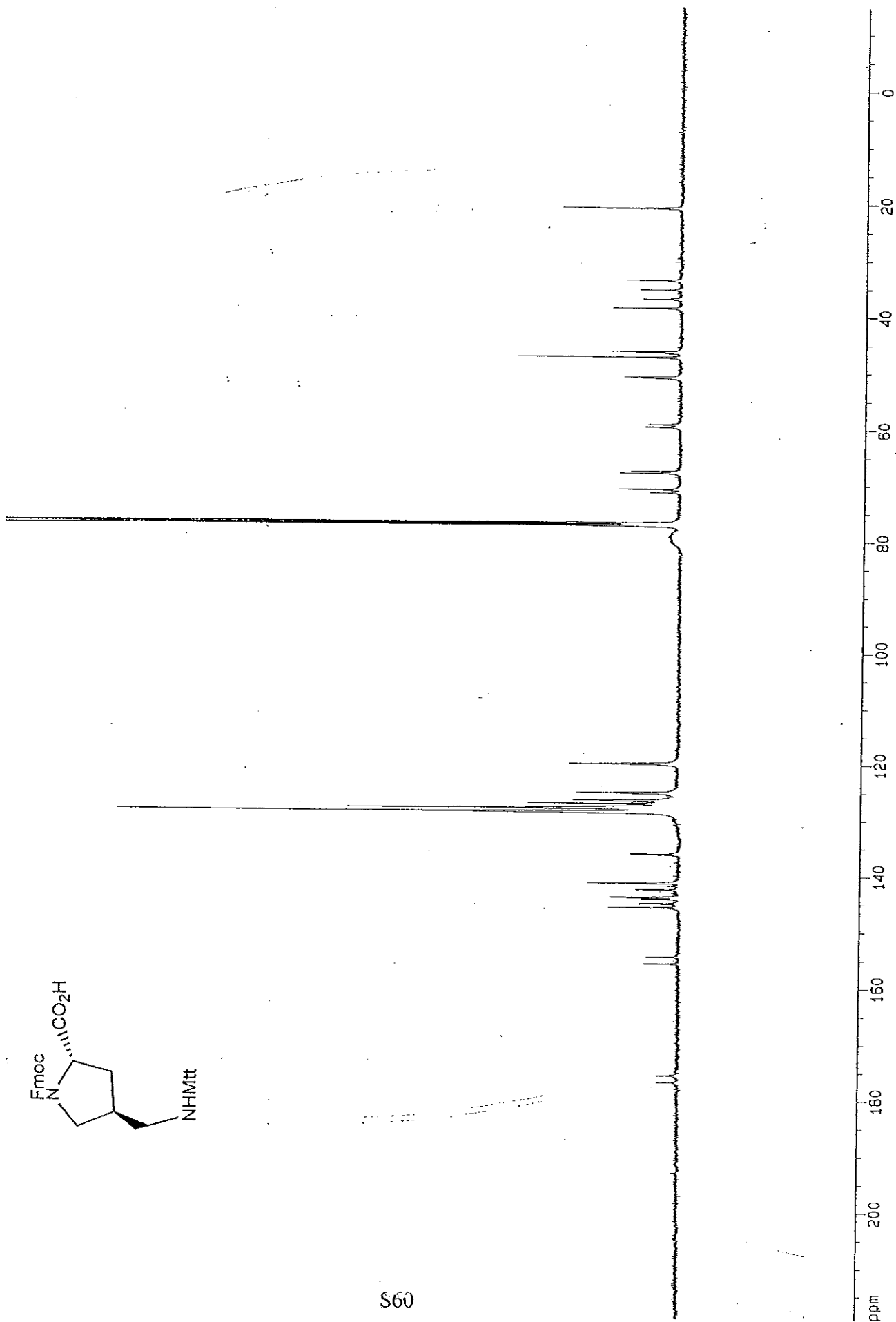
31, $^1\text{H NMR}$, $\text{CD}_3\text{OD} + \text{CDCl}_3$



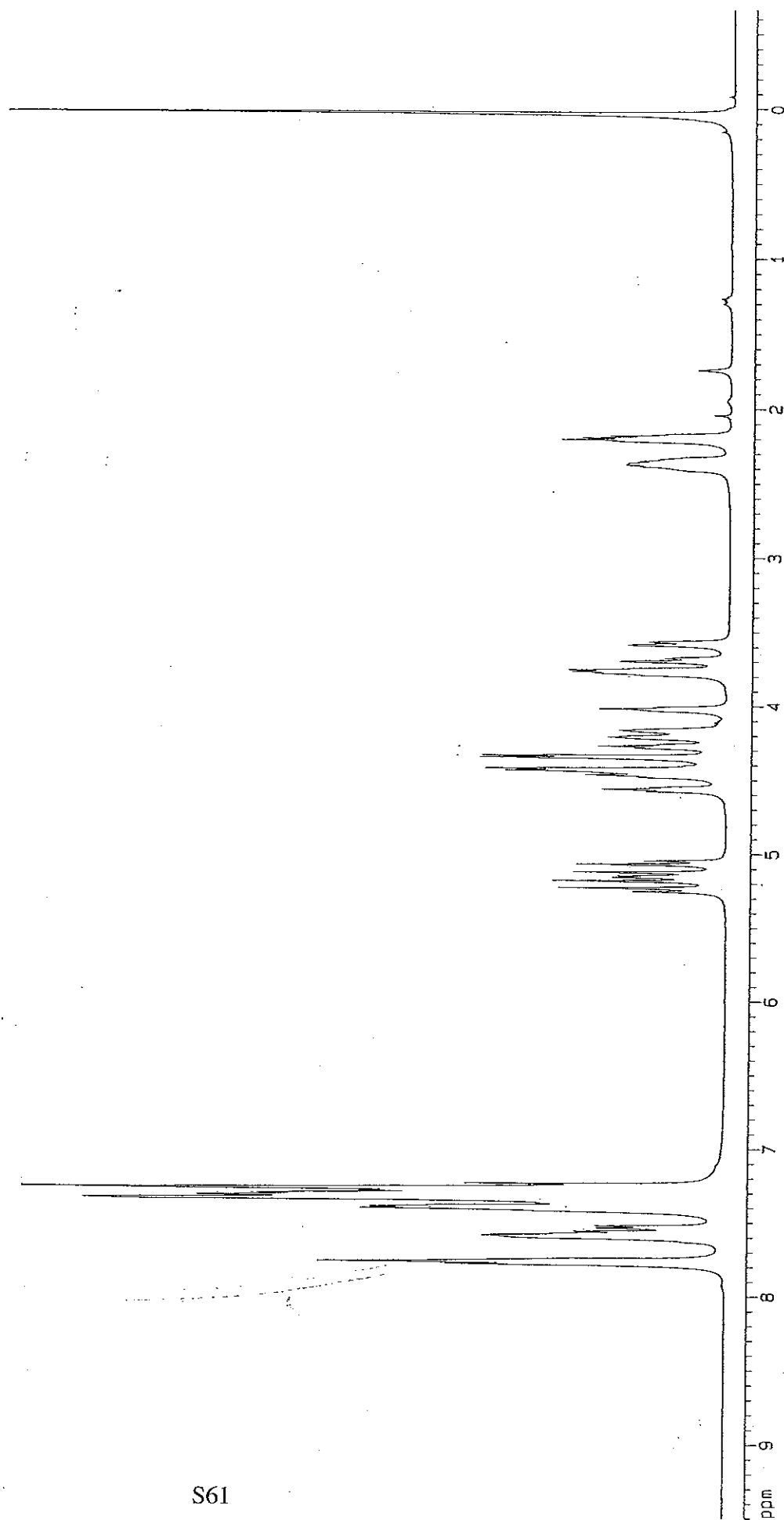
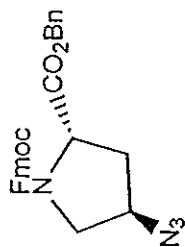
31, ^{13}C NMR, $\text{CD}_3\text{OD} + \text{CDCl}_3$



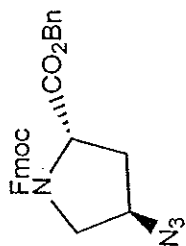
S60



35, ^1H NMR, CDCl_3



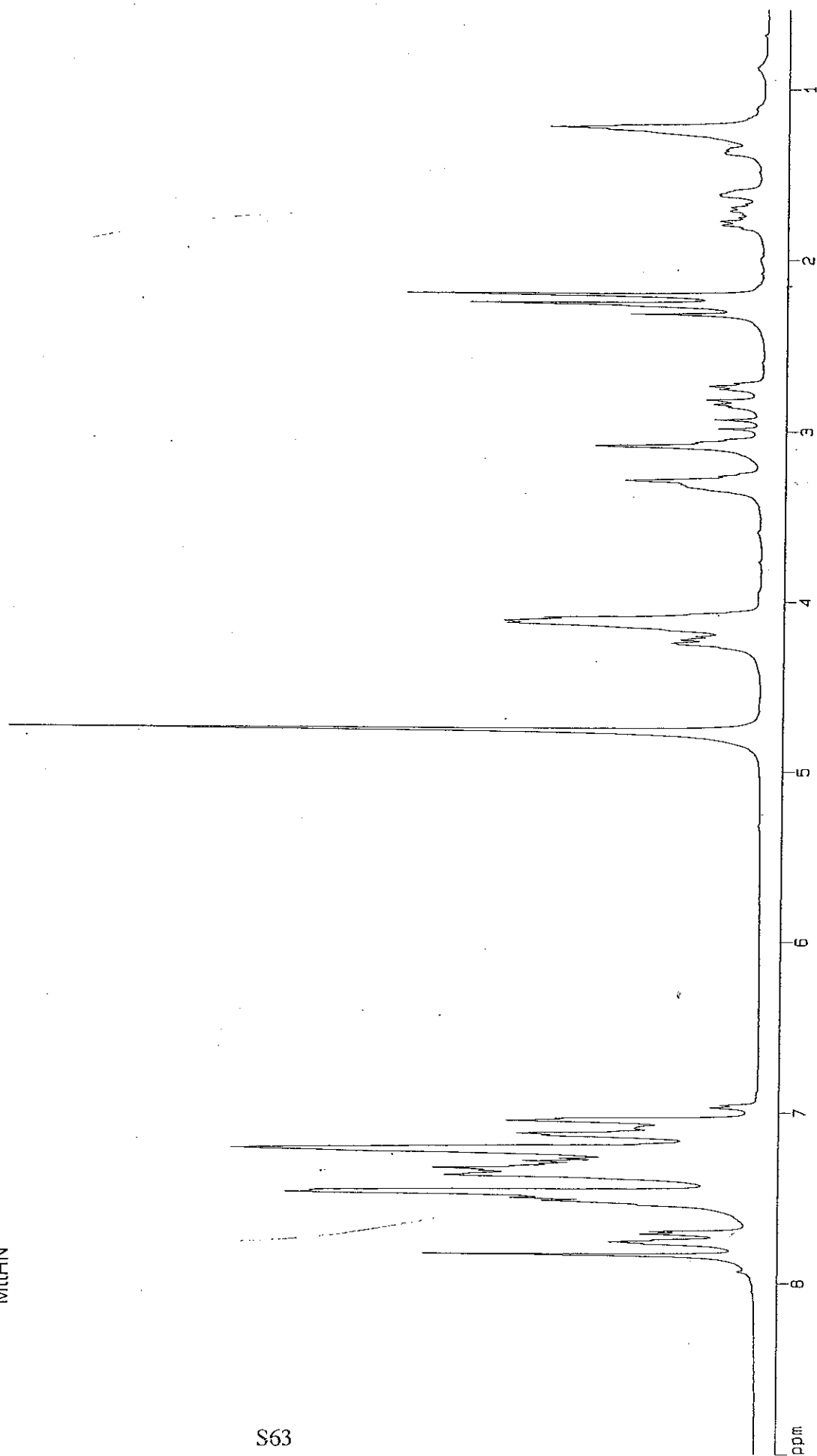
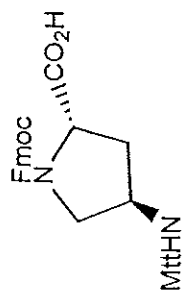
35, ^{13}C NMR, CDCl_3



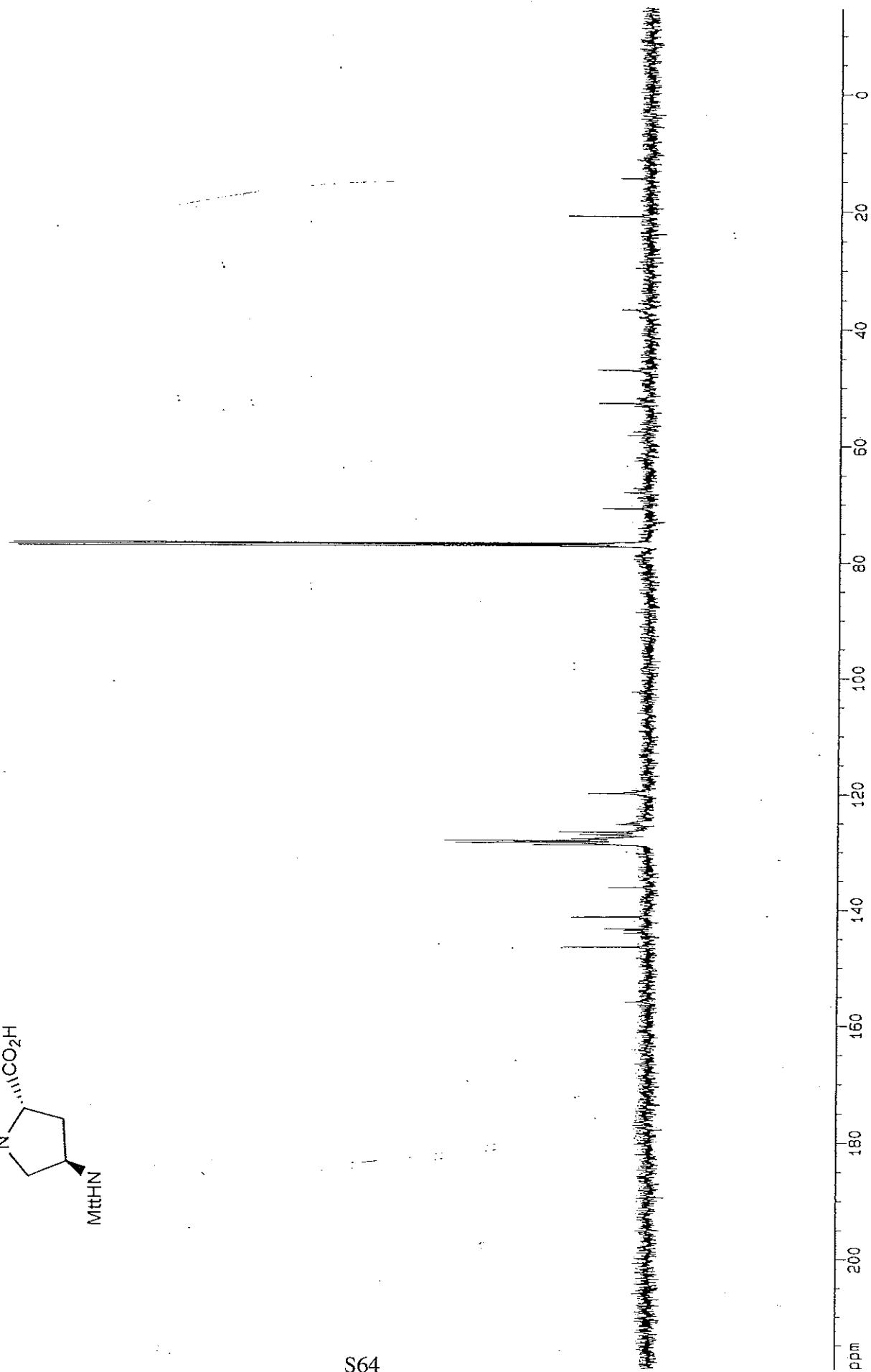
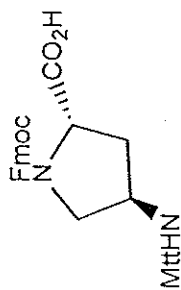
S62



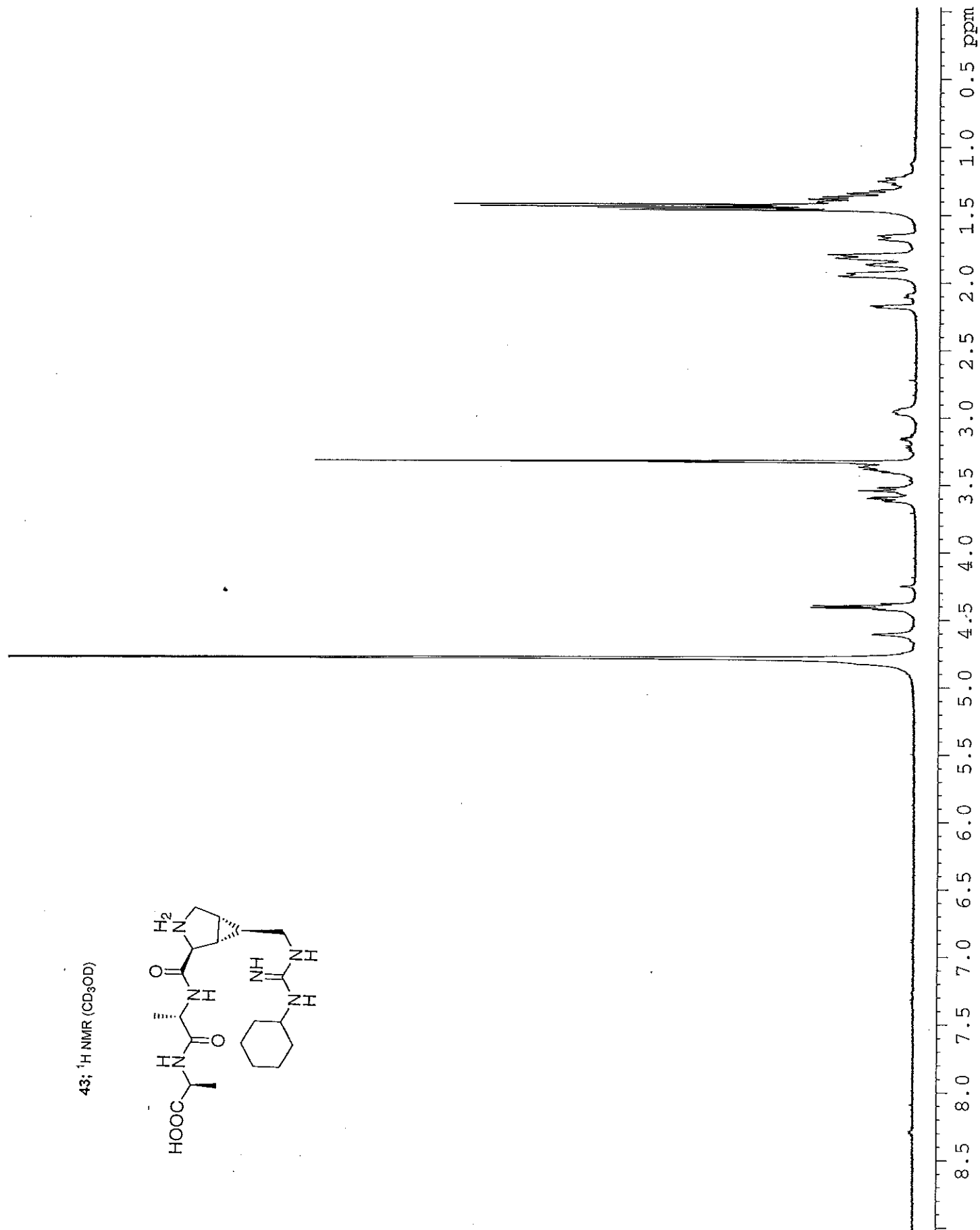
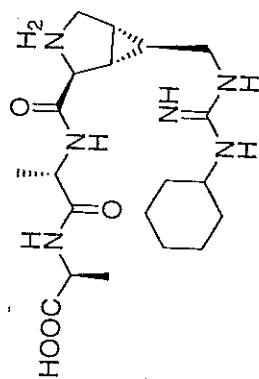
37, ^1H NMR, $\text{CD}_3\text{OD} + \text{CDCl}_3$



37, ^{13}C NMR, $\text{CD}_3\text{OD} + \text{CDCl}_3$



43; ^1H NMR (CD_3OD)



PEC: cd031804 (18-MAR-02)

Samp: sf-6-132

Comm: scan 250 2000 2s

Oper: MJennings

Base: 423.33

Peak: 1000.0 mmu

REG #9 @ 1.10 min (ESI +QIMS LMR UP LR) (/31<41 -/2<12)

Study : lcms

Masses: 100.00 > 1000.04

Intensity: 4262772

43; MS (ESI)

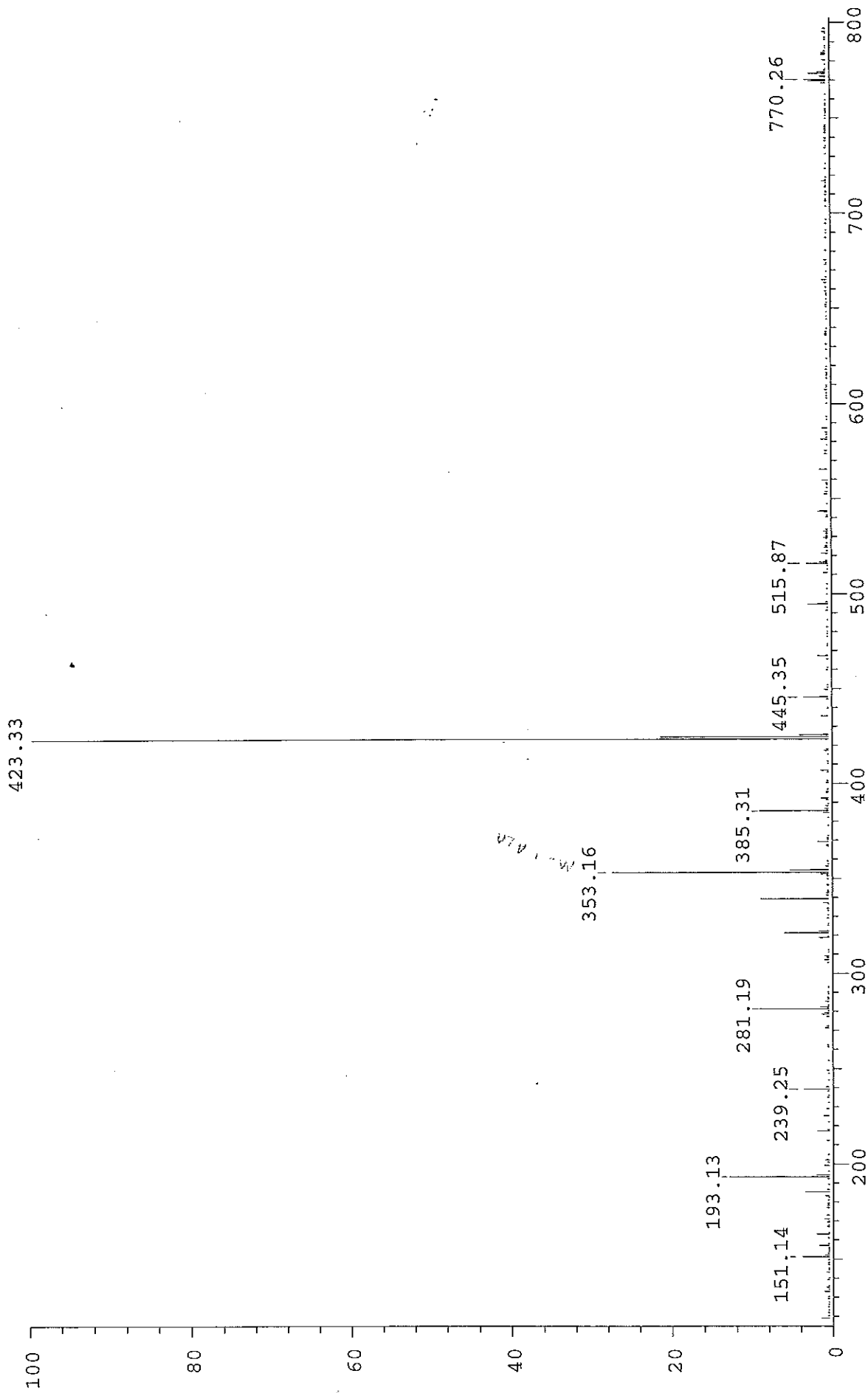
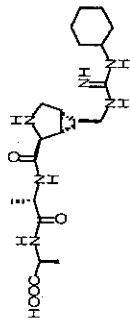
Scans : 1 > 111

Client:

#Peaks: 498

RIC : 13920542

4.3E+06

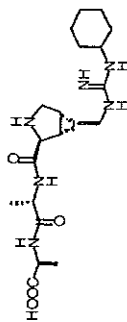


SF-6-132-2 (0.019) Is (1.00,1.00) C20H35O4N6

423.2720

Theoretical $[M+H]^+$

TOF MS ES+
7.73e12



43; HRMS

%

S67

SF-6-132-2 15 (0.275) AM (Cen.3, 80.00, Ht.8000.0, 413.27, 1.00); Sm (SG, 2x3.00); Cm (13:15)

423.2714

KX4

TOF MS ES+
414

Acceptable = 2.1 mmu
Observed Δ = 0.6 mmu

%

cal.

413.1838

414.2752

419.3206

424.2751

425.2826

429.2478

432.2817

433.2892

437.2356

440.3103

445.2562

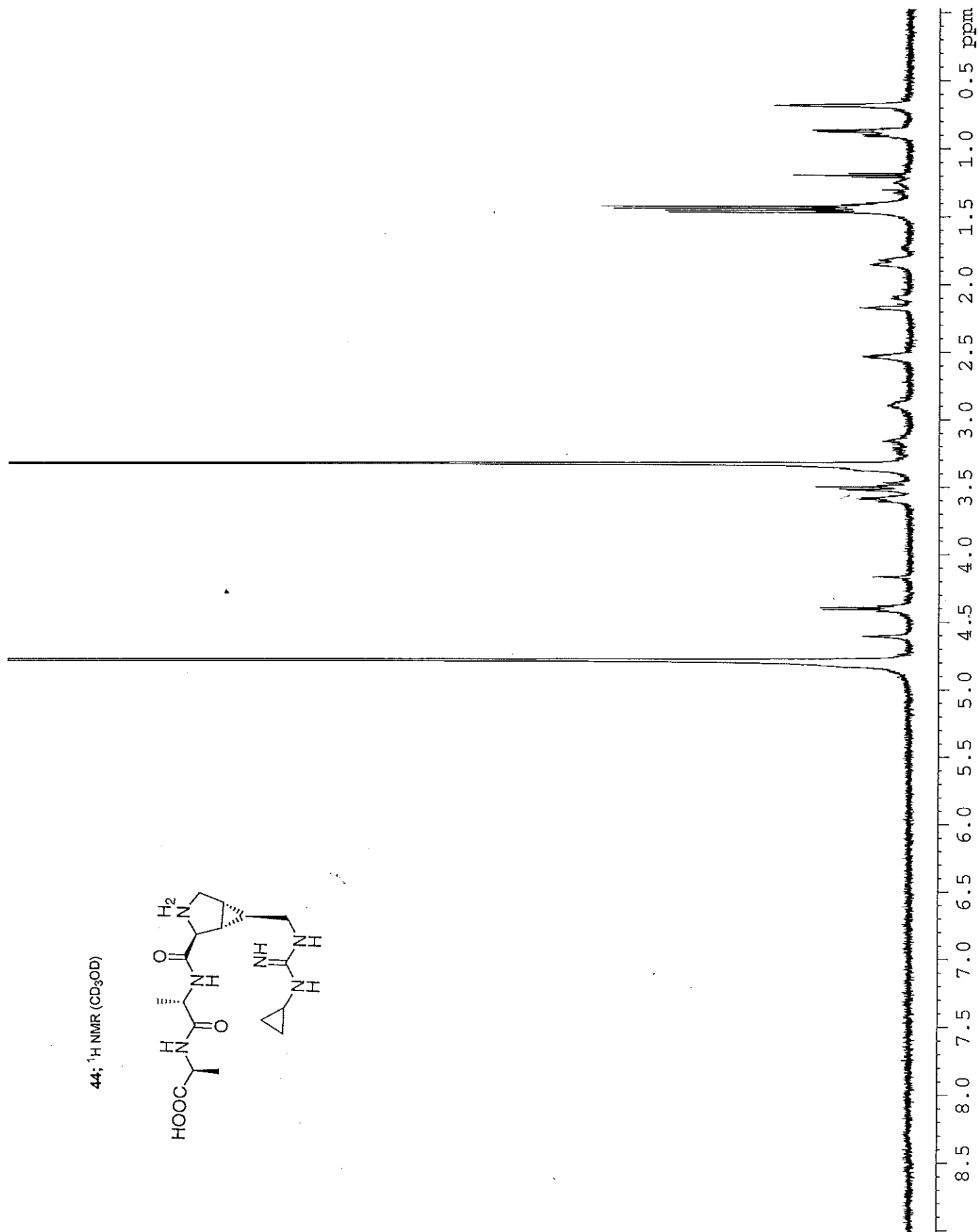
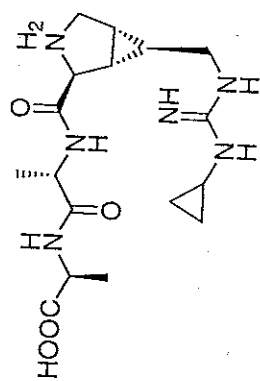
446.2761

449.3526

m/z

450

44; ^1H NMR (CD_3OD)



SC: cd031807 (18-MAR-02)

Samp: sf-6-135

Comm: scan 250 1000 2s

Oper: MJennings

Base: 381.18

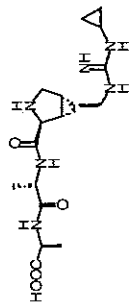
Peak: 1000.0 mmu

Study: lcms

Masses: 100.00 > 1000.04

Intensity: 496229

REG #9 @ 1.13 min (ESI +Q1MS LMR UP LR) (/32<42 -/6<16)



44; MS (ESI)

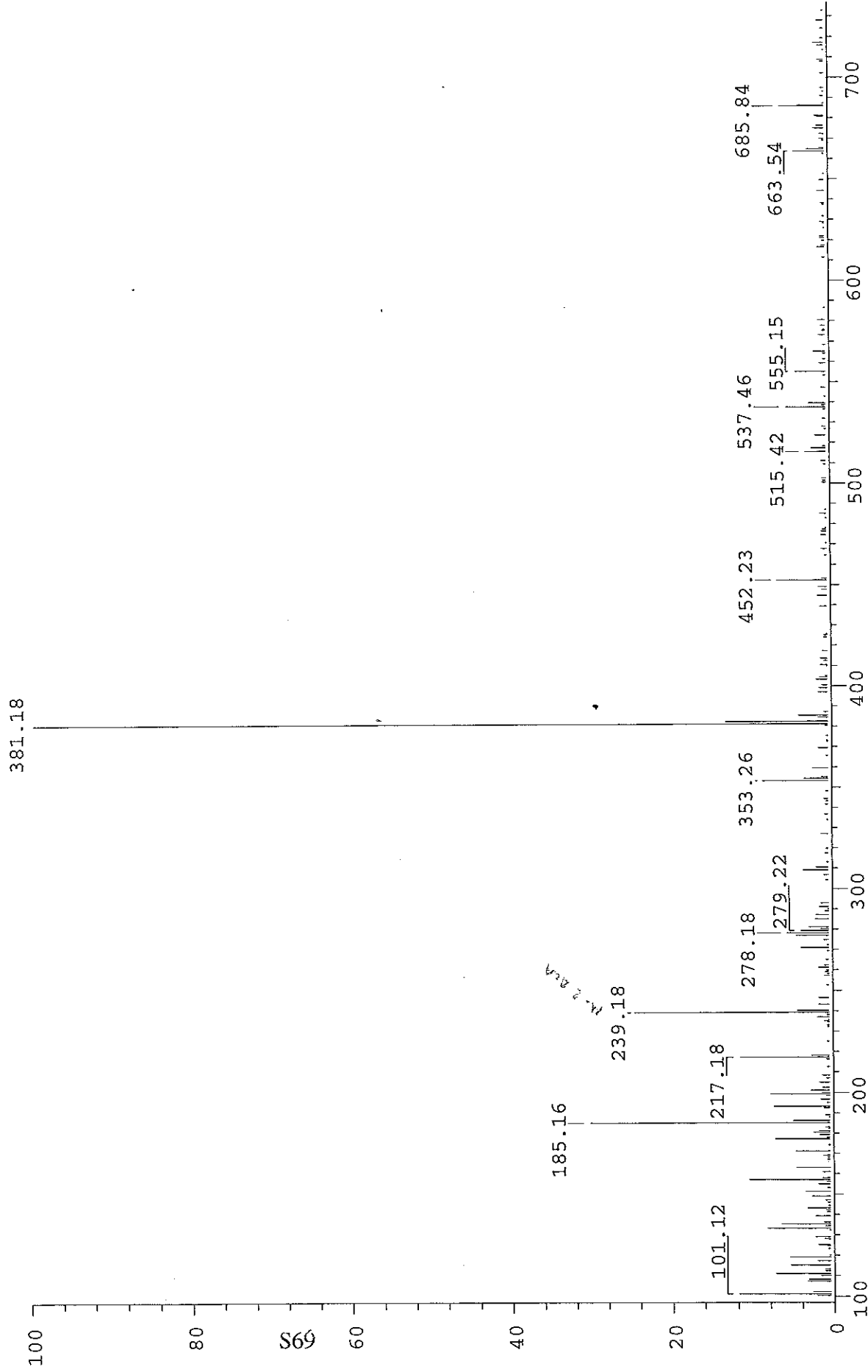
Scans : 1 > 172

Client:

#Peaks: 378

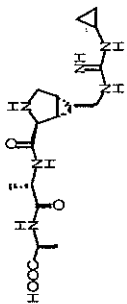
RIC : 2601335

5.0E+05



SF-6-135-1 (0.019) Is (1.00,1.00) C17H29O4N6

TOF MS ES+
7.99e12



44; HRMS

381.2250

Theoretical [M+H]⁺

382.2278

383.2302

SF-6-135-1 34 (0.624) AM (Cen, 3, 80.00, Ht, 8000.0, 349.18, 1.00); Sm (SG, 2x3.00); Cm (34:36)

TOF MS ES+
249

381.2250

*Acceptable = 1.9 m.u.
Observed Δ = 0*

382.2282

383.2302

349.1838

393.2141

345.2302

381.0965

350.1888

403.2141

371.0616

358.2363

407.1187

356.2668

391.2878

m/z

405

400

395

390

385

380

375

370

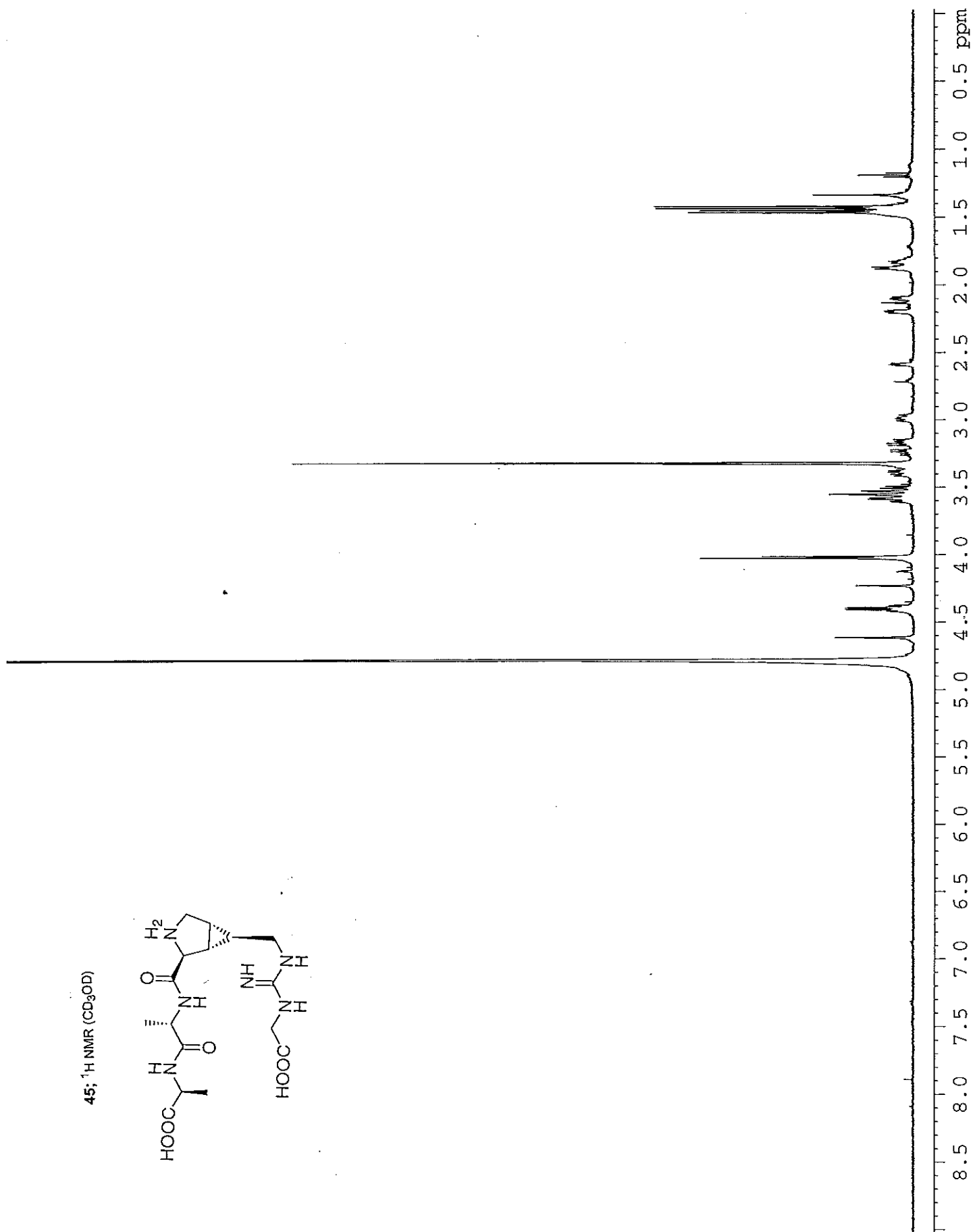
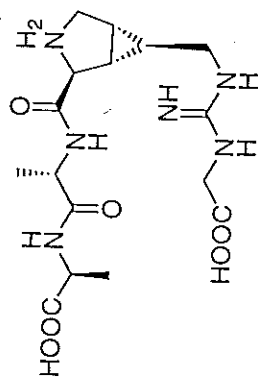
365

360

355

350

45; ^1H NMR (CD_3OD)



C: cd0322208

Sample: sf-6-133.1

Comm: Scan 100 1000 2s

Oper: MJennings

Base: 399.20

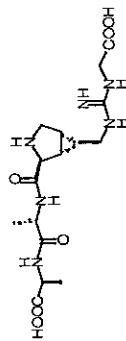
Peak: 1000.0 mmu

REG #9 @ 6.24 min (ESI +Q3MS LMR UP LR) (/181<194 -/120<130)

Study : ESI-MS, pos ion

Masses: 100.00 > 2000.02

Intensity: 35897



45; MS (ESI)

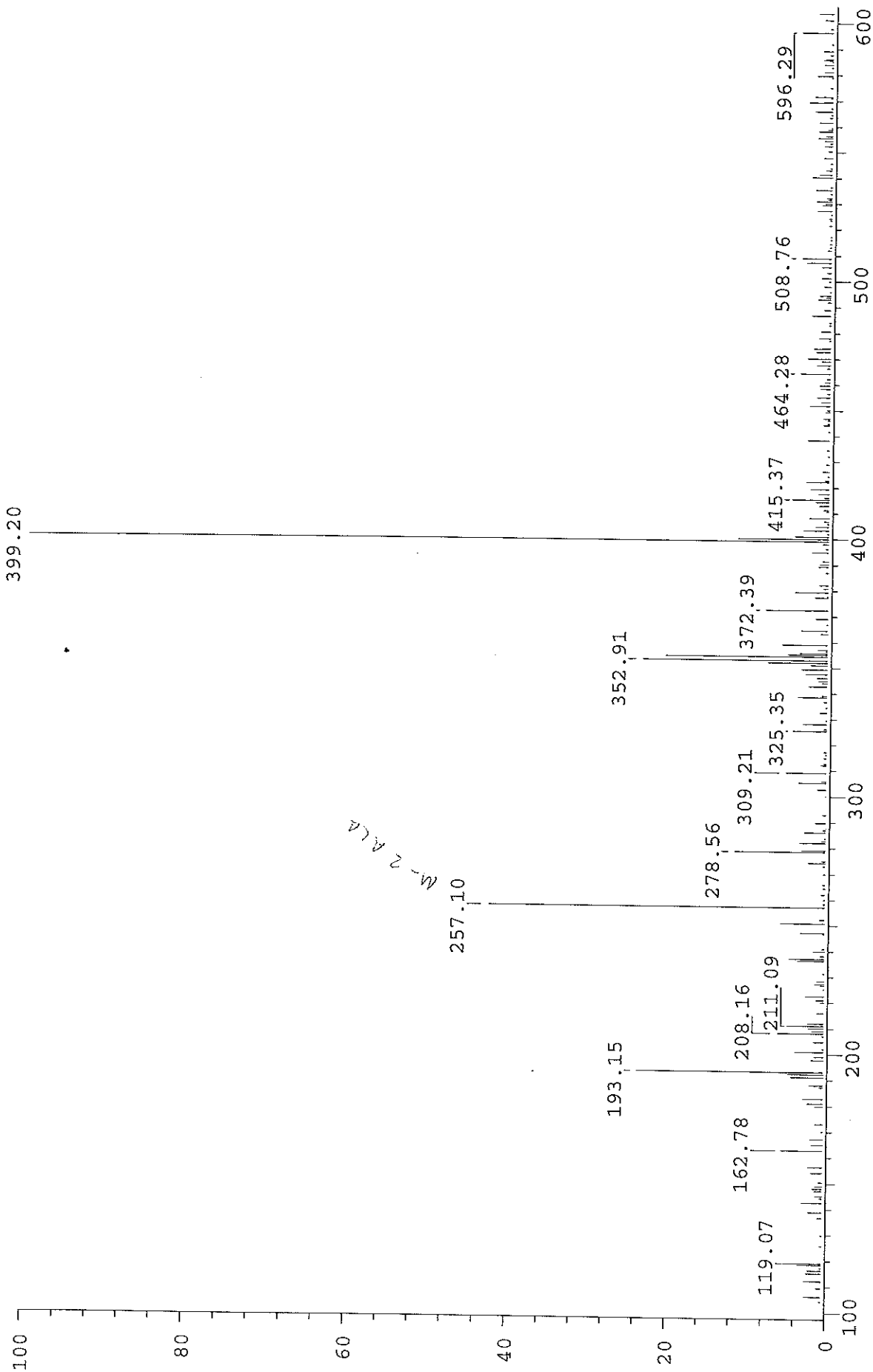
Scans : 1 > 206

Client: Steve Flemer

#Peaks: 1053

RIC : 308300

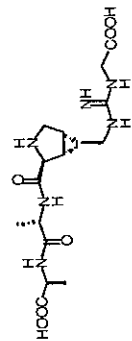
3.6E+04



S72

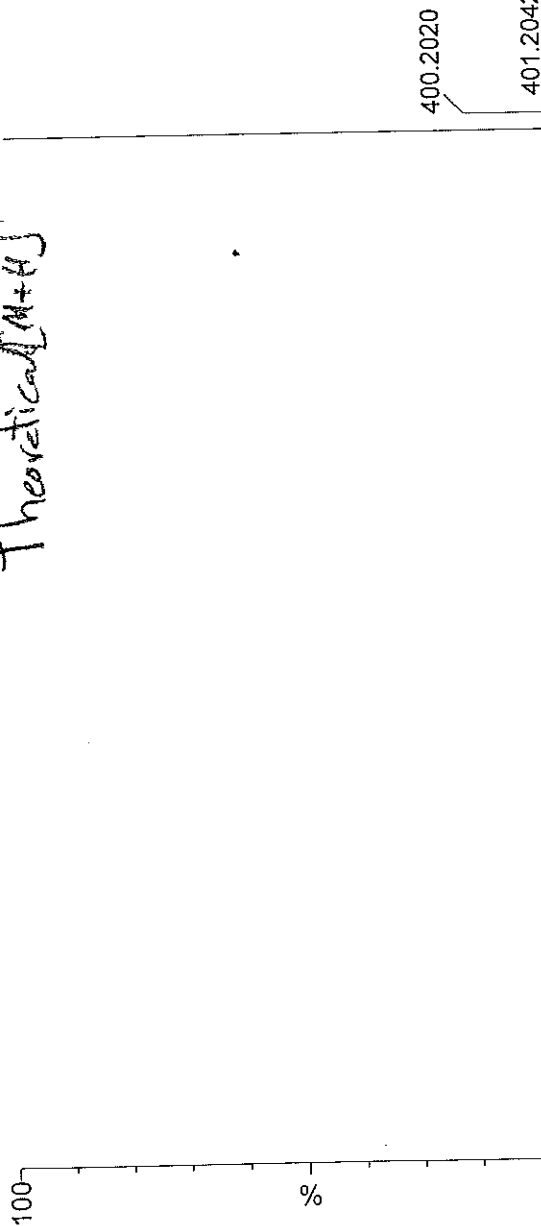
TOF MS ES+
8.05e12

SF-6-194-1 (0.019) Is (1.00, 1.00) C16H27O6N6



45; HRMS

Theoretical [M+H]⁺ 399.1992



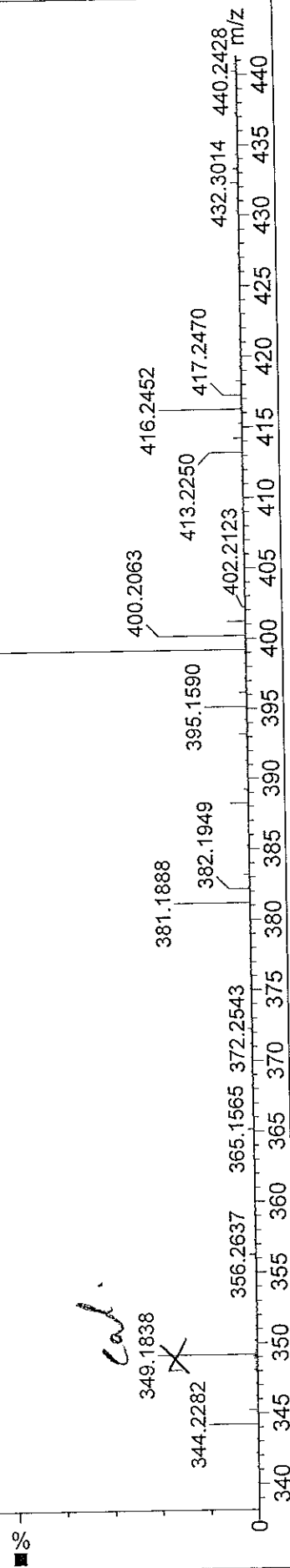
SF-6-194-1 38 (0.697) AM (Cen, 3, 80.00, Ht, 8000.0, 349.18, 1.00); Sm (SG, 2x3.00); Cm (38;40)

399.2004

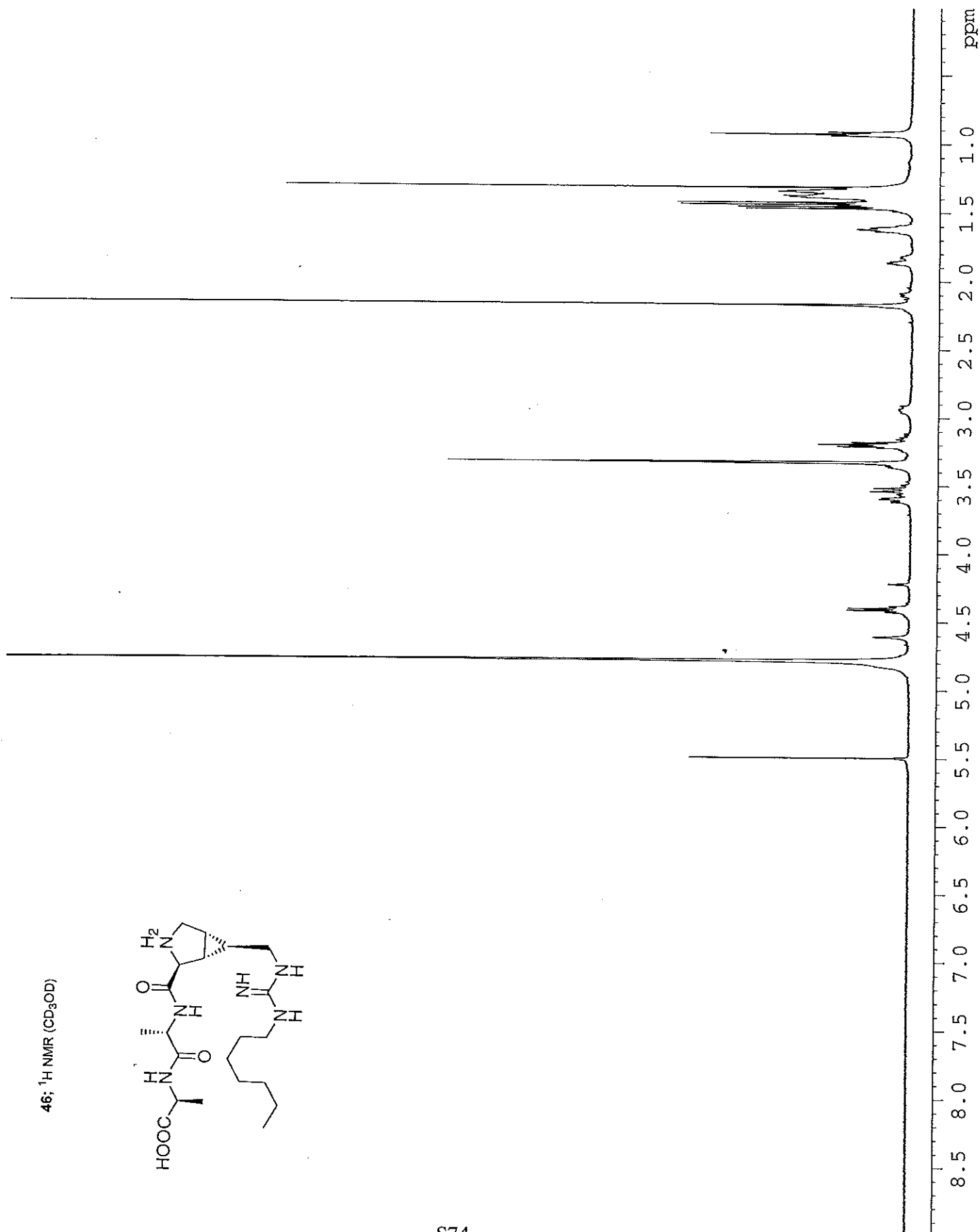
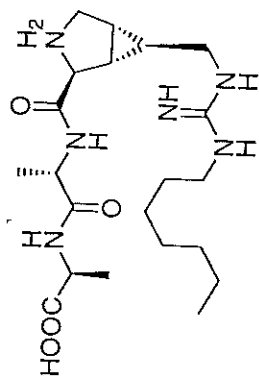
K X6

*Acceptable = 2.0 mmu
Observed Δ = 1.2 mmu*

TOF MS ES+
1.35e3



46; ^1H NMR (CD_3OD)



cd032202 (22-MAR-02)

sf-6-138

Comm: Scan 100 1000 2s

Oper: MJennings

Base: 439.24

Peak: 1000.0 mmu

REG #9 @ 1.55 min (ESI +Q3MS LMR UP LR) (/44<57 -/9<20)

Study : ESI-MS, pos ion

Masses: 100.00 > 1000.04

Intensity: 127053

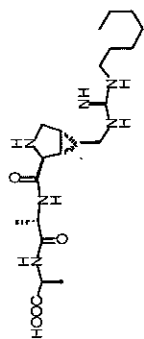
Scans : 1 > 68

Client: Steve Flemer

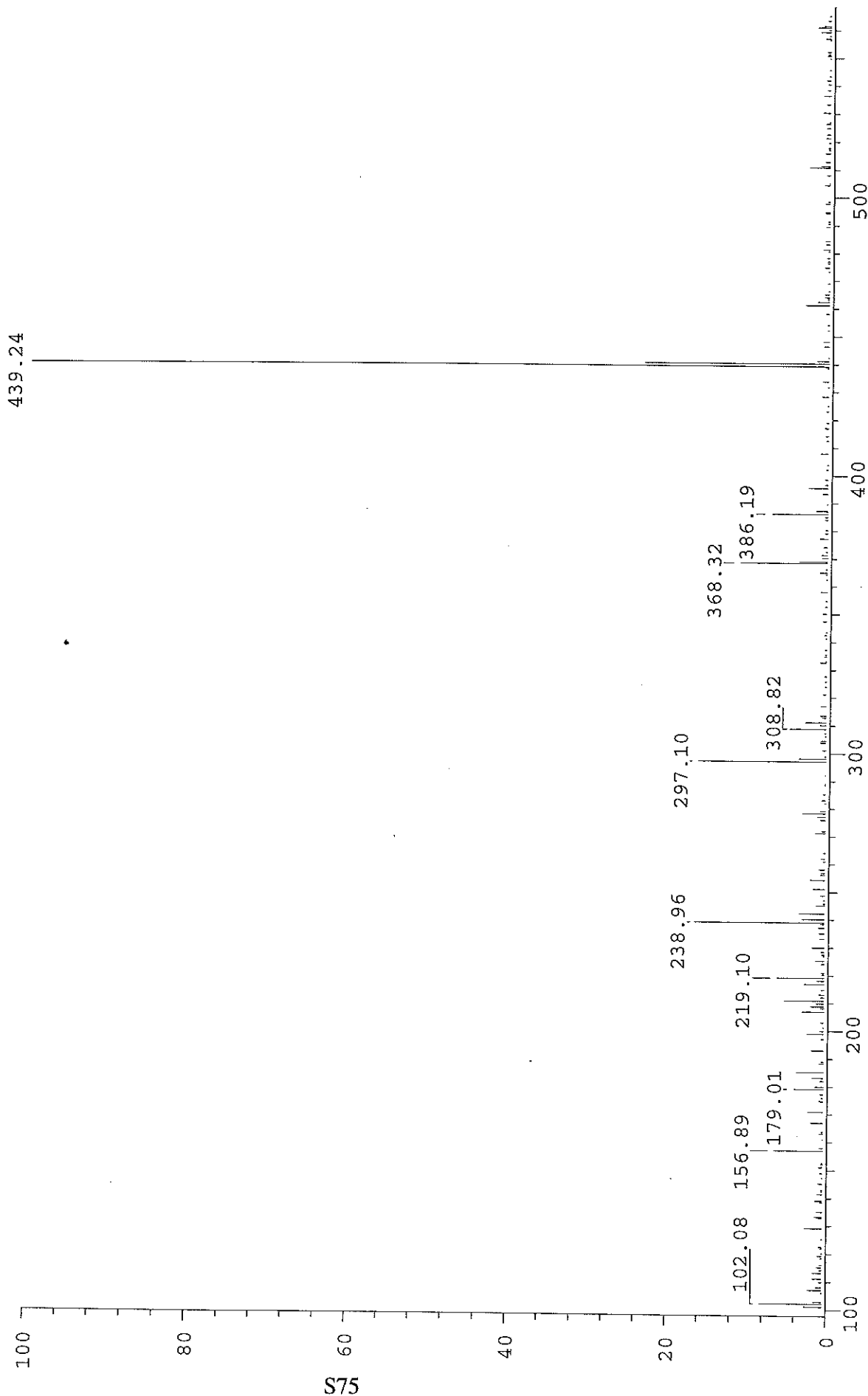
#Peaks: 495

RIC : 500555

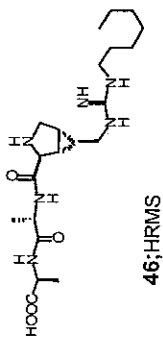
1.3E+05



46; MS (ESI)



TOF MS ES+
7.64e12



SF-6-138-1 (0.019) Is (1.00, 1.00) C21H39O4N6

Theoretical [M+H]⁺

439.3033

440.3062

441.3087

TOF MS ES+
418

SF-6-138-1 41 (0.752) AM (Cen. 3, 80.00, Ht. 8000.0, 413.27, 1.00); Sm (SG, 2x3.00); Cm (41.45)

*Acceptable = 2.2 mm
observed Δ = 0.1 mm*

439.3034

440.3072

413.2667

409.1854

413.3065

417.1884

423.1912

432.2778

437.2397

446.2614

447.2347

453.2157

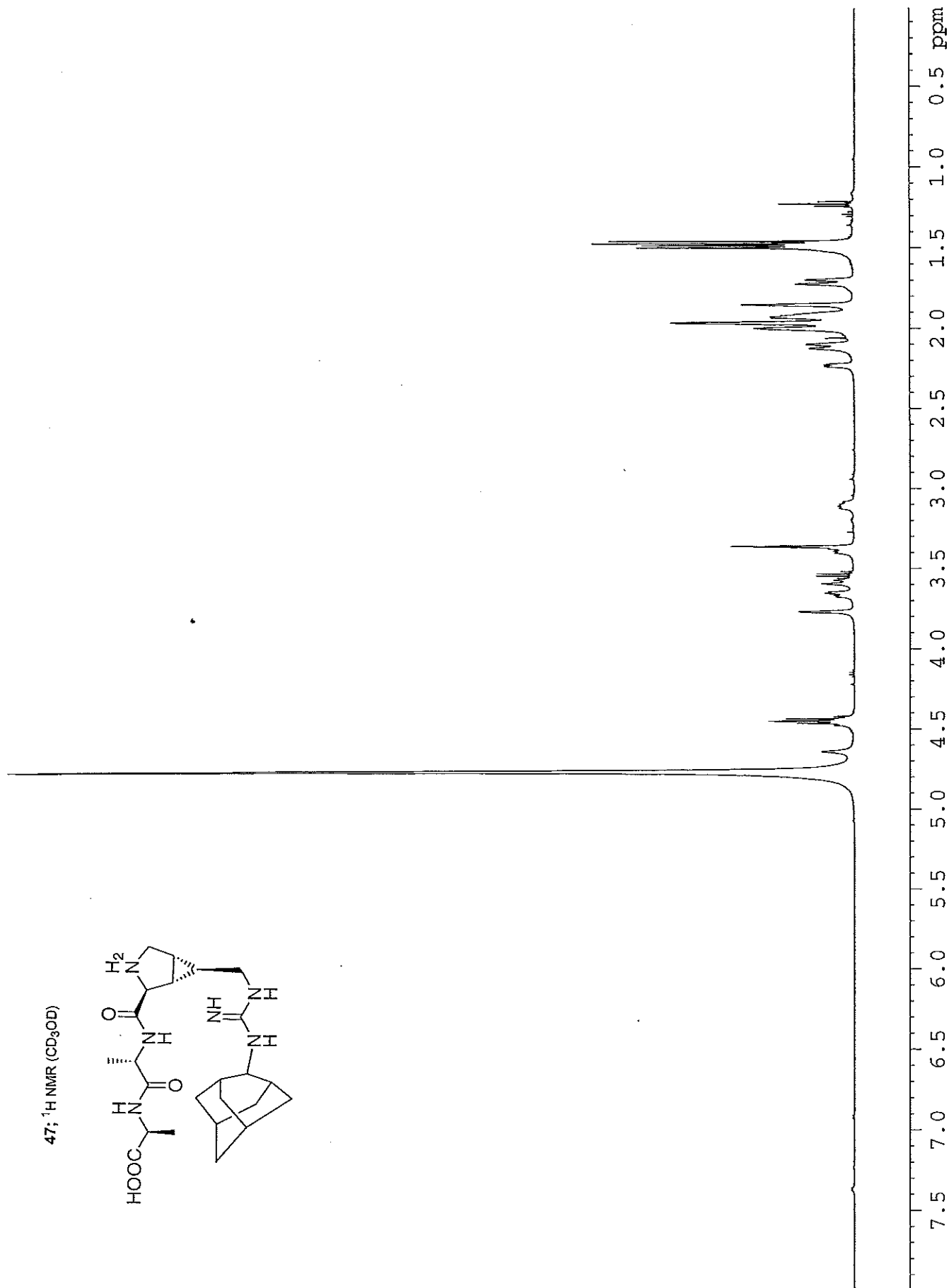
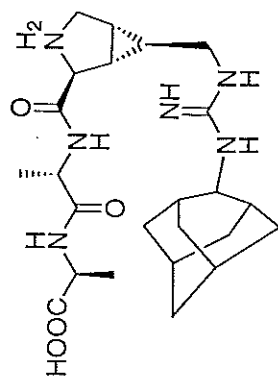
456.3360

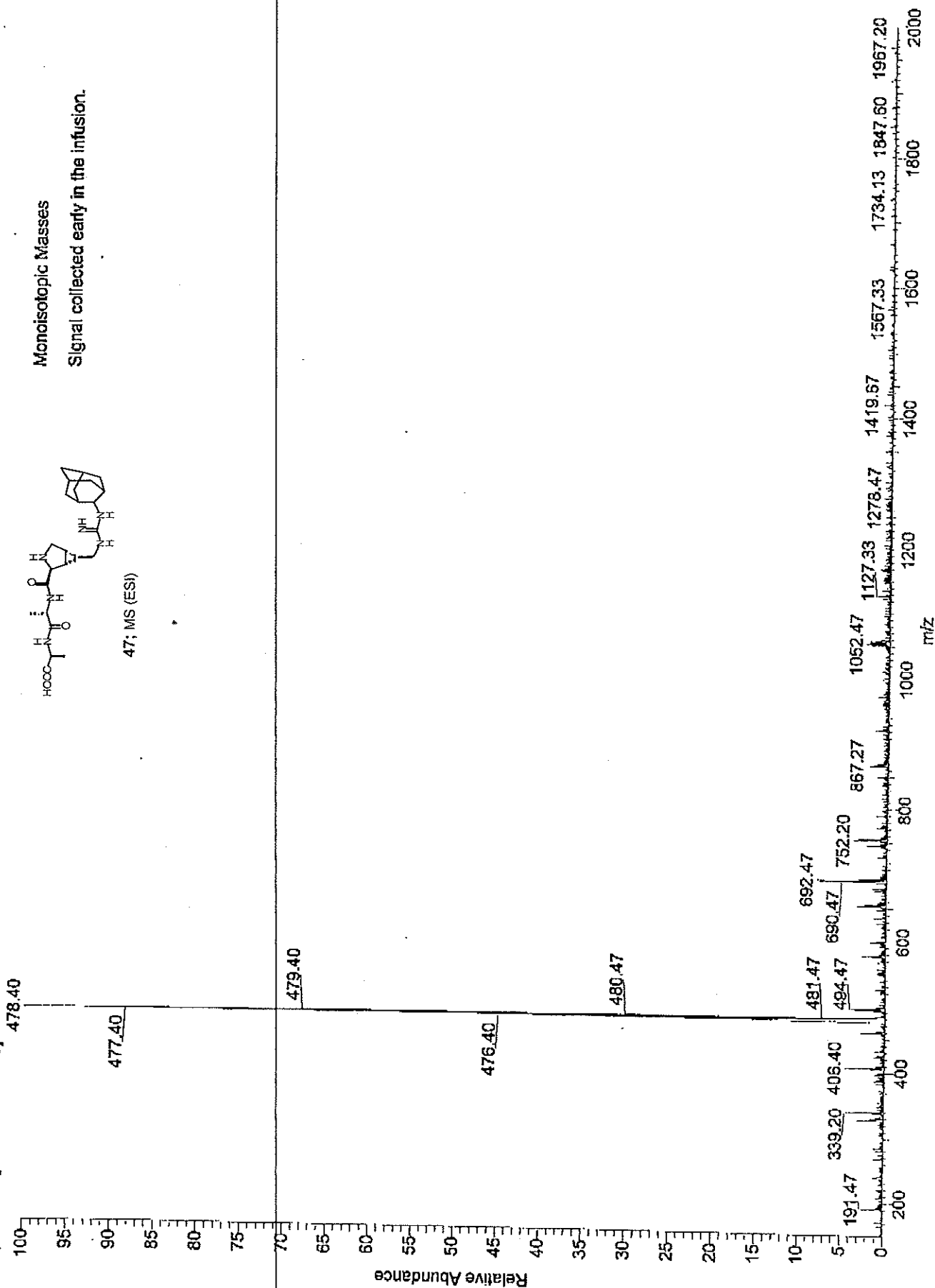
461.2860

467.3678

m/z

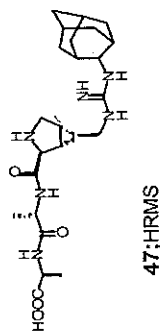
47; ^1H NMR (CD_3OD)



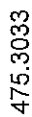


SF-6-176-2 (0.019) Is (1.00,1.00) C24H39O4N6

TOF MS ES+
7.39e12



Theoretical $[M+H]^+$



476.3062

477.3089

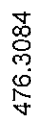
S79

SF-6-176-2 36 (0.660) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (36:39)

TOF MS ES+
419

475.3035

Acceptable = 2-4 mm
Observed = 40.2 mm



413.2667

296

1
 2
 3
 4
 5
 6
 7

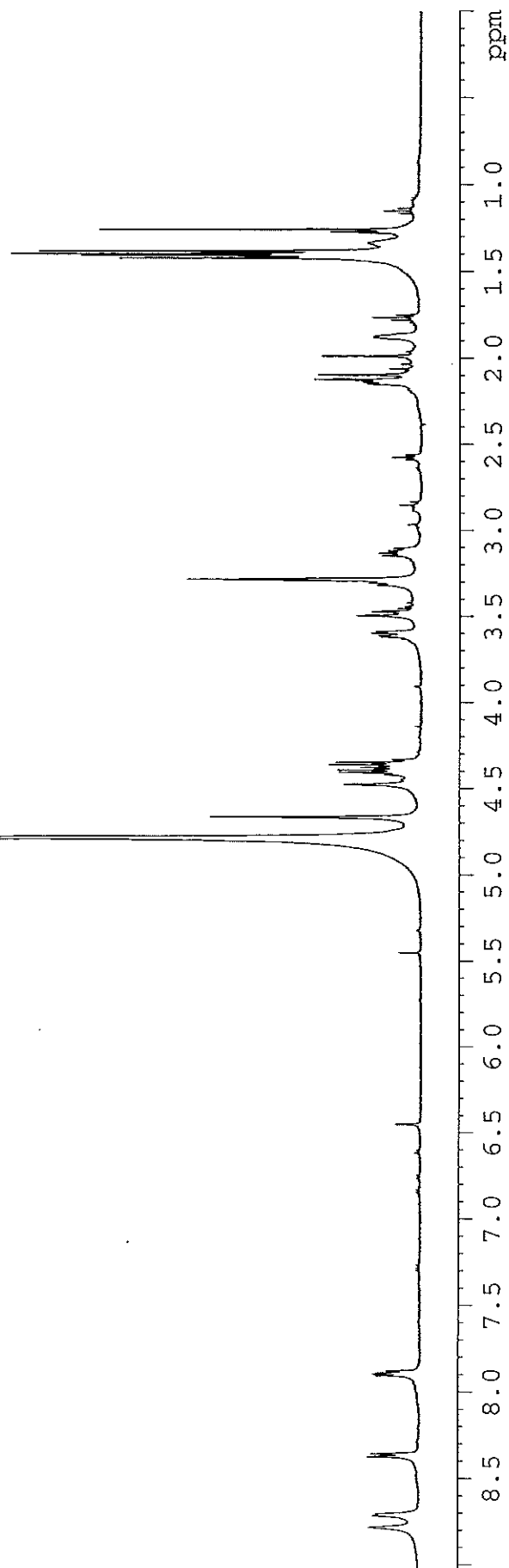
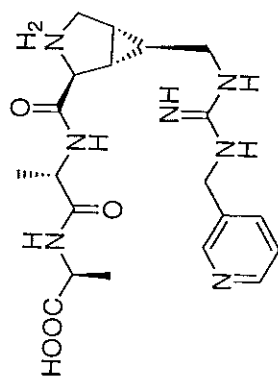
1
2
3
4
5

74

3

④

48; ^1H NMR (CD_3OD)

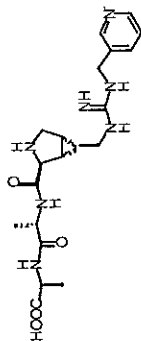


6-179-1 (0.019) Is (1.00,1.00) C20H30O4N7

Theoretical $[M+H]^+$

432.2359

TOF MS ES+
7.70e12



433.2387

434.2412

6-179-1 28 (0.514) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (28:30)

x 4

432.2368

Acceptable = 2.2 m.u.

observed $\Delta = 0.9$ m.u.

TOF MS ES+
355

cal.
413.2667

449.2718

433.2402

409.1868

417.1389 419.3364 427.2591 431.2427

434.2468

446.2563

450.2728

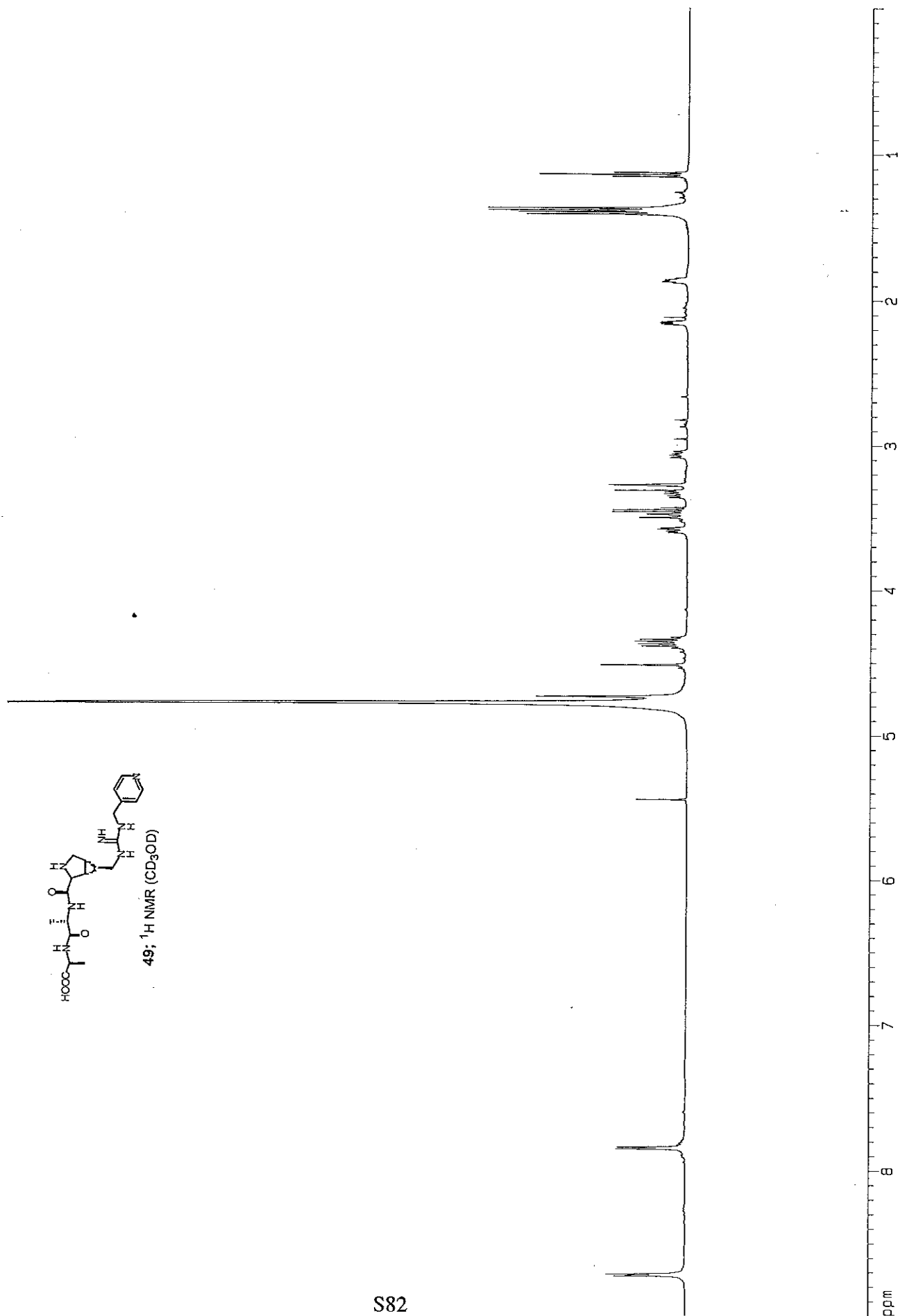
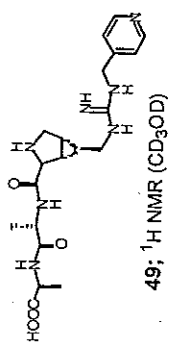
454.2191

455.2367

463.3028

469.3264

m/z

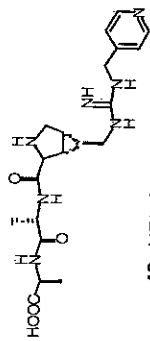


SF-6-187-1 (0.019) Is (1.00,1.00) C20H30O4N7

432.2359

Theoretical $[M+H]^+$

TOF MS ES+
7.70e12



433.2387

434.2412

433.2372

SF-6-187-1 33 (0.605) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (33:35)

TOF MS ES+
292

434.2437

Acceptable = 2.2 mmu
Observed Δ = 0.3 mmu

432.2356

Cal.

431.2361

409.1814 413.2667 417.2541

427.2689

447.2412 450.2730

446.2460

435.2488

436.2548

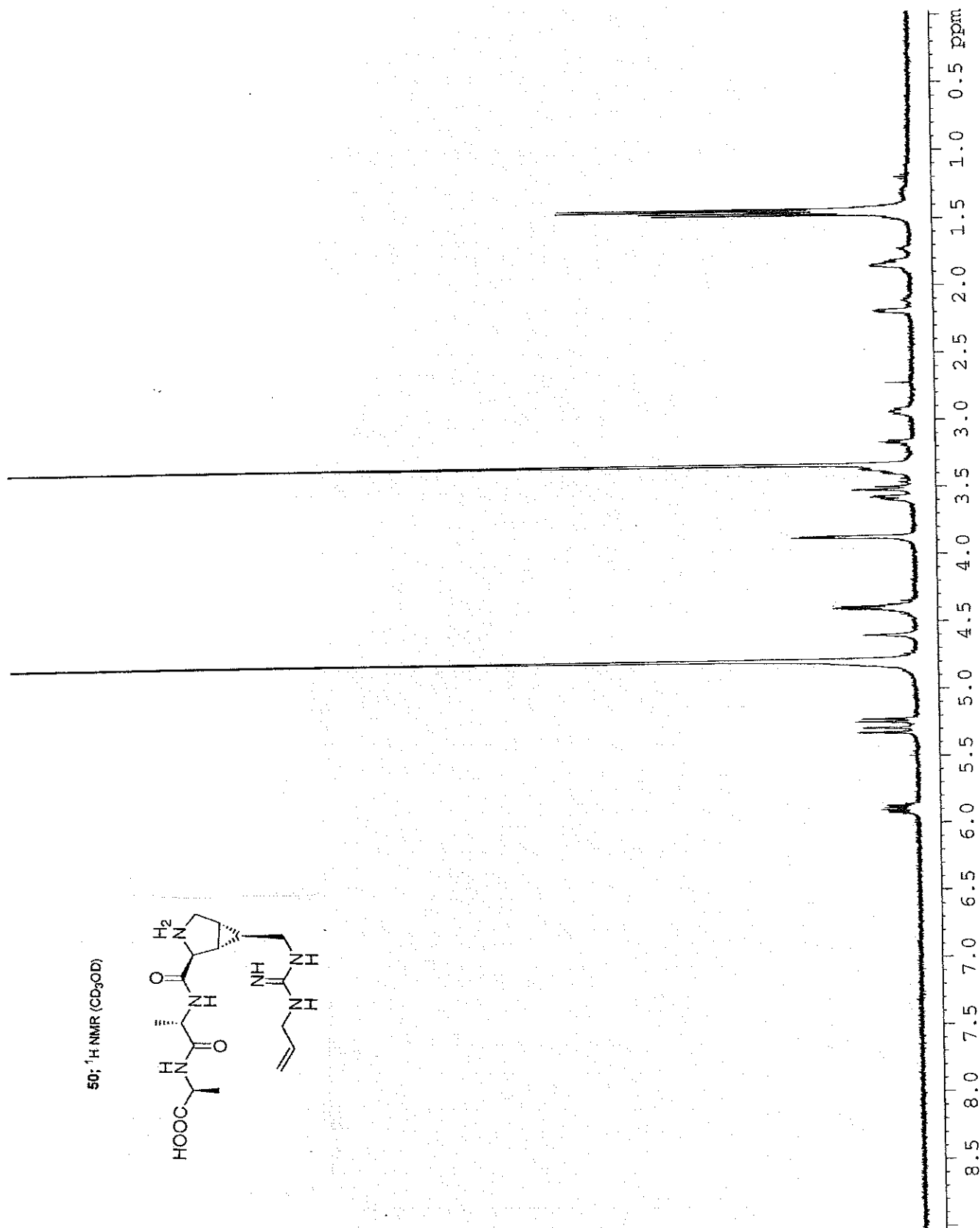
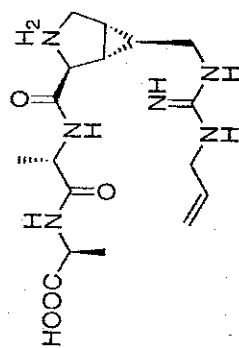
452.2789

456.2326

464.2625 465.6891

m/z

50, ¹H NMR (CD₃OD)



cd031806 (18-MAR-02)

Op: sf-6-134

Comm: scan 250 1000 2s

Oper: MJennings

Base: 381.22

Peak: 1000.0 mnu

REG #9 @ 1.09 min (ESI +QIMS LMR UP LR) (/31<41 -/5<15)

Study : lcms

Masses: 100.00 > 1000.04

Intensity: 1325246

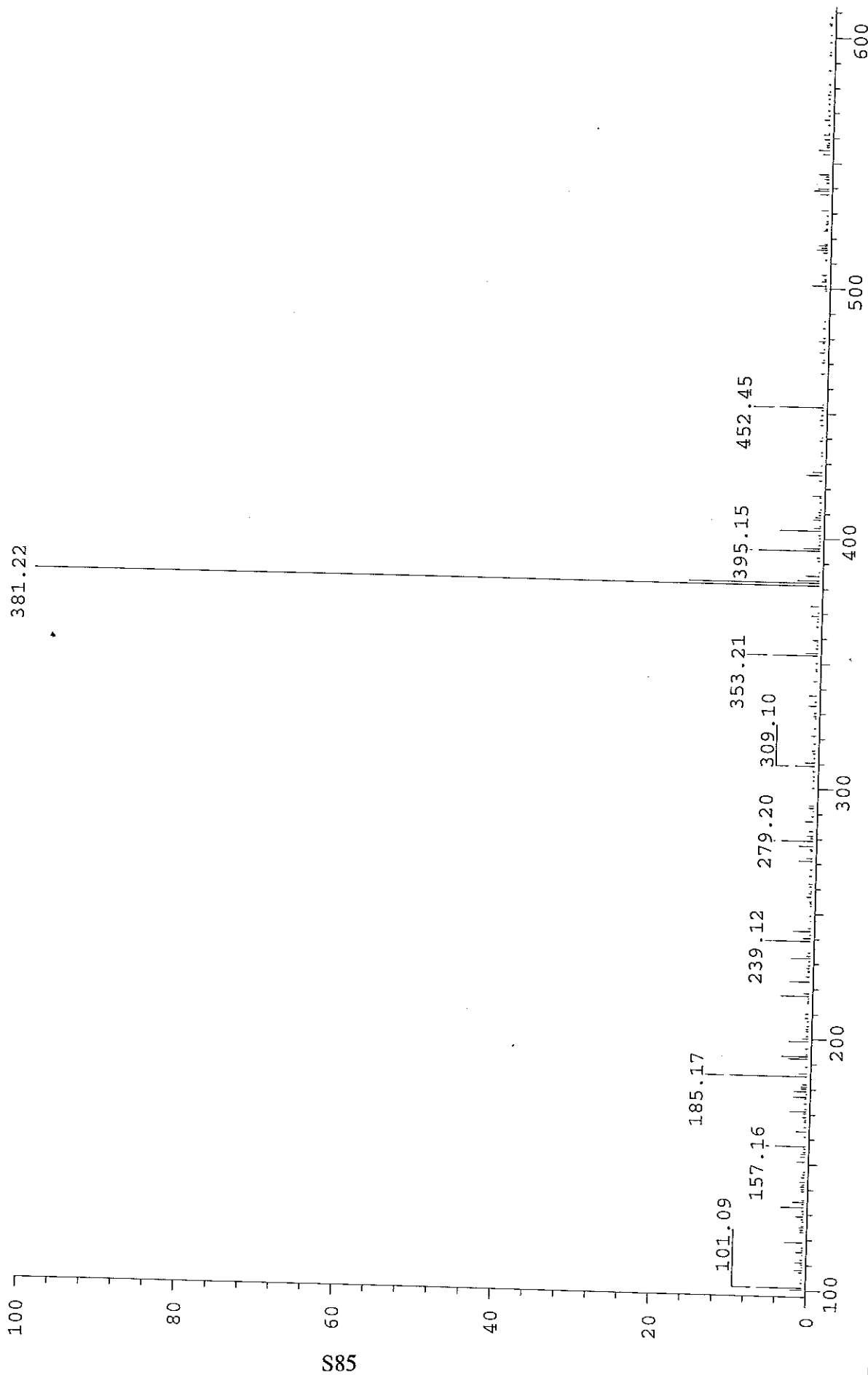
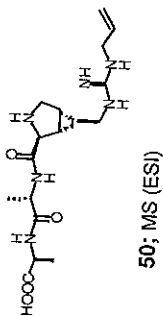
Scans : 1 > 176

Client:

#Peaks: 522

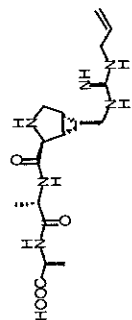
RIC : 4573387

1.3E+06



SF-6-134-2 (0.019) Is (1.00,1.00) C17H29O4N6

TOF MS ES+
7.99e12



Theoretical [M+H]⁺

381.2250

382.2278

383.2302

586

SF-6-134-2 24 (0.440) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (24:27)

TOF MS ES+
465

381.2246

4x2

Acceptable 1.9 mmu

observed 1 = 0.4 mmu

%

413.2667

403.2074

382.2303

393.2102

352.2469

365.1588

360.3245

367.1656

377.1924

388.2557

393.2955

404.2080

414.2679

417.1359

423.2735

427.2578

m/z

425

420

415

410

405

400

395

390

385

380

375

370

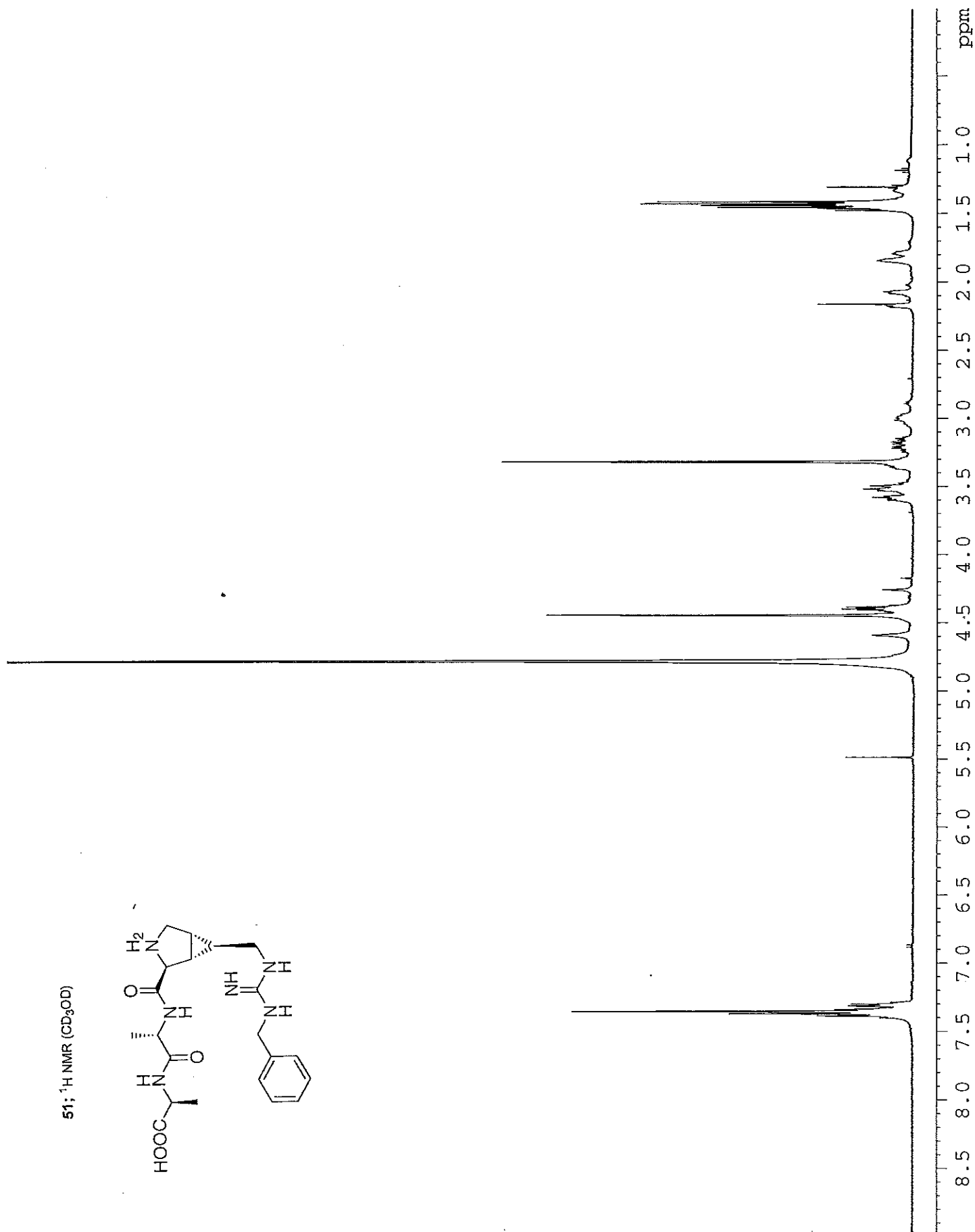
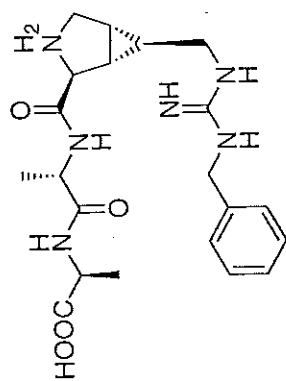
365

360

355

cal.

51; ^1H NMR (CD_3OD)



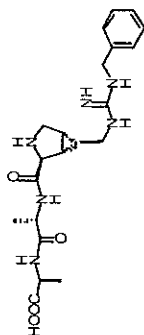
cd0322205
mp: sf-6-139
Comm: Scan 100 1000 2s
Oper: MJennings
Base: 431.12
Peak: 1000.0 mmu

Study : ESI-MS, pos ion
Masses: 100.00 > 2000.02
Intensity: 134343
REG #9 @ 1.14 min (ESI +Q3MS LMR UP LR) (/32<52 -/6<16)

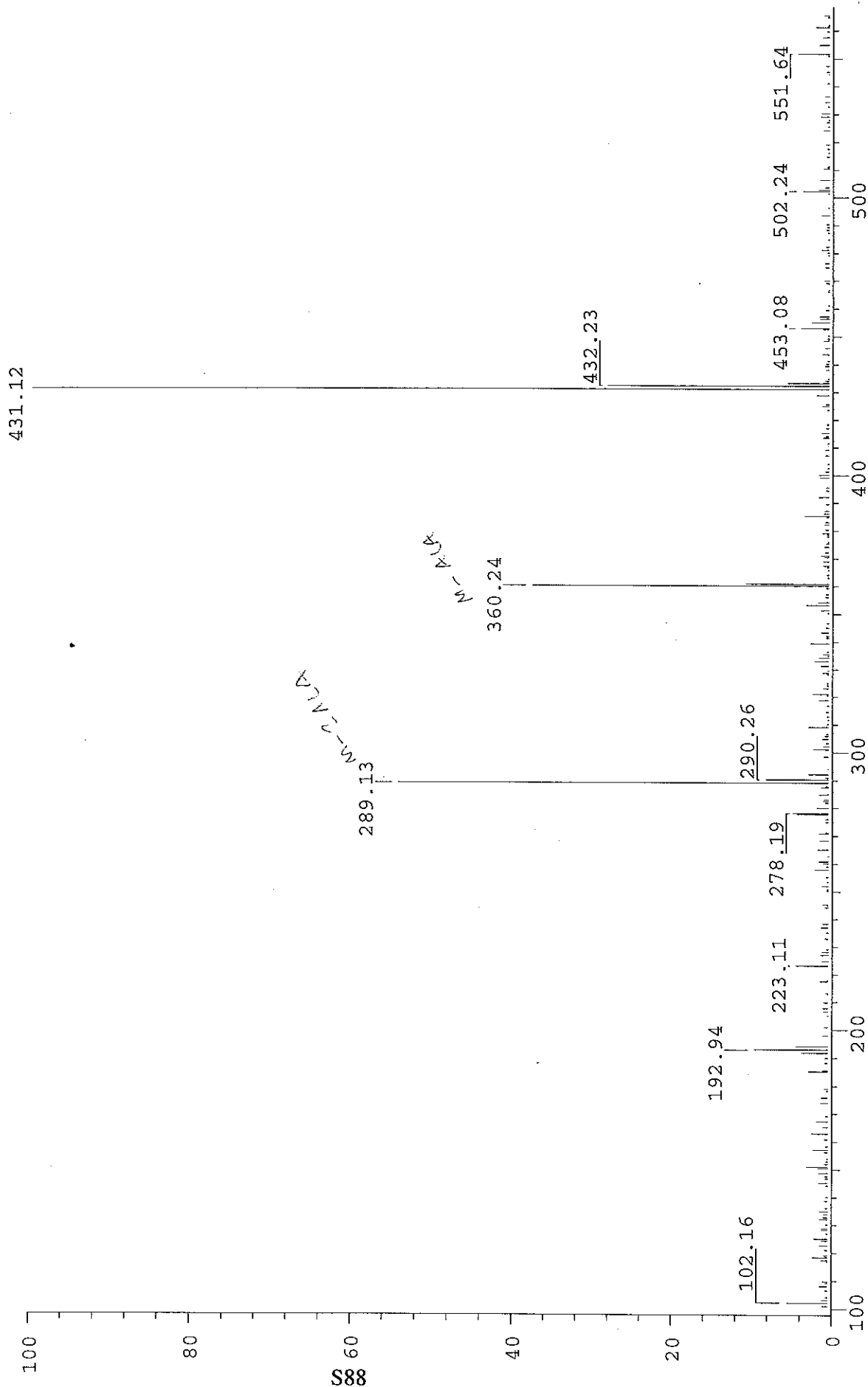
Scans : 1 > 79

Client: Steve Flemer
#Peaks: 1014
RIC : 709811

1.3E+05

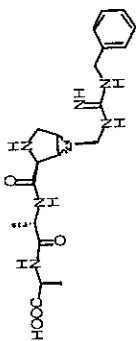


51; MS (ESI)



SF-6-192-2 (0.019) Is (1.00,1.00) C21H31O4N6

TOF MS ES+
7.65e12



Theoretical [M+H]⁺

431.2407

432.2436

433.2461

SF-6-192-2 32 (0.587) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (32:34)

431.2421

*Acceptable = 2.2 mmu
observed Δ = 1.4 mmu*

TOF MS ES+
186

432.2514

448.2771

449.2819

445.2460

433.2473

455.2300

469.3006

476.3059

489.2067

497.2172

m/z

490

485

480

475

470

465

460

455

450

445

440

435

430

425

420

415

410

405

400

cal.

413.2667

413.3174

424.2925

433.2473

449.2819

455.2300

469.3006

476.3059

489.2067

497.2172

m/z

490

485

480

475

470

465

460

455

450

445

440

435

430

425

420

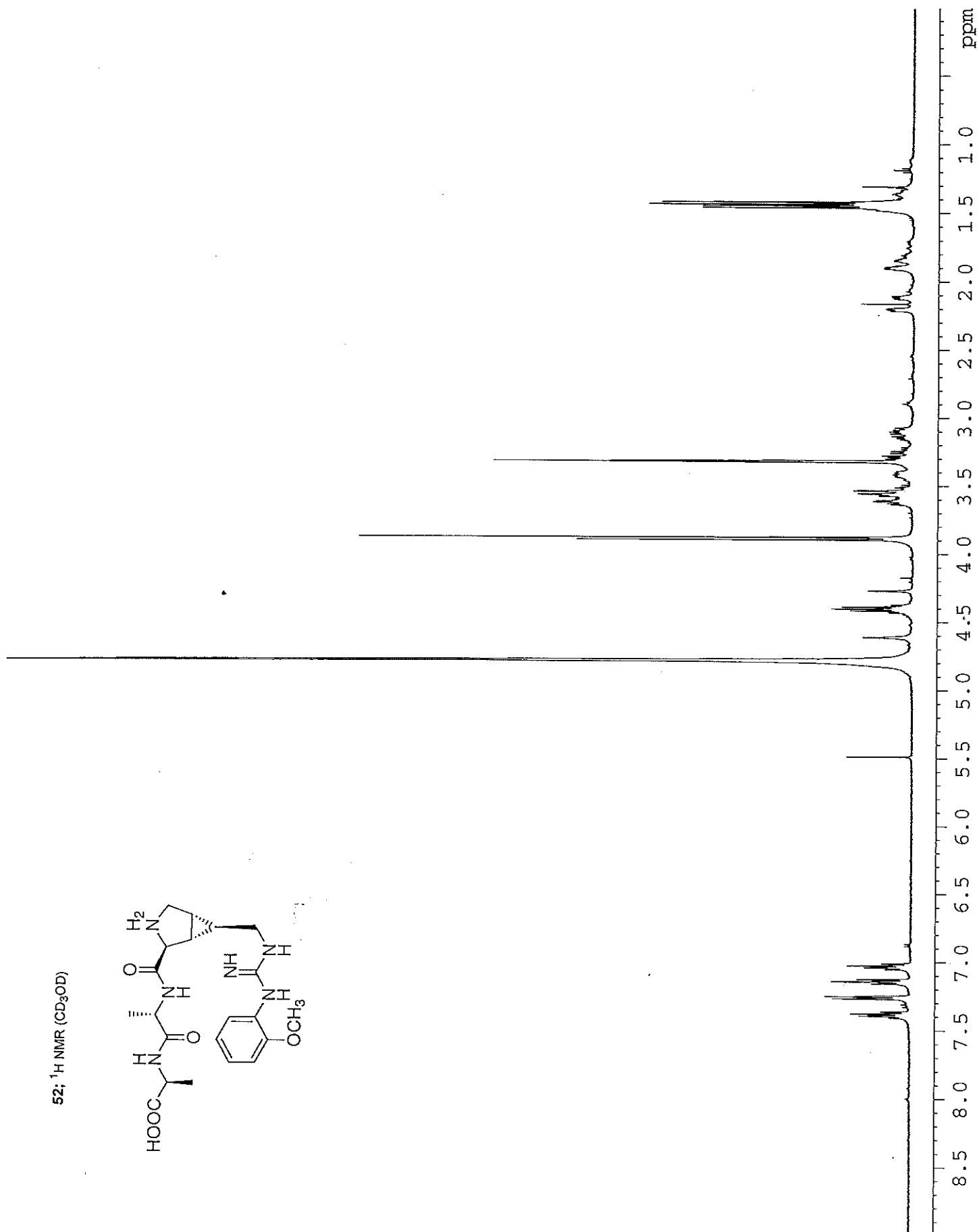
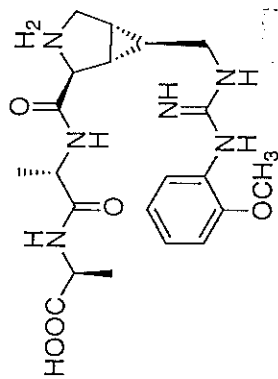
415

410

405

400

52; ^1H NMR (CD_3OD)



cd0322206

sf-6-139 140

per: MJennings

Base: 447.15

Peak: 1000.0 mmu

REG #9 @ 1.26 min (ESI +Q3MS LMR UP LR) (/35<45 -/5<15)

Study : ESI-MS, pos ion

Masses: 100.00 > 2000.02

Intensity: 282911

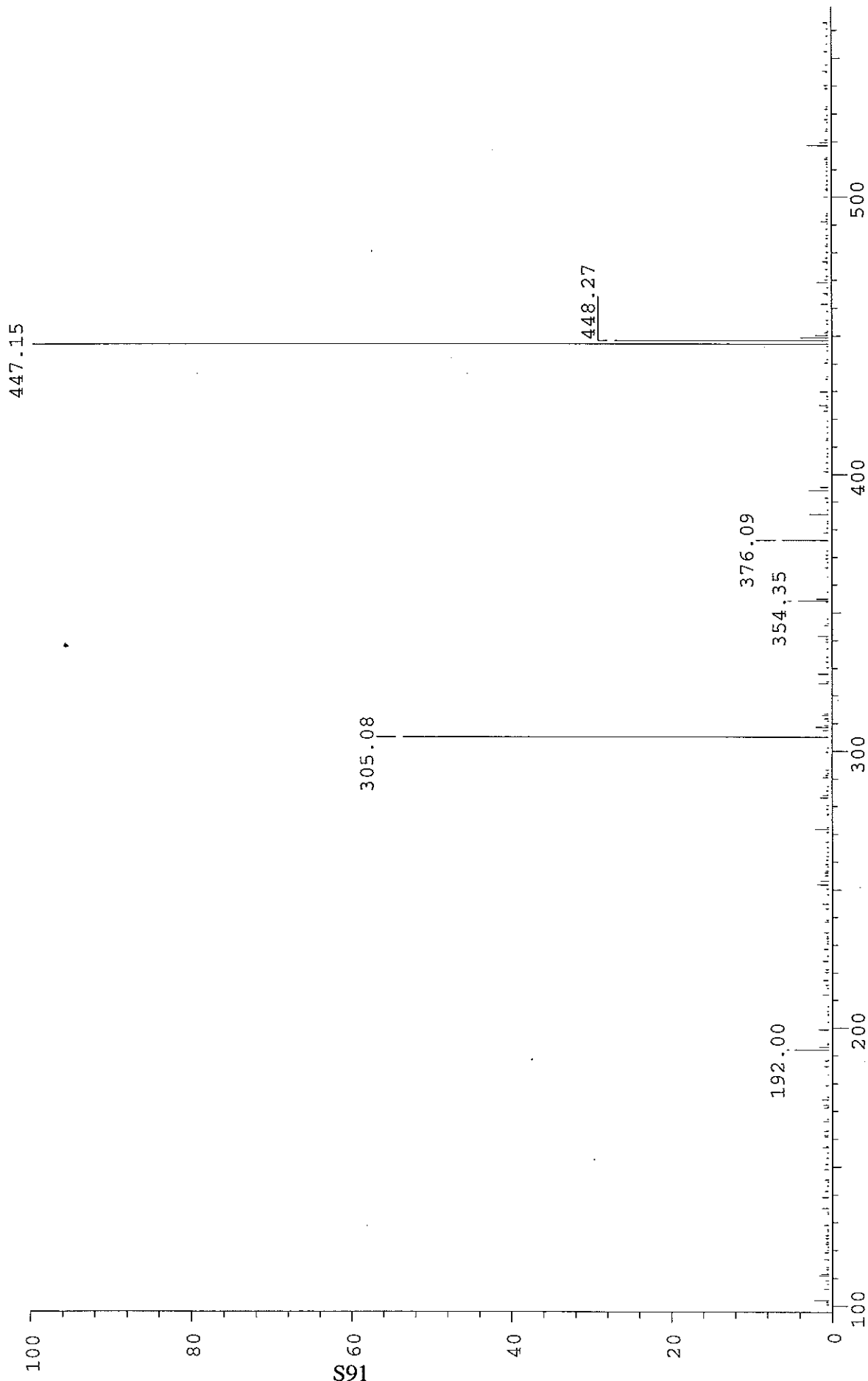
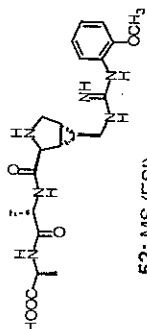
Scans : 1 > 56

Client: Steve Flemer

#Peaks: 886

RIC : 898105

2.8E+05

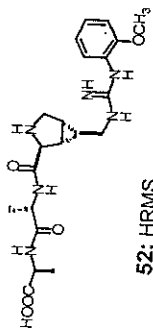


6-140-1 (0.019) Is (1.00,1.00) C21H31O5N6

447.2356

Theoretical [M+H]⁺

TOF MS ES+
7.63e12



448.2385

449.2410

SF-6-140-1 42 (0.770) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (40:42)

447.2350

Acceptable = 2.2 mm u

Observed Δ = 0.6 mm u

TOF MS ES+
320

Cal.
413.2667

432.2804

437.2328 446.2902

448.2409

449.2453

464.2708

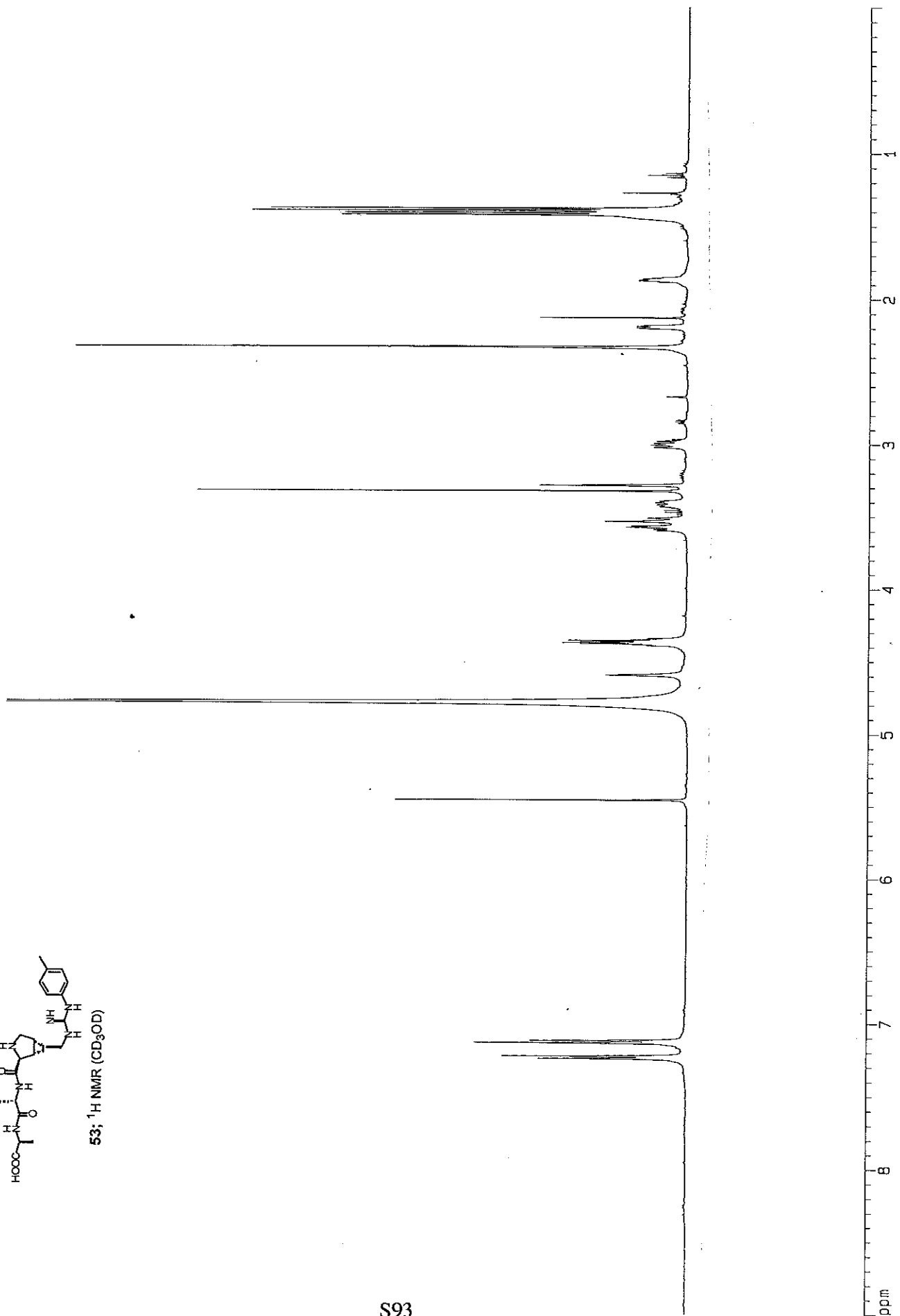
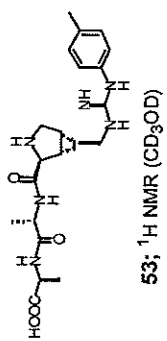
461.2521 465.2608

476.3063

477.3078

491.2572 497.2339

m/z

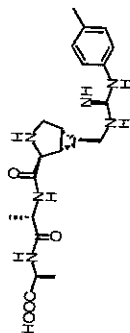


SF-188-1 (0.019) Is (1.00, 1.00) C21H31O4N6

431.2407

Theoretical [M+H]⁺

TOF MS ES+
7.65e12



53; HRMS

432.2436

433.2461

594

SF-6-188-1 45 (0.825) AM (Cen, 3, 80.00, Ht, 8000.0, 413.27, 1.00); Sm (SG, 2x3.00); Cm (45.48)

431.2405

Acceptable = 2.2 mm ea
observed Δ = 0.2 mm ea

TOF MS ES+
278

cal.
409.1846 413.2667

447.2360

432.2576

407.2010

414.2686

419.3036

437.2351

439.2500

445.2544

448.2626

453.2129

454.2157

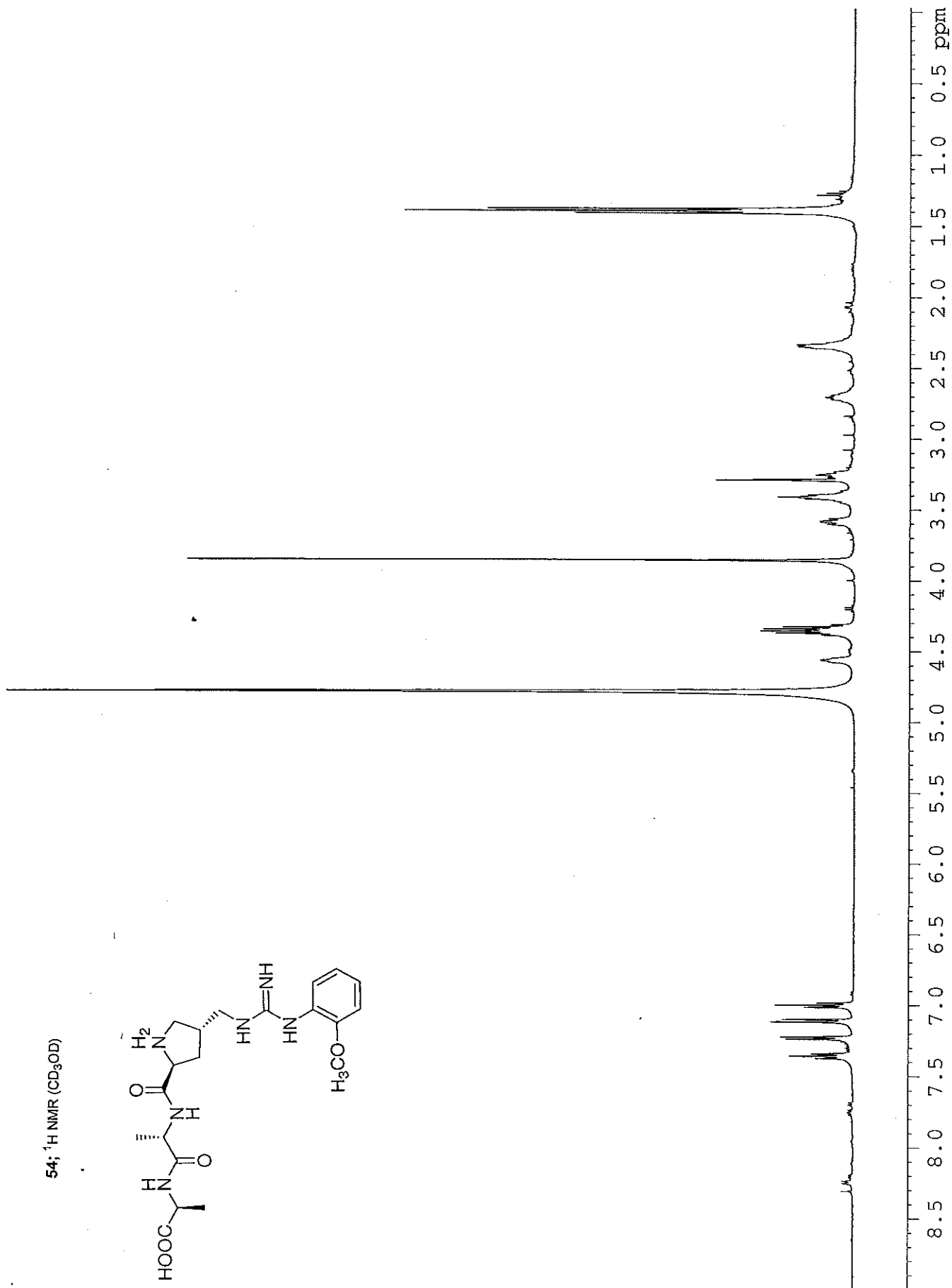
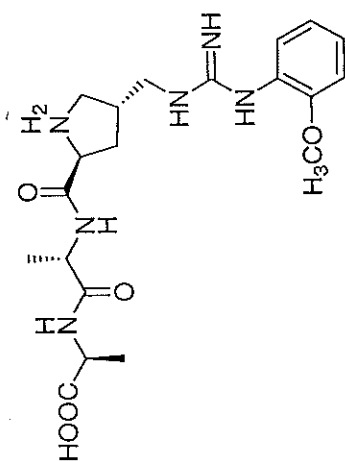
461.2406

464.2691

469.2206

m/z

54; ^1H NMR (CD_3OD)



PEC: cd022201

Samp: sf-6-111

Comm: s 200-1000 2

Oper: MJennings

Base: 435.28

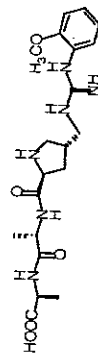
Peak: 1000.0 mmu

REG #9 @ 1.43 min (ESI +Q1MS LMR UP LR) (/41<51 -/13<23)

Study : esi-ms

Masses: 200.00 > 1000.04

Intensity: 383534



54; MS (ESI)

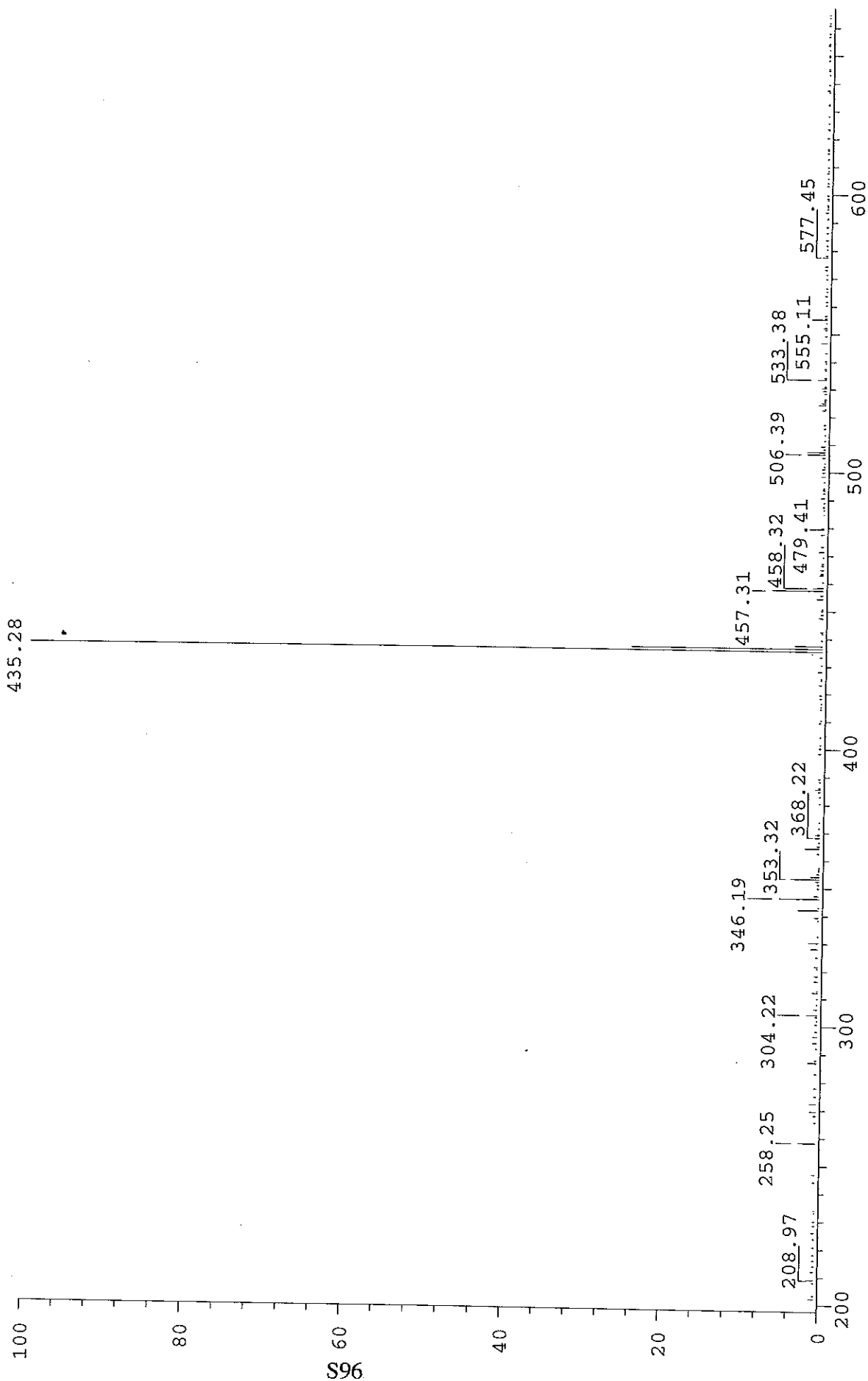
Scans : 1 > 71

Client: Steve Flemer

#Peaks: 416

RIC : 838763

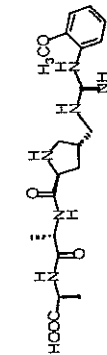
3.8E+05



SF-6-184-2 (0.019) Is (1.00, 1.00) C₂₀H₃₁O₅N₆

Theoretical [M+H]⁺

TOF MS ES+
7.71e12



54; HRMS

435.2356

436.2385

437.2409

SF-6-184-2 27 (0.495) AM (Cen, 3, 80.00, Ht, 8000.0, 413.27, 1.00); Sm (SG, 2x3.00); Cm (27:29)

xx2

435.2350

TOF MS ES+
361

*Acceptable = 2.2 min
observed = 0.6 min*

cal.

413.2667

409.1848

414.2678

431.2422

429.2409

437.2373

448.2754

449.2526

452.2705

457.2178

458.2204

476.2986

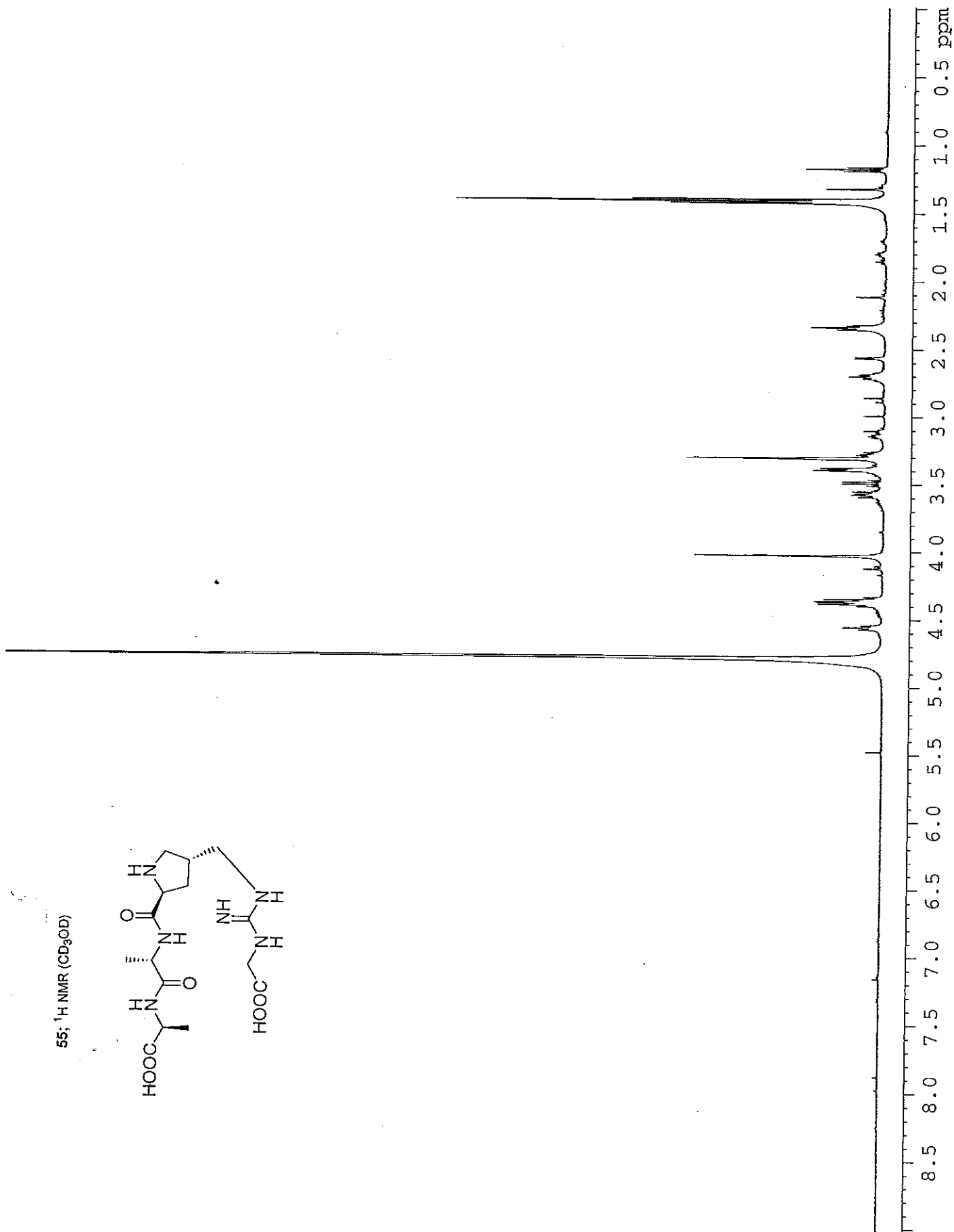
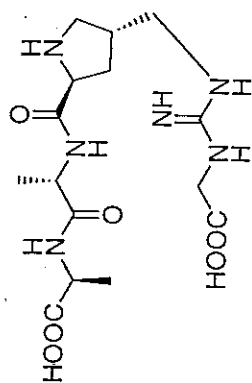
481.2665

489.3203

m/z

490

55; ^1H NMR (CD_3OD)



Flemer/Madalengitia UVM SF-6-185; MW=386.40

07/25/2002 01:51:47 PM

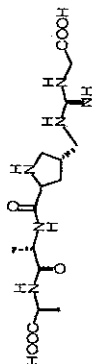
D:\Xcalibur\Data\107250205

107250205 #123-128 RT: 3.72-3.87 AV: 6 SM: 7G NL: 2.92E5

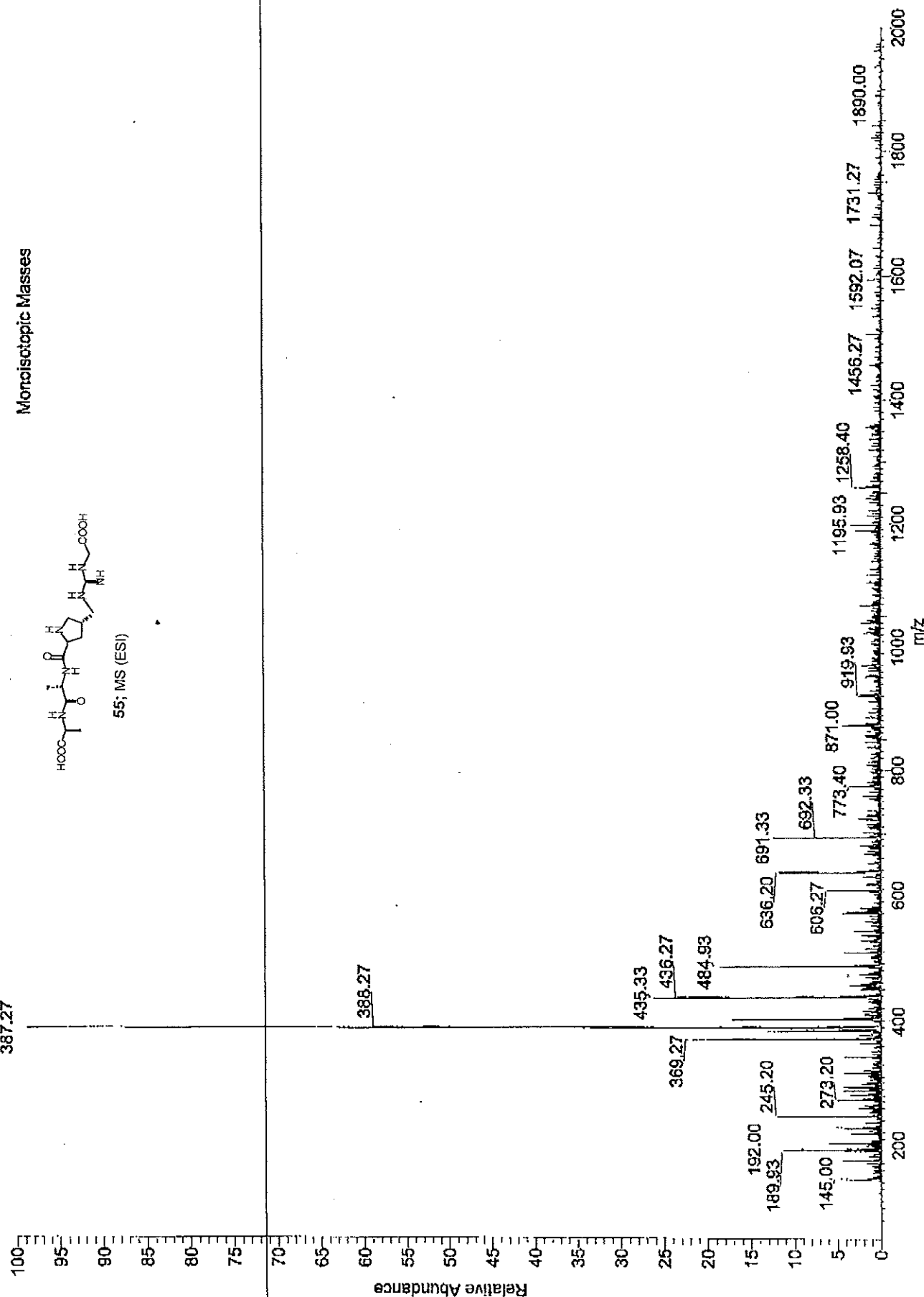
T: + p ESI Full ms [50.00-2000.00]

387.27

Monoisotopic Masses



55: MS (ESI)

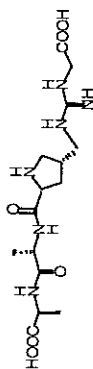


SF-6-239R-1 (0.019) Is (1.00,1.00) C15H27N6O6

387.1992

TOF MS ES+
8.14e12

Theoretical [M+H]⁺



55; HRMS

388.2019
389.2041

SI 100

SF-6-239R-1 16 (0.294) AM (Cen,4, 80.00, Ht,8000.0,393.21,1.00); Sm (SG, 2x3.00); Cm (7:16)

387.1980

TOF MS ES+
188

*Acceptable 1.9 mmu
observed 1.2 mmu*

383.1534

388.2509

393.2100

386.2255

400.1926

370.1890

382.2392

374.2403

371.1852

378.2586

385.1567

389.2530

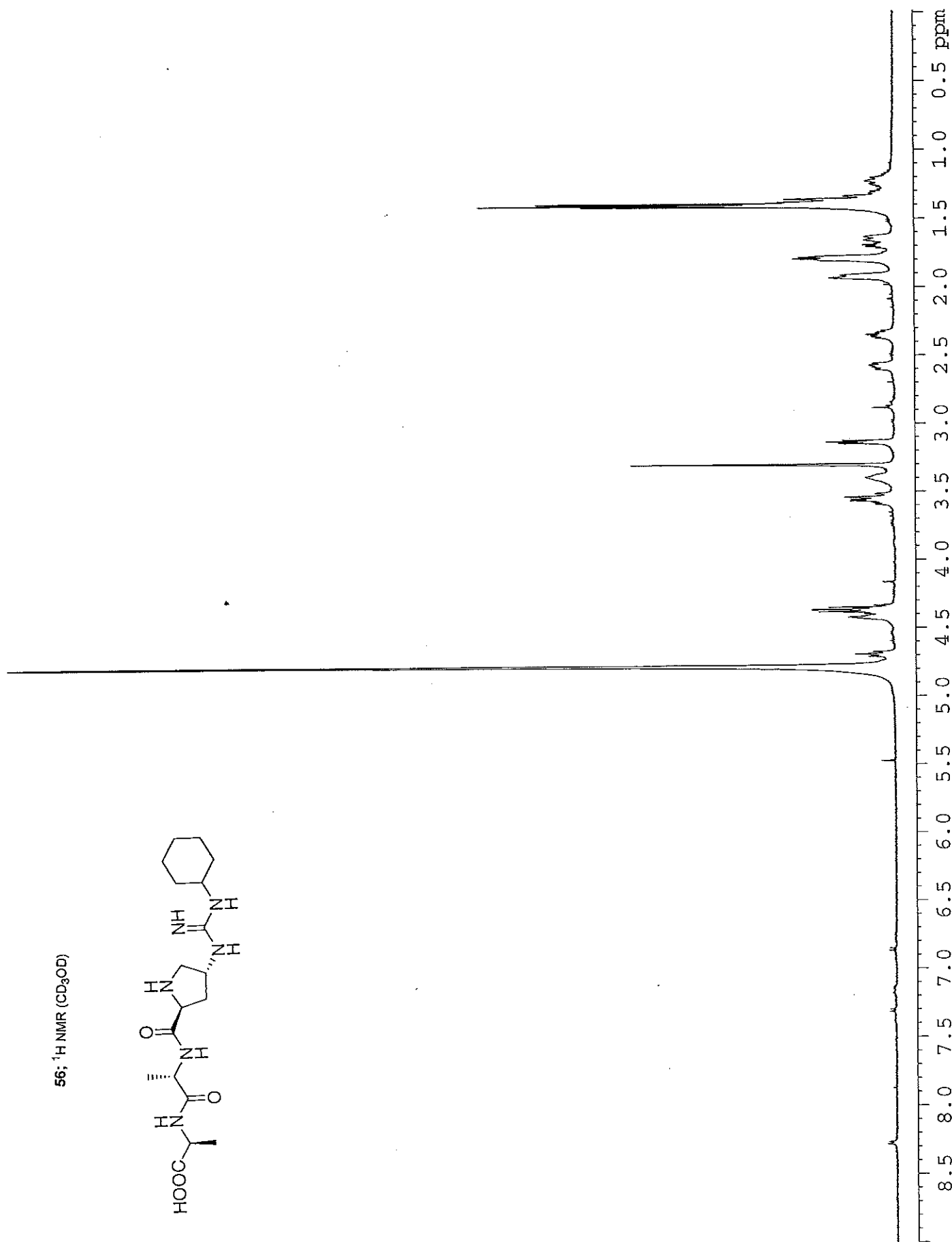
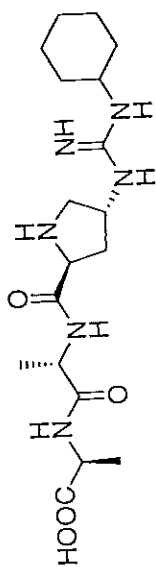
394.2170

397.2517

399.2217

m/z

56; ^1H NMR (CD_3OD)



Flemer/Madalengiotia UVM SF-6-182; MW=3

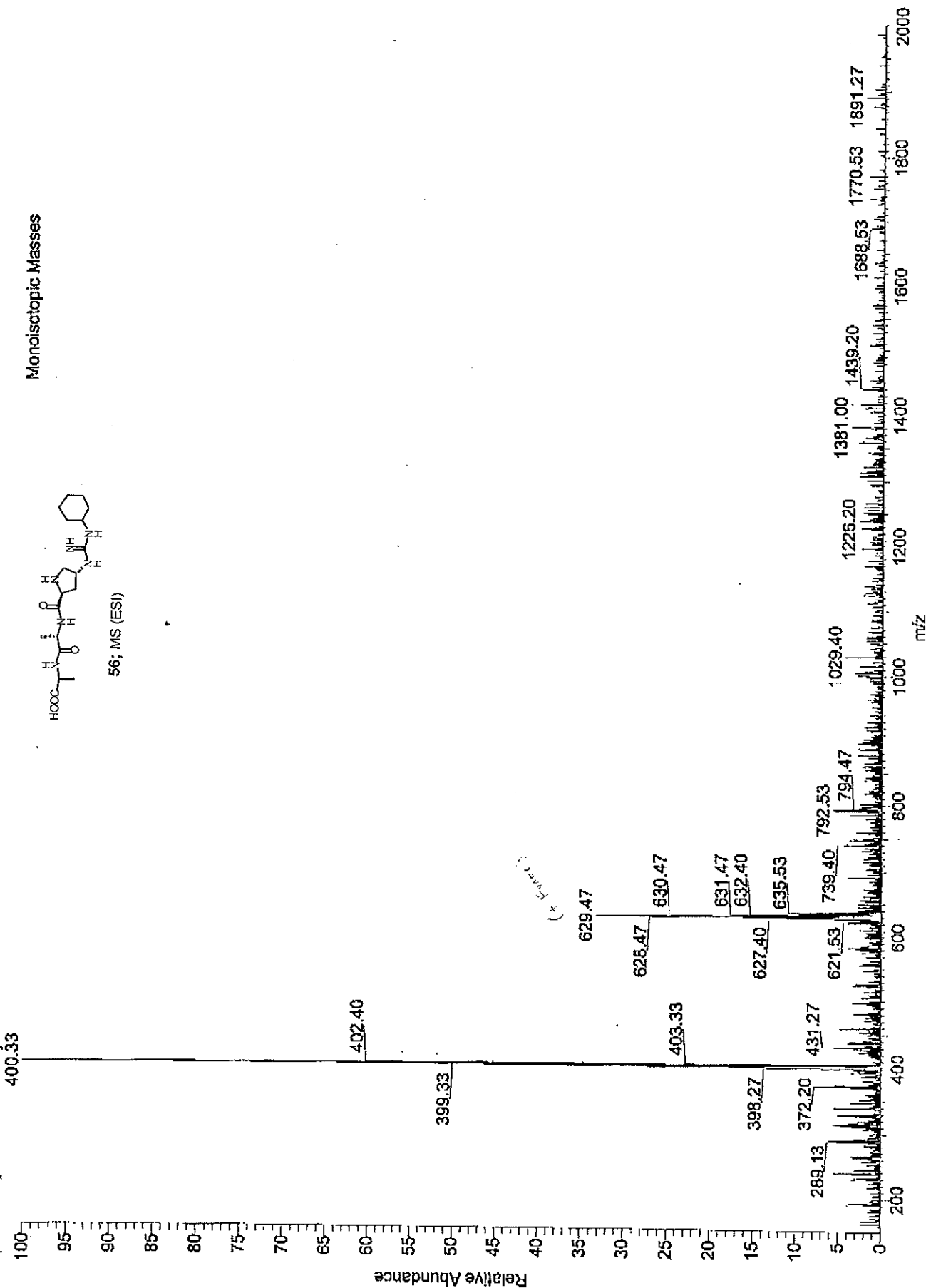
07/25/2002 04:14:12 PM

D:\Xcalibur\Data\107250210

Infusion: 25 uL/min

107250210 #14-37 RT: 0.41-1.10 AV: 24 SM: 7G NL: 1.23E4

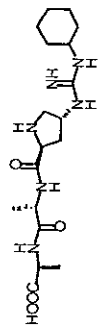
T: + p Full ms [150.00-2000.00]



SF-6-210-1 (0.019) Is (1.00,1.00) C₁₈H₃₃O₄N₆

Theoretical [M+H]⁺

TOF MS ES+
7.90e12



56; HRMS

397.2563

398.2592

399.2616

SF-6-210-1 35 (0.642) AM (Cen, 3, 80.00, Ht, 8000.0, 349.18, 1.00); Sm (SG, 2x3.00); Cm (35:37)

397.2558

*Acceptable = 2.0 mmu
observed Δ = 0.5 mmu*

TOF MS ES+
429

344.2292

349.1838

388.2548

350.1825

365.1573

366.1644

398.2607

411.2718

419.2409

432.2834

437.2266

453.2038

468.2986

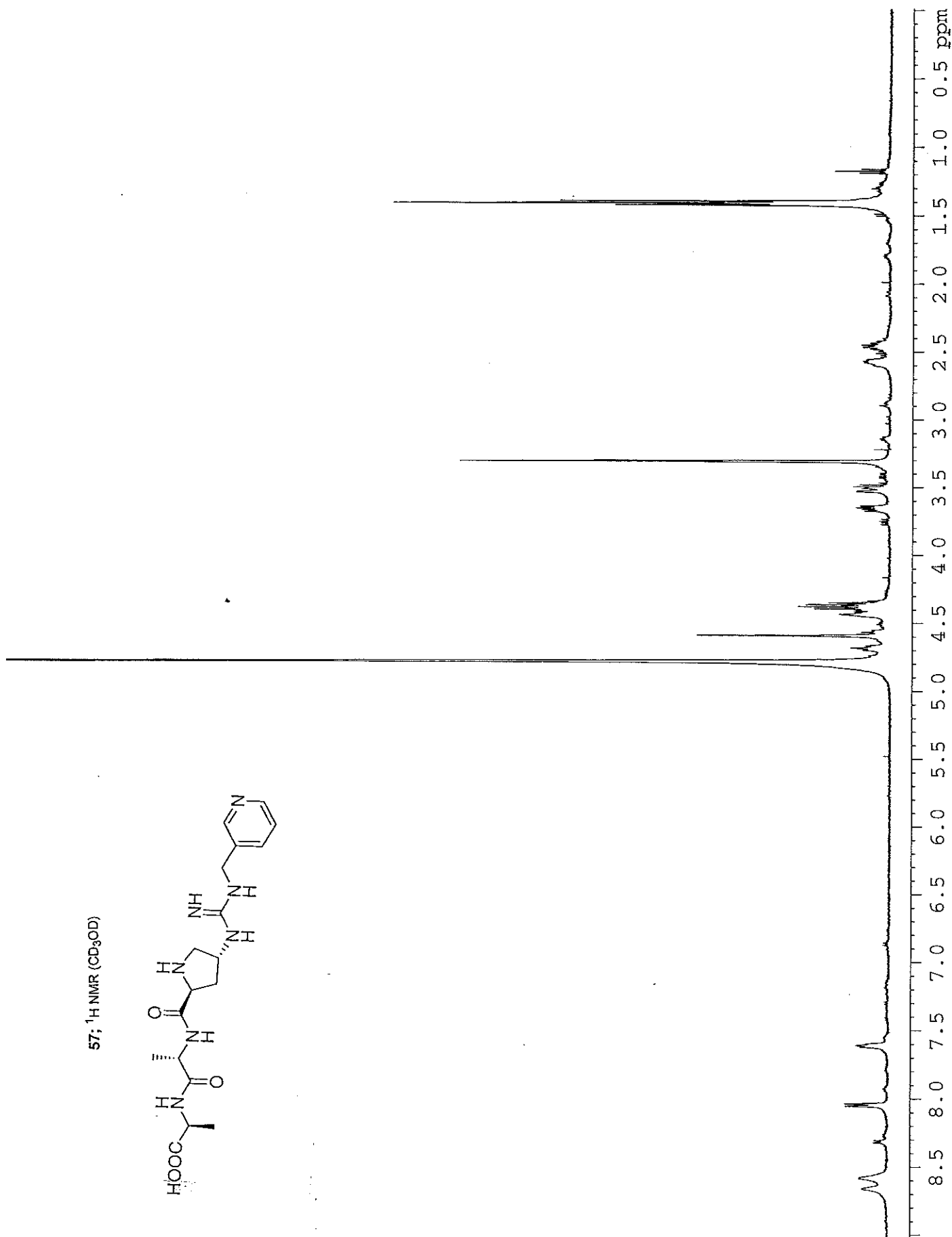
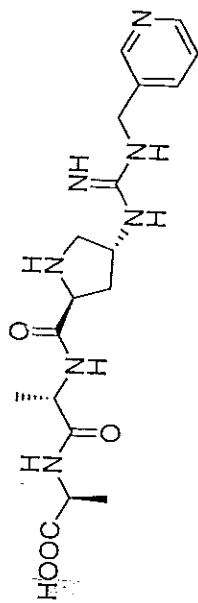
476.3114

481.2787

495.2228

m/z

57; ¹H NMR (CD₃OD)



Flemer/Madalengiotia UVM SF-6-180; MW=4

07/25/2002 03:56:37 PM

XcaliburData\107250209

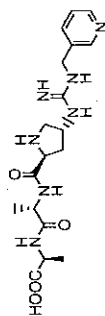
Infusion: 25 uL/min

107250209#31-78 RT: 0.91-2.30 AV: 48 SM: 7G NL: 1.58E4

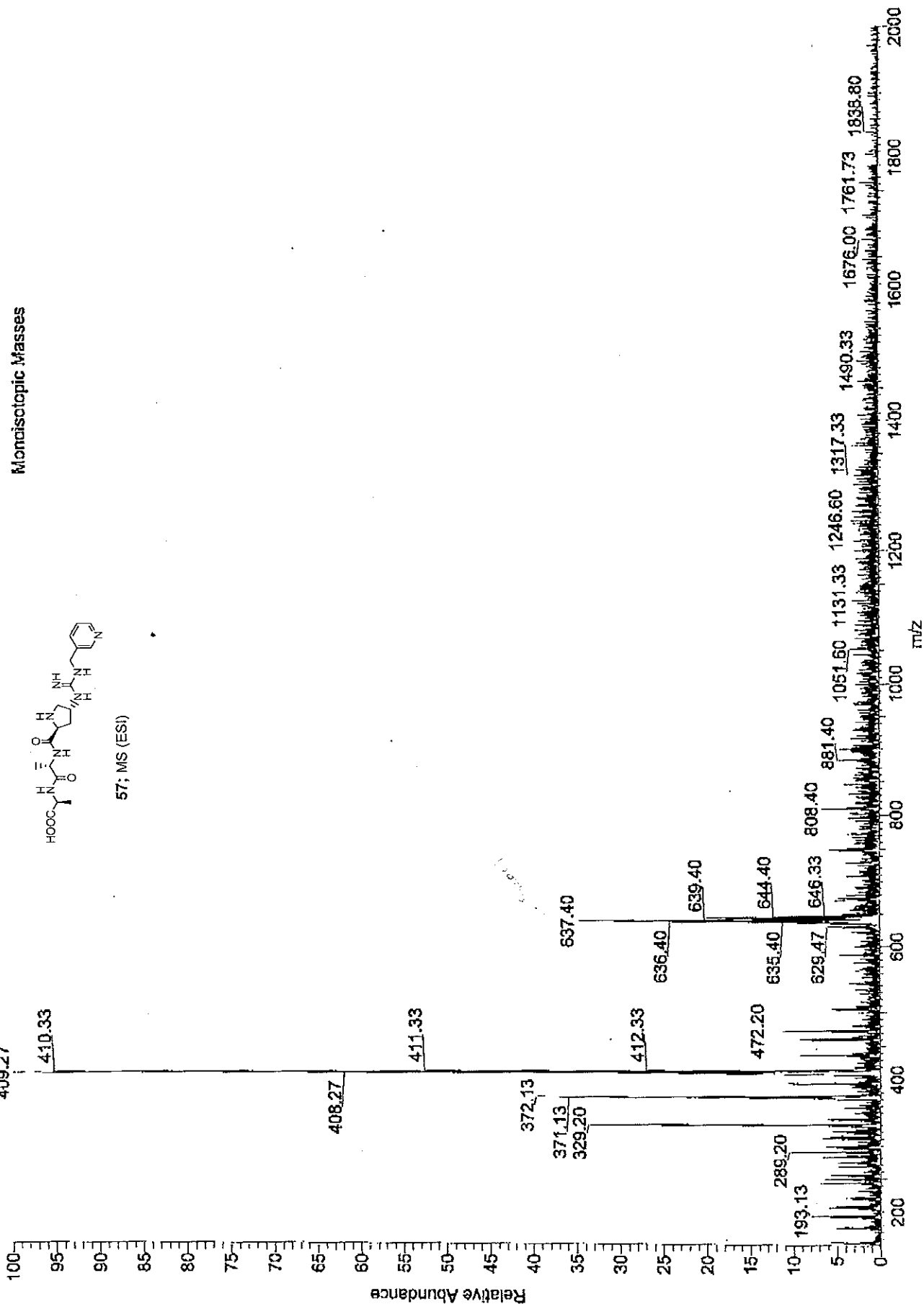
T: + p Full ms [150.00-2000.00]

409.27

Monoisotopic Masses

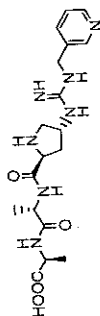


57; MS (ESI)



6-211-4 18 (0.330) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (14:18)

TOF MS ES+
1.58e3



57; HRMS

→ provided exact mass = 406.2203

$\Delta = 0.3 \text{ mmu}$

acceptable = 2.0 mmu

Second compound
exact mass indicates
 C_{12} difference
(still within 5 ppm
that are acceptable
limits for inclusion
and publication)

413.2667

420.2373

~~Calculated~~

407.2253

414.2736

428.2056

421.2418

393.2141

394.2161

405.1391

408.2312

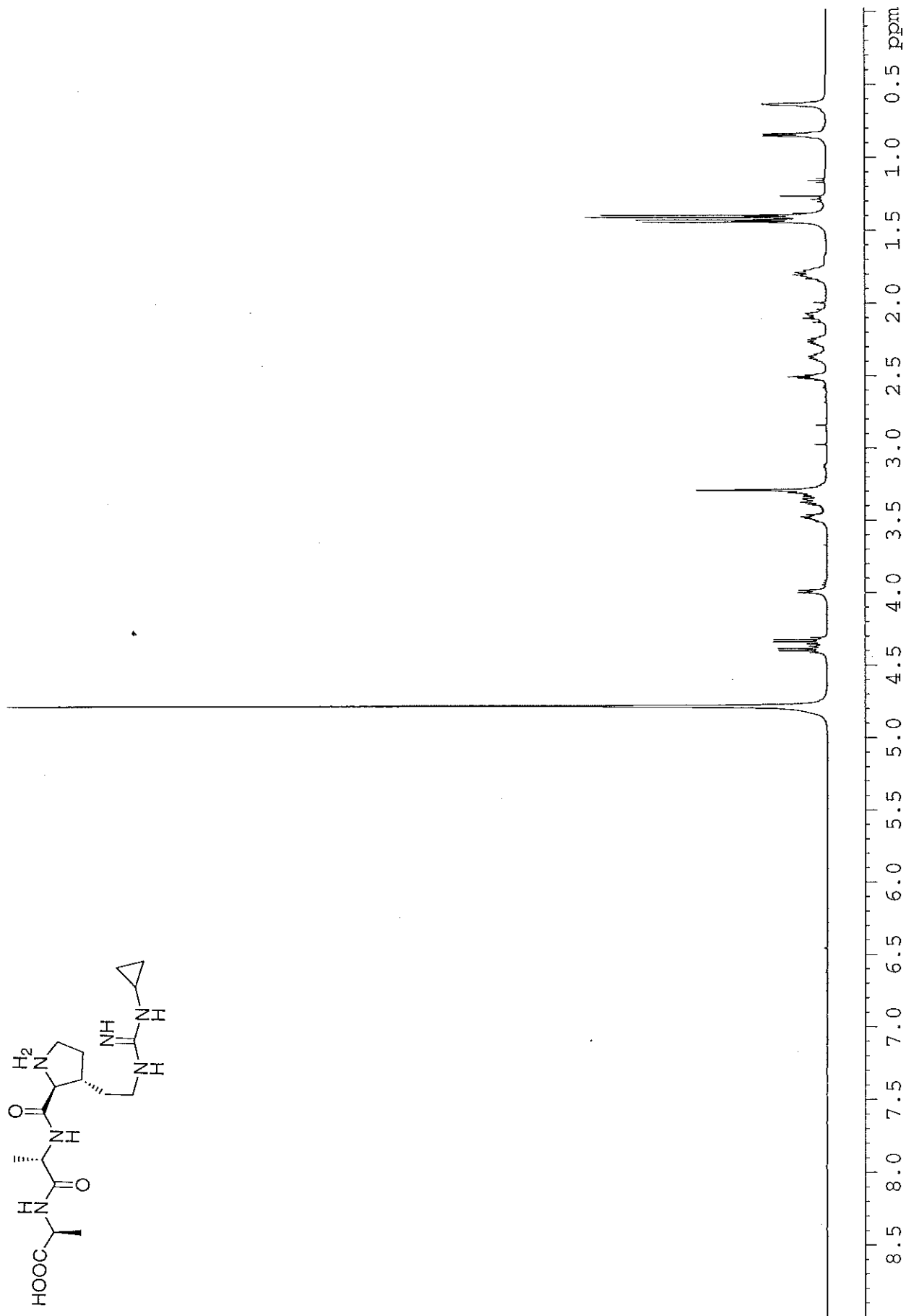
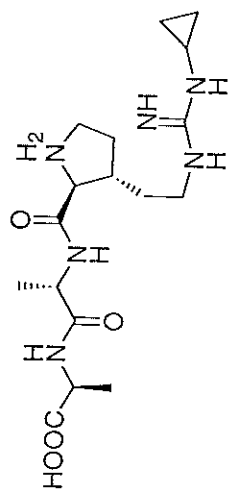
415.2754

422.2438

429.2178

m/z

58; ^1H NMR (CD_3OD)



SPEC: cd021904

Samp: sf-6-105, 1:50

Comm: Scan 200-1000 2s

Oper: MJennings

Base: 383.27

Peak: 1000.0 mmu

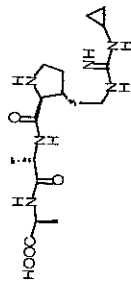
REG #9 @ 1.00 min (ESI +QIMS LMR UP LR) (/28<38)

Study : MS, mw=383.5

Masses: 249.99 > 1000.01

Intensity: 2118683

58; MS (ESI)



Scans : 1 > 64

Client: Steve Flemer

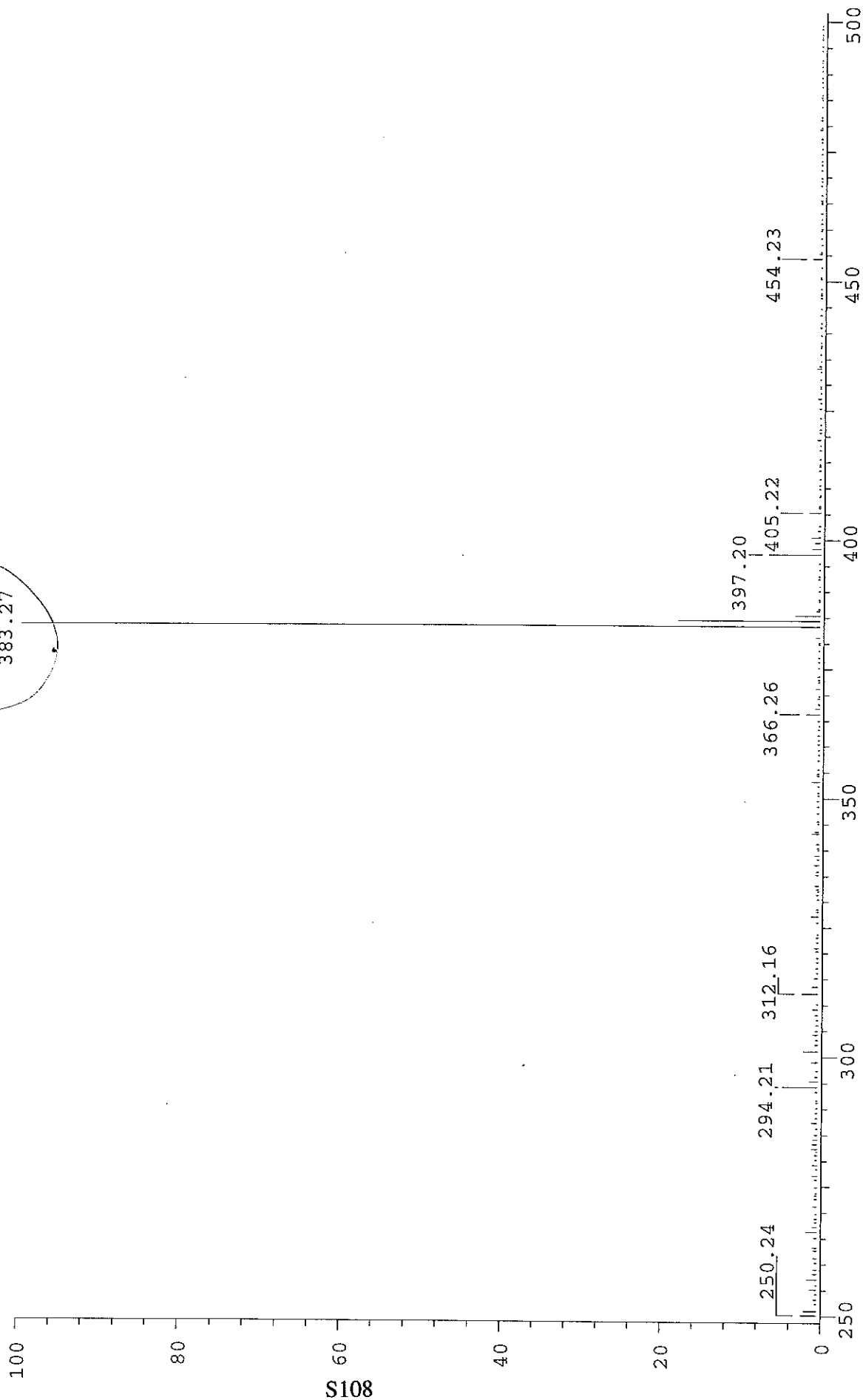
#Peaks: 751

RIC : 4159716

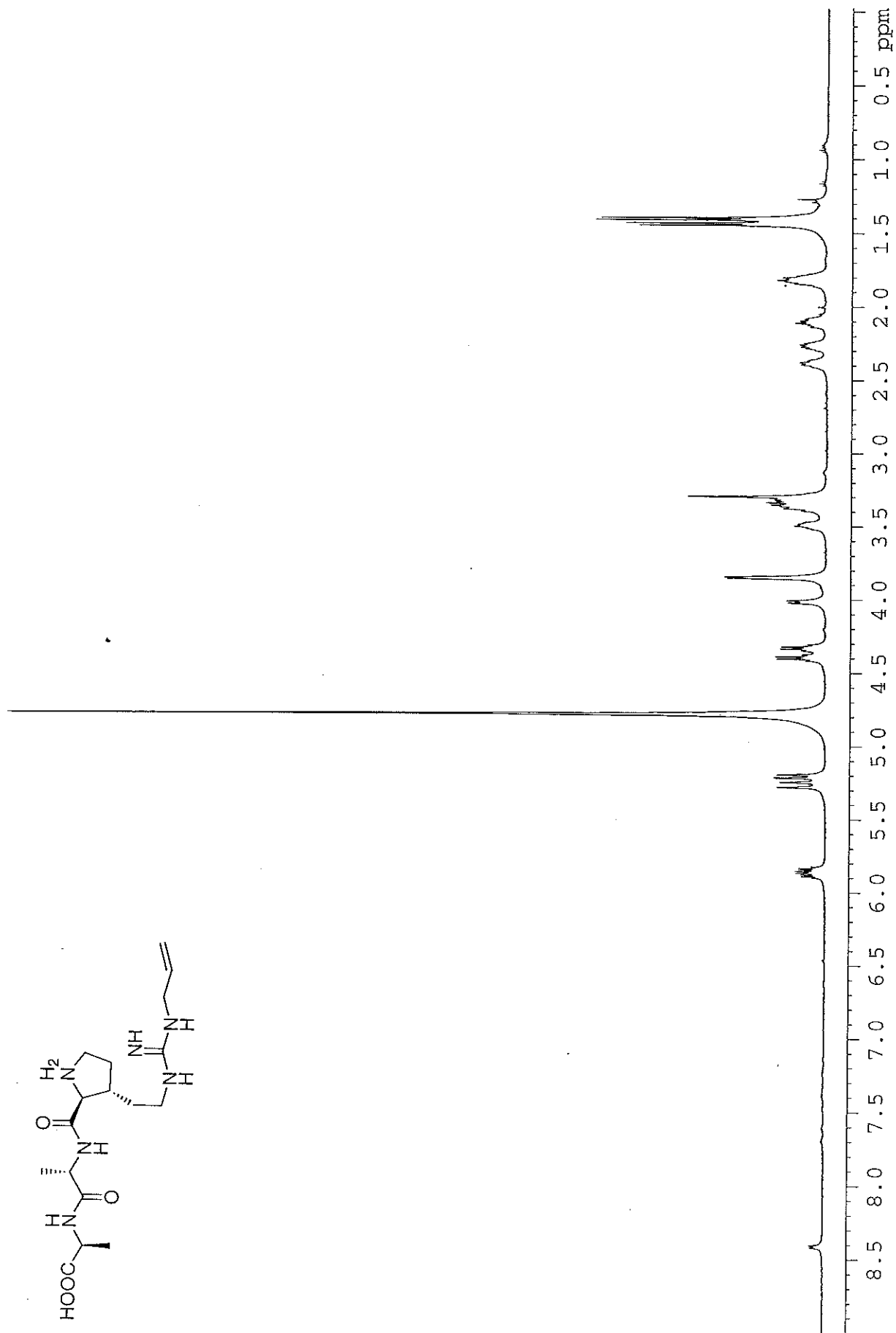
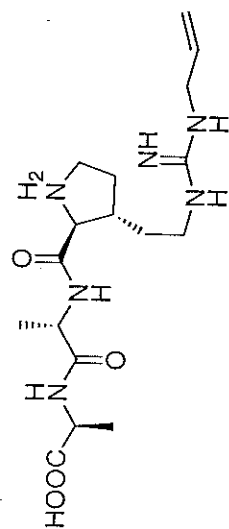
2.1E+06

M+H

383.27



59; ^1H NMR (CD_3OD)



S: cd021902 (19-FEB-02)

Samp: sf-6-103, 1:50

Comm: Scan 200-1000 2s

Oper: MJennings

Base: 383.27

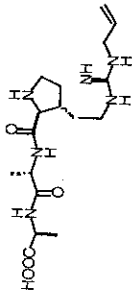
Peak: 1000.0 mmu

Study : MS, mw=383.5

Masses: 249.99 > 1000.0:

Intensity: 1449724

REG #9 @ 1.07 min (ESI +Q1MS LMR UP LR) (/30<40)



59; MS (ESI)

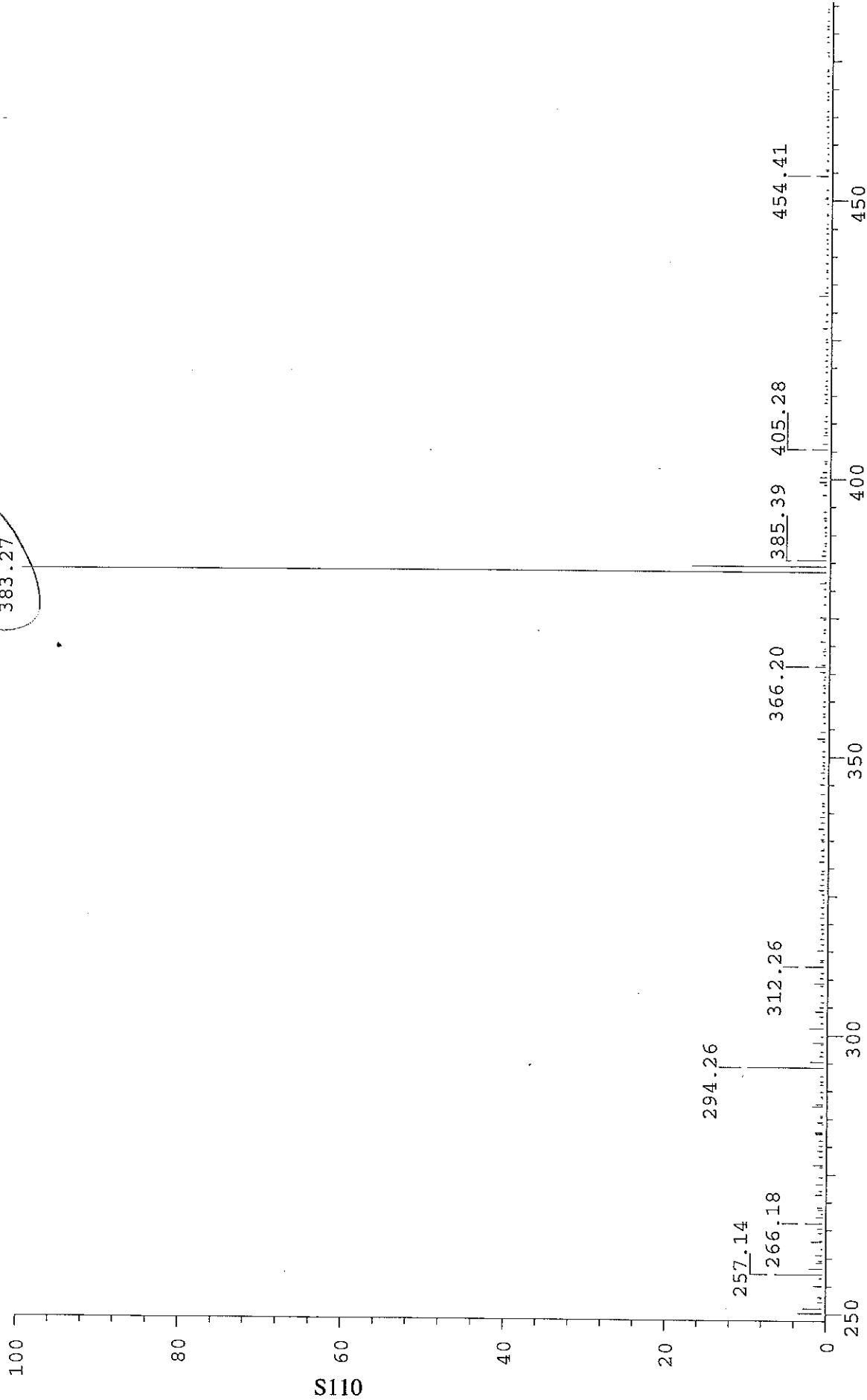
1.4E+06

Scans : 1 > 57

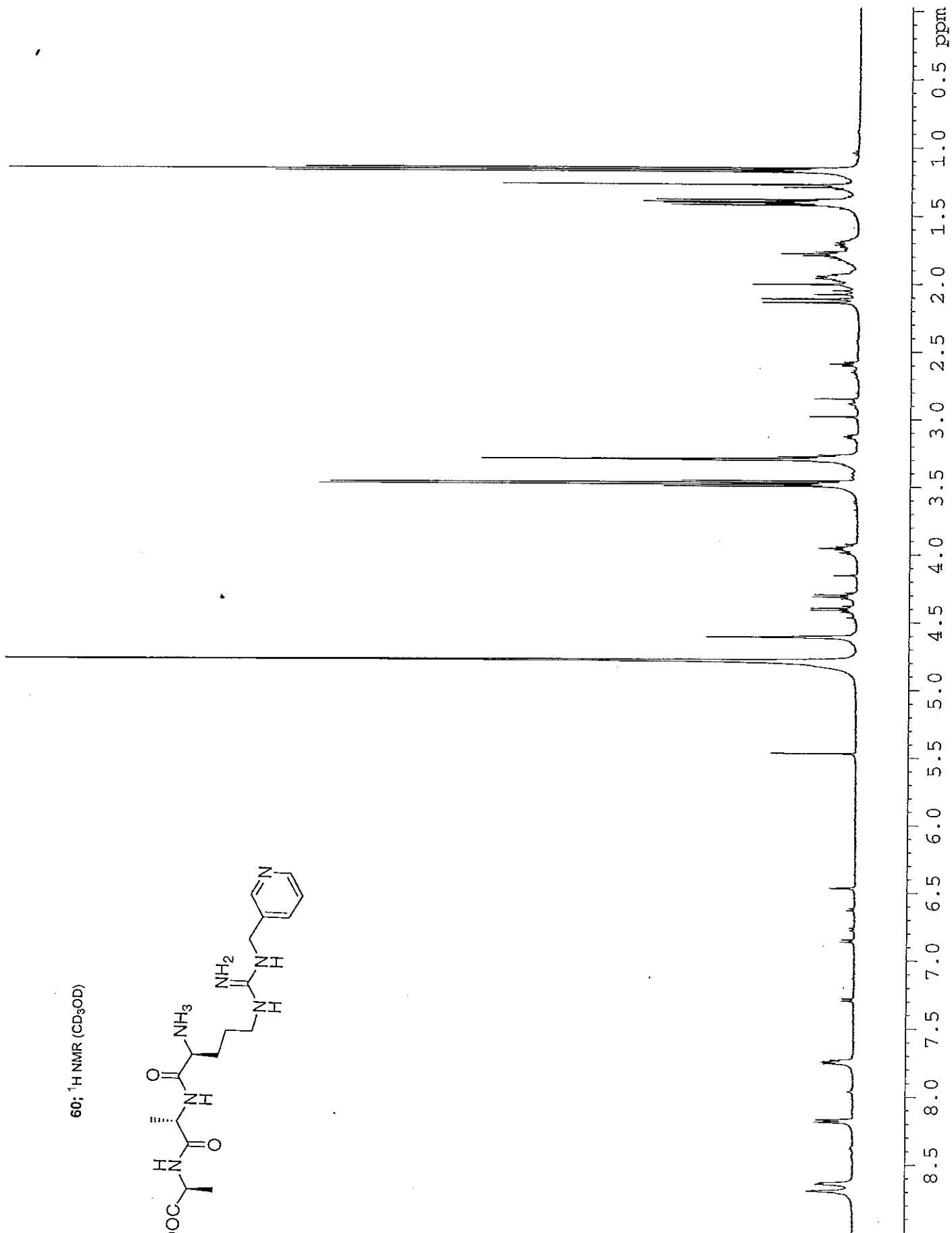
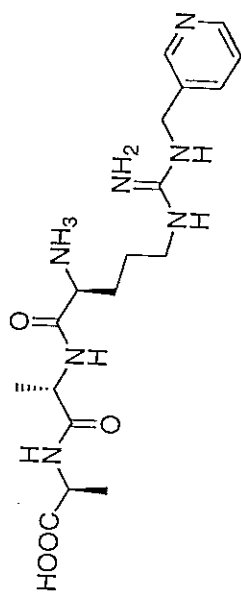
Client: Steve Flemer

#Peaks: 763

RIC : 3316105



60; ^1H NMR (CD_3OD)



cd030807 (08-MAR-02)

Temp: sf-122 1:50

Comm: scan 100-700 2s

Oper: mjennings

Base: 408.20

Peak: 1000.0 mmu

Study: eis-ms, pos ion

Masses: 100.00 > 699.99

Intensity: 516842

REG #9 @ 0.83 min (ESI +Q1MS LMR UP LR) (/23<33 -/8<16)

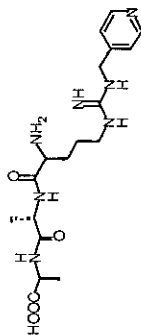
Scans: 1 > 47

Client: Steve Flemer

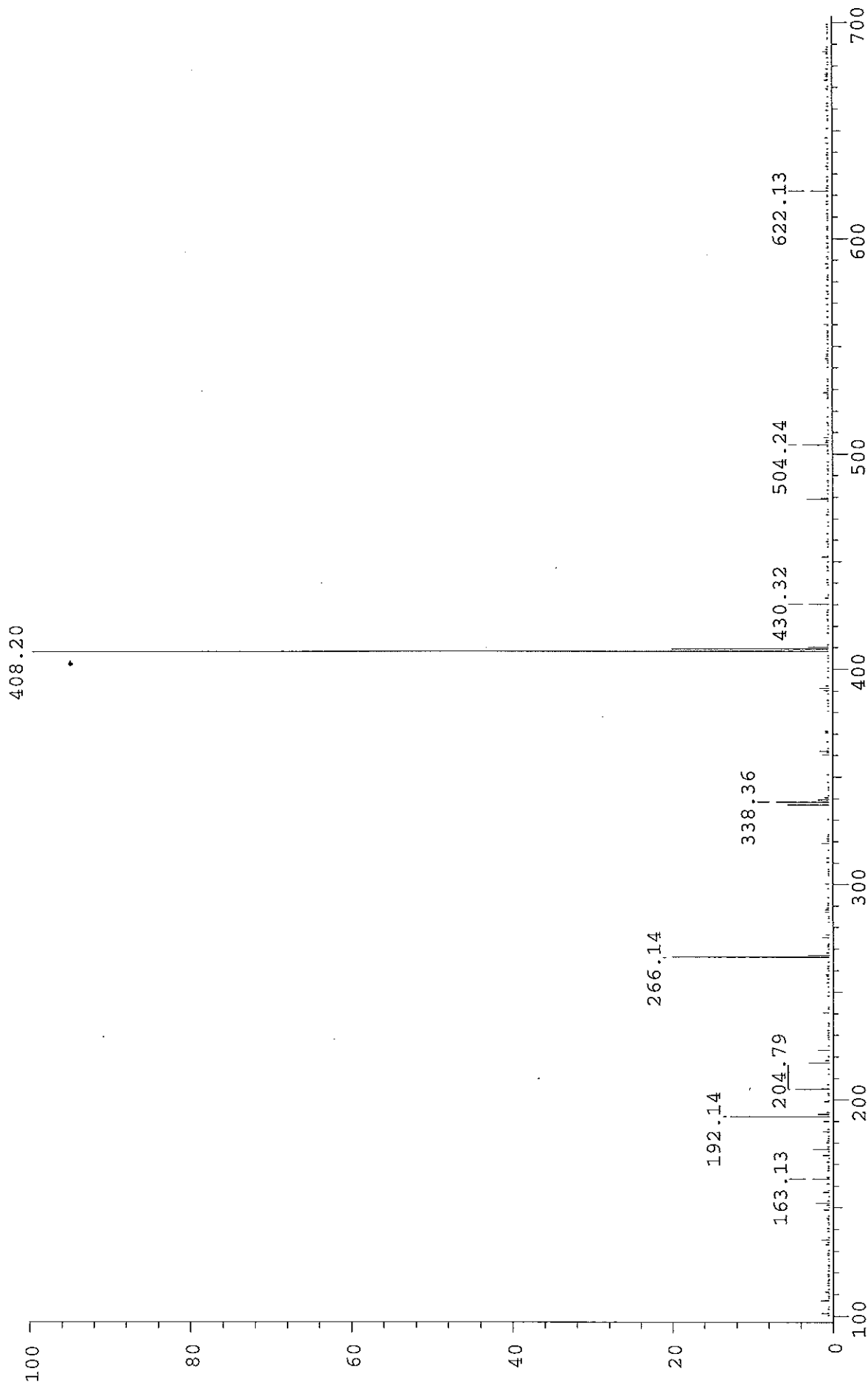
#Peaks: 346

RIC: 1296689

5.2E+05



60: MS (ESI)

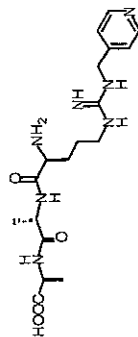


S112

SF-6-209-2 (0.019) Is (1.00, 1.00) C18H30O4N7

TOF MS ES+
7.88e12

Theoretical [M+H]⁺



60; HRMS

408.2359

409.2386

410.2411

S113

SF-6-209-2 22 (0.404) AM (Cen, 3, 80.00, Ht, 8000.0, 413.27, 1.00); Sm (SG, 2x3.00); Cm (19:22)

TOF MS ES+
528

408.2345

Acceptable = 2.0 mmu

Observed Δ = 1.4 mmu

413.2667

422.2506

Leak

409.2371

414.2705

407.1517

393.2095

393.2968

401.2471

397.2543

423.2546

415.2716

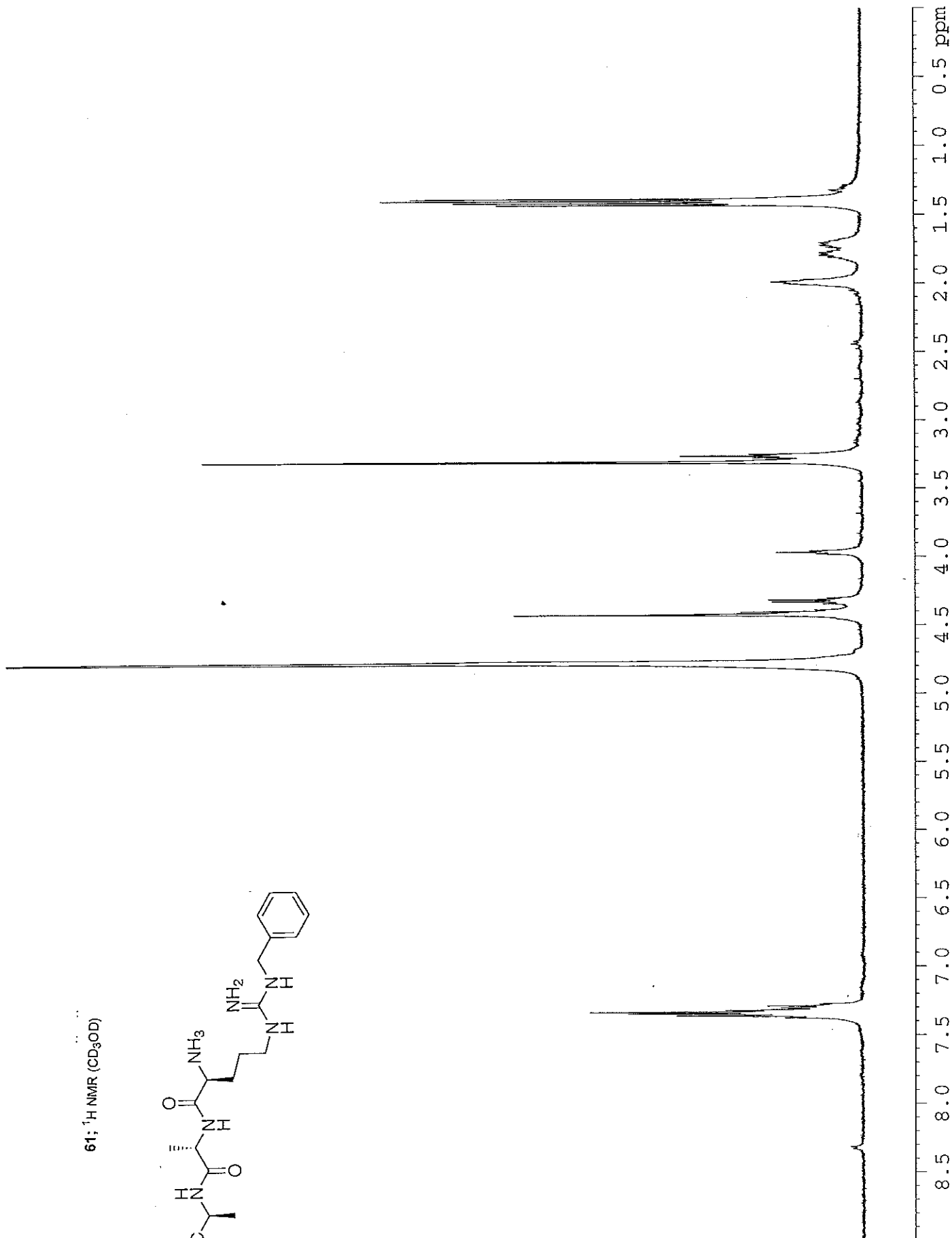
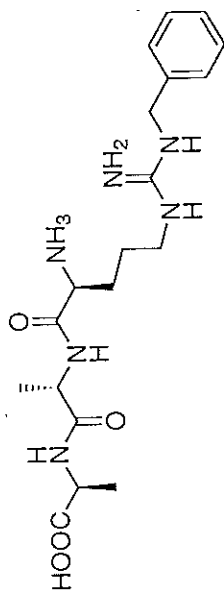
419.2395

427.2486

429.2428

m/z

61; ^1H NMR (CD_3OD)



C: sf021203

amp: sf-6-93

Comm: scan 100-1000 2s

Oper: MJennings

Base: 407.20

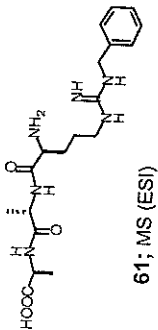
Peak: 1000.0 mmu

Study : ESI MS

Masses: 100.00 > 1000.04

Intensity: 6935588

REG #9 @ 0.86 min (ESI +QIMS LMR UP LR) (/24<34)



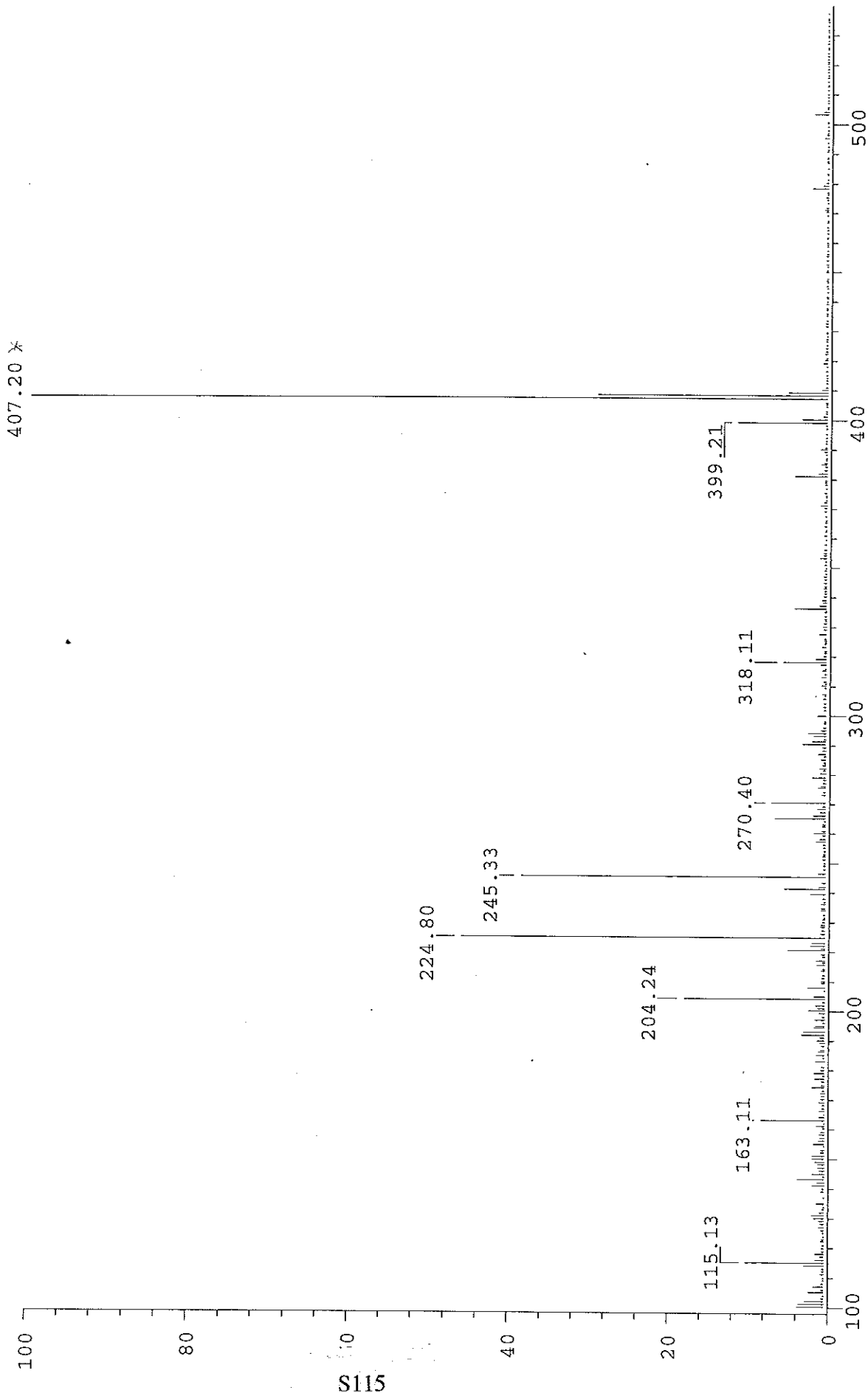
Scans : 1 > 39

Client: Steve Flemer

#Peaks: 901

RIC : 33046387

6.9E+06

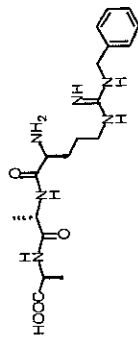


SF-6-228-1 (0.019) Is (1.00,1.00) C19H31O4N6

407.2407

Theoretical [M+H]⁺

TOF MS ES+
7.82e12



61; HRMS

408.2435

409.2460

SF-6-228-1 13 (0.239) AM (Cen,3, 80.00, Ht,8000.0,393.21,1.00); Sm (SG, 2x3.00); Cm (11:13)

407.2396

1x2 H

*Acceptable = 2.0 mm
Observed Δ = 1.1 mm*

TOF MS ES+
246

388.2566

393.2100

393.1346

380.2378

393.2747

397.2547

407.1673

408.2451

409.1846

413.2715

424.2753

432.2836

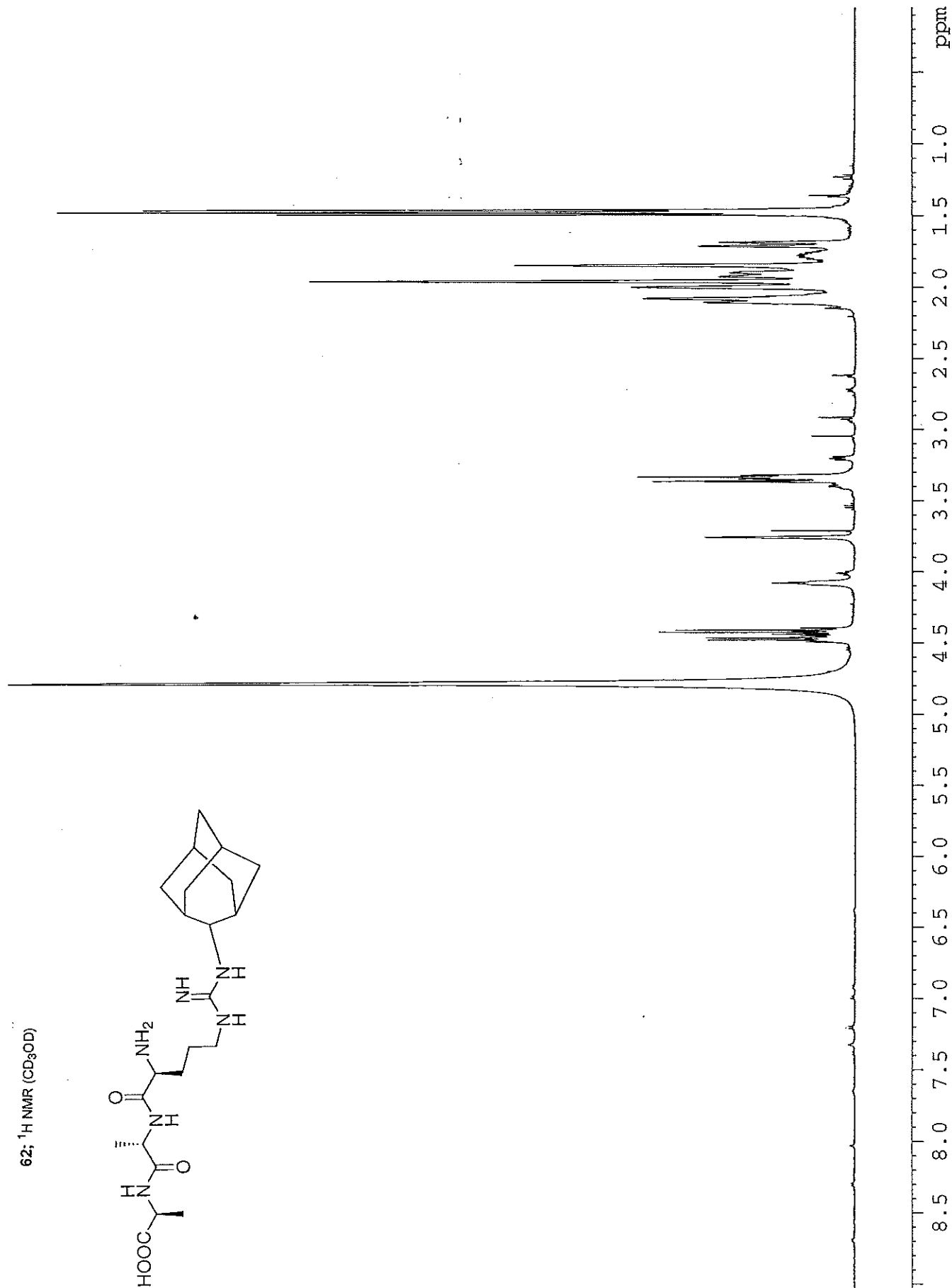
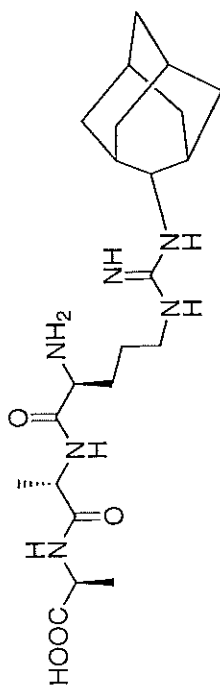
437.2410

441.1213

445.2001

m/z

62; ^1H NMR (CD_3OD)



XcaliburData\07250207

infusion; 25 μ L/min

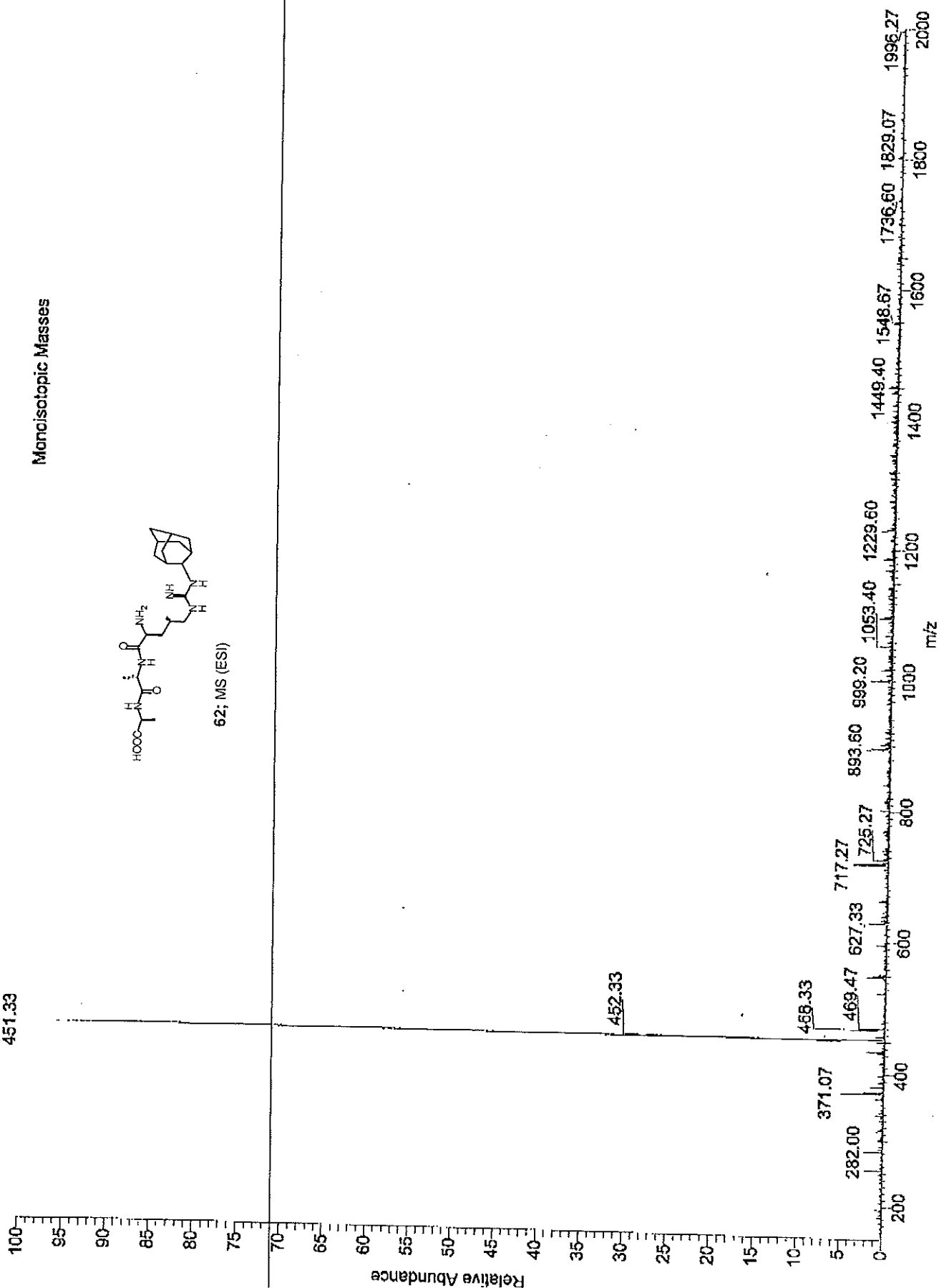
07/25/2002 02:59:10 PM

Flemer/Madalengictia UVM SF-6-175; MW = 450.58

IT07250207#27-51 RT: 0.77-1.49 AV: 25 SM: 7G NL: 7.05E4

T: + p Full ms [150.00-2000.00]

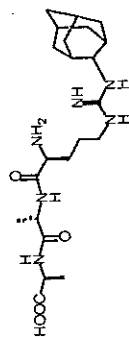
451.33



-6-229-1 (0.019) ls (1.00,1.00) C22H39O4N6

TOF MS ES+
7.55e12

Theoretical [MATH] 451.3033



62;HRMS

452.3062

453.3088

SF-6-229-1 16 (0.294) AM (Cen,3, 80.00, Ht,8000.0,413.27,1.00); Sm (SG, 2x3.00); Cm (13:16)

TOF MS ES+
320

451.3029

Acceptable = 2.3 mm

Observed A. O. C. for m

413 2667

452.3083

409.1861

425 1538

432.2803

437.2433

451.2348

453.3119

468 3466

473.2857

4
3087

491.2659

497 2108

451.2400
m/z

495

490

485

488

47

4

40

5

50

45

440

435

430

425

42

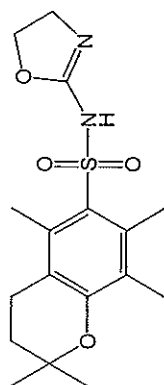
4

4

70

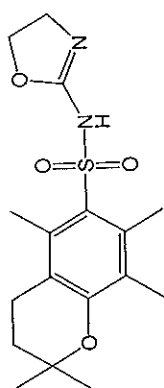
1

S119

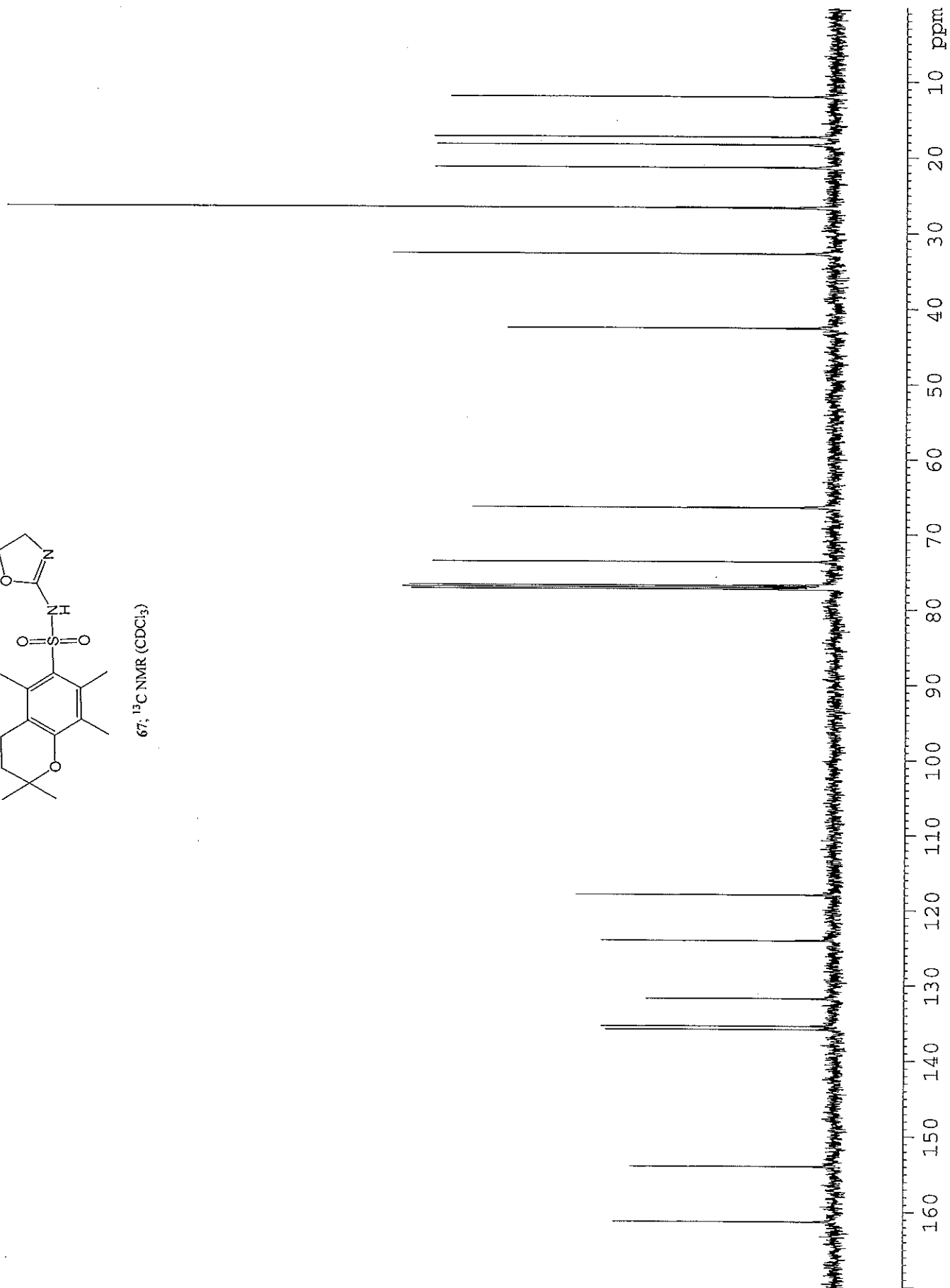


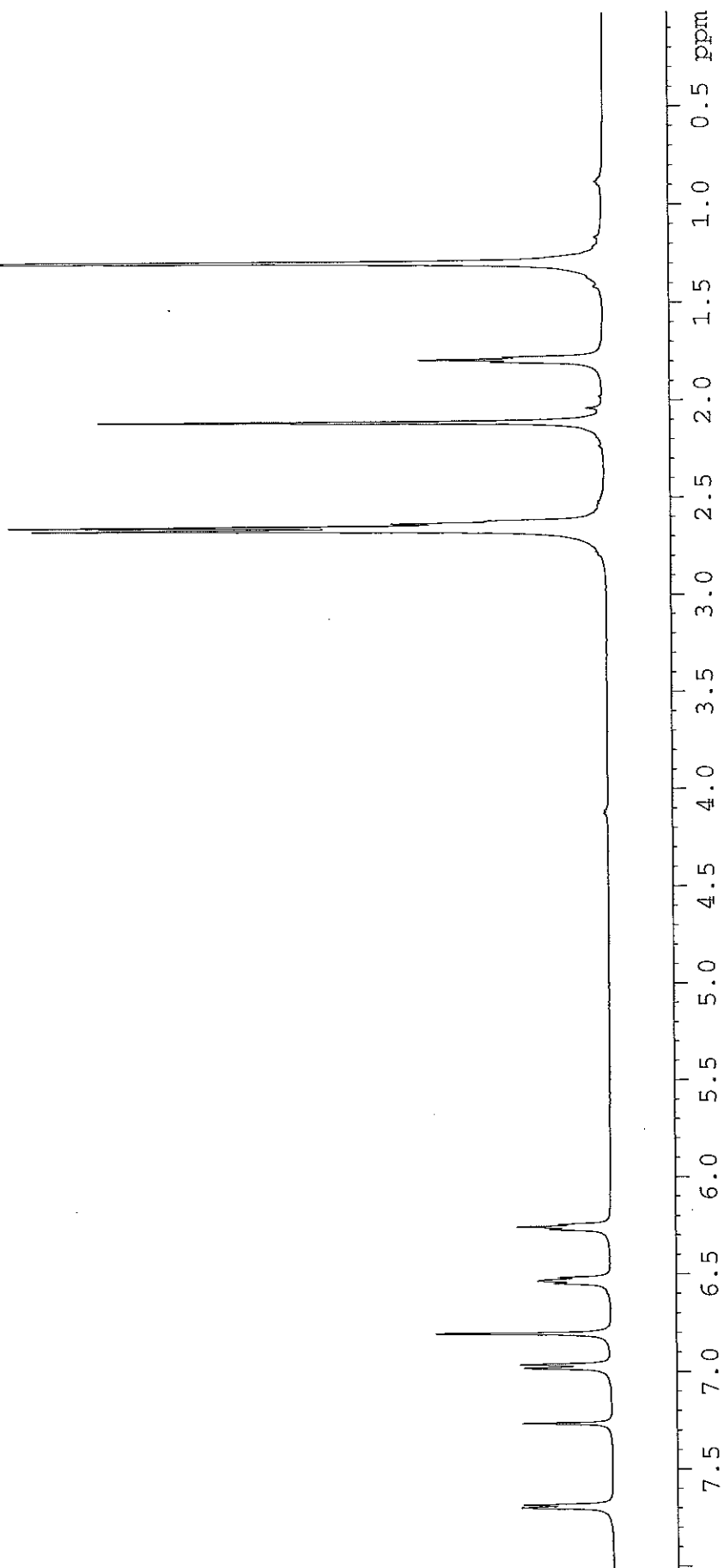
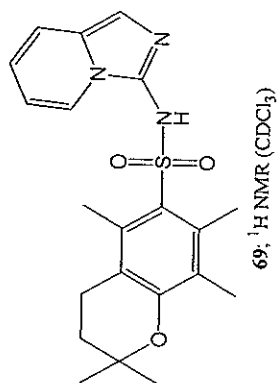
67; ^1H NMR (CDCl_3)

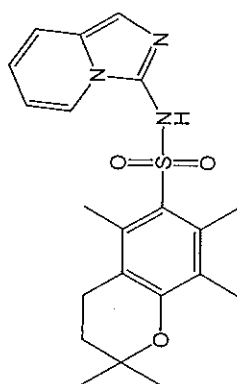




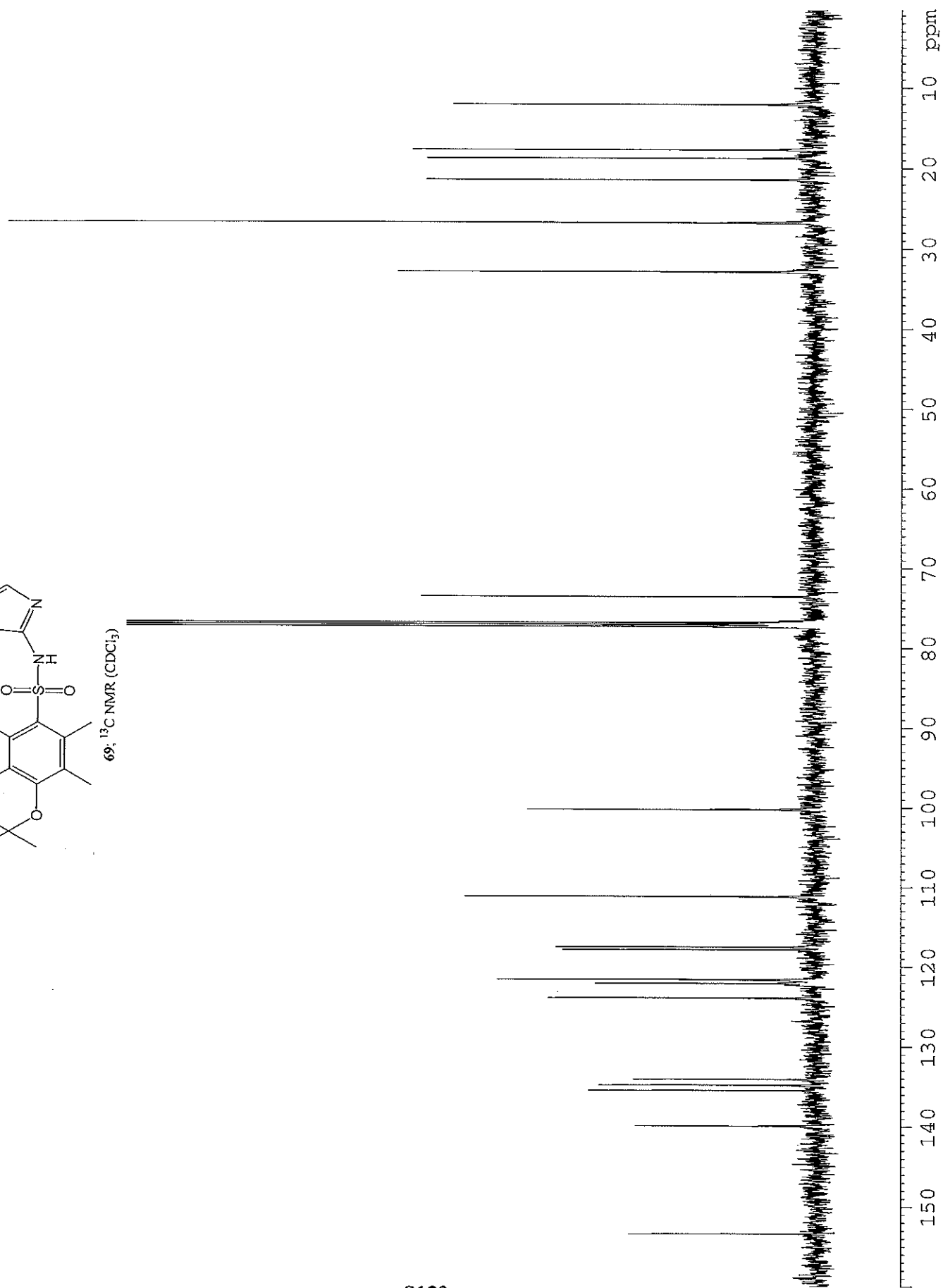
67, ^{13}C NMR (CDCl_3)

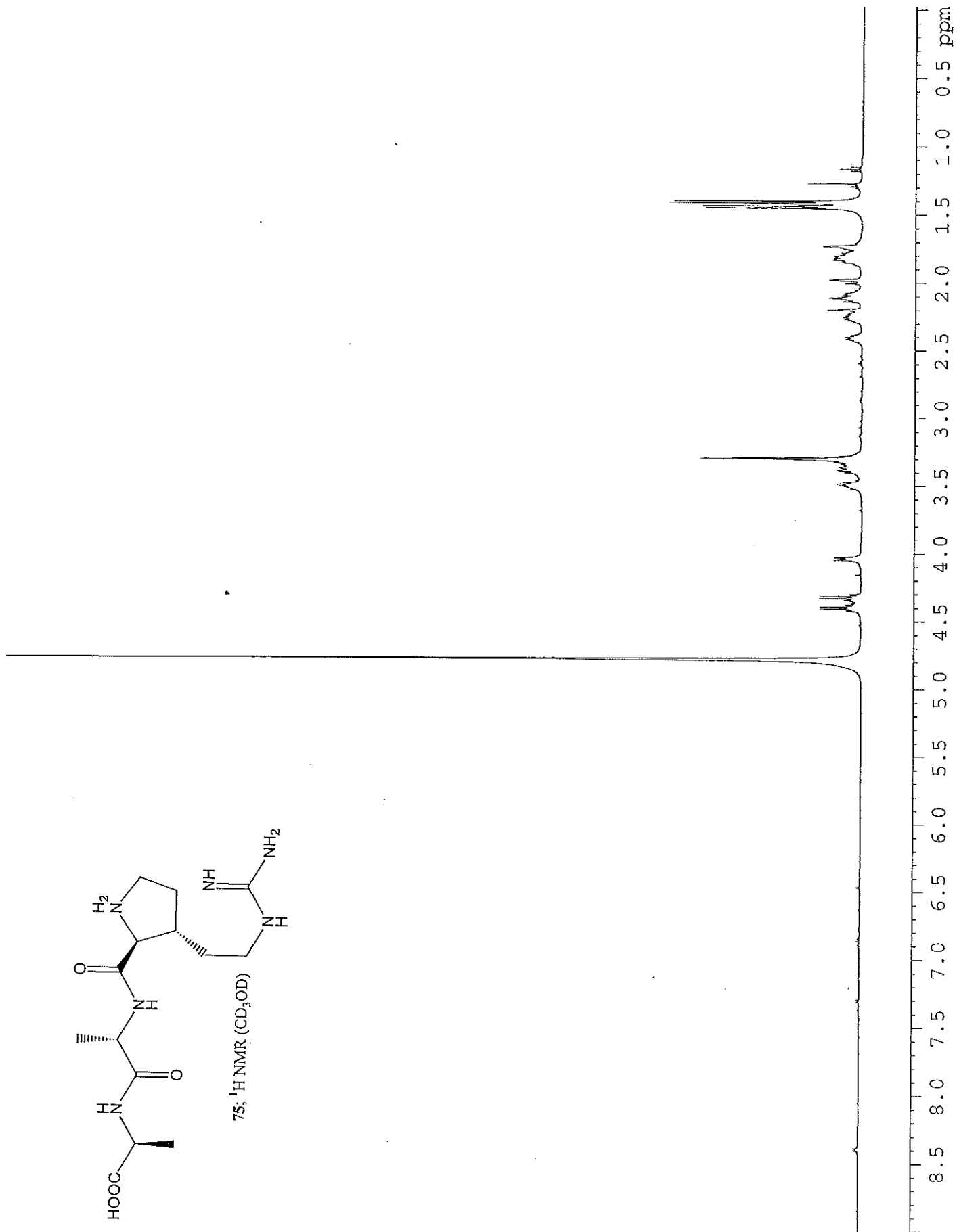
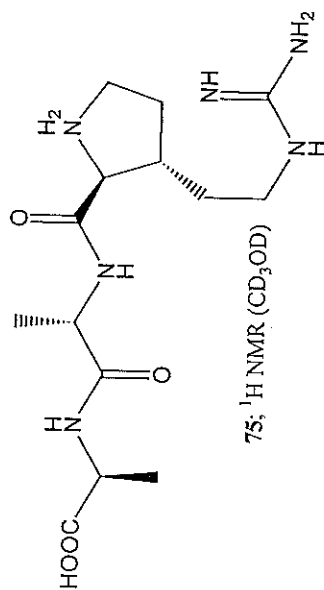






69: ^{13}C NMR (CDCl_3)





SPEC: cd021903 (19-FEB-02)

Samp: sf-6-95-2, ~~104~~

Comm: Scan 200-1000 2s

Oper: MJennings

Base: 343.21

Peak: 1000.0 mmu

REG #9 @ 1.15 min (ESI +Q1MS LMR UP LR) (/32<42)

Study : MS, mw=~~636.8~~ **423.7**

Masses: 249.99 > 1000.01

Intensity: 587226

Scans : 1 > 83

Client: Steve Flemer

#Peaks: 773

RIC : 2500276

5.9E+05

343.21
(M - DOMINANT YL)

100

80

S125

60

40

20

0

250

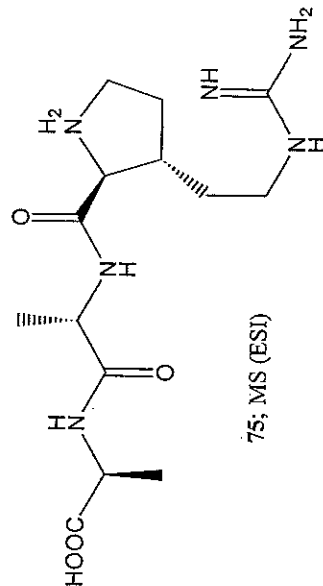
300

350

400

450

500



477.35

478.39

383.40

433.27

414.29

397.18

365.26

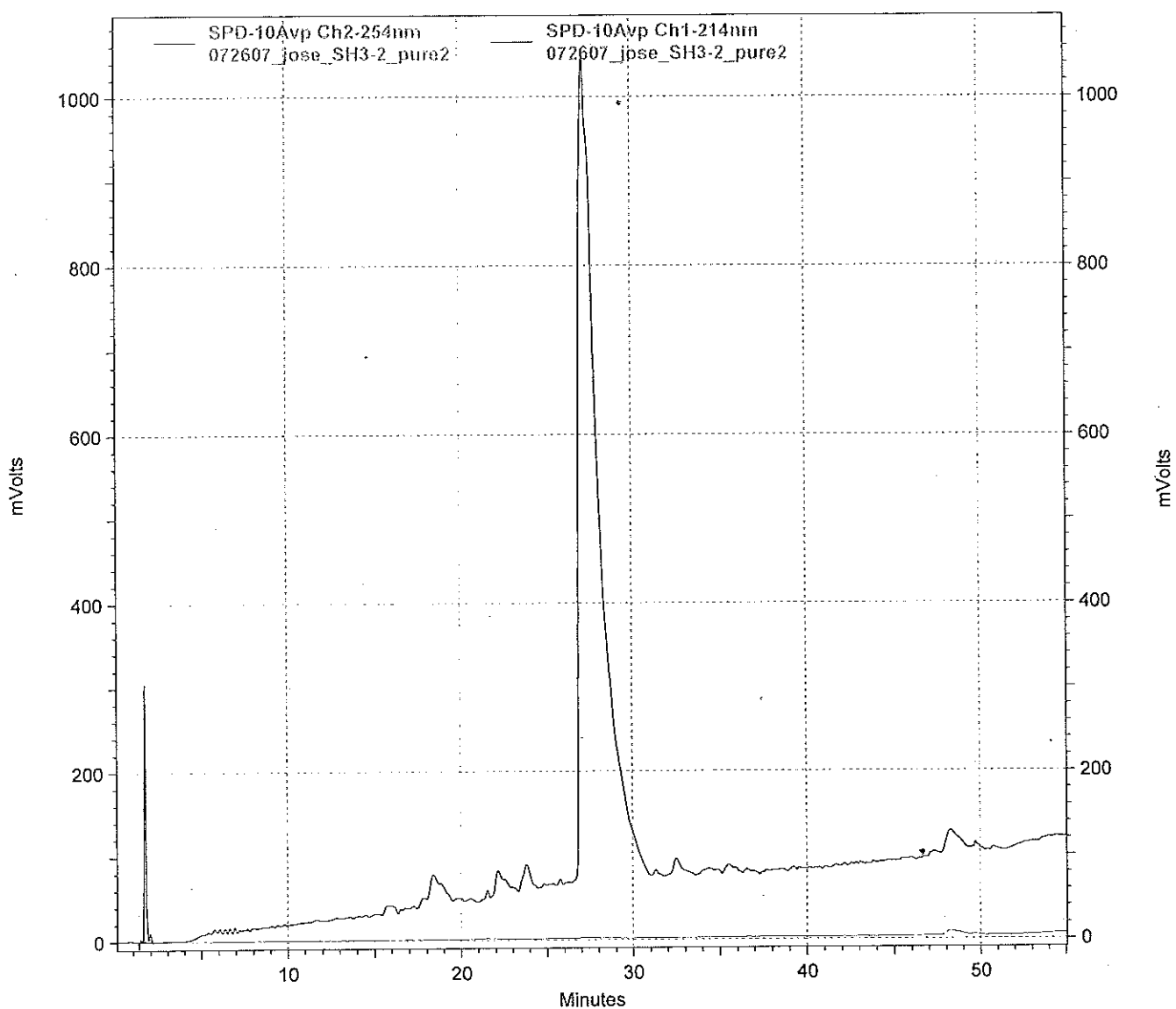
344.25

304.19

271.21

251.13

309.15



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