

SUPPORTING MATERIAL

A Novel Route to Pyrrolo[2,1-c][1,4]Benzodiazepine-5-ones (PBDs). Formal

Total Synthesis of (±)-DC-81

By Tiansheng Wang, Alfred S. Lui and Ian S. Cloudsdale

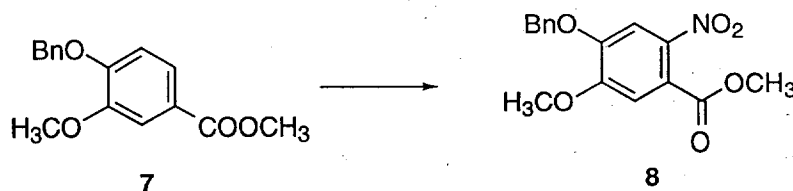
Experimental Section

N-allylisatoic anhydride **5a** was purchased from Maybridge. Reagents and solvents were used as received from commercial suppliers. TLC was performed on pre-coated silica gel 60 F₂₅₄ plates from Merck using reagent-grade solvents. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). ¹H-NMR were performed at 300 MHz and ¹³C NMR at 75 MHz in CDCl₃ unless otherwise specified. Chemical shifts are in ppm downfield from internal tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer. Mass spectra were recorded on a HP 5989B spectrometer. HRMS were performed by Mass Spectrometry Facility of University of California, Berkeley. Elemental analyses were conducted by Galbraith Laboratories, Inc.



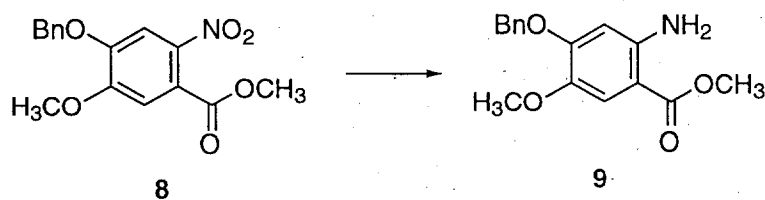
Methyl 4-benzyloxy-3-methoxybenzoate (7): A suspension containing 4-benzyloxy-3-methoxybenzoic acid **6** (14.69 g, 56.88 mmol), potassium carbonate (15.7 g, 114 mmol) and methyl iodide (5.3 ml, 85.5 mmol) in acetone (300 ml) was heated under reflux for 3 h. After filtration and washing with dichloromethane, the combined filtrates were concentrated under vacuum to a residue,

which was re-dissolved in dichloromethane (200 ml). The resulting solution was washed with water (2 x 50 ml), dried (Na_2SO_4) and concentrated. The residue was triturated with methanol to afford **7** (9.07 g, 58.6%) as white solid. Mp. 80.5-82°C (MeOH); TLC (SiO_2 , hexane/ethyl ether, 1:1) R_f = 0.55; ^1H -NMR (300 MHz, CDCl_3) δ 7.62-7.32 (m, 7 H), 6.89 (d, J = 8.4 Hz, 1 H), 5.20 (s, 2 H), 3.92 (s, 3 H), 3.87 (s, 3 H); ^{13}C -NMR (75 MHz, CDCl_3) δ 166.77, 152.07, 149.11, 136.33, 128.59, 128.00, 127.17, 123.32, 122.96, 112.47, 70.74, 56.02, 51.89; API-TIS m/z : 272 (M). Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C 70.58; H 5.92. Found: C 70.29; H 5.77.



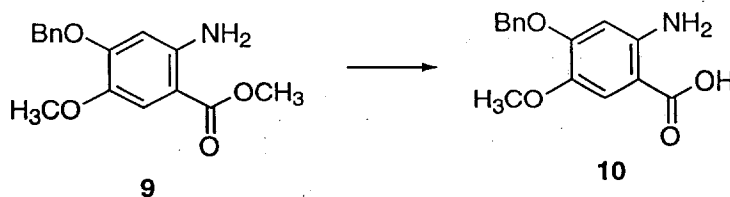
Methyl 4-benzyloxy-5-methoxy-2-nitrobenzoate (8): To a solution of methyl ester **7** (8.76 g, 32.17 mmol) in dichloromethane at -25°C (dry ice/carbon tetrachloride bath) was added a fresh prepared mixture consisting of tin (IV) chloride (40 ml of 1M in dichloromethane solution, 40 mmol) and fuming nitric acid (2.14 ml, 51 mmol) in 3 min. The resulting mixture was kept at -20°C for 10 min. Water (100 ml) was added to the reaction and the mixture was separated. The aqueous phase was extracted by ethyl acetate (2 x 80 ml) and the combined organic phases were washed with brine and dried under sodium sulfate. Concentration under vacuum then gave a residue that was triturated with methanol to generate **8** as a white solid (8.43 g, 82.6%). Mp. 126-127°C (needles from MeOH); TLC (SiO_2 , hexane/ethyl ether, 1:1) R_f = 0.32; ^1H -NMR (300 MHz, CDCl_3) δ 7.66 (s, 1 H), 7.63-7.34 (m, 5 H), 7.08 (s, 1 H), 5.21 (s, 2 H), 3.98 (s, 3 H), 3.91 (s, 3 H); ^{13}C -NMR (75 MHz, CDCl_3) δ 166.30, 153.08, 149.38, 140.97, 135.13, 128.82, 128.55, 127.51, 121.97, 111.06, 108.95, 71.44, 56.61, 53.21;

API-TIS m/z: 317 (M). Anal. Calcd. for $C_{16}H_{15}NO_6$: C 60.57; H 4.77; N 4.41. Found: C 60.47; H 4.59; N 4.38.

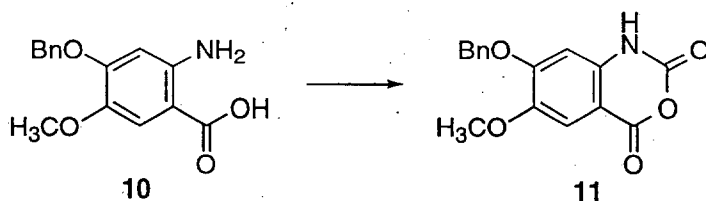


Methyl 2-amino-4-benzyloxy-5-methoxybenzoate (9): To a solution of **8** (6.34 g, 19.98 mmol) in dichloromethane (100 ml) and methanol (50 ml) was added nickel (II) chloride hexahydrate (1.5 g, 6.3 mmol). Sodium borohydride (2.5 g, 66 mmol) was then added in portions to the reaction at 0-5°C in 30 min. The solvents were evaporated under vacuum and to the resulting residue was added cold 2 N hydrochloric acid (100 ml). The mixture was extracted with ethyl acetate (3 x 80 ml). After washing with brine (30 ml) and drying (Na_2SO_4), the organic layer was evaporated under vacuum.

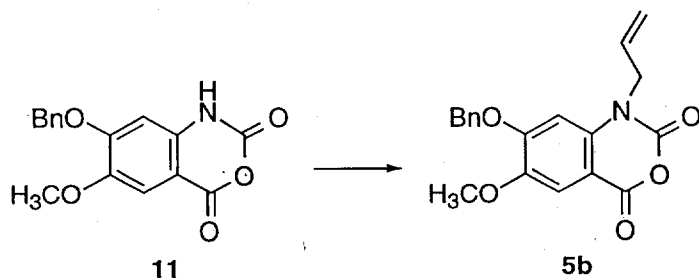
Recrystallization of the residue gave **9** as an amorphous solid (5.50 g, 95.8%). Mp. 128-128.5°C (needles from MeOH); TLC (SiO_2 , hexane/ethyl ether, 1:1) R_f = 0.41; 1H -NMR (300 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5 H), 7.34 (s, 1 H), 6.15 (s, 1 H), 5.49 (b s, 2 H), 5.11 (s, 2 H), 3.84 (s, 3 H), 3.82 (s, 3 H); ^{13}C -NMR (75 MHz, $CDCl_3$) δ 168.07, 153.91, 146.85, 140.81, 136.14, 128.59, 127.98, 127.05, 113.10, 102.27, 101.01, 70.35, 56.51, 51.29; API-TIS m/z: 288 (M). Anal. Calcd. for $C_{16}H_{17}NO_4$: C 66.89; H 5.96; N 4.87. Found: C 66.70; H 5.69; N 4.81.



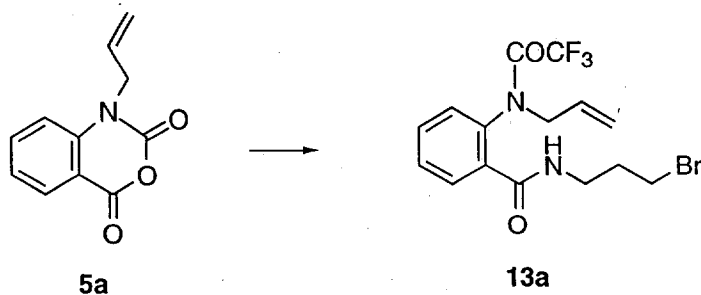
2-Amino-4-benzyloxy-5-methoxybenzoic acid (10): A solution of **9** (4.88 g, 16.98 mmol) in 2 N sodium hydroxide (60 ml) and methanol (60 mL) was heated at reflux for 1 h. Methanol was removed by a rotary evaporator and the aqueous residue was acidified to pH 2 with cold concentrated hydrochloric acid. Filtration and washing with water then gave the acid **10** as solid (4.55 g, 98.0%). Mp. 190-193°C (MeOH); $^1\text{H-NMR}$ (300 MHz, DMSO- d_6) δ 7.84-7.45 (m, 5H), 7.37 (s, 1H), 7.09 (s, 1H), 5.22 (s, 2H), 3.82 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, DMSO- d_6) δ 167.67, 152.42, 143.82, 136.93, 136.11, 128.57, 128.25, 128.18, 113.41, 108.90, 105.13, 69.86, 55.97; API-TIS m/z: 274 (M+1).



7-Benzyloxy-6-methoxyisatoic anhydride (11): A suspension of the acid **10** (2.88 g, 10.54 mmol) in 2N sodium hydroxide (30 ml) was warmed to a clear solution and then cooled to room temperature. A 20% phosgene-toluene solution (15 ml) was then added. After stirring at room temperature for 2 h, the reaction was filtered and the resulting solid was washed with 2% methanol in water (20 ml). Drying under vacuum then gave **11** as a tan solid (2.5 g, 81.1%). Mp. 234-235°C (acetonitrile-ether); $^1\text{H-NMR}$ (300 MHz, DMSO- d_6) δ 11.74 (s, 1 H), 7.58-7.52 (m, 5H), 7.39 (s, 1H), 6.86 (s, 1H), 5.31 (s, 2H), 3.93 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, DMSO- d_6) δ 159.35, 155.40, 147.32, 145.80, 137.47, 135.56, 128.52, 128.27, 128.07, 108.84, 101.41, 99.01, 70.25, 55.93; API-TIS m/z: 300 (M+1).

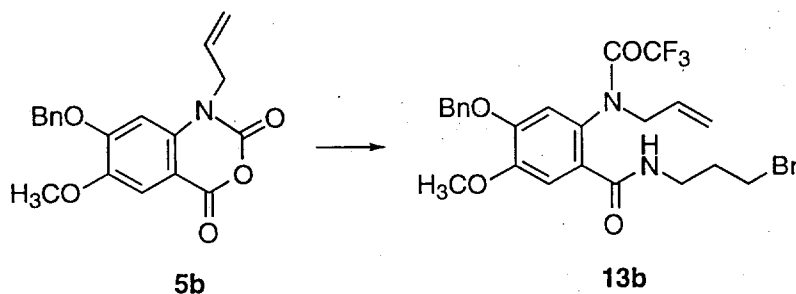


N-Allyl-7-benzyloxy-6-methoxyisatoic anhydride (5b): To a solution of **11** (2.00 g, 6.68 mmol) in N,N-dimethyl acetamide (30 ml) was added sodium hydride (0.245 g, 10.2 mmol) in 3 min. The resulting solution was stirred at room temperature for 30 min. Allyl bromide (1.05 ml, 12.1 mmol) was added. After stirring at room temperature for 12 h, water (60 ml) was added. The mixture was extracted with dichloromethane (3 x 20 ml). The combined extracts were washed with brine and dried. Removal of solvent under vacuum gave the residue, which was washed with small amount of ether to afford **5b** as white solid (1.98 g, 87.3%). Mp. 148-149°C (ethyl acetate-hexane); TLC (SiO₂, hexane / ethyl ether, 1:1) R_f = 0.10; ¹H-NMR (300 MHz, CDCl₃) δ 7.49 (s, 1 H), 7.41-7.35 (m, 5 H), 6.54 (s, 1 H), 5.82-5.70 (m, 1 H), 5.27 (s, 2 H), 5.19 (d, J = 10.4 Hz, 1 H), 5.11 (d, J = 17.2 Hz, 1 H), 4.52 (d, J = 4.9 Hz, 2 H), 3.95 (s, 3 H); ¹³C-NMR (75 MHz, CDCl₃) δ 158.21, 155.61, 148.15, 146.50, 137.17, 135.10, 130.18, 128.98, 128.56, 126.87, 118.37, 110.37, 103.55, 99.65, 71.38, 56.42, 47.23; API-TIS m/z : 340 (M+1); Anal. Calcd for C₁₉H₁₇NO₅: C 67.25; H 5.05; N 4.13. Found: C 67.10; H 4.93; N 4.01.



2-(Allyl-trifluoroacetyl-amino)-N-(3-bromopropyl)-benzamide (13a) : To a solution of N-allylisatoic anhydride (2.03 g, 10 mmol) in 20 ml acetonitrile was added triethylamine (2.7 ml, 20 mmol), followed by 3-bromopropylamine hydrobromide (3.0g, 13.7 mmol). After stirring at room temperature for 5 h, the reaction was evaporated under vacuum and the residue was purified by flash chromatography (SiO₂, hexane/ethyl ether, 3:1) to give 2.869 g of allylaminobenzamide **12**. During the condensation of the purified fractions, a new, nonpolar spot gradually appeared on TLC. Therefore it was immediately acetylated as follows. The purified product was dissolved in 70 ml dichloromethane and triethylamine (1.5 mmol, 10.8 mmol) was added. To the ice-cooled reaction was added dropwise trifluoroacetic anhydride (1.48 ml, 10.5 mmol). After stirring at 0°C for 5 min, the reaction was washed with water and the aqueous phase was extracted with dichloromethane (2 X 10 ml). The combined organic phase was dried (Na₂SO₄) and evaporated. The residue was purified by flash chromatography (SiO₂, hexane / ethyl ether, 1:1) to afford 3.1154 g of the **13a** as a white solid (79.2% over 2 steps). TLC (SiO₂, hexane/ethyl ether, 1:1) R_f = 0.26; ¹H-NMR (300 MHz, CDCl₃) δ 7.61 (dd, *J* = 7.1 and 1.6 Hz, 1 H), 7.52-7.41 (m, 2 H), 7.21 (d, *J* = 7.4 Hz, 1 H), 6.93 (br t, *J* = 5.4 Hz, 1 H), 5.89-5.76 (m, 1 H), 5.17 (d, *J* = 10.0 Hz, 1 H), 5.09 (d, *J* = 17.1 Hz, 1 H), 4.74 (dd, *J* = 14.6 and 5.6 Hz, 1H), 3.87 (dd, *J* = 14.6 and 7.6 Hz, 1 H), 3.52 (br d, *J* = 6.6 Hz, 2 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 2.13 (t, *J* = 6.6 Hz, 2 H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.66, 156.21 (q, *J* = 35 Hz, CO-CF₃), 136.55, 133.90, 130.81, 130.58, 130.48, 129.31, 128.00, 119.73, 116.07 (q, *J* = 287 Hz, CF₃), 54.74, 38.34, 31.68, 30.48; IR (film) ν_{max}: 3346, 2934, 1697, 1650, 1599, 1534, 1488, 1450, 1303, 1195, 1152, 931, 757 cm⁻¹; MS *m/z* (rel intens) 395 (3), 393 (3), 325 (3), 323 (2), 314 (1), 313 (7), 297 (2), 295 (3), 281 (7), 280 (26), 279 (10), 278 (25), 265 (2), 263 (2), 256 (17), 153 (7), 251 (7), 244 (4), 243 (21), 228 (2), 226 (1), 217 (2), 216 (10), 215 (9), 199 (12), 186 (14), 172 (14), 171 (38), 168 (5), 160 (7), 159 (19), 158 (100), 157 (36), 147 (7), 146 (52), 144 (11), 142 (6), 132 (16), 131 (18), 130 (42),

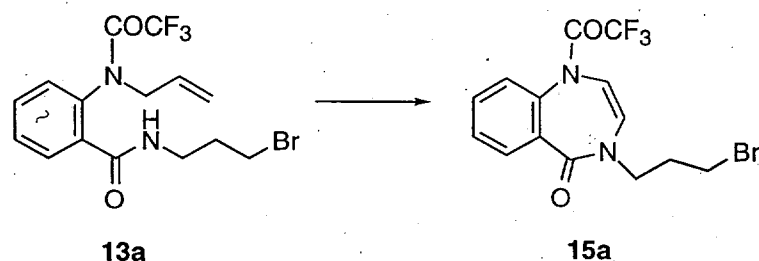
129 (8), 118 (11), 105 (17), 104 (14), 103 (18), 102 (11); Anal. Calcd. for $C_{15}H_{16}BrF_3N_2O_2$: C 45.82; H 4.10; N 7.12; Br 20.32; F 15.11. Found: C 46.09; H 4.22; N 7.32; Br 20.09; F 15.03.



2-(Allyl-trifluoroacetyl)-amino-4-benzyloxy-N-3-(bromopropyl)-5-methoxy-benzamide (13b):

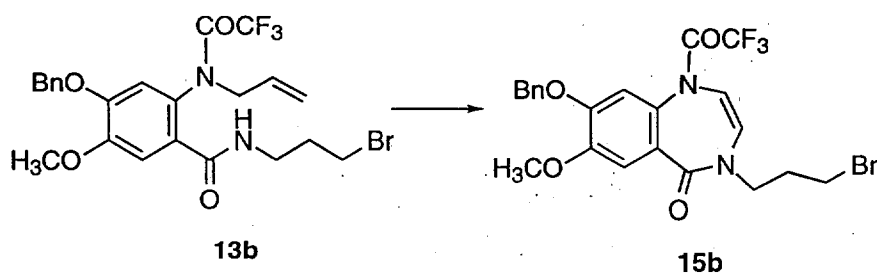
To a solution of **5b** (0.339g, 1.0 mmol) and triethylamine (0.18 ml, 1.3 mmol) in dichloromethane (5 ml) was added 3-bromopropylamine hydrobromide (0.259 g, 1.2 mmol). After stirring at room temperature for 2 h, additional triethylamine (0.18 ml) and 3-bromopropylamine hydrobromide (0.259 g) were added. After 2 h, the TLC (SiO_2 , ethyl acetate/hexane, 1:1) indicated that most of the **5b** had been consumed. The solvents were evaporated and the residue was partitioned between water (30 ml) and dichloromethane (50 ml). The separated organic layer was dried and concentrated in vacua. The crude product was dissolved in dichloromethane (5ml) and cooled to 0°C. Triethylamine (0.21 ml, 1.5 mmol) and trifluoroacetic anhydride (0.2 ml, mmol) were added. After 10 min, the reaction was warmed to room temperature and concentrated under vacuum. The residue was dissolved in dichloromethane (30 ml) and washed with water (15 ml). Drying (Na_2SO_4) and evaporating gave the crude product which was purified by flash chromatography (SiO_2 , ethyl acetate / hexane 1:2) to generate **13b** as an oil (0.31 g, 58%). TLC (SiO_2 , ethyl acetate / hexane, 1:1) R_f = 0.60; 1H -NMR (300 MHz, $CDCl_3$) δ 7.37-28 (m, 5 H), 7.11 (s, 1 H), 6.62 (s, 1 H), 6.31 (t, J = 6.4 Hz, 1 H), 5.71-5.62 (m, 1 H), 5.25-4.92 (m, 4 H), 4.72 (dd, J = 14.4 and 5.6 Hz, 1 H), 3.93 (s, 3H), 3.78 (dd, J = 14.4 and 7.8

Hz, 1 H), 3.56-3.43 (m, 4 H), 2.16-2.04 (m, 2 H); ^{13}C -NMR (75 MHz, CDCl_3) δ 166.23, 156.34 (q, J = 35 Hz, COCF_3), 149.55, 149.03, 135.61, 130.62, 129.57, 128.54, 127.48, 127.00, 126.47, 120.00, 116.16 (q, J = 287 Hz, CF_3), 116.15, 110.84, 70.99, 56.14, 54.91, 38.52, 31.75, 30.74; IR (film) ν_{max} : 3350, 3066, 3014, 2940, 1694, 1650, 1601, 1504, 1454, 1354, 1269, 1204, 1150, 1038, 1020, 915, 871, 755, 698 cm^{-1} ; MS m/z (rel intens) (CI) 531 (19), 529 (20), 489 (3), 477 (5), 452 (4), 451 (16), 450 (29), 449 (100), 439 (3), 409 (15), 392 (6), 379 (18), 359 (27), 132 (8), 115 (48), 114 (17); Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{BrF}_3\text{N}_2\text{O}_4$: C 52.19; H 4.57; N 5.29. Found: C 52.32; H 4.86; N 5.27.



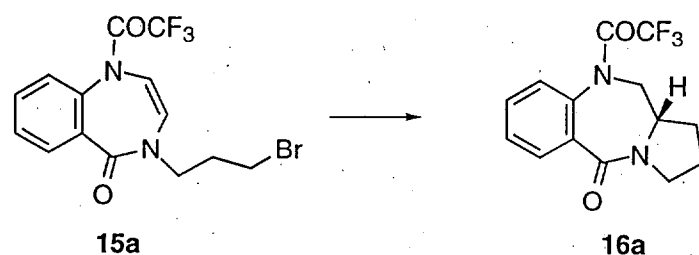
4-(3-Bromopropyl)-1-trifluoroacetyl-1, 4-dihydrobenzo[e][1,4]diazepin-5-one (15a): Ozone was bubbled through a solution containing **13a** (2.5778 g, 6.56 mmol) in dichloromethane (60 ml) and methanol (10 ml) at -78°C until a blue color persisted for 5 min. After bubbling with nitrogen for 5 min, dimethyl sulfide (0.53 ml, 7.2 mmol) was added and the reaction was warmed from -78°C to room temperature in 2 h. The solvents were removed under vacuum and the residue was dissolved in dichloromethane (100 ml). Washing with water, drying (Na_2SO_4) and evaporation then gave the crude hemi-aminal which was dissolved in benzene (45 ml). After addition of camphorsulfonic acid (0.2 g) and connection to a Dean-Stark trap, the benzene solution was refluxed overnight. Evaporation followed by purification by flash column (SiO_2 , ethyl ether / hexane, 1:1) then afforded pure **15a** as a viscous oil (1.7144 g, 69.3%), TLC (SiO_2 , hexane/ethyl ether, 1:1) R_f = 0.35; ^1H -NMR (300 MHz, CDCl_3) δ 7.92 (dd, J = 7.8 and 1.3 Hz, 1 H), 7.59 (td, J = 7.7 and 1.5 Hz, 1 H), 7.45 (br t, J = 7.5 Hz, 1 H), 7.31 (br d, J = 7.9 Hz, 1 H), 6.44 and 6.39 (br s, 1 H), 6.14 (d, J = 5.6 Hz, 1 H), 4.31-4.10 (m, 1

H), 3.54-3.44 (m, 3 H), 2.28-2.20 (m, 2 H); ^{13}C -NMR (75 MHz, CDCl_3) δ 166.22, 155.20 (q, $J = 36$ Hz, COCF_3), 141.29, 132.74, 132.10, 129.88, 129.46, 128.50, 125.61, 116.95, 115.94 (q, $J = 286$ Hz, CF_3), 47.79, 31.12, 30.03; IR (film) ν_{max} : 3084, 1719, 1648, 1602, 1578, 1455, 1407, 1306, 1280, 1230, 1203, 1113, 1084, 923, 885, 746 cm^{-1} ; MS m/z (rel intens) 379 (4), 378 (26), 377 (6), 376 (26), 361 (1), 359 (1), 331 (1), 329 (1), 310 (10), 309 (63), 308 (13), 307 (64), 298 (4), 297 (23), 281 (11), 279 (10), 265 (4), 242 (4), 229 (38), 200 (4), 187 (27), 171 (6), 146 (6), 145 (9), 144 (21), 143 (5), 133 (10), 132 (100), 130 (5), 123 (16), 121 (16), 117 (10), 116 (10), 104 (10), 103 (10), 89 (9), 77 (22), 76 (16), 69 (9), 51 (4); Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{BrF}_3\text{N}_2\text{O}_2$: C 44.58; H 3.21; N 7.43; Br 21.19; F 15.11. Found: C 44.46; H 3.31; N 7.61; Br 21.05; F 15.03.



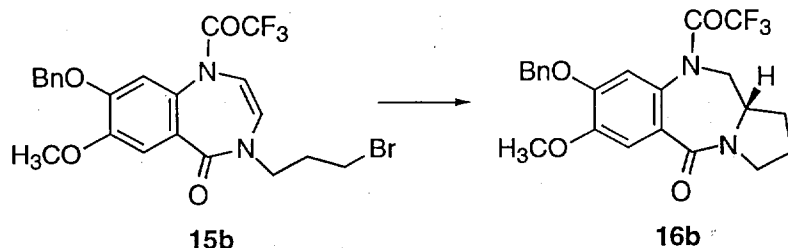
8-Benzyloxy-4-(3-bromopropyl)-7-methoxy-1-trifluoroacetyl-1,4-dihydrobenzo[e] 1,4]diazepin-5-one (15b): The process for 15a was repeated, starting from 0.1464 g (0.28 mmol) of 13b, 0.064 g product 15b was obtained (45.1%), TLC (SiO_2 , ethyl ether/hexane, 1:1) $R_f = 0.31$; ^1H -NMR (300 MHz, CDCl_3) δ 7.45-7.31 (m, 6 H), 6.81 (s, 1 H), 6.32 (br s, 1 H), 6.09 (d, $J = 5.4$ Hz, 1 H), 5.19 (d, $J = 12.1$ Hz, 1 H), 5.08 (d, $J = 12.1$ Hz, 1 H), 4.29-4.11 (m, 1 H), 3.91 (s, 3 H), 3.49-3.13 (m, 3 H), 2.26-2.18 (m, 2 H); IR (film) ν_{max} : 2937, 1711, 1643, 1604, 1515, 1454, 1418, 1265, 1227, 1198, 1153, 1063, 1026, 871, 751 cm^{-1} ; MS m/z (rel intens) 515 (25), 514 (98), 513 (29), 512 (100), 497 (2), 495 (3), 446 (17), 445 (65), 444 (18), 443 (69), 435 (3), 434 (12), 433 (29), 432 (8), 423 (8), 417 (8), 415 (7), 401 (9), 399 (8), 395 (6), 393 (6), 365 (8), 355 (10), 354 (11), 353 (15), 352 (10), 325 (7), 298 (7), 296 (8),

274 (9), 268 (11), 246 (25), 189 (13), 178 (20), 177 (12), 176 (21), 175 (19), 147 (28), 123 (29), 121 (37); EI-HRMS m/z calcd for $C_{22}H_{20}BrF_3N_2O_4$ (M^+) 512.0558 and 514.0538, found 512.0564 and 514.0542.

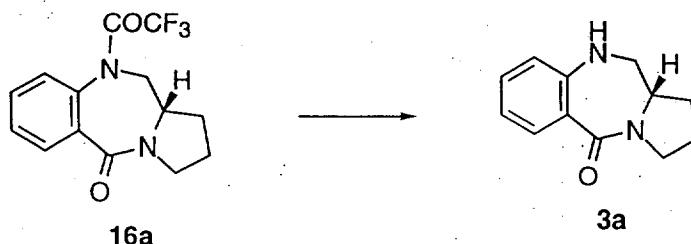


10-Trifluoroacetyl-1,2,3,10,11,11a-hexahydro-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one (16a): A solution containing the benzodiazepinone **15a** (1.00 g, 2.65 mmol), tributyltin hydride (0.655 ml, 3.31 mmol) and AIBN (0.20 g) in benzene (177ml) was degassed with argon for 5 min and then refluxed for 2 h. After cooling and adding more tributyltin hydride (0.6 ml) and AIBN (0.2 g), the reflux was continued for another 2 h. Cooling and evaporation then gave a residue which was purified by flash chromatography (SiO_2 , 1:1 hexane/ethyl acetate) to afford 0.7145 g of **15** as a white solid (90.3%), mp 154-155°C; TLC (SiO_2 , hexane /ethyl acetate, 1:1) R_f = 0.17; 1H -NMR (300 MHz, $CDCl_3$) δ 7.84-7.81 (m, 1H), 7.56-7.53 (m, 2H), 7.27-7.24 (m, 1H), 4.41 (t, J = 12.6 Hz, 1 H), 3.83-3.72 (m, 2 H), 3.61-3.55 (m, 1 H), 3.51 (dd, J = 12.8 and 4.7Hz, 1 H), 2.18-2.02 (m, 3 H), 1.88-1.85 (m, 1 H); ^{13}C -NMR (75 MHz, $CDCl_3$) δ 165.95, 157.74, (q, J = 36 Hz, $COCF_3$), 135.04, 134.33, 131.48, 129.91, 129.50, 127.85, 115.94 (q, J = 286 Hz, CF_3), 55.79, 54.41, 46.12, 28.20, 23.09; IR (film) ν_{max} : 2978, 2880, 1698, 1650, 1602, 1488, 1458, 1413, 1355, 1201, 1157, 1120, 1010, 898, 776, 757, 719, 698 cm^{-1} ; MS m/z (rel intens) 299 ($M+1$, 1), 298 (M , 6), 279 (1), 270 (3), 230 (6), 229 (29), 216 (4), 201 (7), 187 (7), 186 (48), 166 (2), 160 (6), 146 (3), 133 (10), 132 (100), 116 (2), 105 (6), 104 (7), 90 (5), 83

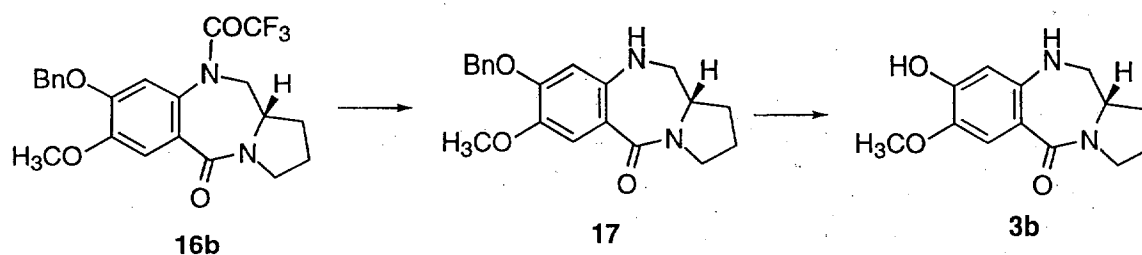
(34), 77 (23), 70 (39), 51 (5); Anal. Calcd for $C_{14}H_{13}F_3N_2O_2$: C 56.38; H 4.39; N 9.39. Found: C 56.01; H 4.40; N 9.31.



8-Benzoyloxy-7-methoxy-10-trifluoroacetyl-1,2,3,10,11,11a-hexahydro-benzo[e] pyrrolo[1,2-a] [1,4] diazepin-5-one (16b): A solution containing the bicyclic bromide **15b** (0.084 g, 0.16 mmol), tributyltin hydride (0.057 ml, 0.029 mmol) and AIBN (5 mg) in benzene (13 ml) was degassed with argon for 5 min, and then heated to reflux for 2 h. After cooling and evaporation, the residue was purified by flash chromatography (SiO_2 , ethyl acetate/hexane 2.5:1) to afford pure product as a white solid (0.065 g, 91%). Mp 199-200°C (ether/hexane); TLC (SiO_2 , hexane/ethyl acetate, 1:3) R_f = 0.34; 1H -NMR (300 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5 H), 7.28 (s, 1 H), 6.72 (s, 1 H), 5.13 (s, 2 H), 4.34 (t, J = 12.6 Hz, 1 H), 3.93 (s, 3 H), 3.79-3.70 (m, 2 H), 3.57-3.48 (m, 1 H), 3.43 (dd, J = 12.8 and 4.8 Hz, 1 H), 2.12-1.97 (m, 3 H), 1.84-1.79 (m, 1 H); ^{13}C -NMR (75 MHz, $CDCl_3$) δ 166.19, 157.31 (q, J = 36 Hz, $COCF_3$), 150.25, 149.84, 135.67, 128.64, 128.02, 127.79, 127.25, 127.12, 115.95 (q, J = 286 Hz, CF_3), 113.24, 111.56, 71.31, 56.16, 56.04, 54.70, 46.19, 28.38, 23.14; IR (film) ν_{max} : 2956, 2878, 1698, 1642, 1603, 1515, 1454, 1430, 1381, 1280, 1197, 1158, 1044, 1002, 875, 753, 698, cm^{-1} ; MS m/z (rel intens) 435 ($M+1$, 3), 434 (M , 10), 365 (2), 343 (1), 315 (1), 190 (1), 176 (1), 175 (1), 149 (1), 122 (2), 105 (3), 92 (9), 91 (100), 89 (1); EI-HRMS m/z calcd for $C_{22}H_{21}F_3N_2O_4$ (M^+) 434.1453, found 434.1463.



1,2,3,10,11,11a-hexahydro-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one (3a): The trifluoroacetamide 16a (0.7145 g, 2.40 mmol) was dissolved in methanol (10 ml) and water (2 ml). After addition of potassium carbonate (0.5 g), the reaction was stirred at room temperature overnight. Evaporation gave a white residue, which was washed three times with water and dried under vacuum to afford pure product 3a (0.466g, 96.2%) as a white solid. Mp 175.5-177°C; TLC (SiO₂, 5% methanol in dichloromethane) R_f = 0.37; ¹H-NMR (300 MHz, CDCl₃) δ 8.00 (d, J = 8.1 Hz, 1 H), 7.17 (t, J = 7.6 Hz, 1 H), 6.74 (t, J = 7.5 Hz, 1 H), 6.57 (d, J = 8.1 Hz, 1 H), 4.54 (d, J = 6 Hz, 1 H), 3.89-3.77 (m, 2 H), 3.70-3.61 (m, 1 H), 3.52 (dd, J = 12.4 and 6.8 Hz, 1 H), 3.27 (dd, J = 11.8 and 10.3 Hz, 1 H), 2.27-2.13 (m, 1 H), 1.96-1.76 (m, 2 H), 1.71-1.62 (m, 1 H); ¹³C-NMR (75 MHz, CDCl₃) δ 166.79, 145.65, 132.87, 131.73, 118.67, 117.88, 117.47, 57.01, 52.98, 48.09, 30.68, 22.77; IR (film) $\nu_{\max}$: cm⁻¹; MS m/z (rel intens): 203 (M+1, 21), 202 (M, 100), 173 (2), 146 (2), 134 (5), 133 (46), 132 (23), 117 (3), 106 (4), 105 (41), 104 (44), 92 (4); Anal. Calcd for C₁₂H₁₄N₂O: C 71.26; H 6.98; N 13.85 . Found: C 70.95; H 7.03; N 13.83.



8-Hydroxy-7-methoxy-1,2,3,10,11,11a-hexahydro-benzo[e]pyrrolo[1,2-a][1,4] diazepin-5-one (3b): To tricyclic compound **16b** (0.1245 g, 0.29 mmol) in acetonitrile (9 ml) and water (2 ml) was added potassium carbonate (0.3 g). After stirring at room temperature overnight, the solvents were removed under vacuum. Water (50 ml) was added and the resulting suspension was extracted with dichloromethane (3 x 20 ml). The combined organic layers were dried (Na_2SO_4) and evaporated to give the secondary amine **17** (0.0918 g, 94.7%) as a single spot in TLC as a white solid, which was used directly for next step. TLC (SiO_2 , 4% methanol in dichloromethane) $R_f = 0.40$; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.60 (s, 1 H), 7.36-7.25 (m, 5 H), 6.07 (s, 1 H), 4.99 (s, 2 H), 4.53 (d, $J = 6.0$ Hz, 1 H), 3.81 (s, 3 H), 3.79-3.65 (m, 2 H), 3.60 (dd, $J = 12$ and 7 Hz, 1 H), 3.43 (dd, $J = 11.8$ and 7 Hz, 1 H), 3.11 (dd, $J = 11.8$ and 9 Hz, 1 H), 2.18-2.10 (m, 1 H), 1.90-1.55 (m, 3 H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) 166.25, 151.63, 141.79, 141.43, 136.47, 128.45, 127.81, 127.12, 115.19, 110.24, 102.53, 70.36, 57.66, 56.22, 52.62, 48.33, 30.76, 22.72.

The crude amine **17** was dissolved in methanol (5 ml). After addition of 10% palladium on carbon (10 mg) and ammonium formate (0.3 g), the suspension was heated to reflux for 1 h. The reaction was cooled, filtrated through celite and washed with methanol-dichloromethane (1:2). Evaporation gave the residue which was absorbed on silica gel and was chromatographic (SiO_2 , 4% methanol in dichloromethane) to afford pure **3b** as a white solid (0.0523 g, 53.9% over 2 steps). Mp 248-250°C (methanol); TLC (SiO_2 , 4% methanol in dichloromethane) $R_f = 0.20$; $^1\text{H-NMR}$ (300 MHz, methanol- d_4) δ 7.29 (s, 1 H), 6.08 (s, 1 H), 3.74 (s, 3 H), 3.64 (dd, $J = 7.2$ and 5 Hz, 1 H), 3.56-3.49 (m, 1 H),

3.23 (br s, 1 H), 3.45 (dd, $J = 12.7$ and 1.7 Hz, 1 H), 3.04 (dd, $J = 12.7$ and 8.8 Hz, 1 H), 2.20-2.12 (m, 1 H), 1.89-1.61 (m, 3 H); ^{13}C -NMR (75 MHz, methanol- d_4) δ 169.54, 152.76, 145.10, 142.18, 116.04, 110.22, 105.42, 59.90, 57.13, 54.09, 31.92, 31.07, 24.06; CI MS: 249 ($M+1$); MS m/z (rel intens) 248 (M , 100); EI HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$: M^+ , 248.1161, found 248.1160.

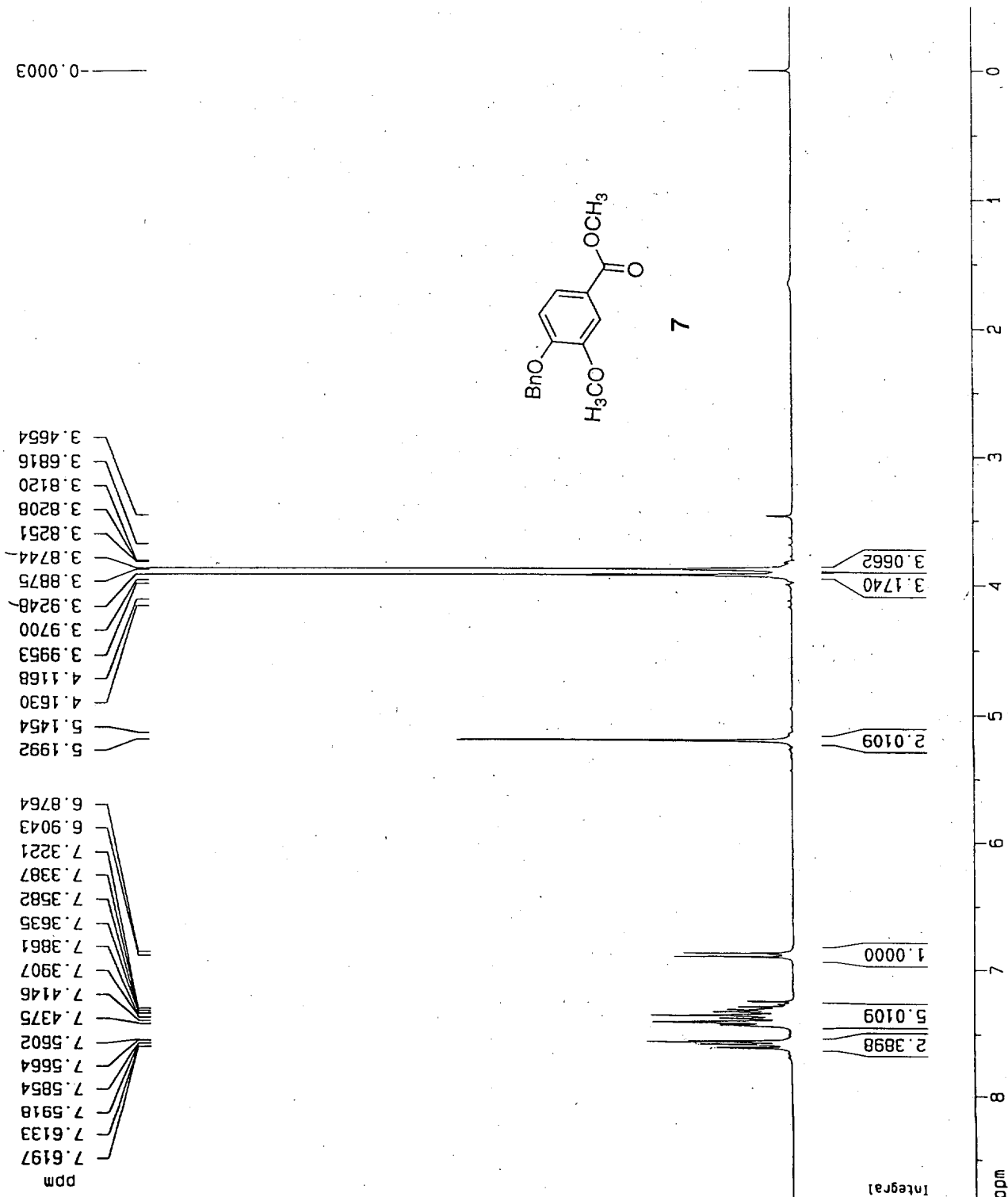
S-15

Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameters
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 SOLVENT CDCl3
 AQ 2.6214600 sec
 FIDRES 0.190735 Hz
 DK 80.0 usec
 RG 256
 NUCLEUS 1H
 HL1 1 dB
 D1 1.0000000 sec
 P1 8.0 usec
 DE 100.0 usec
 SF01 300.1351622 MHz
 SWH 6250.00 Hz
 TD 32768
 NS 8
 DS 2

F2 - Processing parameters
 SI 16384
 SF 300.1333689 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
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 F2P -0.497 ppm
 F2 -149.28 Hz
 PPMCM 0.46506 ppm/cm
 HZCM 139.58037 Hz/cm



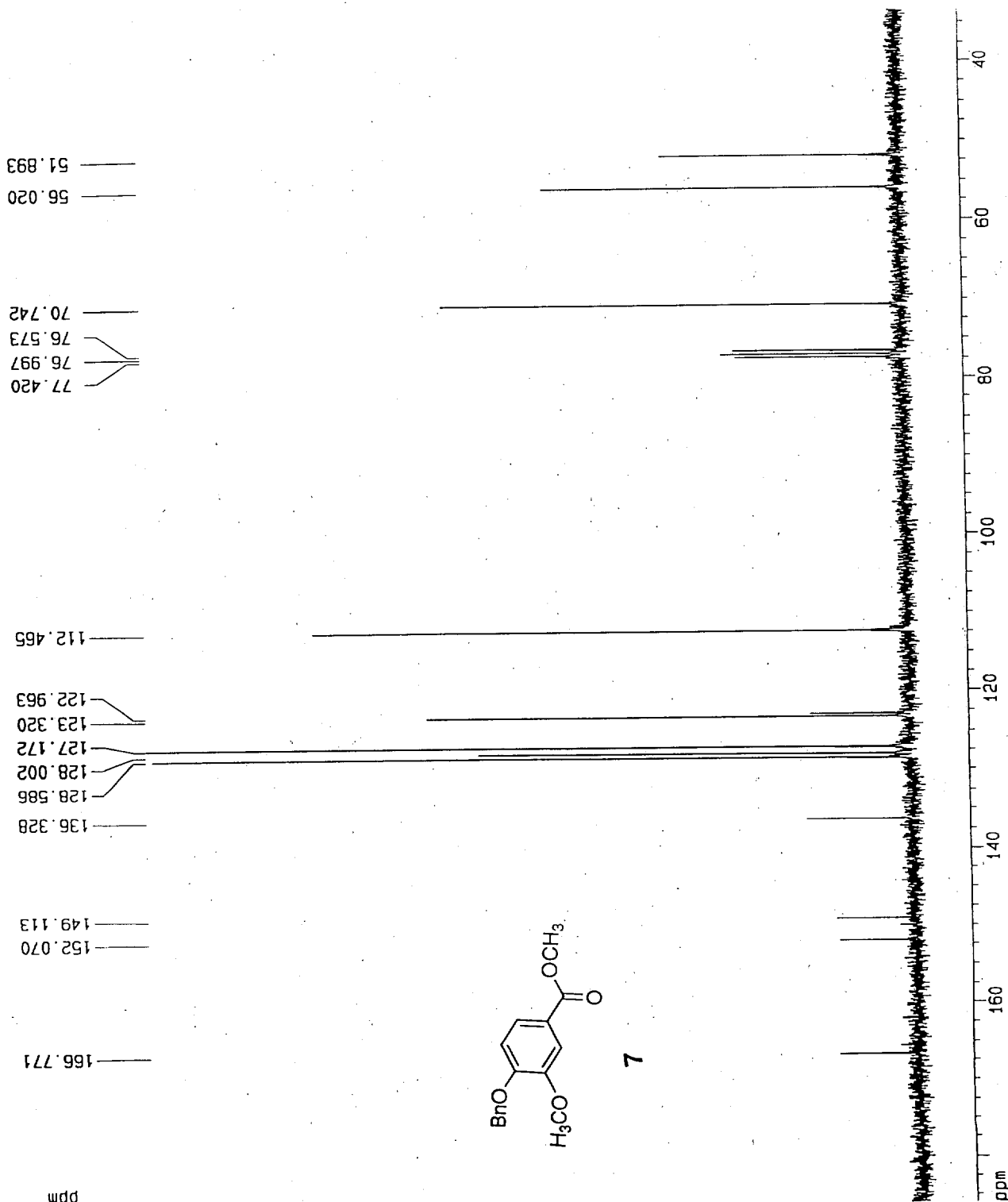
S-16

Current Data Parameters
NAME tsw-213-b37
EXPNO 2
PROCNO 1

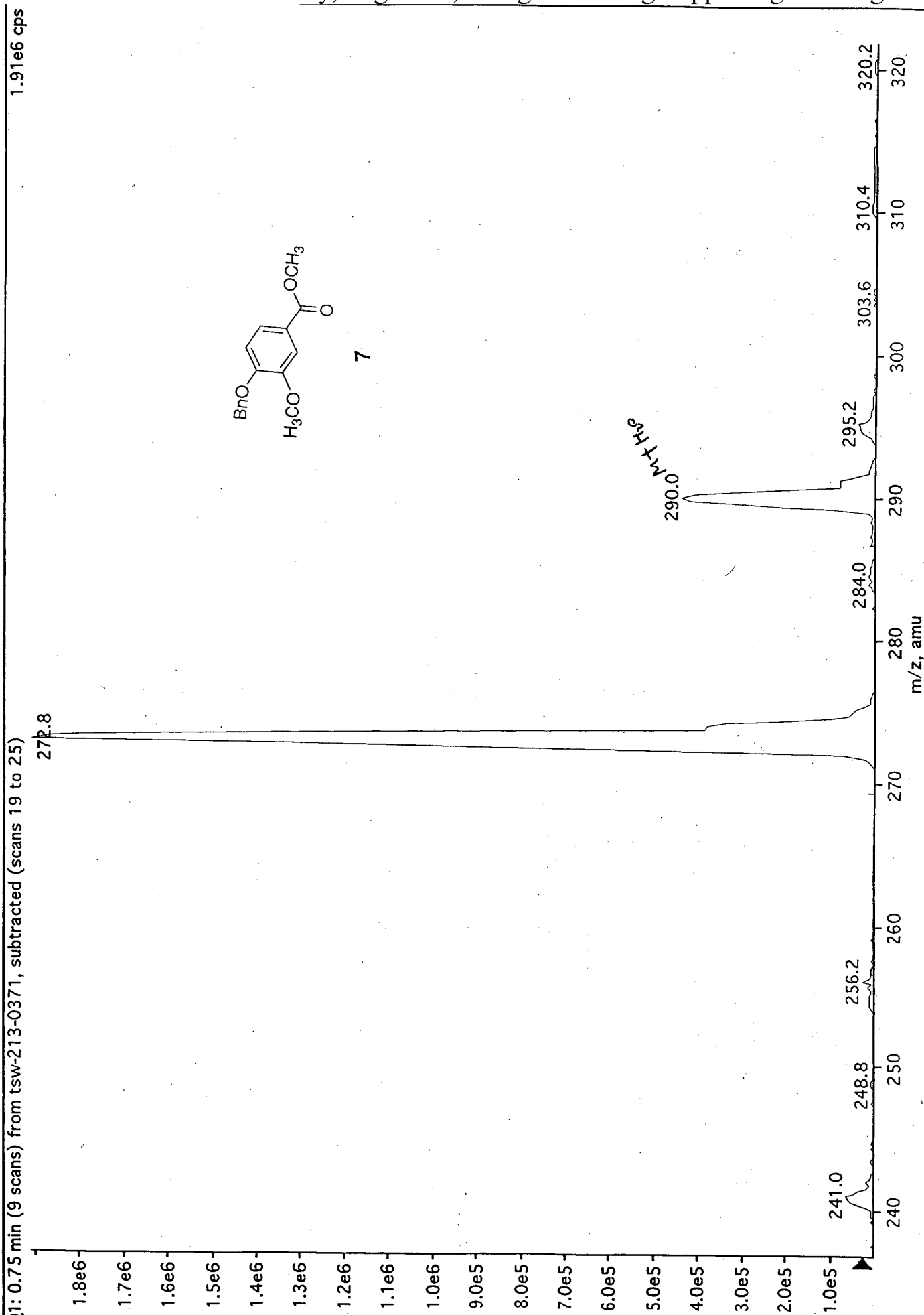
F2 - Acquisition Parameters
Date 990427
Time 17.39
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SOLVENT CDCl3
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FIDRES 0.363304 Hz
DQ 21.0 usec
RG 16384
NUCLEUS 13C
HL1 3 dB
D1 1.0000000 sec
P31 100.0 usec
S4 26 dB
D11 0.0300000 sec
S2 26 dB
P1 14.0 usec
DE 30.0 usec
SF01 75.4753021 MHz
SWH 23809.52 Hz
TD 65536
NS 344
DS 2

F2 - Processing parameters
SI 32768
SF 75.4685988 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1p 185.983 ppm
F1 14035.88 Hz
F2p 33.399 ppm
F2 2520.60 Hz
PPMCM 7.62918 ppm/cm
HZCM 575.76367 Hz/cm



Q1: 0.75 min (9 scans) from tsw-213-0371, subtracted (scans 19 to 25)
riond 1, Expt. 1; Mass range: 100.0 to 1000.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 5.0 ms
q. Time: Fri, Aug 13, 1999 at 06:20:11 PM; Exp. Comment: Default Comment.



S-18

Current Data Parameters
 NAME tsw-213-038
 EXPNO 1
 PROCNO 1

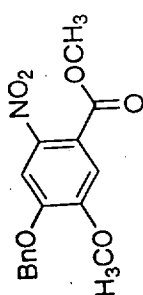
F2 - Acquisition Parameters
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 Time 17.00
 PULPROG zg30
 SOLVENT COC13
 AQ 2.6214600 sec
 FIDRES 0.190735 Hz
 DM 80.0 usec
 RG 2048
 NUCLEUS ¹H
 HL1 1 dB
 D1 1.0000000 sec
 P1 8.0 usec
 DE 100.0 usec
 SF01 300.1351622 MHz
 SWH 6250.00 Hz
 TD 32768
 NS 8
 DS 2

F2 - Processing parameters
 SI 16384
 SF 300.1333663 MHz
 EM
 WDW 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 9.879 ppm
 F1 2965.06 Hz
 F2P -0.429 ppm
 F2 -128.83 Hz
 PPMCH 0.51542 ppm/cm
 HZCM 154.69415 Hz/cm

ppm

8.30301
8.27309
8.65962
7.51962
7.45722
7.43221
7.40716
7.38150
7.37424
7.35259
7.33736
7.26396
7.20507
7.19241
7.11611
7.08366
5.30188
5.28563
5.21772
4.22140
4.06758
4.01040
3.98168
3.92231
3.90789
3.84770
3.73733
3.65878
3.49691
2.05049
1.59353
1.26263
1.25253
0.01000
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8

Integral

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3.1834
3.3161

ppm

0 2 4 6 8

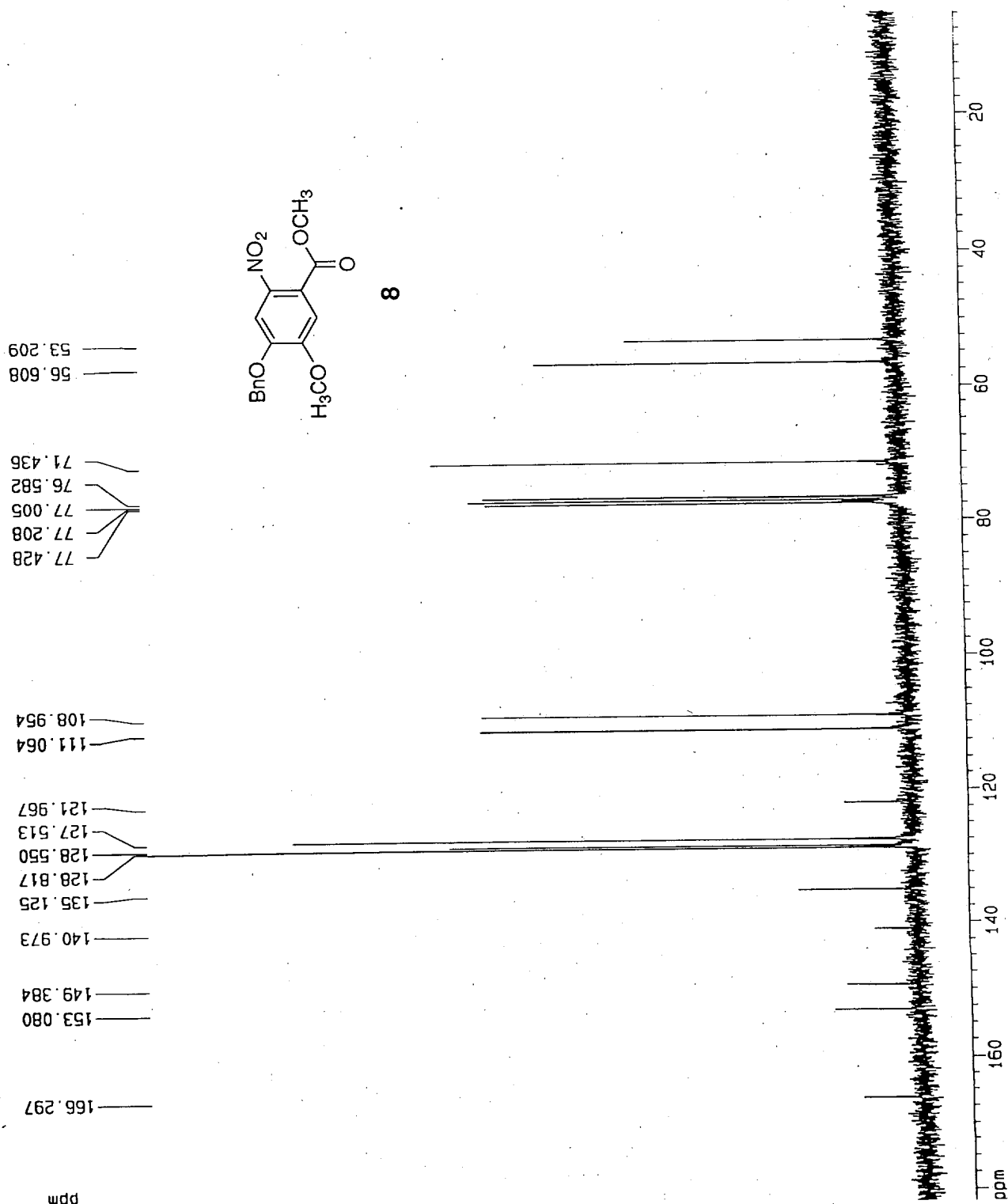
S-19

Current Data Parameters
NAME tsw-213-b33
EXPNO 2
PROCNO 1

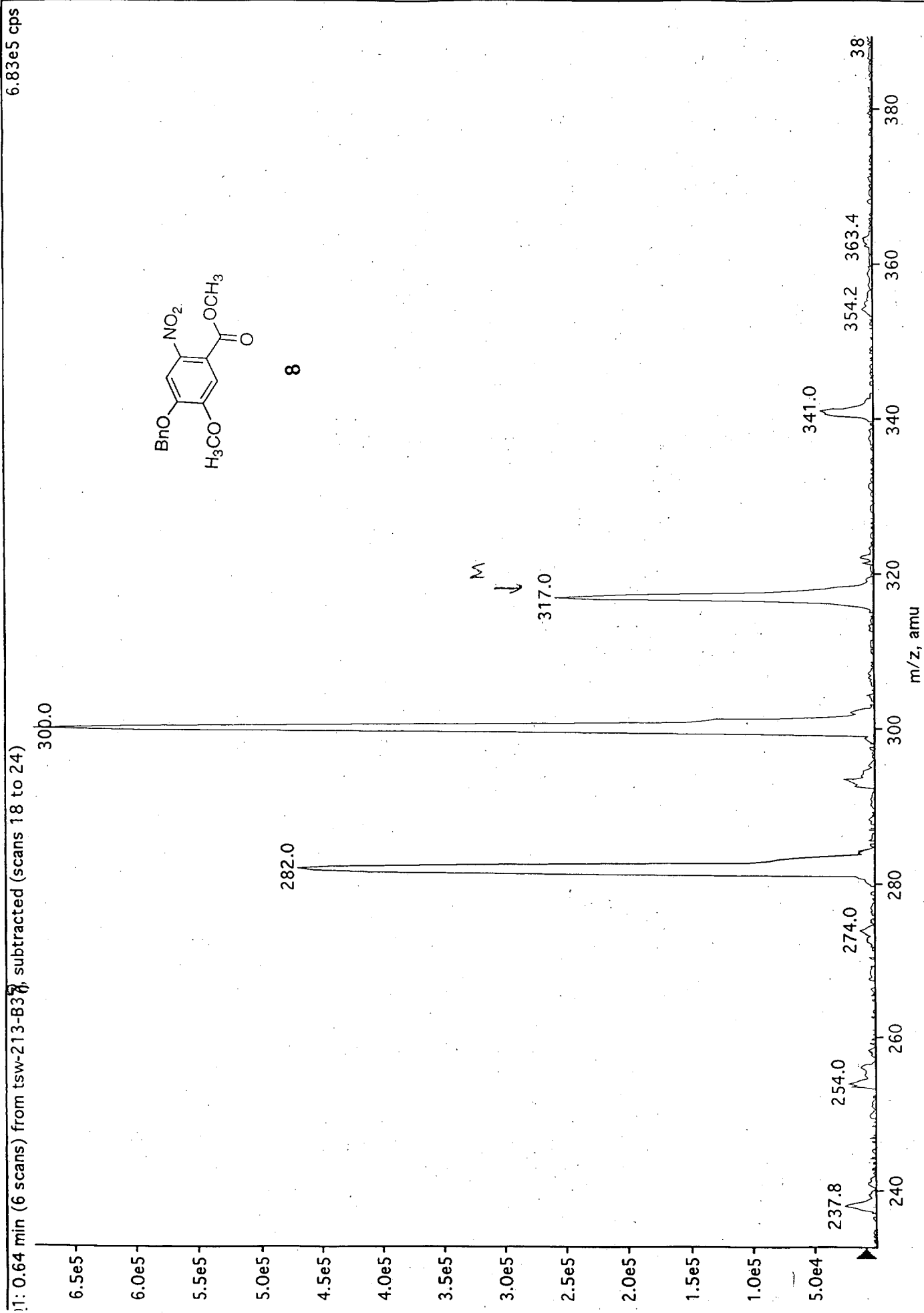
F2 - Acquisition Parameters
Date 990409
Time 8.34
PULPROG zgpg30
SOLVENT CDCl3
AQ 1.3762760 sec
FIDRES 0.363304 Hz
AQ 21.0 usec
RG 32768
NUCLEUS 13C
HL1 3 dB
D1 1.0000000 sec
P31 100.0 usec
S4 26 dB
D11 0.0300000 sec
S2 26 dB
P1 14.0 usec
DE 30.0 usec
SF01 75.4753021 MHz
SWH 23809.52 Hz
TO 65536
NS 1177
DS 2

F2 - Processing parameters
SI 32768
SF 75.4685959 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 181.983 ppm
F1 13733.97 Hz
F2P 4.716 ppm
F2 355.93 Hz
PPMCM 8.86332 ppm/cm
HZCM 688.90198 Hz/cm



213-031 (LSW 13W-213-031)
Mod 1, Expt. 1; Mass range: 100.0 to 1000.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 5.0 ms
Time: Fri, Apr 23, 1999 at 03:30:01 PM; Exp. Comment: Default Comment.



S-21

213-B40

Current Data Parameters

NAME tsm-213-040
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 990503
Time 17.59
PULPROG zg30
SOLVENT CDCl3
AQ 2.6214600 sec
FIDRES 0.190735 Hz
RG 256
NUCLEUS 1H
HL1 1 dB
D1 1.0000000 sec
P1 8.0 usec
DE 100.0 usec
SF01 300.1351622 MHz
SMH 6250.00 Hz
TD 32768
NS 4
DS 2

F2 - Processing parameters

SI 16384
SF 300.1333682 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 8.481 ppm
F1 2545.30 Hz
F2P -0.524 ppm
F2 -157.41 Hz
PPMCM 0.45025 ppm/cm
HZCM 135.13512 Hz/cm

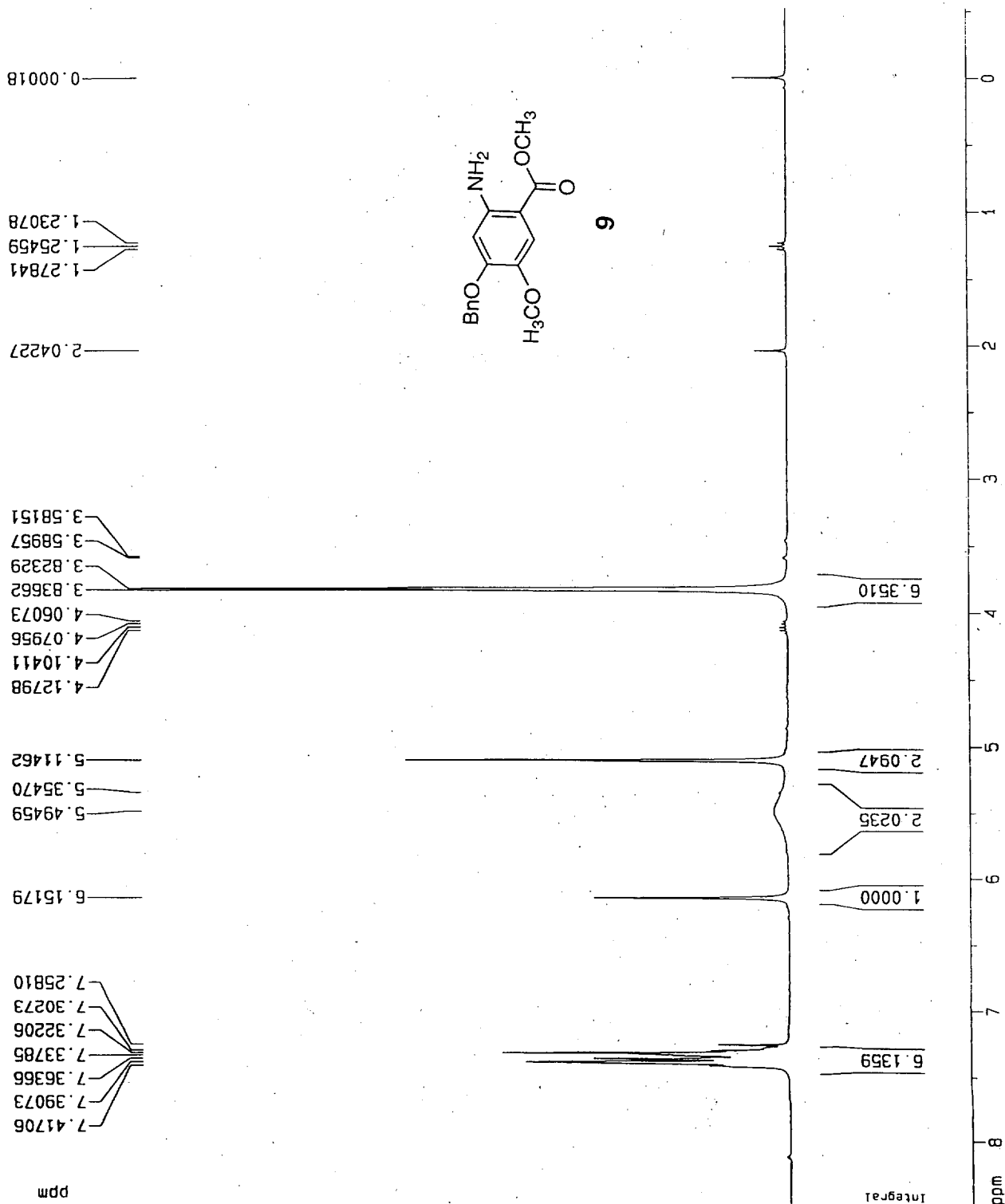
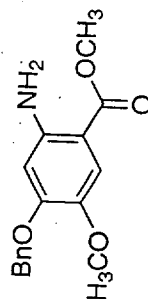
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1.27841
2.04227

3.58151
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4.06073
4.07956
4.10411
4.12798

5.11462
5.35470
5.49459

6.15179

7.41706
7.39073
7.36366
7.33785
7.32206
7.30273
7.25810



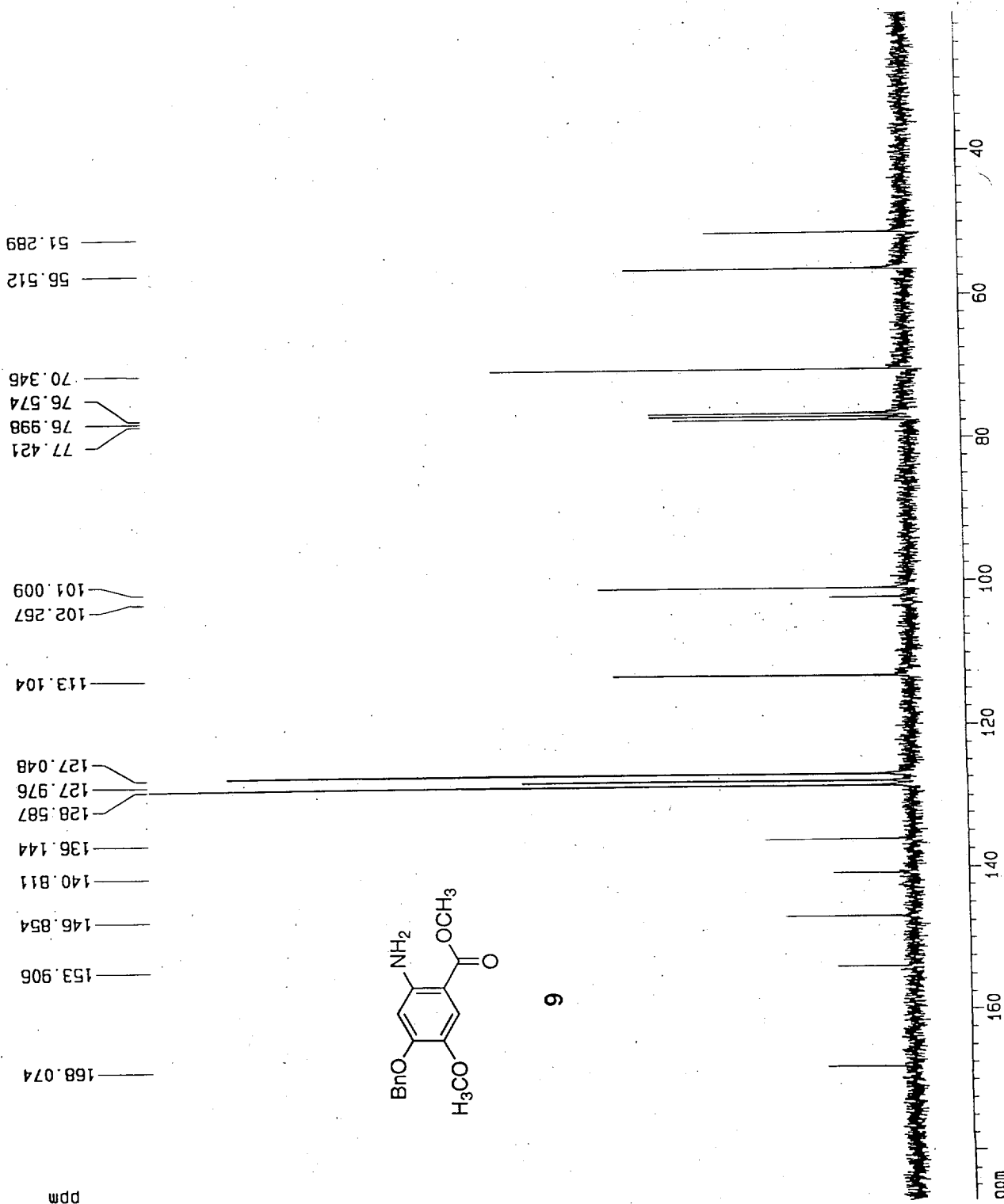
S-22

Current Data Parameters
NAME tsw-213-040
EXPNO 2
PROCNO 1

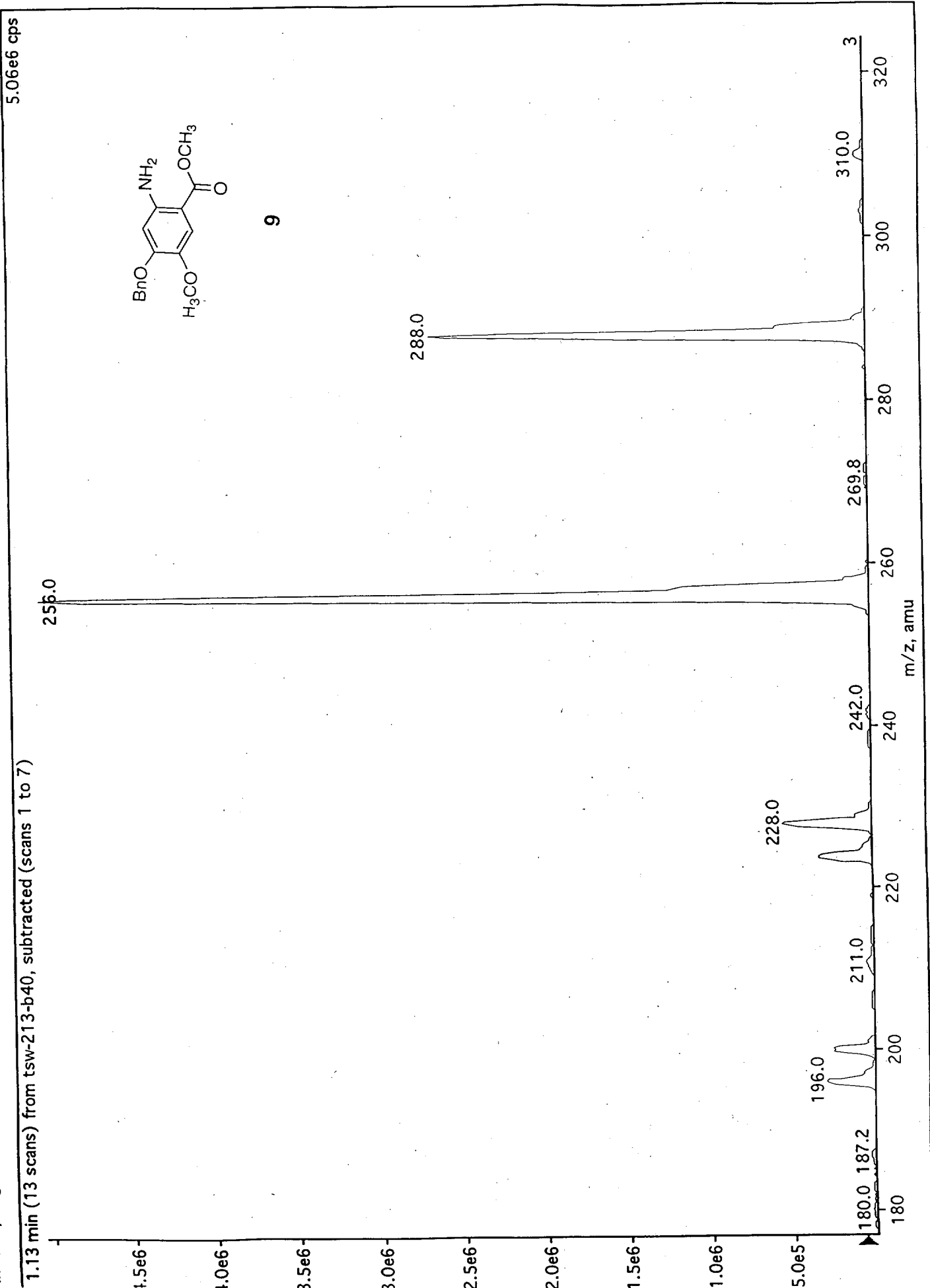
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Date 990503
Time 18.04
PULPROG zgpg30
SOLVENT CDCl3
AQ 1.3762760 sec
FIDRES 0.363304 Hz
DQ 21.0 usec
RG 16384
NUCLEUS 13C
HL1 3 dB
D1 1.0000000 sec
P31 100.0 usec
S4 26 dB
D11 0.0300000 sec
S2 26 dB
P1 14.0 usec
DE 30.0 usec
SF01 75.4753021 MHz
SWH 23809.52 Hz
T0 65536
NS 293
DS 2

F2 - Processing parameters
SI 32768
SF 75.4686017 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 187.291 ppm
F1 14134.58 Hz
F2P 20.795 ppm
F2 1569.38 Hz
PPMCM 8.32478 ppm/cm
HZCM 628.25983 Hz/cm



1.13 min (13 scans) from tsw-213-b40, subtracted (scans 1 to 7)
 1.1, Expt. 1; Mass range: 100.0 to 1000.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 5.0 ms
 Time: Fri, Aug 13, 1999 at 06:16:23 PM; Exp. Comment: Default Comment. S-23



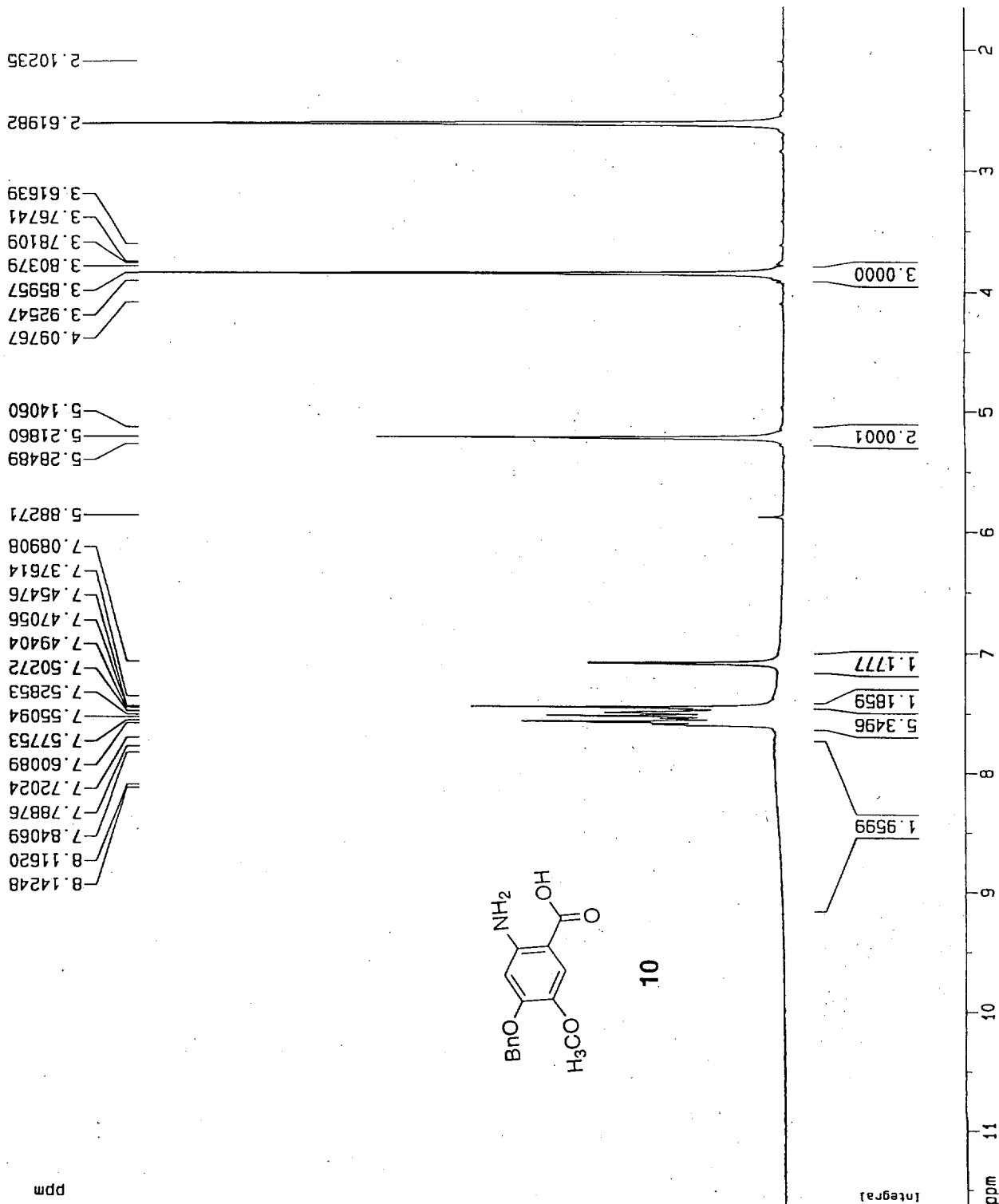
S-24

Current Data Parameters
 NAME tsw-213-d41
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 990505
 Time 13.29
 PULPROG zg30
 SOLVENT CDCl3
 AQ 2.621460 sec
 FIDRES 0.190735 Hz
 DM 80.0 usec
 RG 1024
 NUCLEUS 1H
 HL1 1 dB
 D1 1.000000 sec
 P1 8.0 usec
 DE 100.0 usec
 SFO1 300.1351622 MHz
 SWH 6250.00 Hz
 TO 32768
 NS 8
 DS 2

F2 - Processing parameters
 SI 16384
 SF 300.1347520 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
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 F1 3490.77 Hz
 F2P 1.648 ppm
 F2 494.68 Hz
 PPMCM 0.49912 ppm/cm
 HZCM 149.80443 Hz/cm



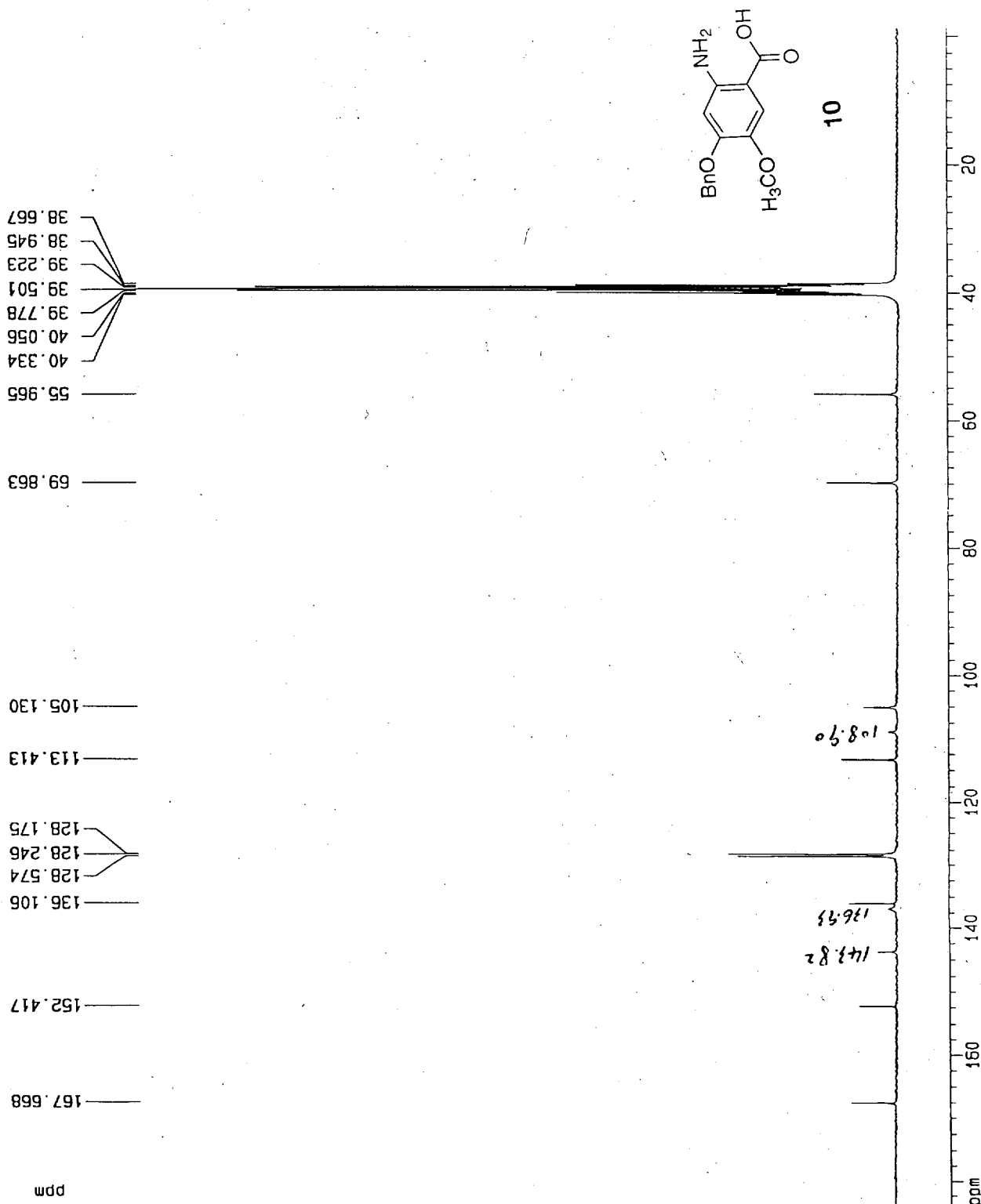
S-25

Current Data Parameters
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 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
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 Time 19.31
 PULPROG zgpg30
 SOLVENT CDCl3
 AQ 1.3762760 sec
 FIDRES 0.363304 Hz
 DW 21.0 usec
 RG 16384
 NUCLEUS 13C
 HL1 3 dB
 D1 1.0000000 sec
 P31 100.0 usec
 S4 26 dB
 D11 0.0300000 sec
 S2 26 dB
 P1 14.0 usec
 DE 30.0 usec
 SF01 75.4753021 MHz
 SWH 23809.52 Hz
 TD 65536
 NS 12000
 DS 2

F2 - Processing parameters
 SI 32768
 SF 75.4689831 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
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 F1 13888.67 Hz
 F2P -1.312 ppm
 F2 -99.01 Hz
 PPMCH 9.26717 ppm/cm
 HZCH 699.38361 Hz/cm



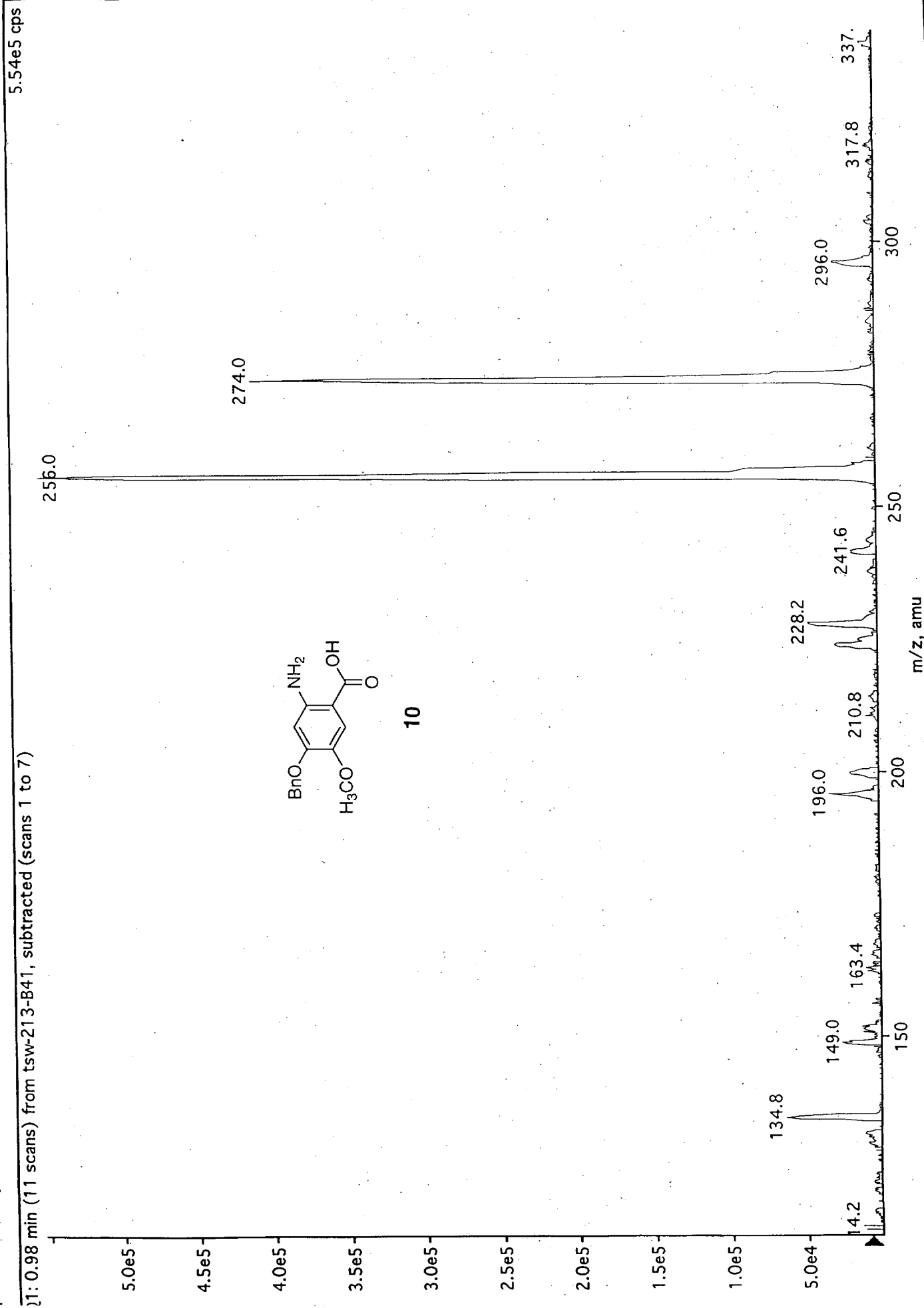
Friday, May 1, 3 02:31 PM

tiView 1.3

-213-B41 (Low TSW-213-B41)

iod 1, Expt. 1; Mass range: 100.0 to 1000.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 5.0 ms

1. Time: Fri, May 7, 1999 at 02:53:42 PM; Exp. Comment: Default Comment. S-26



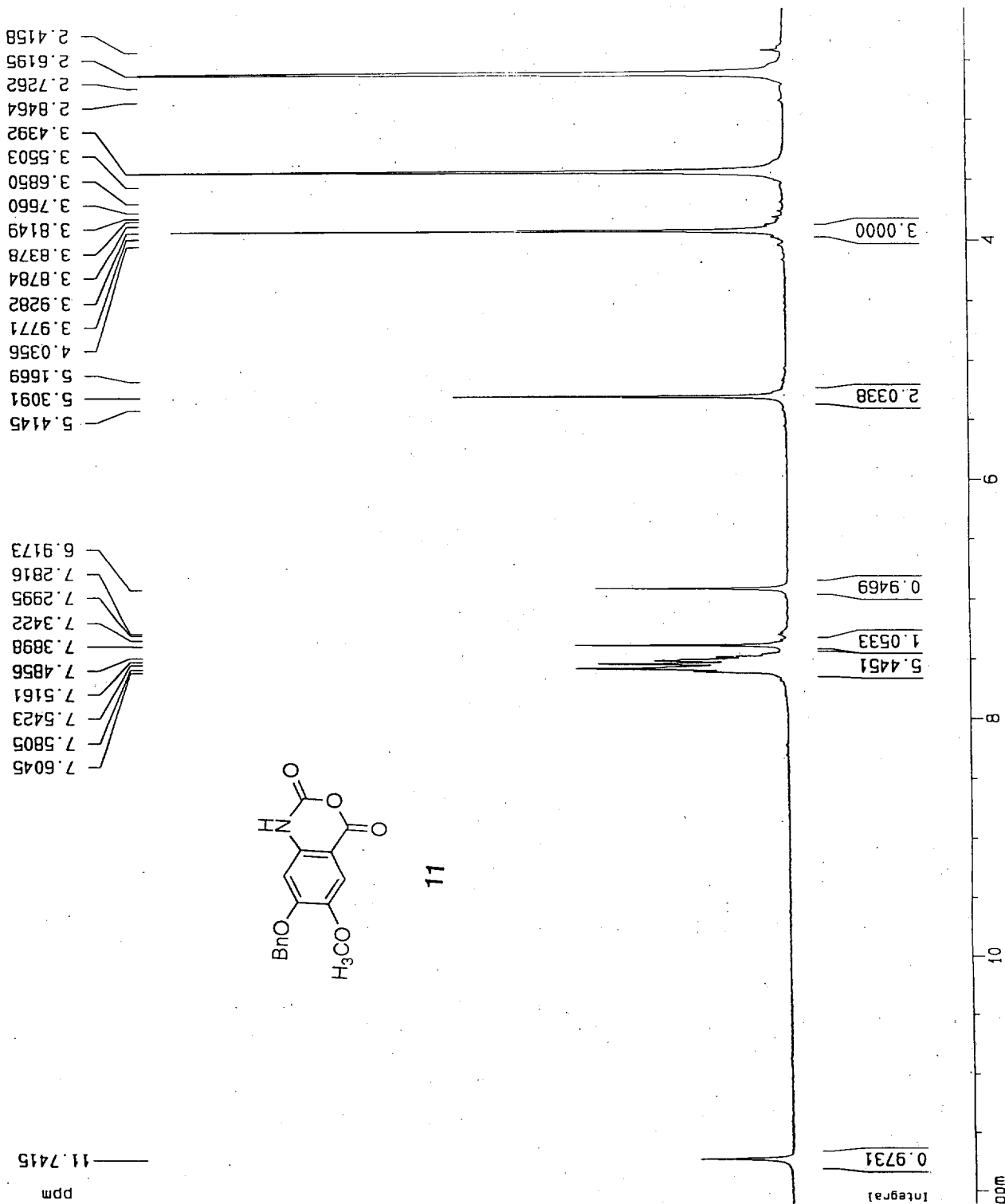
S-27

Current Data Parameters
 NAME tsw-213-046
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date 990815
 Time 18.25
 PULPROG zg30
 SOLVENT CDCl3
 AQ 2.1527080 sec
 FIDRES 0.231194 Hz
 DM 66.0 usec
 RG 1024
 NUCLEUS ¹H
 HL1 1 dB
 D1 1.0000000 sec
 P1 8.0 usec
 DE 94.3 usec
 SF01 300.1351622 MHz
 SWH 7575.76 Hz
 TD 32768
 NS 8
 DS 2

F2 - Processing parameters
 SI 16384
 SF 300.1347523 MHz
 WDW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

10 NMR plot parameters
 CX 20.00 cm
 F1P 12.119 ppm
 F1 3637.48 Hz
 F2P 2.066 ppm
 F2 620.11 Hz
 PPMCH 0.50267 ppm/cm
 HZCM 150.86858 Hz/cm



11

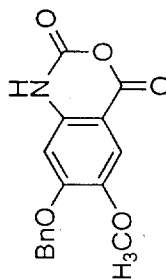
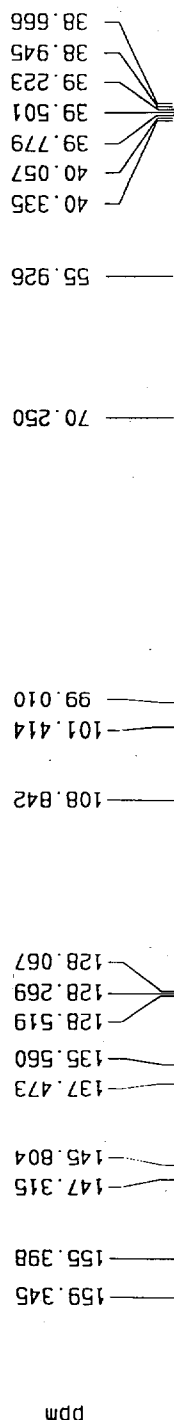
S-28

Current Data Parameters
NAME tsw-213-045
EXPNO 2
PROCNO 1

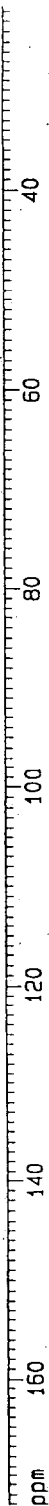
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Date 990816
Time 18.29
PULPROG zgpg30
SOLVENT CDCl3
AQ 1.3762760 sec
FIDRES 0.363304 Hz
DQ 21.0 usec
RG 16384
NUCLEUS 13C
HL1 3 dB
D1 1.0000000 sec
P31 100.0 usec
S4 26 dB
D11 0.0300000 sec
S2 26 dB
P1 14.0 usec
DE 30.0 usec
SF01 75.4753021 MHz
SHH 23809.52 Hz
TD 65536
NS 12000
DS 2

F2 - Processing parameters
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SF 75.4689511 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

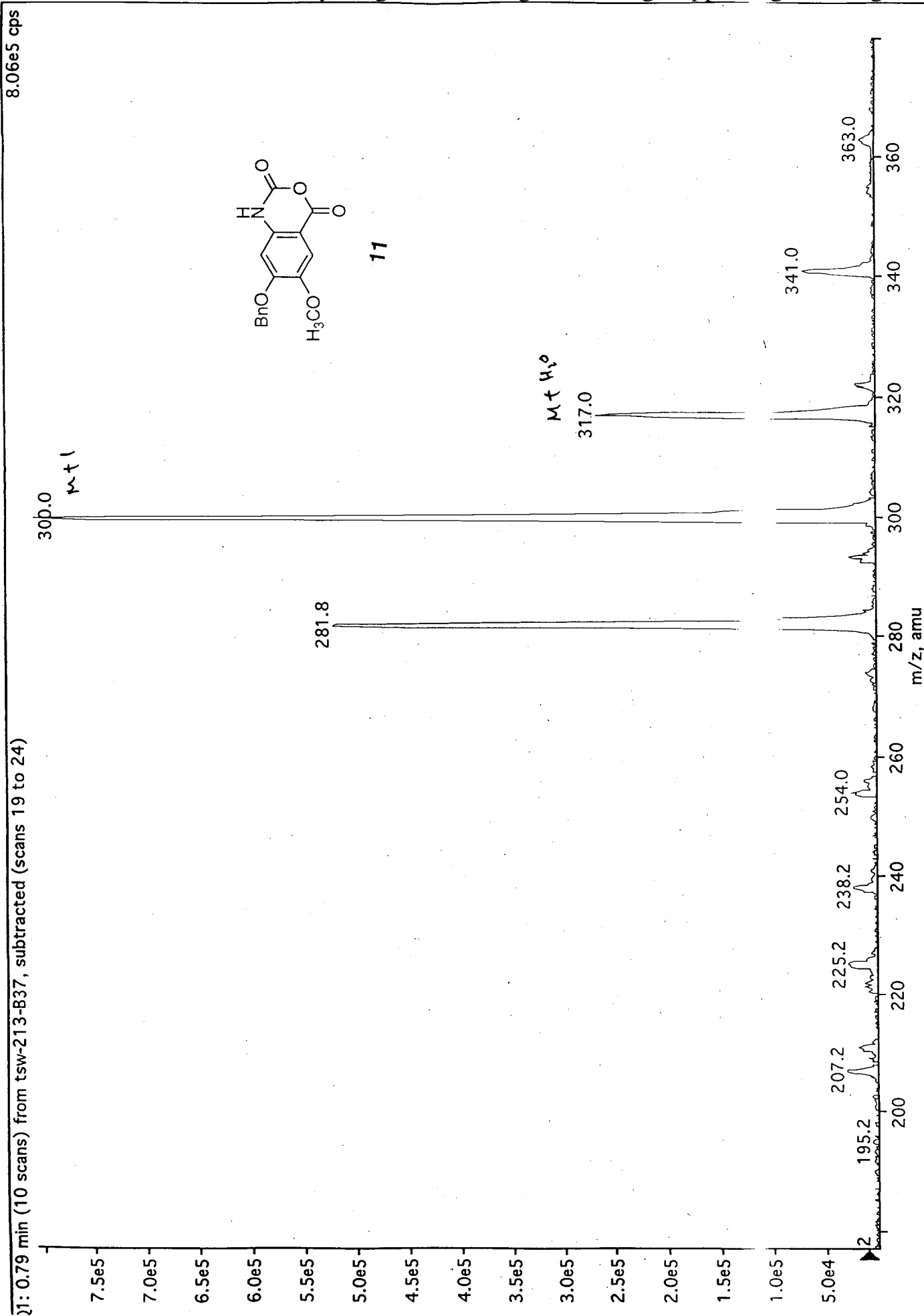
1D NMR plot parameters
CX 20.00 cm
F1P 173.155 ppm
F1 13067.83 Hz
F2P 21.470 ppm
F2 1620.30 Hz
PPMCM 7.58427 ppm/cm
HZCM 572.37683 Hz/cm



11



213-B37 (tsw 1SW-213-B37)
iod 1, Expt. 1; Mass range: 100.0 to 1000.0 by 0.2 amu; Dwell: 1.0 ms; Pause: 5.0 ms
1. Time: Fri, Apr 23, 1999 at 03:30:01 PM; Exp. Comment: Default Comment. S-29



S-30

Current Data Parameters
 NAME tsw-213-b43
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 990510
 Time 17:33
 PULPROG zg30
 SOLVENT CDCl3
 AG 2.6214600 sec
 FIDRES 0.190735 Hz
 DW 80.0 usec
 RG 2048
 NUCLEUS ¹H
 HL1 1 dB
 D1 1.0000000 sec
 P1 8.0 usec
 DE 100.0 usec
 SF01 300.1351622 MHz
 SWH 6250.00 Hz
 TD 32768
 NS 8
 DS 2

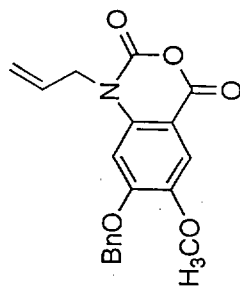
F2 - Processing parameters
 SI 16384
 SF 300.1333659 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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 F1P 10.414 ppm
 F1 3125.47 Hz
 F2P -0.606 ppm
 F2 -181.79 Hz
 PPMCM 0.55096 ppm/cm
 HZCM 165.36272 Hz/cm

-0.0006

1.2110
 1.2347
 1.2531
 1.6117

3.7036
 3.8355
 3.8746
 3.9471
 4.1866
 4.5250
 4.5413
 5.0771
 5.1346
 5.1688
 5.2035
 5.2254
 5.2724
 5.3029
 5.6976
 5.7141
 5.7313
 5.7491
 5.7711
 5.7885
 5.8062
 5.8231
 6.5369
 7.2650
 7.3497
 7.3789
 7.3959
 7.4062
 7.4921
 7.6112

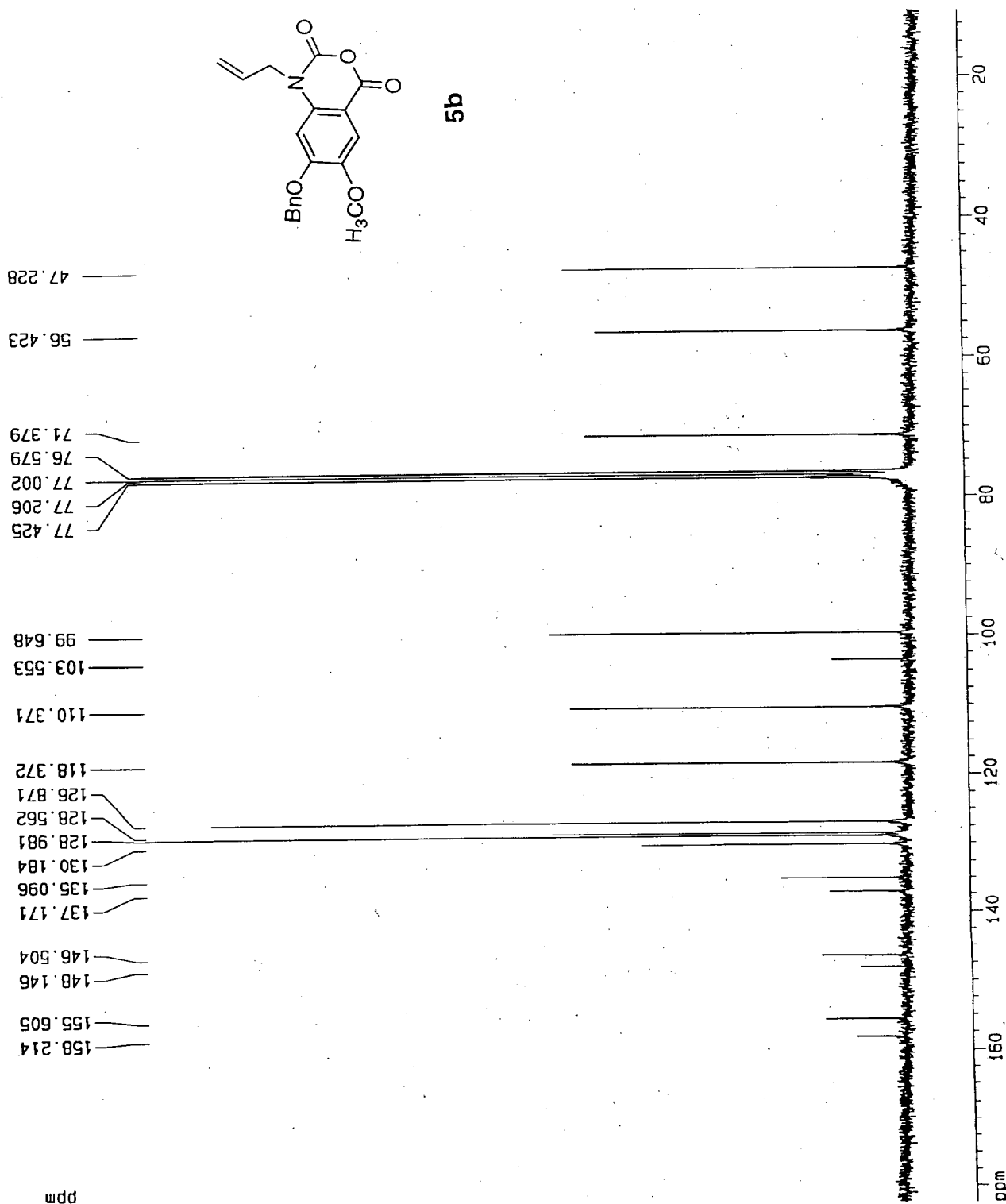


Integral

1.1181
 5.2605
 1.2054
 1.0000
 1.0229
 2.0010
 1.0560
 1.1063
 2.0663
 3.2814

ppm

S-31

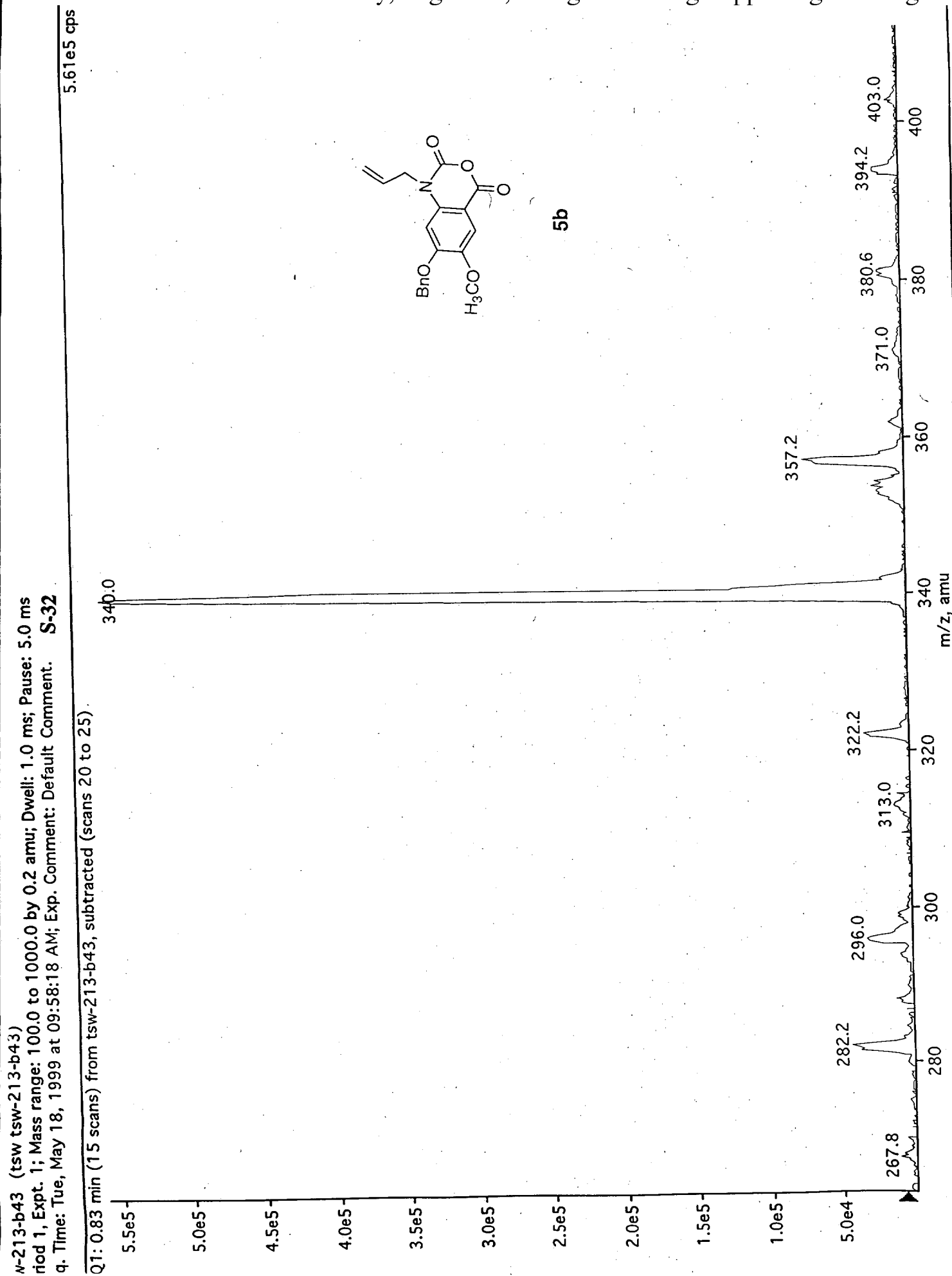


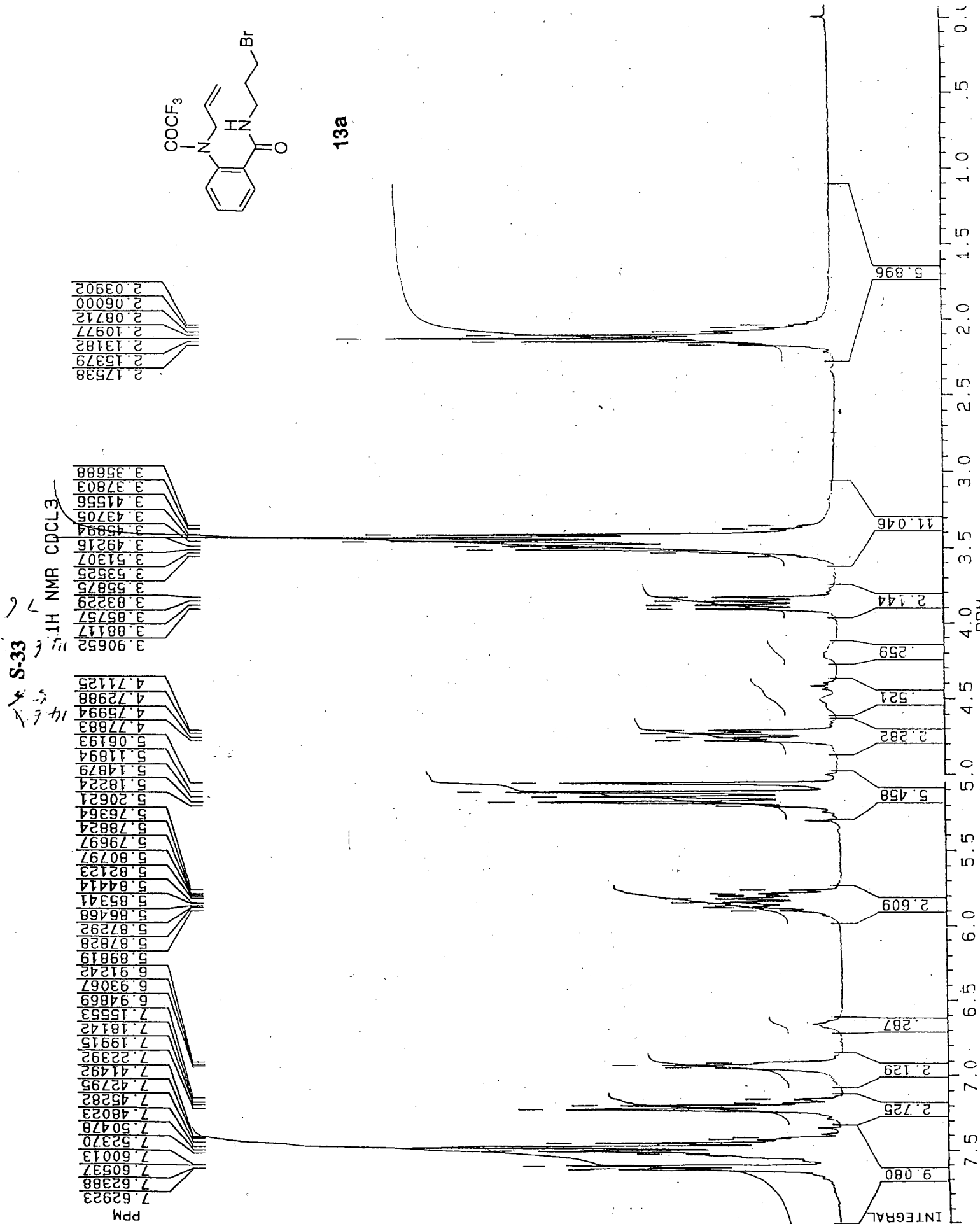
Current Data Parameters
 NAME tsw-213-043
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date 990510
 Time 17.39
 PULPROG zgpg30
 SOLVENT CDCl3
 AQ 1.3762760 sec
 FIDRES 0.363304 Hz
 DQ 21.0 usec
 RG 16384
 NUCLEUS 13C
 HL1 3 dB
 D1 1.0000000 sec
 P31 100.0 usec
 S4 26 dB
 D11 0.0300000 sec
 S2 26 dB
 P1 14.0 usec
 DE 30.0 usec
 SF01 75.4753021 MHz
 SWH 23809.52 Hz
 TD 65536
 NS 16000
 DS 2

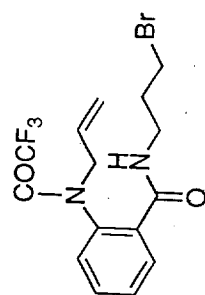
F2 - Processing parameters
 SI 32768
 SF 75.4685973 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 182.412 ppm
 F1 13765.38 Hz
 F2P 10.531 ppm
 F2 794.77 Hz
 PRMCM 8.59405 ppm/cm
 HZCM 648.58087 Hz/cm

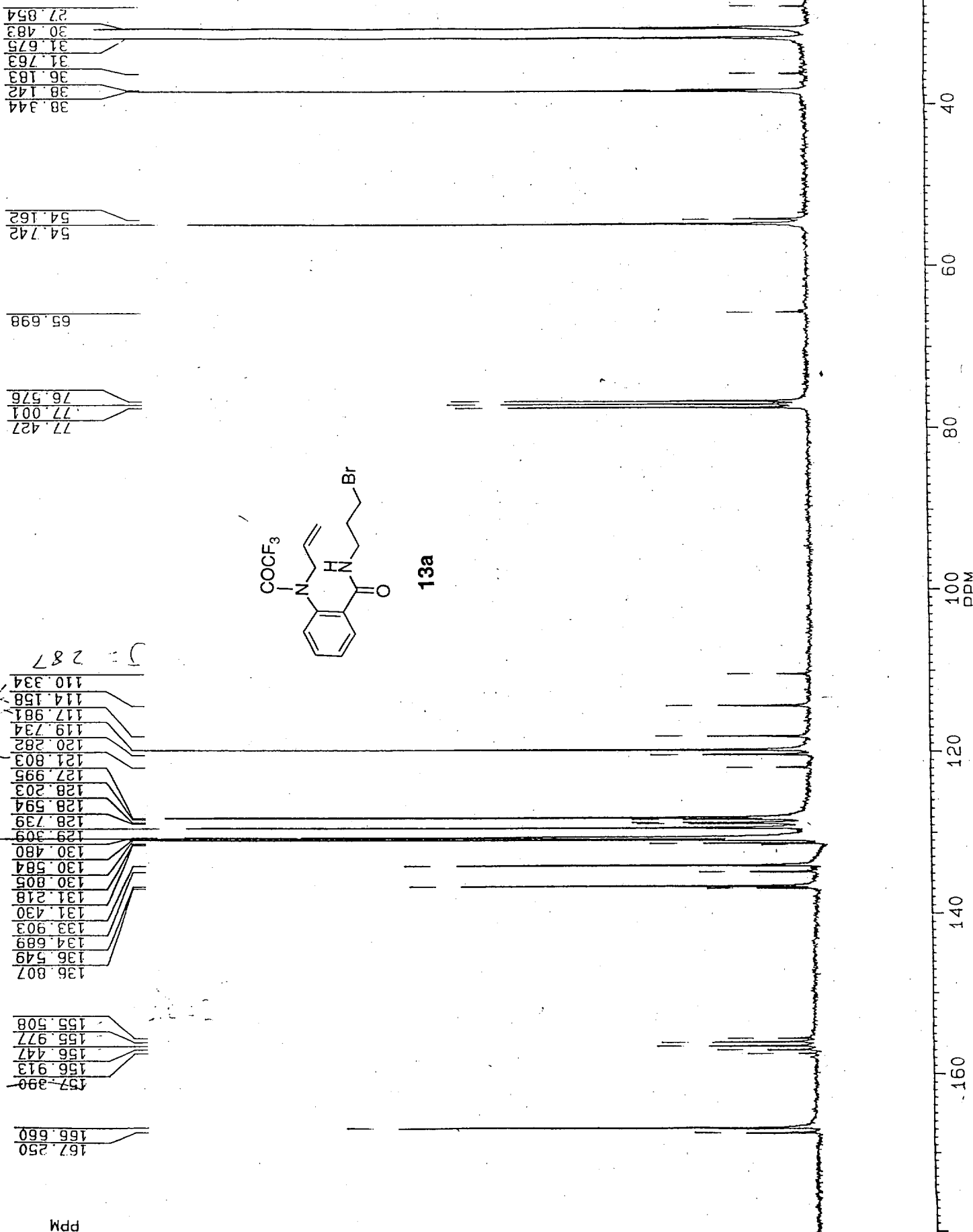




S-34 C13 NMR-CDCL3



13a



S-35

File : C:\HPCHEM\1\DATA\1297028A.D

Operator : rsl

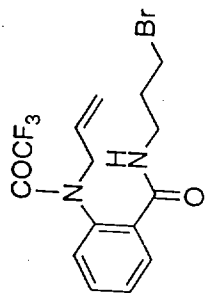
Acquired : 17 Dec 97 3:40 pm using AcqMethod LPEI

Instrument : 5989x - I

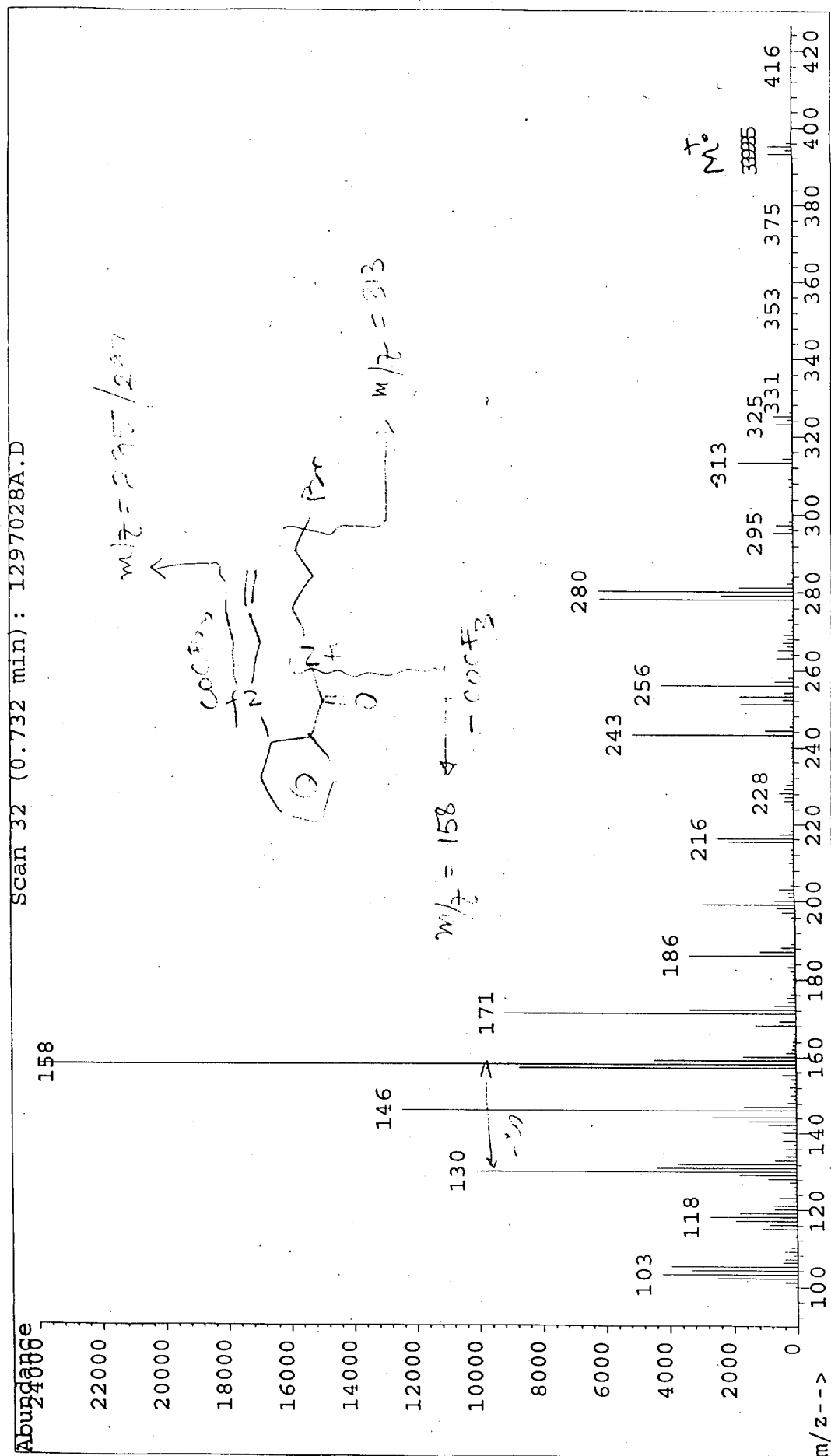
Sample Name: ar1297028

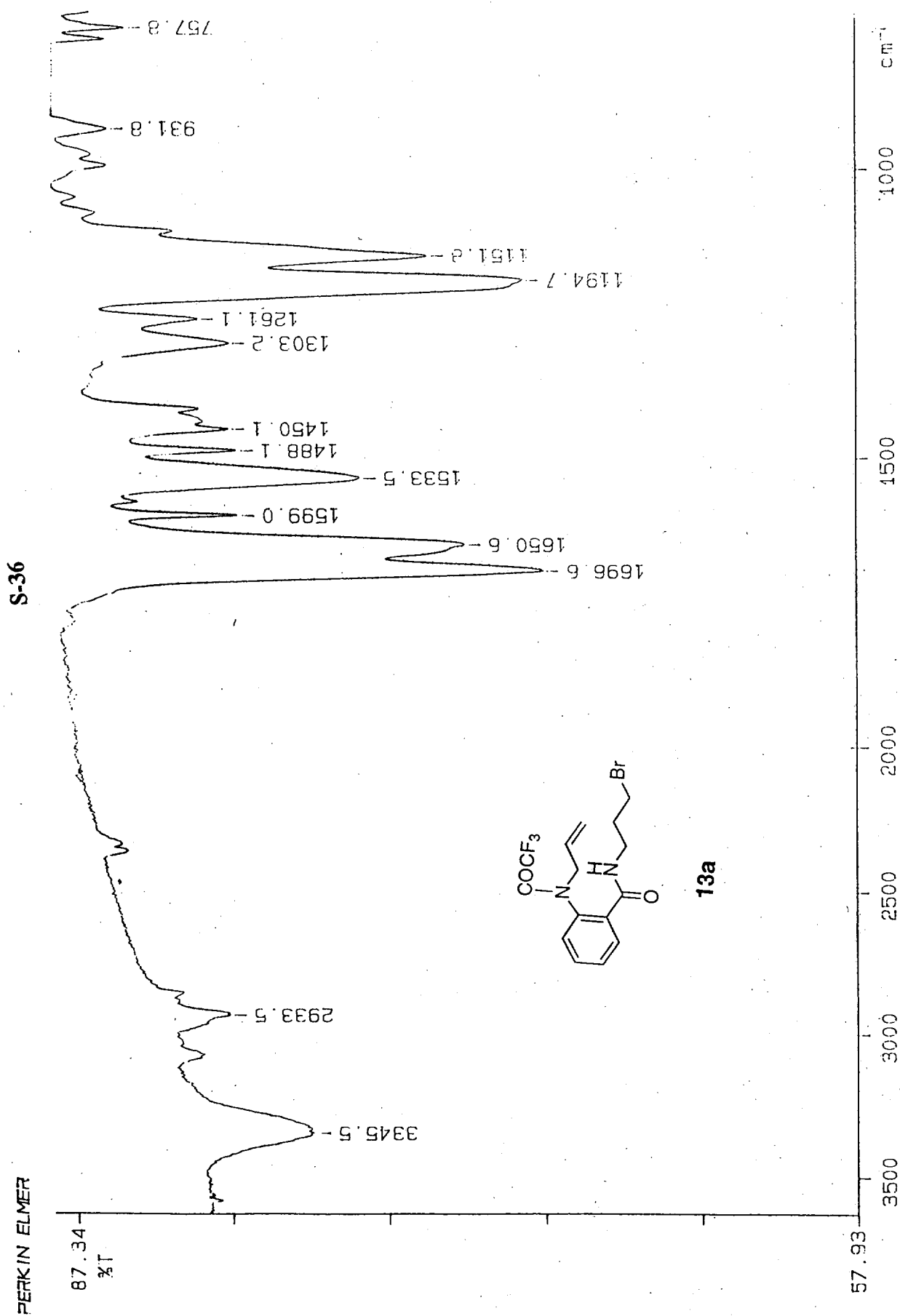
Misc Info : pb/ei/loop

Vial Number: 1

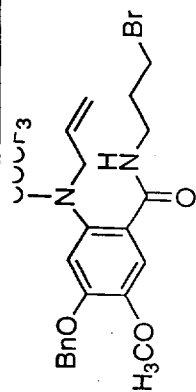


13a





98/05/27 15:24
X: 4 scans, 4.0cm⁻¹



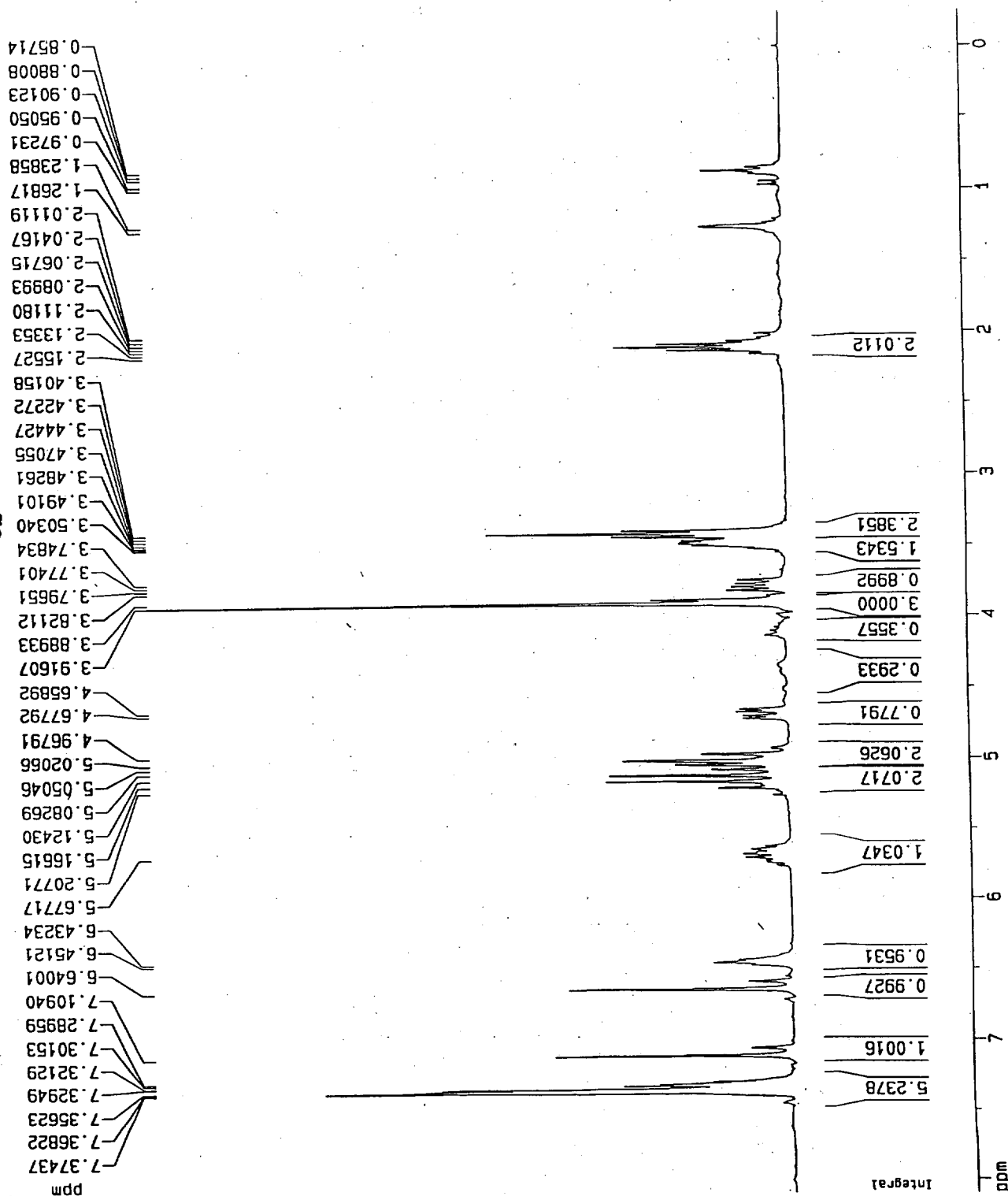
13b

Current Data Parameters
 NAME tsm-213-050
 EXPNO 1
 PROCNO 1

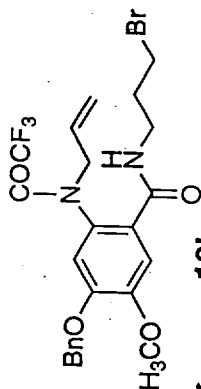
F2 - Acquisition Parameters
 Date 990621
 Time 16.07
 PULPROG zg30
 SOLVENT CDCl3
 AQ 2.6214500 sec
 FIDRES 0.190735 Hz
 DW 80.0 usec
 RG 128
 NUCLEUS 1H
 HL1 1 dB
 D1 1.0000000 sec
 P1 8.0 usec
 DE 100.0 usec
 SF01 300.1351622 MHz
 SMH 6250.00 Hz
 TD 32768
 NS 4
 DS 2

F2 - Processing parameters
 SI 16384
 SF 300.1333579 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 8.100 ppm
 F1 2431.13 Hz
 F2P -0.253 ppm
 F2 -75.98 Hz
 PPMCM 0.41767 ppm/cm
 HZCM 125.35561 Hz/cm



S-37



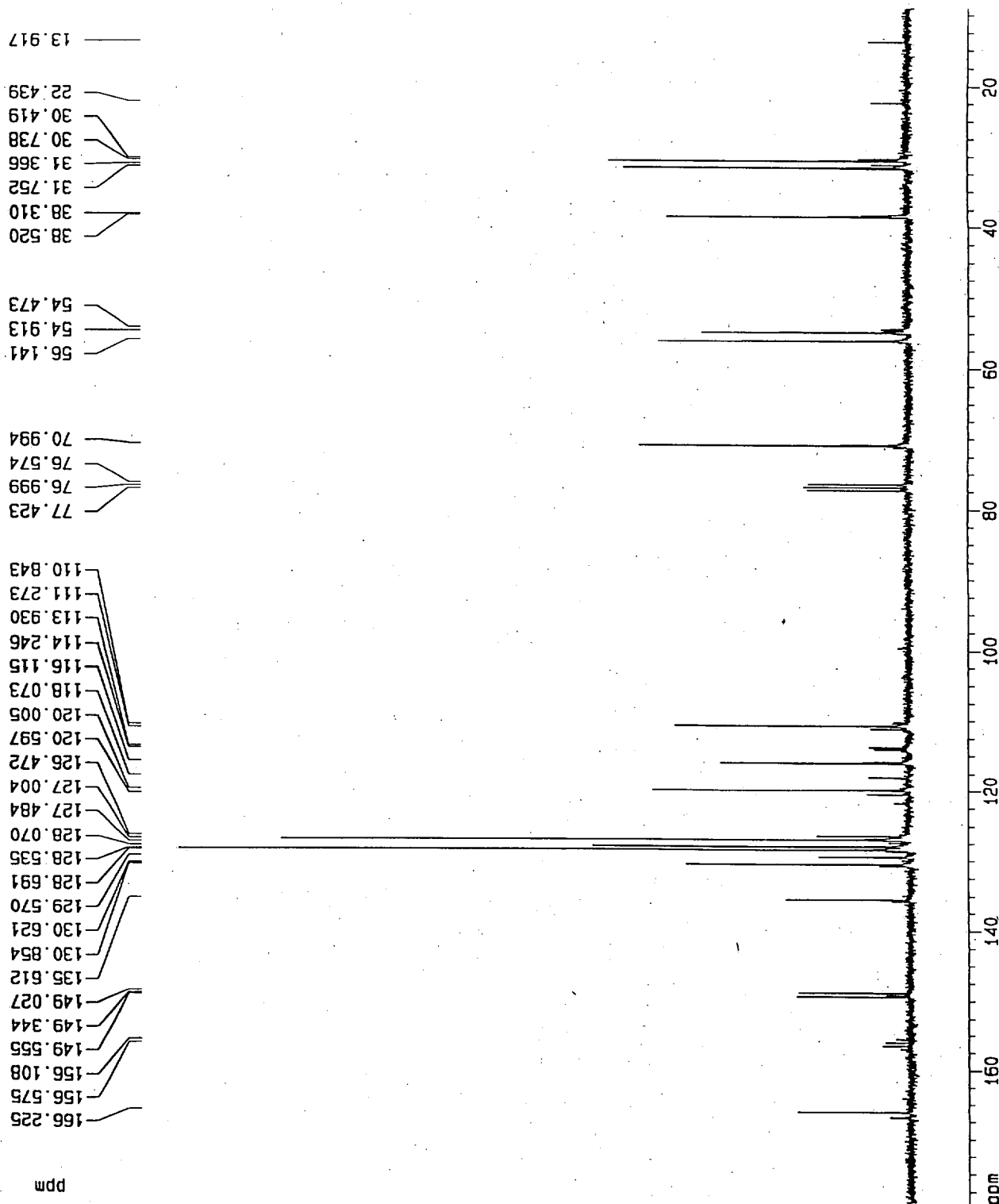
13b

Current Data Parameters
 NAME tsw-213-550
 EXPNO 2
 PROCNO 1

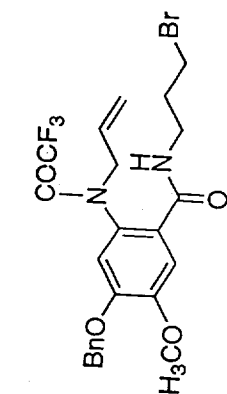
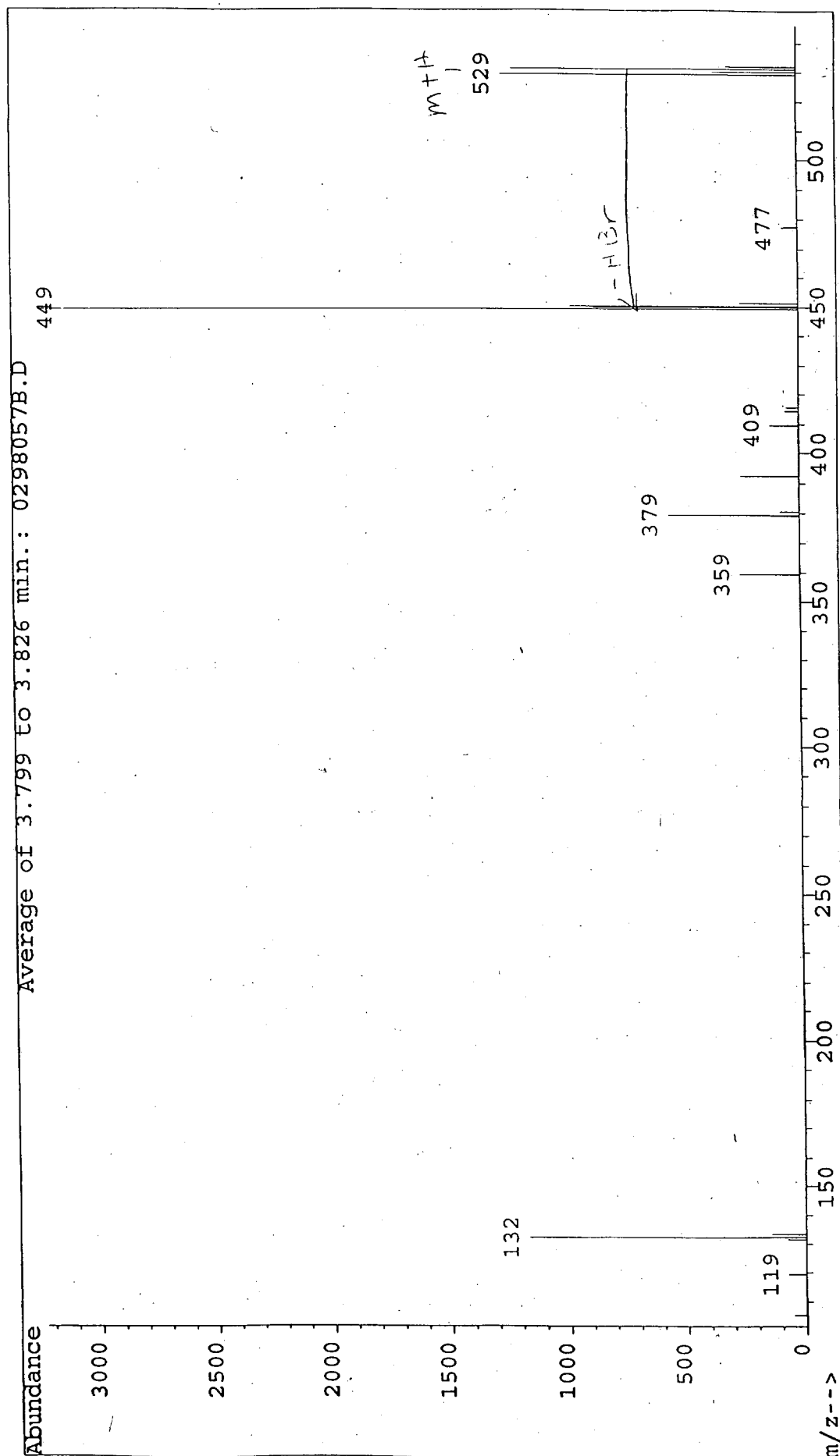
F2 - Acquisition Parameters
 Date 990521
 Time 16.13
 PULPROG zgpg30
 SOLVENT CDCl3
 AQ 1.3762760 sec
 FIDRES 0.363304 Hz
 DK 21.0 usec
 RG 32768
 NUCLEUS 13C
 HL1 3 dB
 D1 1.0000000 sec
 P31 100.0 usec
 S4 26 dB
 D11 0.0300000 sec
 S2 26 dB
 P1 14.0 usec
 DE 30.0 usec
 SF01 75.4753021 MHz
 SMH 23809.52 Hz
 TD 65536
 NS 426
 DS 2

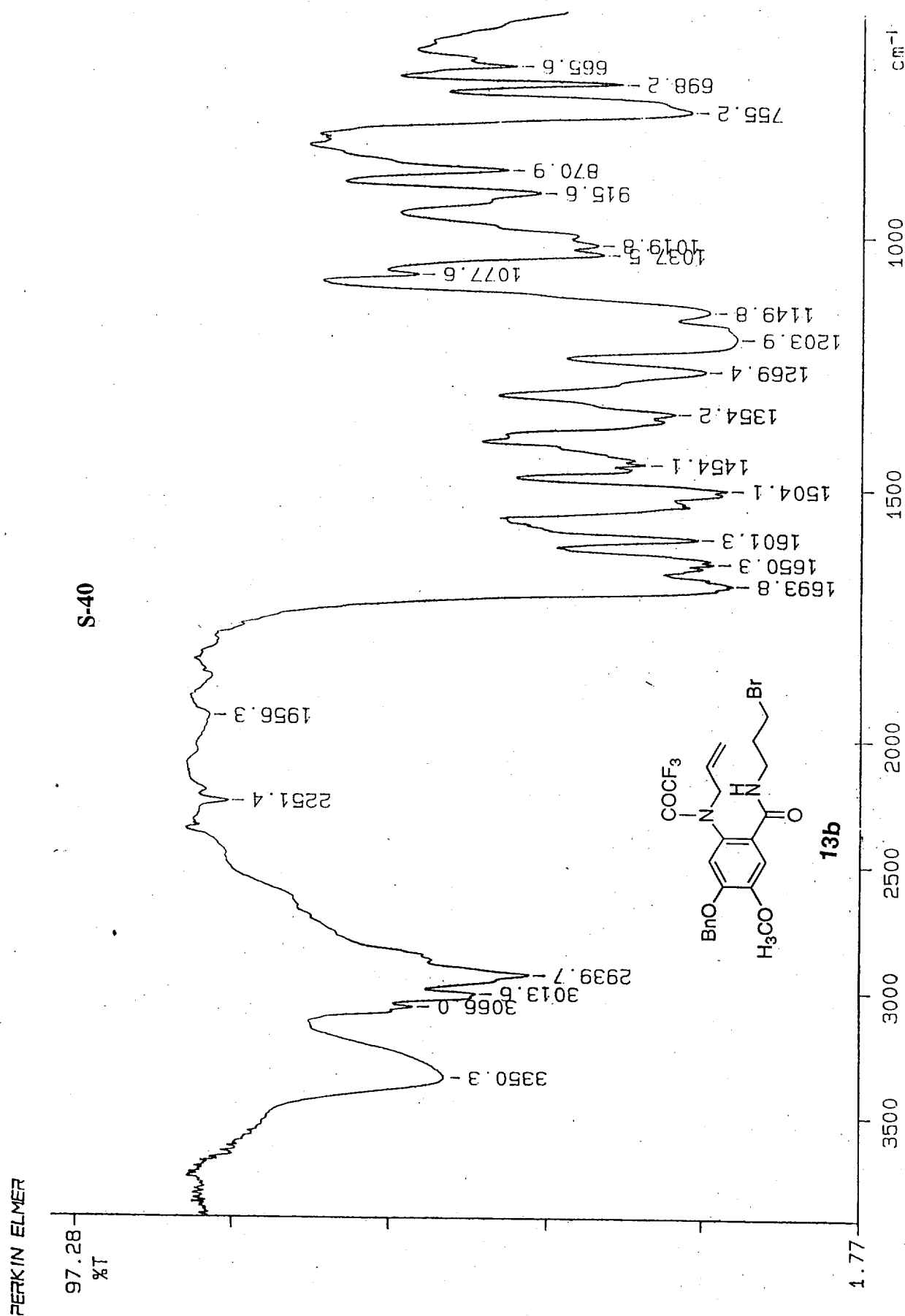
F2 - Processing parameters
 SI 32768
 SF 75.4686068 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 171.645 ppm
 F1 12953.83 Hz
 F2P 106.805 ppm
 F2 8060.39 Hz
 PPMCM 3.24203 ppm/cm
 HZCM 244.67186 Hz/cm



File : C:\HPCHEM\1\DATA\0298057B.D
Operator : acs
Acquired : 27 Feb 98 10:23 am using AcqMethod PBGCII1
Instrument : 5989x - I
Sample Name: ar0298057 scan 100-600
Misc Info : pb/ci/ch4/loop
Vial Number: 1

**13b**



98/05/28 17:18

X: 4 scans, 4.0cm⁻¹