SUPPLEMENTARY MATERIAL

Trisubstituted (*E*)-Alkene Dipeptide Isosteres as β-Turn Promoters in the Gramicidin S Cyclodecapeptide Scaffold

Jingbo Xiao,[§] Bernard Weisblum[#] and Peter Wipf*[,§]

[§]*Department of Chemistry and Center for Chemical Methodologies & Library Development, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and*

[#]*Pharmacology Department, University of Wisconsin Medical School, 1300 University Avenue, Madison, Wisconsin 53706*

pwipf@pitt.edu

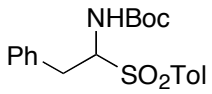
Experimental procedures and spectral data for all new compounds, including copies of ^{1}H and ^{13}C NMR spectra for **3**, **4**, **5**, **6**, **7**, **8**, **10** (298 and 338 K), **Cbz$_2$GS** and 2D NMR spectra of **10** and **Cbz$_2$GS**; T-shift plots for **10** and **Cbz$_2$GS**.

General. All moisture-sensitive reactions were performed using syringe-septum cap techniques under an N_2 atmosphere and all glassware was dried in an oven at 150 °C for 2 h prior to use. Reactions carried out at -78 °C employed a CO_2-acetone bath. THF was distilled over sodium / benzophenone ketyl; CH_2Cl_2, toluene and Et_3N were distilled from CaH_2. Me_2Zn was purchased from Aldrich Company.

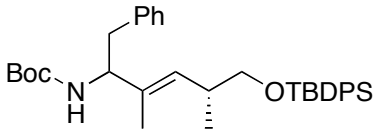
Reactions were monitored by TLC analysis (EM Science pre-coated silica gel 60 F_{254} plates, 250 μm layer thickness) and visualization was accomplished with a 254 nm UV light and by staining with a PMA solution (5 g of phosphomolybdic acid in 100 mL of 95% EtOH) or a Vaughn's reagent (4.8 g $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$, 0.2 g $Ce(SO_4)_2\bullet 4H_2O$ in 10 mL conc. H_2SO_4 and 90 mL H_2O). Flash chromatography on SiO_2 or deactivated SiO_2 (1% Et_3N in mobile phase) was used to purify the crude reaction mixtures.

Infrared spectra were determined on a Nicolet Avatar 360 FT-IR spectrometer. Circular dichroism spectra were obtained on a JASCO 715 spectrometer at 0.1 mM concentration in anhydrous EtOH solution. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker Avance 300, 500 or 600 MHz instruments. ^1H NMR spectra are tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet), number of protons, and coupling constant(s). Mass spectra were obtained on a Waters Autospec double focusing mass spectrometer (EI) or a Waters Q-Tof mass spectrometer (ESI). A Varian HPLC system a Gilson 215 Liquid Handler

equipped with a *semi*-prep C_{18} column (Varian 250 mm × 10 mm, 10 μm particle size, 60 Å, with 5 mL/min flow rate, or a Varian Dynamax 250 mm × 21.4 mm, Microsorb 60-8, with 10 mL/min flow rate) and a fraction collector was used for purification. A Varian HPLC system equipped with an analytical chiral column (Chiralcel OD, 250 × 4.6 mm, 1.0 mL/min) was used for normal phase HPLC analysis. LC-MS data were obtained on an Agilent 1100 instrument, using an analytical C_{18} column (Waters Xterra MS 100 × 4.6 mm, 3.5 μm, 0.4 mL/min).

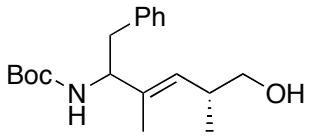


[1-(4-Methylbenzenesulfonyl)-2-phenylethyl]carbamic acid *tert*-butyl ester (3). A mixture of 5.43 g (46.4 mmol) of H_2N-Boc, 8.35 g (69.5 mmol) of phenylacetaldehyde, and 10.8 g (69.1 mmol) of $TolSO_2H$ in 200 mL of dry ether was stirred at room temperature overnight. The resulting white precipitate was filtered off, washed with ether, and dried *in vacuo* to yield 10.5 g (61%) of **3** as a colorless powder: IR (neat) 3431, 1697, 1639, 1454, 1313, 1303, 1141, 1087 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 8.05 (d, 1 H, J = 9.8 Hz), 7.74 (d, 2 H, J = 8.2 Hz), 7.42 (d, 2 H, J = 8.0 Hz), 7.27-7.24 (m, 4 H), 7.21-7.18 (m, 1 H), 4.91 (ddd, 1 H, J = 10.8, 10.8, 2.5 Hz), 3.32 (dd, 1 H, J = 14.0, 2.4 Hz), 2.94 (dd, 1 H, J = 13.8, 12.1 Hz), 2.36 (s, 3H), 1.06 (s, 9 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 154.1, 144.4, 136.0, 133.8, 129.6, 129.2, 129.1, 128.3, 126.7, 78.8, 72.5, 31.3, 27.7, 21.0; HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NO_4SNa$ (M+Na) 398.1402, found 398.1422.



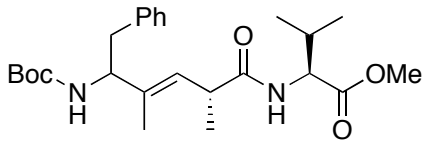
[(1*SR*,2*E*,4*R*)-1-Benzyl-5-(*tert*-butyldiphenylsilanyloxy)-2,4-dimethylpent-2-enyl]carbamic acid *tert*-butyl ester (4). A solution of 337 mg (1.00 mmol) of **2** in 2.00 mL of dry CH_2Cl_2 was treated at room temperature with 335 mg (1.30 mmol) of Cp_2ZrHCl. The reaction mixture was stirred at room temperature for 20 min, until a clear yellow solution was formed. The resulting yellow solution was cooled to –78 ˚C, treated over a period of 30 min with 500 μL (1.00 mmol) of Me_2Zn (2.0 M solution in toluene), stirred at –78 ˚C for 10 min, warmed to 0 ˚C over a period of 5 min and treated at 0 ˚C with another solution of 188 mg (500 μmol) of **3** in 1.50 mL of dry CH_2Cl_2. The reaction mixture was stirred at 0 ˚C for 2 h, quenched with saturated NH_4Cl solution, diluted with Et_2O, filtered through a thin pad of celite, and extracted with Et_2O. The organic layer was dried ($MgSO_4$), concentrated *in vacuo*, and purified by chromatography on SiO_2 (100 : 1, $CHCl_3/Et_2O$) to yield 180 mg (64%) of **4** as a colorless, oily ~ 1 : 1 mixture of diastereomers: IR (neat) 3444, 3358, 3274, 3070, 3028, 2961, 2930, 2858, 1701, 1495, 1473, 1390, 1365, 1247, 1169, 1112, 1080, 824, 739, 701 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4 H), 7.45-7.40 (m, 6 H), 7.22-7.09 (m, 5 H), 4.94 (d, 0.5 H, *J* = 8.7 Hz), 4.93 (d, 0.5 H, *J* = 7.9 Hz), 4.52 (b, 1 H), 4.23 (b, 1 H), 3.47 (dd, 0.5 H, *J* = 9.0, 5.5 Hz), 3.40-3.35 (m, 1 H), 3.25 (dd, 0.5 H, *J* = 9.7, 8.0 Hz), 2.87-2.70 (m, 2 H), 2.62-2.52 (m, 1 H), 1.60 (s, 1.5 H), 1.57

(s, 1.5 H), 1.38 (s, 9 H), 1.07 (s, 9 H), 0.99 (d, 1.5 H, J = 6.6 Hz), 0.89 (d, 1.5 H, J = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 138.0, 135.6, 133.9, 129.5, 129.3, 129.0, 128.9, 128.6, 128.1, 127.6, 126.2, 125.1, 79.1, 68.2, 68.1, 57.9, 40.1 (2C), 35.1, 28.3, 26.8, 19.2, 17.2, 17.1, 14.0; HRMS (ESI) *m/z* calcd for $C_{35}H_{47}NO_3SiNa$ (M+Na) 580.3223, found 580.3245.



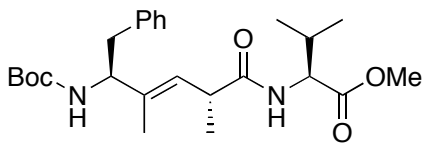
[(1*SR*,2*E*,4*R*)-Benzyl-5-hydroxyl-2,4*R*-dimethylpent-2-enyl]carbamic acid *tert*-butyl ester (5). A solution of 233 mg (418 μmol) of **4** in 10.0 mL of dry THF was treated at 0 ˚C with 835 μL (835 μmol) of TBAF (1.0 M solution in THF). The reaction mixture was stirred at 0 ˚C for 2 h and room temperature overnight, diluted with EtOAc, and washed with brine. The organic layer was dried (Na_2SO_4), concentrated *in vacuo*, and purified by chromatography on SiO_2 (from 4 : 1 to 2 : 1, hexane/EtOAc) to yield 62.3 mg (47%) of **5** as a colorless, oily ~ 1 : 1 mixture of diastereomers: IR (neat) 3424, 3342, 3086, 3062, 3028, 2975, 2929, 2870, 1693, 1497, 1454, 1366, 1249, 1171, 1032, 865, 737, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.14 (m, 5 H), 4.92 (d, 0.5 H, J = 9.7 Hz), 4.83 (d, 0.5 H, J = 9.6 Hz), 4.72 (bd, 0.5 H, J = 6.4 Hz), 4.72 (bd, 0.5 H, J = 6.4 Hz), 4.63 (bd, 0.5 H, J = 5.3 Hz), 4.25-4.15 (m, 1 H), 3.46 (dd, 0.5 H, J = 10.3, 5.1 Hz), 3.34 (dd, 0.5 H, J = 10.6, 5.3 Hz), 3.23 (t, 0.5 H, J = 9.7 Hz), 3.01 (dd, 0.5 H, J = 10.6, 8.9 Hz), 2.91 (dd, 0.5 H, J = 13.5, 6.6 Hz), 2.72-2.86 (m, 2 H), 2.66-2.51 (m, 1 H),

1.67 (s, 3 H), 1.42 (s, 4.5 H), 1.39 (s, 4.5 H), 0.85 (d, 1.5 H, J = 6.7 Hz), 0.79 (d, 1.5 H, J = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 155.1, 138.0, 137.6, 135.7, 129.1, 128.4 (2C), 126.6, 126.5, 125.1, 79.5, 67.6, 59.5, 39.7, 39.4, 35.3, 28.3, 16.4, 16.2; HRMS (ESI) *m/z* calcd for $C_{19}H_{29}NO_3Na$ (M+Na) 342.2045, found 342.2049.



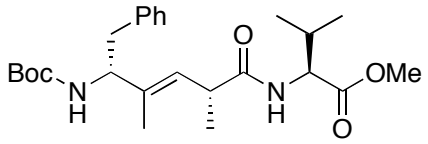
^{D,L}Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-OMe (6 + 7). A solution of 110 mg (0.259 mmol) of **5** in 10.0 mL of dry CH_2Cl_2 was treated at 0 ˚C with 122 mg (0.287 mmol) of Dess-Martin periodinane. The reaction mixture was stirred at 0 ˚C for 1 h and at room temperature for an additional 2 h, quenched with saturated $Na_2S_2O_3$ in a saturated $NaHCO_3$ solution, stirred for 30 min at room temperature, and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated *in vacuo* to give a colorless foam and subsequently dissolved in 6.00 mL of THF. The solution was treated at 0 ˚C with 1.24 mL (2.48 mmol) of 2-methyl-2-butene (2.0 M solution in THF) followed by another solution of 70.3 mg (0.777 mmol) of $NaClO_2$ and 71.5 mg (0.518 mmol) of $NaH_2PO_4 \cdot H_2O$ in 6.00 mL of H_2O. The reaction mixture was stirred at 0 ˚C for 1 h and at room temperature for an additional 4 h, extracted with EtOAc, and washed with H_2O. The organic layer was dried (Na_2SO_4), concentrated *in vacuo* and re-dissolved in 5.00 mL of $CHCl_3$. The solution was treated at 0 ˚C with 38.5 mg (0.285 mmol) of HOBt, 49.7 mg

(0.259 mmol) of EDC, and 65.2 mg (0.389 mmol) of Val-OMe • HCl followed 108 μL (0.777 mmol) of triethylamine. The reaction mixture was stirred at room temperature for 36 h, diluted with $CHCl_3$, and washed with brine. The organic layer was dried (Na_2SO_4), concentrated *in vacuo*, and purified by chromatography on SiO_2 (from 2 : 1 to 1 : 1, hexanes/EtOAc) to yield 145 mg (94%) of **6** and **7** as a colorless, foamy ~ 1 : 1 mixture of diastereomers. The two diastereomers were separated by RP-HPLC (C_{18}; linear gradient 70% to 100% CH_3CN (H_2O) in 30 min; 10 mL/min).

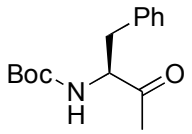


Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-OMe (6). Faster eluting isomer; $[\alpha]^{25}_D$ – 3.9 (*c* 1.0, $CHCl_3$); IR (neat) 3325, 3027, 2968, 2931, 2868, 1744, 1698, 1650, 1519, 1455, 1391, 1366, 1249, 1206, 1171, 1013, 868, 749, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2 H), 7.23-7.21 (m, 1 H), 7.17-7.16 (m, 2 H), 6.23 (b, 1 H), 5.32 (d, 1 H, *J* = 8.3 Hz), 4.59 (b, 1 H), 4.46 (dd, 1 H, *J* = 8.4, 5.3 Hz), 4.27 (bs, 1 H), 3.73 (s, 3 H), 3.22 (dq, 1 H, *J* = 8.6, 7.0 Hz), 2.96 (bd, 1 H, *J* = 7.4 Hz), 2.77 (dd, 1 H, *J* = 14.0, 8.1 Hz), 2.14-2.08 (m, 1 H), 1.76 (s, 3 H), 1.36 (s, 9 H), 1.24 (d, 3 H, *J* = 7.0 Hz), 0.90 (d, 3 H, *J* = 6.8 Hz), 0.87 (d, 3 H, *J* = 6.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 172.5, 155.0, 138.8, 137.4, 129.2, 128.4, 126.6, 124.9, 79.3, 57.1, 52.0, 40.0, 39.6, 30.9, 29.7, 28.3, 18.9, 17.9 (2C), 14.9; HRMS (ESI) *m/z* calcd for $C_{25}H_{38}N_2O_5Na$ (M+Na) 469.2678, found

469.2657; LC-MS (R_t 11.2 min, linear gradient 50% to 80% CH_3CN in 15 min, 0.4 mL/min; *m/z* = 469.3 $[M+Na]^+$).



^{D}Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-OMe (7). Slower eluting isomer; $[\alpha]^{25}_D$ – 11.0 (*c* 1.0, $CHCl_3$); IR (neat) 3325, 3032, 2967, 2930, 2872, 1745, 1701, 1655, 1519, 1455, 1391, 1366, 1248, 1205, 1171, 1001, 866, 741, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2 H), 7.23-7.21 (m, 1 H), 7.17-7.16 (m, 2 H), 6.51 (bs, 1 H), 5.25 (d, 1 H, *J* = 8.1 Hz), 4.64 (b, 1 H), 4.43 (b, 1 H), 4.24 (bd, 1 H, *J* = 5.7 Hz), 3.70 (s, 3 H), 3.15 (dq, 1 H, *J* = 8.9, 7.1 Hz), 2.84 (dd, 1 H, *J* = 13.7, 7.1 Hz), 2.78 (dd, 1 H, *J* = 13.6, 7.7 Hz), 2.17 (octet, 1 H, *J* = 6.6 Hz), 1.70 (s, 3 H), 1.37 (s, 9 H), 1.12 (d, 3 H, *J* = 7.0 Hz), 0.91 (d, 3 H, *J* = 6.6 Hz), 0.87 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 172.5, 155.1, 138.5, 137.4, 129.0, 128.4, 127.0, 126.6, 79.3, 59.6, 57.5, 51.8, 39.6, 30.6, 29.7, 28.3, 19.0, 18.2, 17.5, 12.3; HRMS (ESI) *m/z* calcd for $C_{25}H_{38}N_2O_5Na$ (M+Na) 469.2678, found 469.2661; LC-MS (R_t 11.6 min, linear gradient 50% to 80% CH_3CN in 15 min, 0.4 mL/min; *m/z* = 469.3 $[M+Na]^+$).

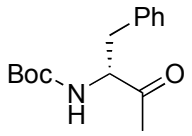


(*S*)-*tert*-Butyl-3-oxo-1-phenylbutan-2-ylcarbamate (12 from ozonolysis of 6). Through a solution of 5.1 mg (11 μmol) of **6** in 1.0 mL of CH_2Cl_2 and 1.0 mL of MeOH was bubbled O_3 at –78 ˚C until a blue color formed. Subsequently, N_2 was bubbled through the solution to remove excess O_3 until the blue color disappeared. The reaction mixture was treated at –78 ˚C with one drop of Me_2S, stirred at –78 ˚C for 2 h and at room temperature overnight, and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 (4 : 1, hexanes/EtOAc) to yield 2.5 mg (83%) of **12** as a colorless foam: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3 H), 7.18-7.14 (m, 2 H), 5.13 (bd, 1 H, *J* = 7.1 Hz), 4.55 (q, 1 H, *J* = 6.6 Hz), 3.11 (dd, 1 H, *J* = 13.9, 6.5 Hz), 2.99 (dd, 1 H, *J* = 14.0, 6.6 Hz), 2.14 (s, 3 H), 1.42 (s, 9 H); HPLC (Chiralcel OD, 250 × 4.6 mm, R_t 7.30 min, 5% *i*-PrOH (hexanes), 1.0 mL/min).

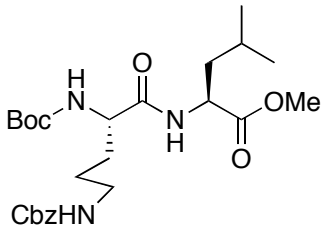
(*S*)-*tert*-Butyl-3-oxo-1-phenylbutan-2-ylcarbamate (12 from Boc-^{L}Phe-OH (11)). According to a literature procedure,[1] **12** was prepared from Boc-^{L}Phe-OH (**11**) as a colorless foam: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3 H), 7.18-7.14 (m, 2 H), 5.13 (bd, 1 H, *J* = 6.4 Hz), 4.55 (q, 1 H, *J* = 6.8 Hz), 3.11 (dd, 1 H, *J* = 13.9, 6.4 Hz), 2.99 (dd, 1 H, *J* = 14.0, 6.4 Hz), 2.14 (s, 3 H), 1.42 (s, 9

[1] Pace, R. D.; Kabalka, G. W. *J. Org. Chem.* **1995**, *60*, 4838.

H); HPLC (Chiralcel OD, 250 × 4.6 mm, R_t 7.27 min, 5% *i*PrOH (hexanes), 1.0 mL/min).

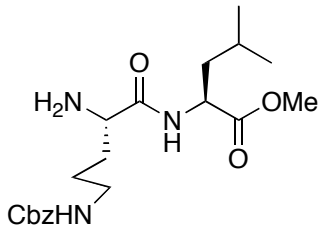


(*R*)-*tert*-Butyl-3-oxo-1-phenylbutan-2-ylcarbamate (12*R* from Boc-^{D}Phe-OH). According to a literature procedure,[1] **12*R*** was prepared from Boc-^{D}Phe-OH as a colorless foam: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.23 (m, 3 H), 7.18-7.14 (m, 2 H), 5.13 (bd, 1 H, *J* = 5.9 Hz), 4.55 (q, 1 H, *J* = 6.7 Hz), 3.11 (dd, 1 H, *J* = 13.9, 6.5 Hz), 2.99 (dd, 1 H, *J* = 13.9, 6.5 Hz), 2.14 (s, 3 H), 1.42 (s, 9 H); HPLC (Chiralcel OD, 250 × 4.6 mm, R_t 6.64 min, 5% *i*-PrOH (hexanes), 1.0 mL/min).

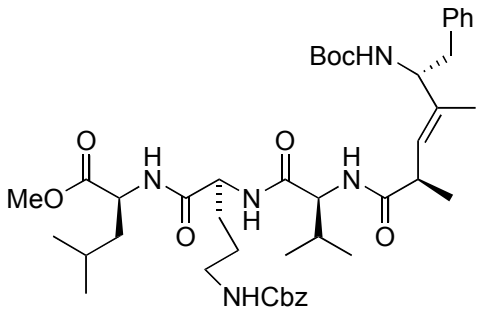


Boc-Orn(Cbz)-Leu-OMe. A mixture of 545 mg (3.00 mmol) of Leu-OMe • HCl, 1.00 g (2.73 mmol) of Boc-Orn(Cbz)-OH, 405 mg (3.00 mmol) of HOBt, and 523 g (2.73 mmol) of EDC in 30.0 mL of $CHCl_3$ was treated at 0 ˚C with 936 μL (6.72 mmol) of triethylamine. The reaction mixture was stirred at 0 ˚C for 1 h and at room temperature overnight, and washed with 5% citric acid, 5% of Na_2CO_3 solution and H_2O. The organic layer was dried (Na_2SO_4) and concentrated *in*

vacuo to yield 1.28 g (95%) of **Boc-Orn(Cbz)-Leu-OMe** as a colorless foam: IR (neat) 3526, 3324, 3066, 2957, 2871, 1701, 1659, 1529, 1455, 1391, 1367, 1251, 1165, 1025, 866, 777, 740, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5 H), 6.92 (b, 1 H), 5.27 (b, 1 H), 5.16 (b, 1 H), 5.11, 5.06 (AB, 2 H, *J* = 12.4 Hz), 4.55 (b, 1 H), 4.31 (b, 1 H), 3.69 (s, 3 H), 3.41 (b, 1 H), 3.20-3.10 (m, 1 H), 1.90-1.80 (m, 1 H), 1.73-1.65 (m, 1 H), 1.65-1.50 (m, 5 H), 1.43 (s, 9 H), 0.92 (d, 3 H, *J* = 6.0 Hz), 0.91 (d, 3 H, *J* = 5.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 172.2, 157.0, 155.7, 136.5, 128.4, 128.0, 79.7, 66.6, 52.8, 52.1, 50.7, 41.0, 39.6, 30.0, 28.2, 26.1, 24.7, 22.8, 21.6; HRMS (ESI) *m/z* calcd for $C_{25}H_{39}N_3O_7Na$ (M+Na) 516.2686, found 516.2656.

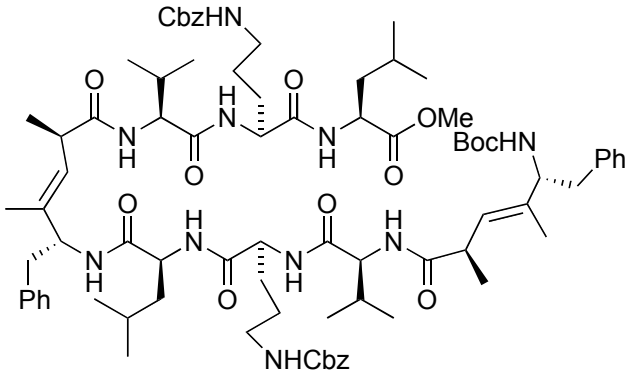


H-Orn(Cbz)-Leu-OMe. A solution of 113 mg (0.228 mmol) of **Boc-Orn(Cbz)-Leu-OMe** in 2.40 mL (9.60 mmol) of HCl (4.0 N solution in 1,4-dioxane) was stirred at 0 ˚C for 10 min and at room temperature for an additional 50 min. 1,4-Dioxane was removed *in vacuo* and the colorless, foamy residue was dissolved in 20.0 mL of $CHCl_3$ and washed with 5% Na_2CO_3 solution and H_2O. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to yield **H-Orn(Cbz)-Leu-OMe** as a colorless foam that was used immediately without further purification.



Boc-^{D}Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-Orn(Cbz)-Leu-OMe (8). A solution of 51.0 mg (0.114 mmol) of **7** in 3.60 mL of MeOH was treated at 0 ˚C with 1.14 mL (1.14 mmol) of 1 N NaOH. The reaction mixture was stirred at room temperature for 6 h, treated at 0 ˚C with 1.14 mL (1.14 mmol) of 1 N HCl, and extracted with $CHCl_3$. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to yield crude acid as a colorless foam which was re-dissolved in 3.50 mL of $CHCl_3$. This solution was treated at room temperature with 0.228 mmol of crude **H-Orn(Cbz)-Leu-OMe**, 16.9 mg (0.125 mmol) of HOBt, 26.3 mg (0.137 mmol) of EDC and 13.9 mg (0.114 mmol) of DMAP and stirred at room temperature for 36 h. The reaction mixture was concentrated *in vacuo* and purified by chromatography on SiO_2 (10 : 1, $CHCl_3$/MeOH) to yield 88.7 mg (96%) of **8** as a colorless foam: $[\alpha]^{25}_{D}$ –22.2 (*c* 1.0, $CHCl_3$); IR (neat) 3290, 3064, 3023, 2961, 2929, 2872, 1693, 1636, 1535, 1454, 1385, 1366, 1250, 1169, 1026, 743, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.14 (m, 10 H), 7.00 (b, 1 H), 6.95 (b, 1 H), 6.68 (b, 1 H), 5.26 (b, 2 H), 5.11, 5.07 (AB, 2 H, *J* = 12.1 Hz), 4.75 (b, 1 H), 4.62 (b, 1 H), 4.56-4.50 (m, 1 H), 4.20 (b, 1 H), 4.15 (b, 1 H), 3.69 (s, 3 H), 3.44-3.32 (m, 1 H), 3.22-3.10 (m, 2 H), 2.82 (dd, 1 H, *J* = 13.7, 6.8 Hz), 2.75 (dd, 1 H,

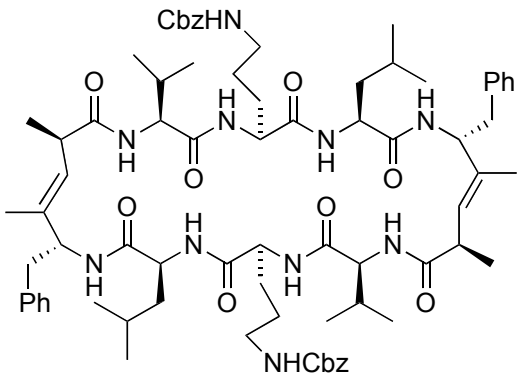
J = 13.4, 8.2 Hz), 2.15 (b, 1 H), 2.03 (b, 1 H), 1.95-1.85 (m, 1 H), 1.75-1.50 (m, 5 H), 1.66 (s, 3 H), 1.37 (s, 9 H), 1.08 (d, 3 H, *J* = 6.9 Hz), 1.00-0.85 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 173.2, 171.5 (2C), 157.1, 155.2, 138.0, 137.5, 136.6, 129.1, 128.5 (2C), 128.0, 126.6, 79.4, 66.6, 59.4, 52.2, 51.7, 50.8, 41.0, 39.7, 30.0, 29.5, 28.3, 26.0, 24.8, 22.8, 21.7, 19.3, 18.5, 17.4, 12.8; HRMS (ESI) *m/z* calcd for $C_{44}H_{65}N_5O_9Na$ (M+Na) 830.4680, found 830.4666; LC-MS (R_t 7.95 min, linear gradient 70% to 95% CH_3CN in 10 min, 95% CH_3CN from 10 to 20 min, 0.4 mL/min; *m/z* = 830.4 $[M+Na]^+$).



Boc-^{D}Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-Orn(Cbz)-Leu-^{D}Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-Orn(Cbz)-Leu-OMe (9). A solution of 33.0 mg (40.8 μmol) of **8** in 4.50 mL of MeOH was treated at 0 ˚C with 408 μL (408 μmol) of 1 N NaOH. The reaction mixture was stirred at 0 ˚C for 1 h and at room temperature for an additional 6 h, treated with 408 μL (408 μmol) of 1 N HCl and extracted with $CHCl_3$. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude acid as a colorless foam.

A solution of 33.0 mg (40.8 μmol) of **8** in 2.64 mL (10.6 mmol) of HCl (4.0 N solution in 1,4-dioxane) was stirred at 0 ˚C for 10 min and at room temperature for an additional 40 min. 1,4-Dioxane was removed *in vacuo* and the colorless, foamy residue was dissolved in 30.0 mL of $CHCl_3$ and washed with 5% Na_2CO_3 solution. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to give the crude amine as a colorless foam.

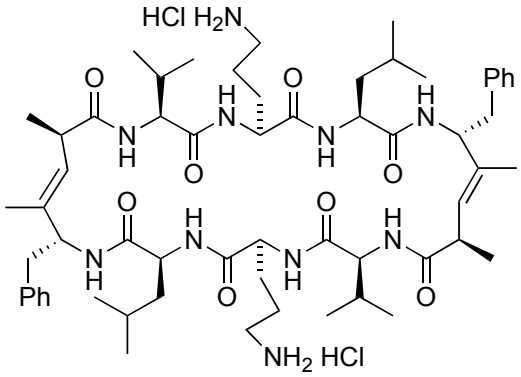
A solution of acid and amine in 8.50 mL of $CHCl_3$ was treated at room temperature with 6.1 mg (44.9 μmol) of HOBt, 9.4 mg (49.0 μmol) of EDC and 5.0 mg (40.8 μmol) of DMAP. The reaction mixture was stirred at room temperature for 60 h, concentrated *in vacuo*, and purified by chromatography on SiO_2 (20 : 1, $CHCl_3$/MeOH) to yield 60.0 mg (99%) of **9** as a colorless foam that was used directly without further purification: HRMS (ESI) *m/z* calcd for $C_{82}H_{118}N_{10}O_{15}Na$ (M+Na) 1505.8676, found 1505.8679; LC-MS (R_t 11.6 min, linear gradient 70% to 95% CH_3CN in 10 min, 95% CH_3CN from 10 to 20 min, 0.4 mL/min; *m/z* = 1383.6 $[M\text{-Boc}]^+$).



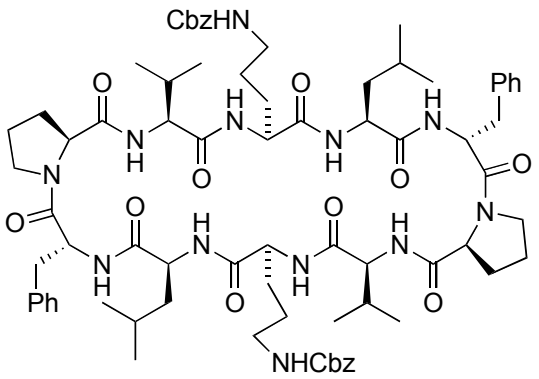
Cyclo[(*D*Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-Orn(Cbz)-Leu)$_2$] (10). A solution of 46.7 mg (31.5 μmol) of **9** in 3.60 mL of MeOH was treated at room temperature with 315 μL (315 μmol) of 1 N NaOH. The reaction mixture was stirred at room temperature for 16 h and treated with 315 μL (315 μmol) of 1 N HCl. Solvents were removed *in vacuo* and 4.00 mL (16.0 mmol) of HCl (4.0 N solution in 1,4-dioxane) was added at 0 ˚C. The solution was stirred at 0 ˚C for 10 min and at room temperature for an additional 40 min. 1,4-Dioxane was removed *in vacuo* and the colorless, foamy residue was dissolved in 10.0 mL of benzene, treated at room temperature with 26.5 mg (315 μmol) of $NaHCO_3$, and evaporated to dryness by azeotropic distillation with benzene at 25 ˚C. The solid residue was diluted with 26.3 mL of $CHCl_3$ and treated at room temperature with 4.7 mg (34.7 μmol) of HOBt, 7.2 mg (37.8 μmol) of EDC, and 3.8 mg (31.5 μmol) of DMAP. The reaction mixture was stirred at room temperature for 36 h, concentrated *in vacuo*, purified by chromatography on SiO_2 (20 : 1, $CHCl_3$/MeOH) and repurified by RP-HPLC (C_{18}; from 90% to 100% MeOH (H_2O) in 20 min, 100% MeOH (H_2O) from 20 to 30 min, 10 mL/min) to yield 21.2 mg (50%) of **10** as a colorless solid: Mp 263-266 ˚C (MeOH/H_2O); $[\alpha]^{25}_D$ –119 (*c* 0.1, $CHCl_3$); IR (neat) 3269, 3065,

2959, 2931, 2871, 1699, 1632, 1525, 1455, 1258, 1142, 1028, 750, 698 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6, 298K) δ 8.37 (bd, 4 H, *J* = 7.5 Hz), 8.08 (d, 2 H, *J* = 6.9 Hz), 7.35-7.27 (m, 10 H), 7.23-7.18 (m, 8 H), 7.16-7.11 (m, 4 H), 7.07 (d, 2 H, *J* = 7.8 Hz), 5.15 (d, 2 H, *J* = 9.7 Hz), 4.98, 4.96 (AB, 4 H, *J* = 13.2 Hz), 4.66 (bq, 2 H, *J* = 7.0 Hz), 4.37 (q, 2 H, *J* = 7.8 Hz), 4.33 (t, 2 H, *J* = 7.8 Hz), 4.19 (q, 2 H, *J* = 7.4 Hz), 3.02-2.95 (m, 2 H), 2.95-2.87 (m, 4 H), 2.84 (dd, 2 H, *J* = 13.6, 8.0 Hz), 2.68 (dd, 2 H, *J* = 13.5, 7.4 Hz), 2.03 (octet, 2 H, *J* = 6.8 Hz), 1.58-1.50 (m, 2 H), 1.50-1.40 (m, 2 H), 1.48 (s, 6 H), 1.35-1.25 (m, 8 H), 1.30-1.18 (m, 2 H), 0.93 (d, 6 H, *J* = 7.0 Hz), 0.79 (d, 6 H, *J* = 6.7 Hz), 0.77 (d, 6 H, *J* = 6.8 Hz), 0.75 (d, 6 H, *J* = 6.3 Hz), 0.73 (d, 6 H, *J* = 6.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6, 298K) δ 172.2, 171.1, 170.7, 170.5, 156.0, 138.5, 137.1, 136.6, 129.0, 128.4, 128.3, 127.9, 127.7 (2C), 126.0, 65.2, 59.9, 57.1, 52.0, 50.7, 41.2, 40.2, 38.5, 36.9, 30.9, 30.1, 26.0, 24.0, 22.5 (2C), 18.9, 18.3, 17.6, 10.4; ^{1}H NMR (600 MHz, DMSO-d_6, 338K) δ 8.19 (d, 2 H, *J* = 8.9 Hz), 8.15 (d, 2 H, *J* = 6.7 Hz), 8.01 (d, 2 H, *J* = 8.7 Hz), 7.34-7.28 (m, 10 H), 7.24-7.19 (m, 8 H), 7.16-7.13 (m, 2 H), 7.00 (d, 2 H, *J* = 9.2 Hz), 6.89 (b, 2 H), 5.18 (dd, 2 H, *J* = 9.6, 1.0 Hz), 4.99 (s, 4 H), 4.67 (q, 2 H, *J* = 7.7 Hz), 4.39 (q, 2 H, *J* = 7.7 Hz), 4.35 (dd, 2 H, *J* = 9.1, 7.0 Hz), 4.24 (q, 2 H, *J* = 7.4 Hz), 3.00-2.90 (m, 6 H), 2.87 (dd, 2 H, *J* = 13.8, 7.9 Hz), 2.71 (dd, 2 H, *J* = 13.8, 7.5 Hz), 2.05 (octet, 2 H, *J* = 6.8 Hz), 1.61-1.55 (m, 2 H), 1.54-1.45 (m, 2 H), 1.49 (s, 6 H), 1.41-1.32 (m, 8 H), 1.27-1.21 (m, 2 H), 0.96 (d, 6 H, *J* = 7.0 Hz), 0.82 (d, 6 H, *J* = 6.8 Hz), 0.80 (d, 6 H, *J* = 6.8 Hz), 0.77 (d, 6 H, *J* = 6.5 Hz), 0.75 (d, 6 H, *J* = 6.3 Hz); ^{13}C NMR (150 MHz, DMSO-d_6, 338K) δ

171.9, 170.9, 170.5, 170.3, 155.7, 138.2, 137.0, 136.4, 128.6, 128.3, 127.9, 127.6, 127.3, 127.2, 125.7, 64.9, 59.5, 56.9, 51.8, 50.5, 40.8, 40.0, 38.4, 36.7, 30.7, 29.8, 25.6, 23.8, 22.2, 22.1, 18.6, 17.9, 17.2, 10.1; HRMS (ESI) *m/z* calcd for $C_{76}H_{106}N_{10}O_{12}Na$ (M+Na) 1373.7889, found 1373.7872; LC-MS (R_t 14.3 min, linear gradient 70% to 95% CH_3CN in 10 min, 95% CH_3CN from 10 to 20 min, 0.4 mL/min; *m/z* = 1351.5 $[M+H]^+$, 1374.4 $[M+Na]^+$).



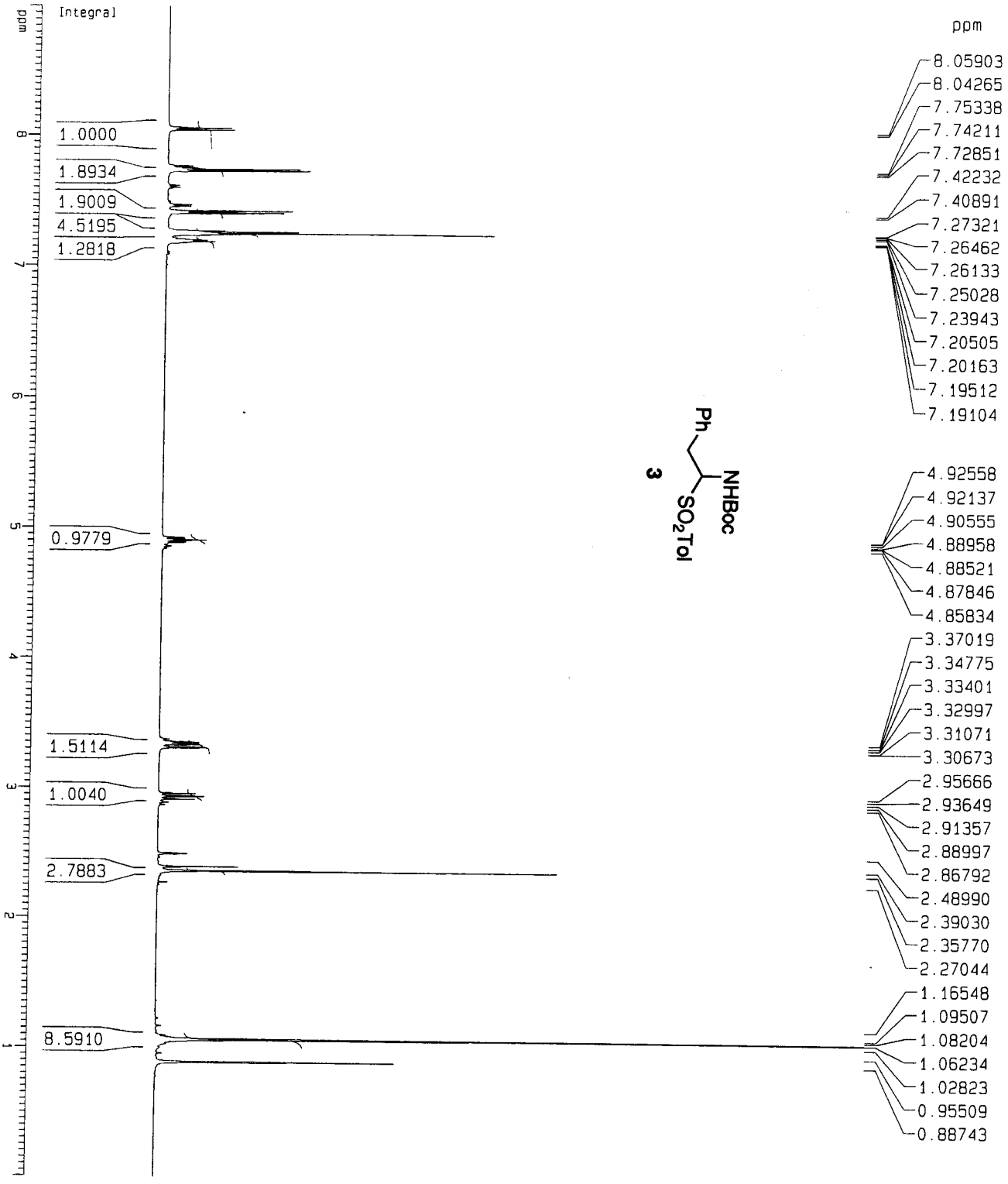
Cyclo[(*D*Phe-ψ[(*E*)-C(CH$_3$)=CH]-Ala-Val-Orn-Leu)$_2$] • 2HCl (1•2HCl). A solution of 1.7 mg (1.3 μmol) of **10** in 0.74 mL of a 0.02 M HCl solution in MeOH was treated at room temperature with 1.8 mg of 10% Pd/C. The reaction mixture was hydrogenated at room temperature under H_2 (1 atm) for 3 h, filtered through a pad of celite, concentrated *in vacuo*, dissolved in H_2O, and lyophilized to yield 1.5 mg (quant.) of **1•2HCl** as a colorless powder: ESI-MS *m/z* 1083.6 (M-2HCl+H), 1106.6 (M-2HCl+Na); HRMS (ESI) *m/z* calcd for $C_{60}H_{95}N_{10}O_8$ (M-2HCl+H) 1083.7334, found 1083.7269.



Cyclo[(Val-Orn(Cbz)-Leu-^{D}Phe-Pro)$_2$] (Cbz$_2$GS). Prepared as a colorless solid:[2] Mp 52-53 °C (hexanes/Et_2O); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 (d, 2 H, J = 3.2 Hz), 8.58 (d, 2 H, J = 9.1 Hz), 8.38 (d, 2 H, J = 8.9 Hz), 7.34-7.27 (m, 12 H), 7.20-7.16 (m, 8 H), 7.13-7.10 (m, 4 H), 4.99, 4.96 (AB, 4 H, J = 12.6 Hz), 4.80-4.75 (m, 2 H), 4.57 (q, 2 H, J = 7.9 Hz), 4.42 (dd, 2 H, J = 9.1, 7.2 Hz), 3.35 (d, 2 H, J = 8.1 Hz), 4.33-4.30 (m, 2 H), 3.51 (bt, 2 H, J = 9.3 Hz), 3.00-2.90 (m, 6 H), 2.83 (t, 2 H, J = 11.4 Hz), 2.39 (q, 2 H, J = 8.8 Hz), 2.05-1.95 (m, 2 H), 1.95-1.87 (m, 2 H), 1.75-1.65 (m, 2 H), 1.50-1.35 (m, 12 H), 1.35-1.20 (m, 6 H), 0.79 (d, 12 H, J = 6.6 Hz), 0.78 (d, 6 H, J = 6.7 Hz), 0.75 (d, 6 H, J = 6.7 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ 171.7, 170.7, 170.5, 170.4, 169.6, 155.9, 137.2, 136.3, 129.2, 128.3, 128.1, 127.7, 127.6, 126.7, 65.2, 59.7, 56.6, 53.7, 51.3, 49.5, 45.7, 41.0, 40.2, 35.7, 31.3, 29.9, 25.2, 24.0, 23.0, 22.7, 22.5, 19.0, 18.0; HRMS (ESI) *m/z* calcd for $C_{76}H_{104}N_{12}O_{14}Na$ (M+Na) 1431.7693, found 1431.7726; LC-MS (R_t

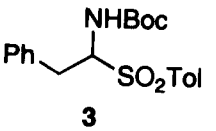
[2] (a) Xiao, J.; Weisblum, B.; Wipf, P. *J. Am. Chem. Soc.* **2005**, *127*, 5742. (b) Wipf, P.; Xiao, J.; Jiang, J.; Belikova, N. A.; Tyurin, V. A.; Fink, M. P.; Kagan, V. E. *J. Am. Chem. Soc.* **2005**, *127*, 12460.

14.2 min, linear gradient 70% to 95% CH_3CN in 10 min, 95% CH_3CN from 10 to 20 min, 0.4 mL/min; *m/z* = 1409.6 $[M+H]^+$).




```
Current Data Parameters
NAME                  xjb-5-179-600
EXPNO                             1
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20050303
Time                         21.13
INSTRUM                       spect
PROBHD     5 mm TBI 1H/
PULPROG                         zg
TD                             65536
SOLVENT                     CD2Cl2
NS                                8
DS                                0
SWH                        8992.806 Hz
FIDRES                     0.137219 Hz
AQ                         3.643515 sec
RG                                1
DW                         55.600 use
DE                          6.00 use
TE                         290.0 K
D1                         3.00000000 sec
============== CHANNEL f1 ===
NUC1                             1H
P1                          9.00 use
PL1                          0.00 dB
SFO1                       600.8336050 MHz

F2 - Processing parameters
SI                             65536
SF                         600.8300107 MHz
WDW                               EM
SSB                               0
LB                           0.10 Hz
GB                                0
PC                             1.00

1D NMR plot parameters
CX                           20.00 cm
F1P                          9.000 ppm
F1                        5407.47 Hz
F2P                          0.000 ppm
F2                           0.00 Hz
PPMCM                        0.45000 ppm
HZCM                      270.37350 Hz
```

xjb-5-179-600, DMSO, rt, 150MHz C13



3

Current Data Parameters

NAME	xjb-5-179-600
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20050303
Time	21.21
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	c13wonoe
TD	65536
SOLVENT	CDCl3
NS	64
DS	2
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ======

NUC1	13C
P1	13.00 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ======

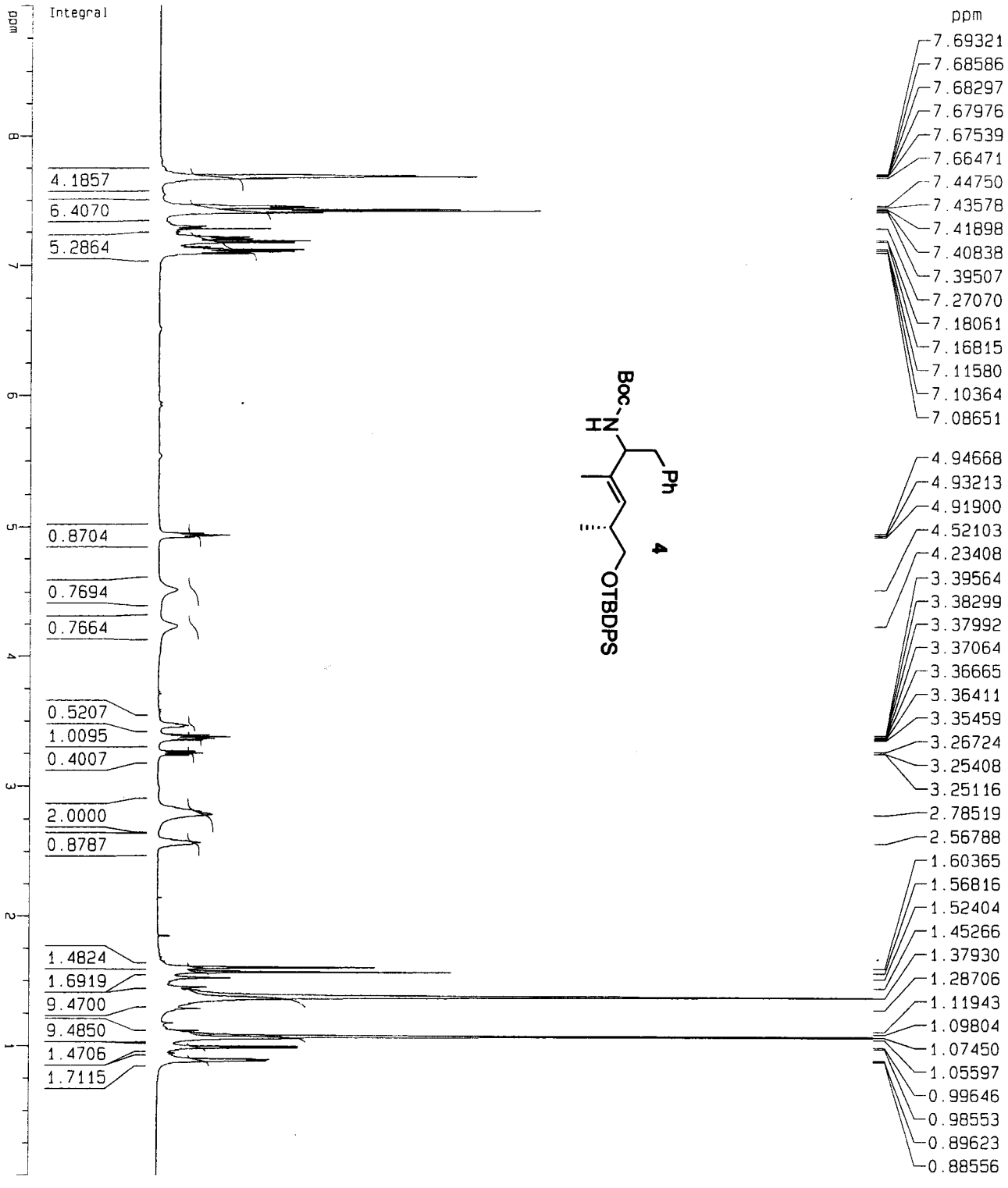
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	151.0788986 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	180.000 ppm
F1	27194.20 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	9.00000 ppm/cm
HZCM	1359.71008 Hz/cm

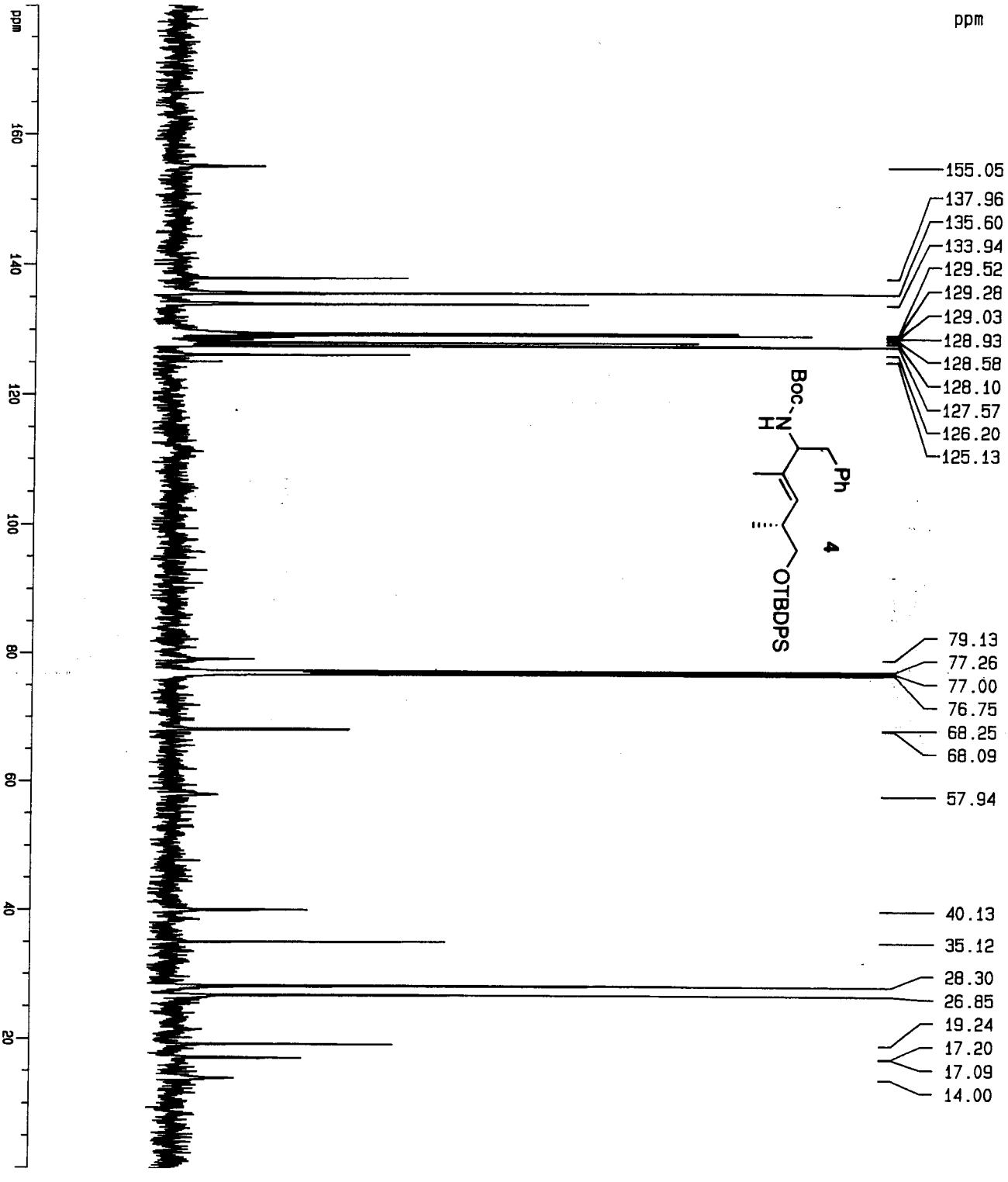


Current Data Parameters
NAME xjb-5-183-600
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050303
Time 18.00
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CD2Cl2
NS 20
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 10
DW 55.600 use
DE 6.00 use
TE 290.0 K
D1 3.00000000 sec
========== CHANNEL f1 ===
NUC1 1H
P1 9.00 use
PL1 0.00 dB
SF01 600.8336050 MHz

F2 - Processing parameters
SI 65536
SF 600.8300261 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 5407.47 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm
HZCM 270.37350 Hz

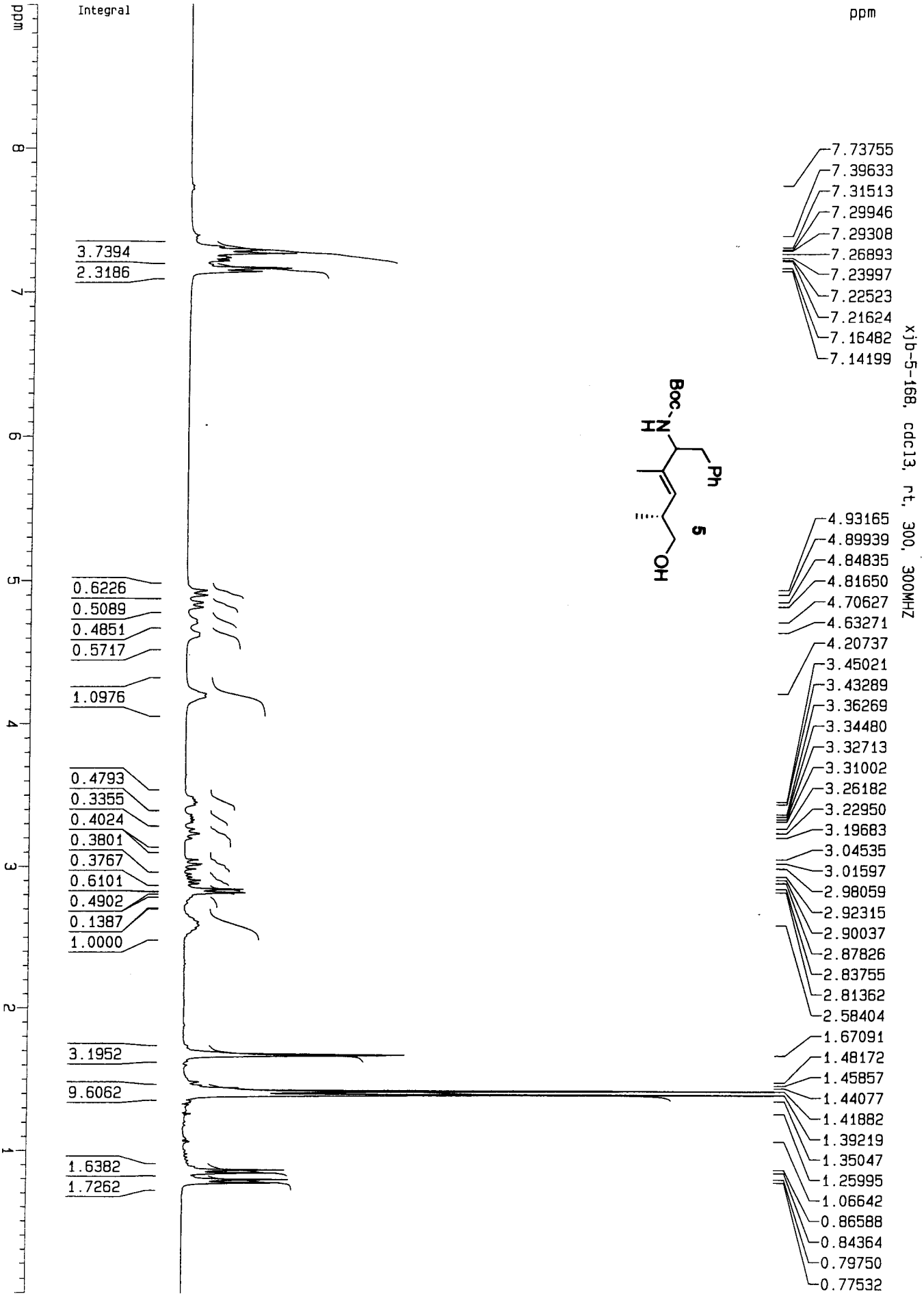


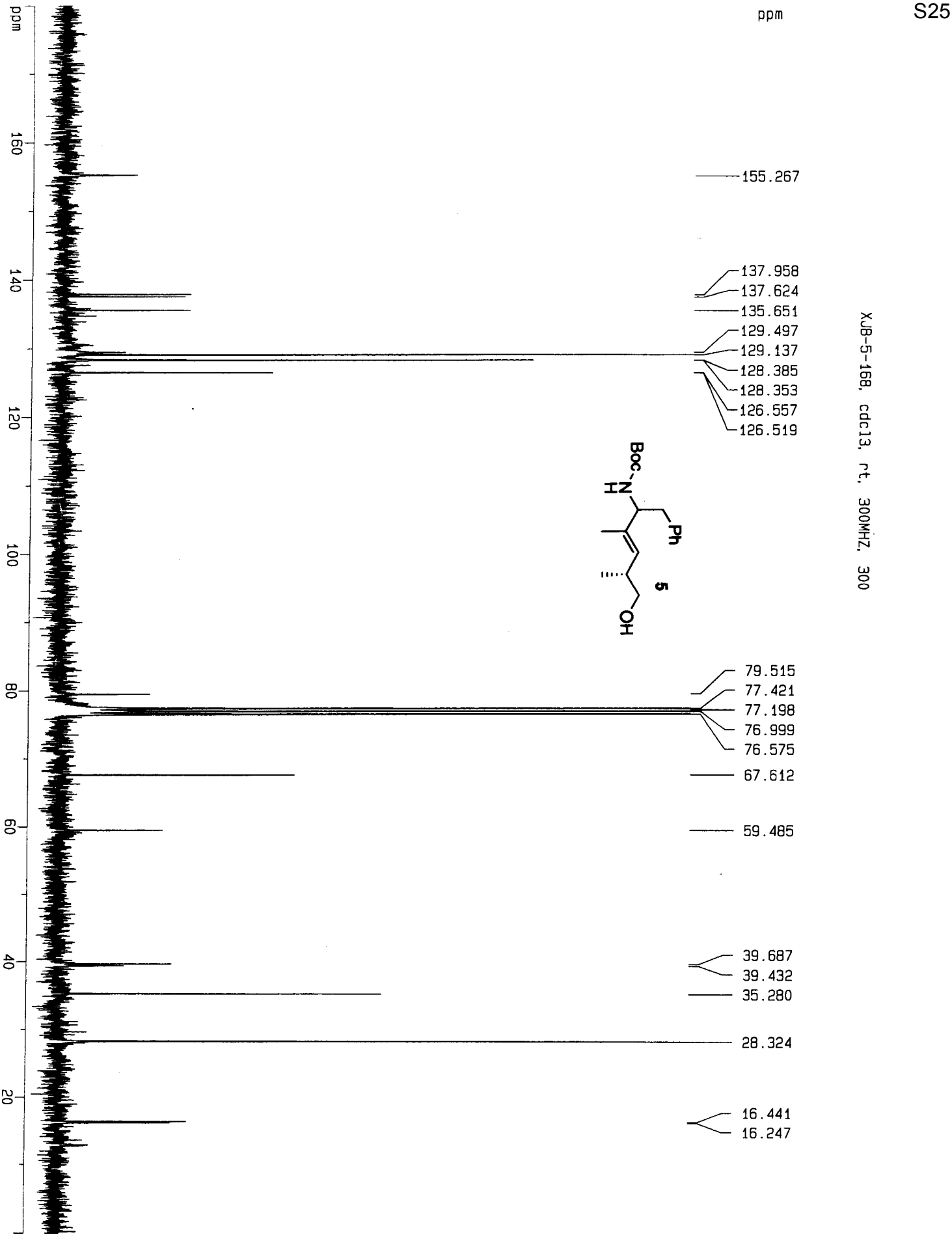
Current Data Parameters
NAME xjb-5-183-500
EXPNO 13
PROCNO 1

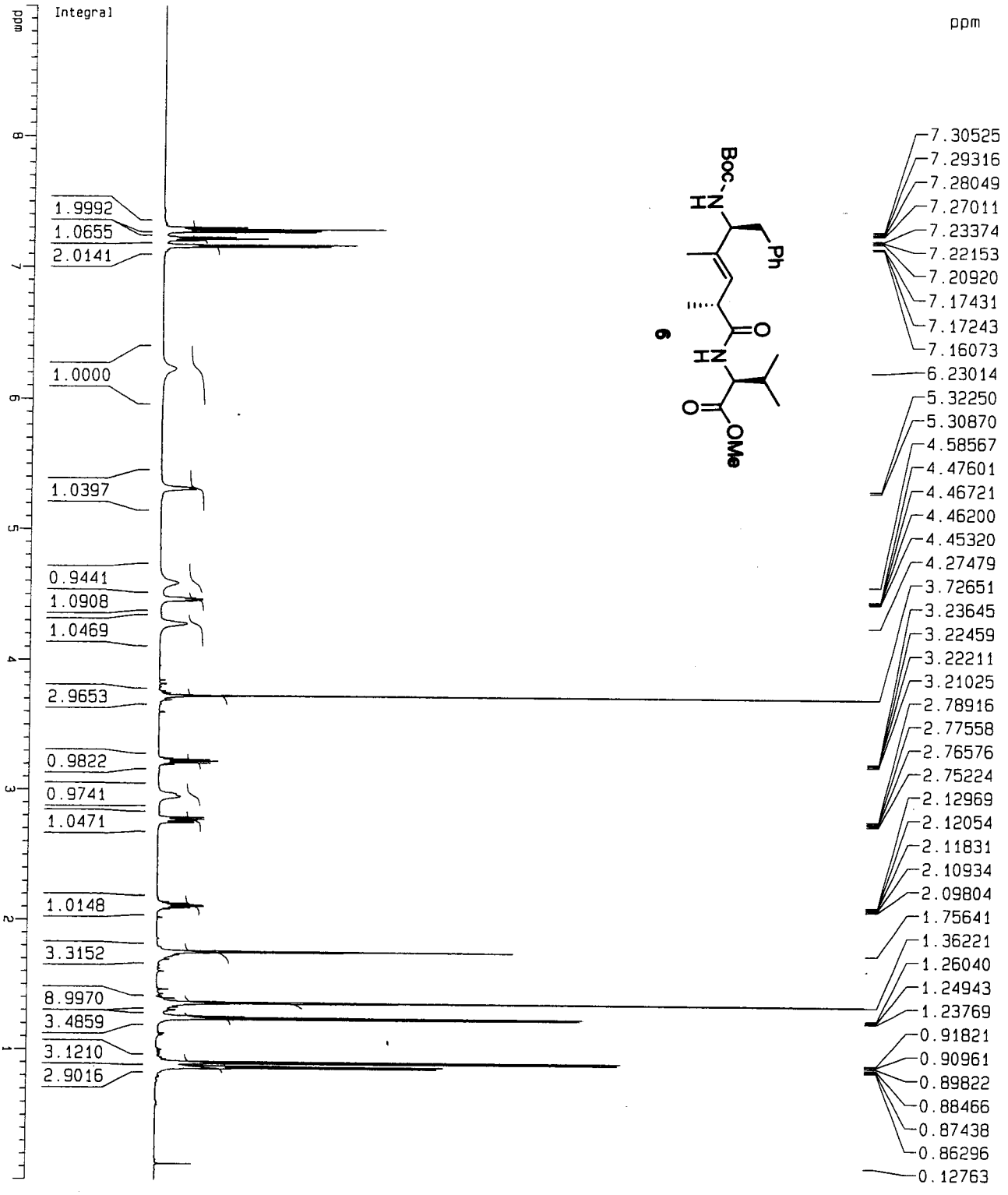
F2 - Acquisition Parameters
Date_ 500000
Time 19.37
INSTRUM spect
PROBHD 5 mm TXI 13C
PULPROG c13wonoe
TD 32768
SOLVENT CDCl3
NS 1035
DS 0
SWH 32679.738 Hz
FIDRES 0.997306 Hz
AQ 0.5014004 sec
RG 32768
DW 15.300 usec
DE 6.00 usec
TE 290.0 K
D3 0.00100000 sec
PL12 6.00 dB
D1 8.00000000 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 500.1330008 MHz
NUC2 1H
PL2 120.00 dB
P1 21.60 usec
DE 6.00 usec
SFO1 125.7715724 MHz
NUC1 13C
PL1 0.00 dB

F2 - Processing parameters
SI 8192
SF 125.7578000 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 180.000 ppm
F1 22636.40 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 9.00000 ppm/cm
HZCM 1131.82019 Hz/cm


Integral
ppm
7.73755
7.39633
7.31513
7.29946
7.29308
7.26893
7.23997
7.22523
7.21624
7.16482
7.14199
xjb-5-168, cdcl3, rt, 300, 300MHZ
Boc
N
H
Ph
5
OH
4.93165
4.89939
4.84835
4.81650
4.70627
4.63271
4.20737
3.45021
3.43289
3.36269
3.34480
3.32713
3.31002
3.26182
3.22950
3.19683
3.04535
3.01597
2.98059
2.92315
2.90037
2.87826
2.83755
2.81362
2.58404
1.67091
1.48172
1.45857
1.44077
1.41882
1.39219
1.35047
1.25995
1.06642
0.86588
0.84364
0.79750
0.77532
3.7394
2.3186
0.6226
0.5089
0.4851
0.5717
1.0976
0.4793
0.3355
0.4024
0.3801
0.3767
0.6101
0.4902
0.1387
1.0000
3.1952
9.6062
1.6382
1.7262


ppm
160
140
120
100
80
60
40
20
155.267
137.958
137.624
135.651
129.497
129.137
128.385
128.353
126.557
126.519
79.515
77.421
77.198
76.999
76.575
67.612
59.485
39.687
39.432
35.280
28.324
16.441
16.247
Boc
N
H
Ph
5
OH
XJB-5-168, cdcl3, rt, 300MHZ, 300



Current Data Parameters
NAME xjb-5-247-1-60
EXPNO 1
PROCNO 1

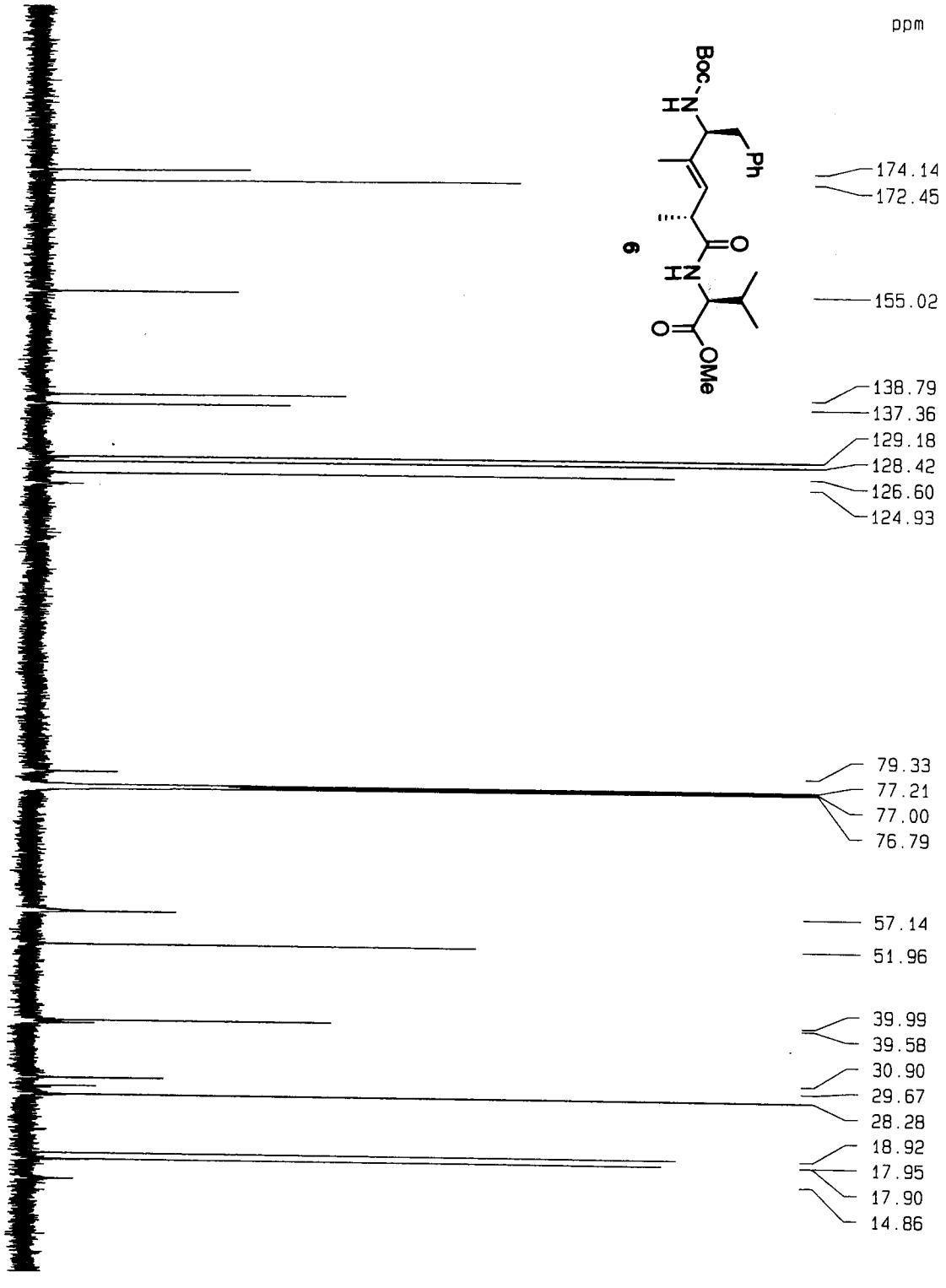
F2 - Acquisition Parameters
Date_ 20050508
Time 13.28
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 40
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.643515 sec
RG 2
DW 55.600 use
DE 6.00 use
TE 290.0 K
D1 6.00000000 sec

========== CHANNEL f1 ==
NUC1 1H
P1 9.00 use
PL1 0.00 dB
SFO1 600.8336050 MHz

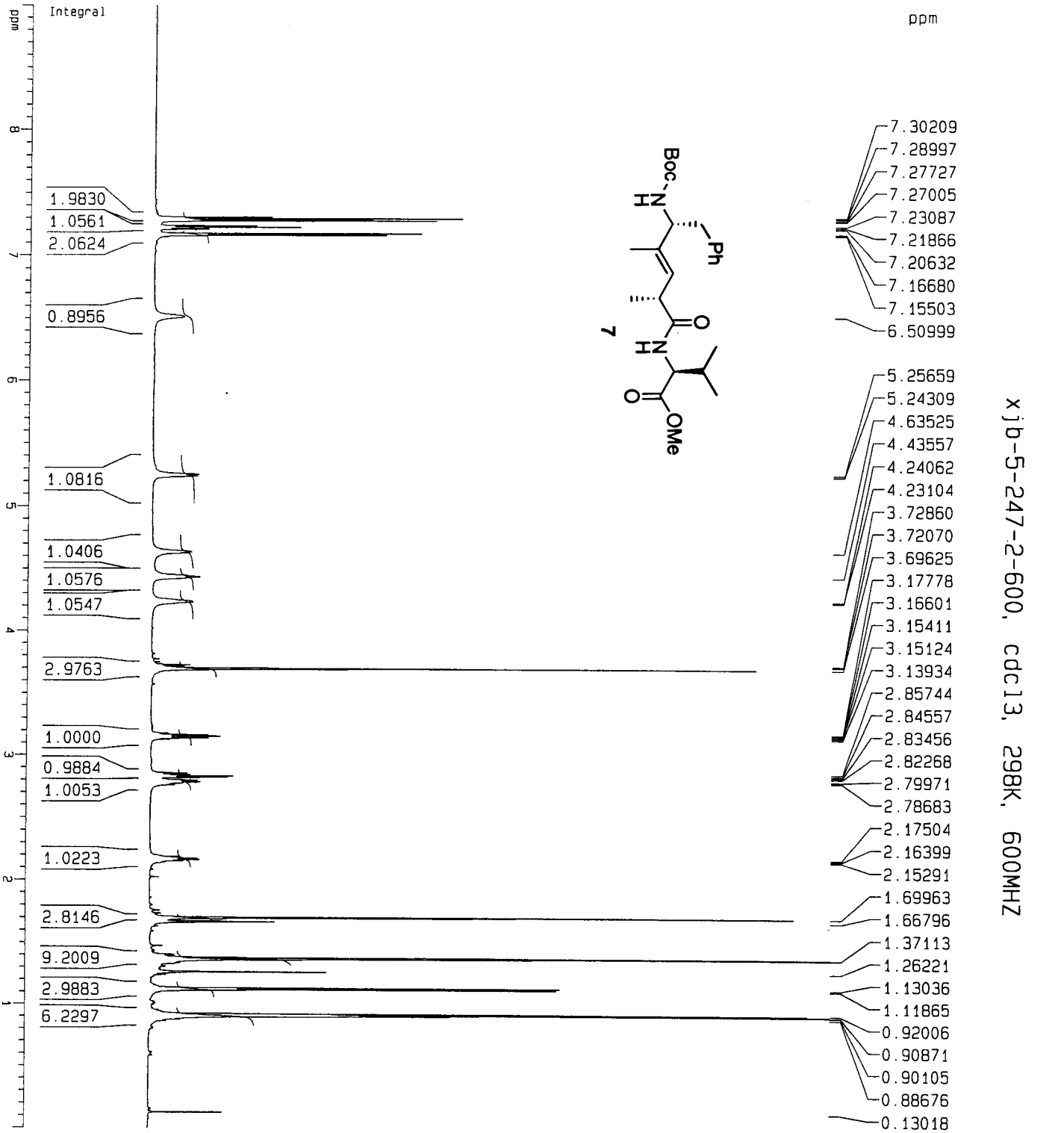
F2 - Processing parameters
SI 65536
SF 600.8300264 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 5407.47 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm
HZCM 270.37350 Hz

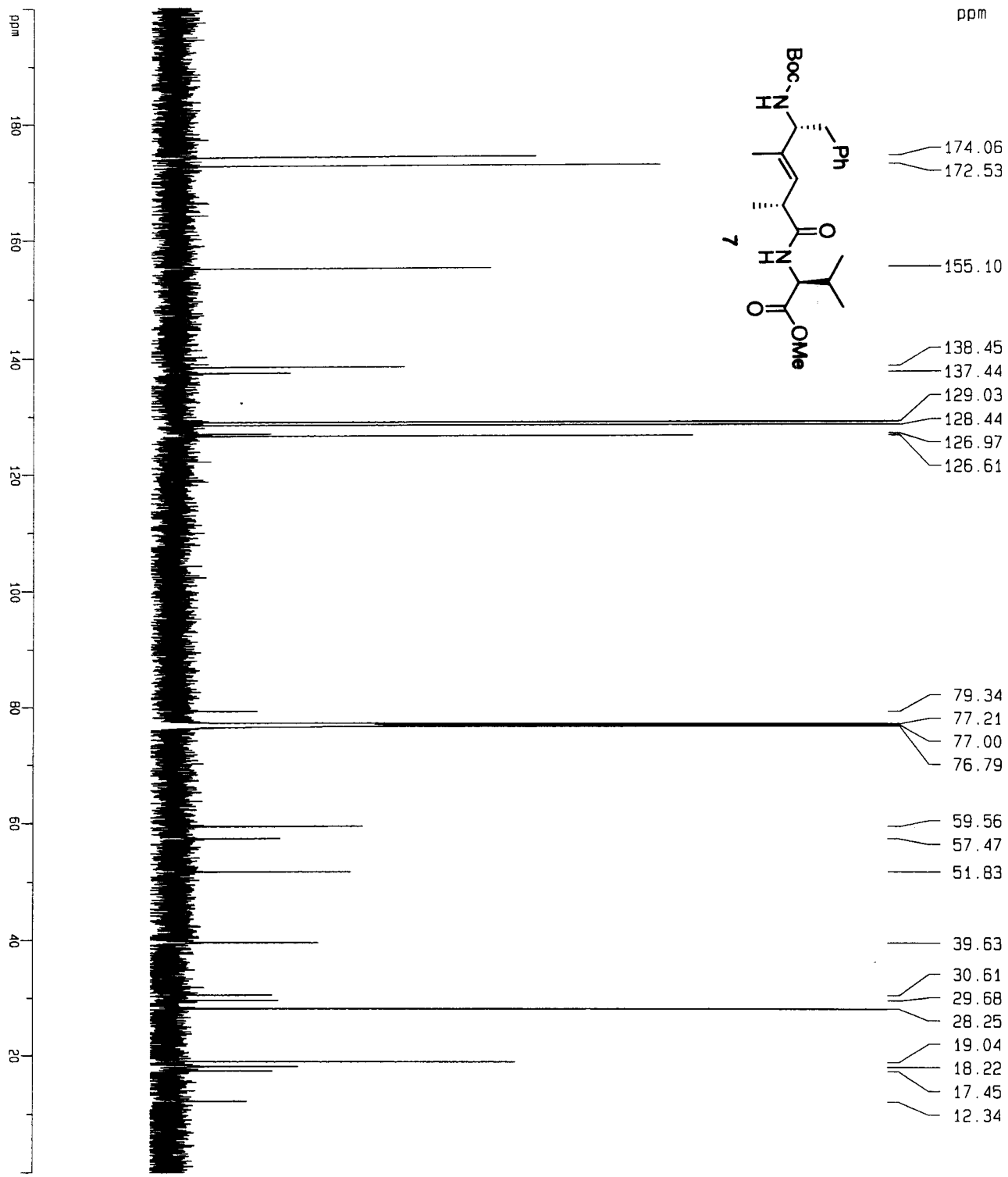
xjb-5-247-1-600, cdcl3, 298K, 151MHz C13




```
Current Data Parameters
NAME          xjb-5-247-1-60
EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20050507
Time                  21.15
INSTRUM                spect
PROBHD  5 mm TBI 1H/
PULPROG             c13wonoe
TD                     65536
SOLVENT                CDCl3
NS                      5343
DS                         0
SWH              37878.789 Hz
FIDRES            0.577984 Hz
AQ                0.8651252 sec
RG                     32768
DW                    13.200 usec
DE                     6.00 usec
TE                   290.0 K
D1                10.00000000 sec
D3                 0.00100000 sec

========== CHANNEL f1 ======
NUC1                      13C
P1                      13.50 usec
PL1                      0.00 dB
SFO1            151.0953827 MHz

========== CHANNEL f2 ======
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                      0.00 dB
PL12                    12.00 dB
SFO2            600.8336050 MHz

F2 - Processing parameters
SI                        65536
SF              151.0788333 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                   200.000 ppm
F1                  30215.77 Hz
F2P                     0.000 ppm
F2                      0.00 Hz
PPMCM                10.00000 ppm/cm
HZCM            1510.78833 Hz/cm
```

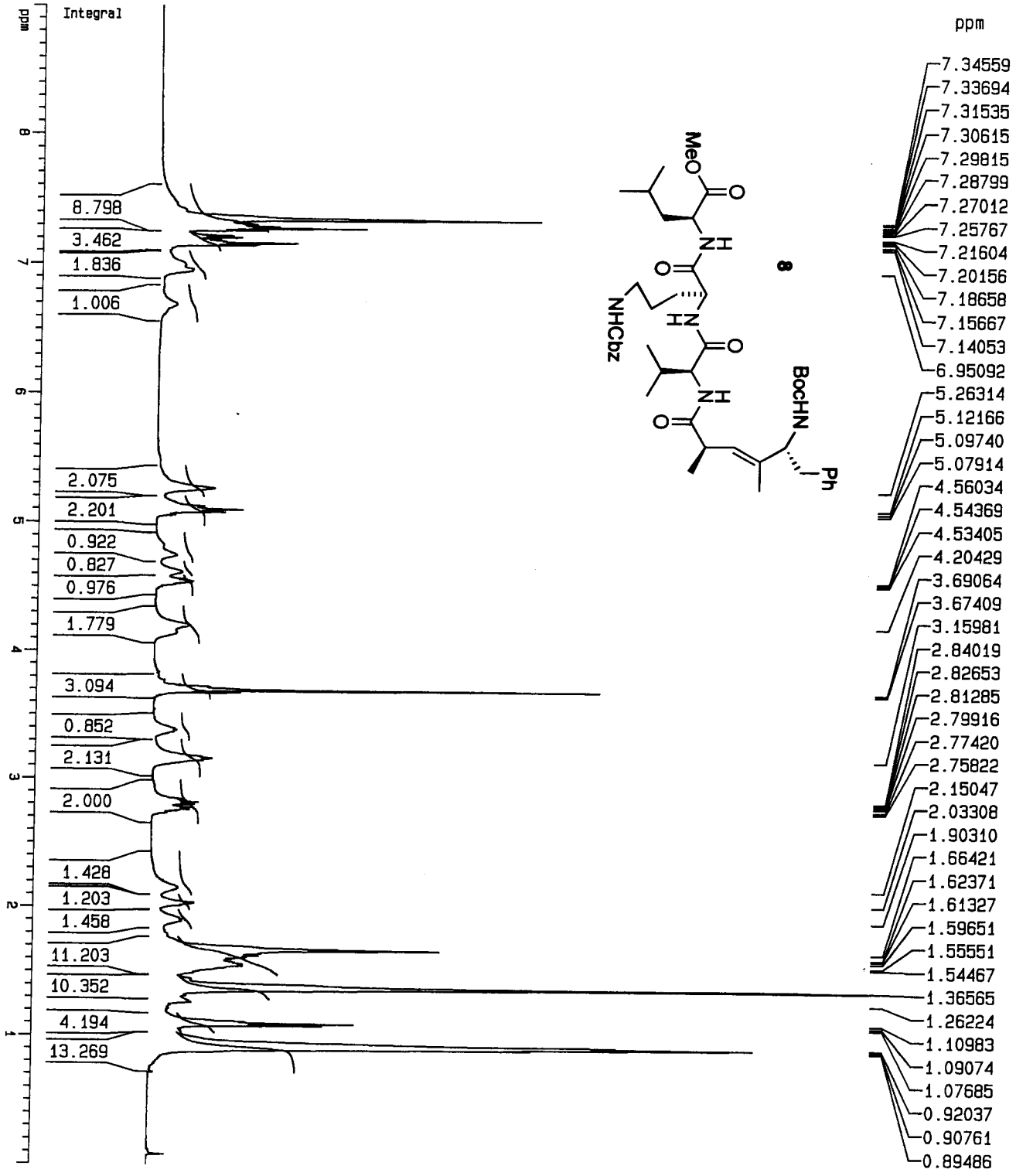



```
Current Data Parameters
NAME                  xjb-5-247-2-60
EXPNO                             1
PROCNO                            1

F2 - Acquisition Parameters
Date_               20050507
Time                   20.56
INSTRUM                spect
PROBHD     5 mm TBI 1H/
PULPROG                 zg
TD                     65536
SOLVENT                CD2C12
NS                        20
DS                         0
SWH                 8992.806 Hz
FIDRES              0.137219 Hz
AQ                  3.643515 sec
RG                        10
DW                  55.600 use
DE                   6.00 use
TE                  290.0 K
D1                  6.00000000 sec
========== CHANNEL f1 ===
NUC1                      1H
P1                   9.00 use
PL1                  0.00 dB
SFO1                600.8336050 MHz

F2 - Processing parameters
SI                        65536
SF                600.8300265 MHz
WDW                        EM
SSB                         0
LB                   0.10 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                  9.000 ppm
F1                 5407.47 Hz
F2P                  0.000 ppm
F2                   0.00 Hz
PPMCM                0.45000 ppm
HZCM               270.37350 Hz/
```




```
Current Data Parameters
NAME          xjb-5-247-2-60
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
Date_           , 20050507
Time                 13.50
INSTRUM              spect
PROBHD    5 mm TBI 1H/
PULPROG          c13wonoe
TD                  65536
SOLVENT             CDCl3
NS                   2938
DS                      0
SWH           37878.789 Hz
FIDRES        0.577984 Hz
AQ            0.8651252 sec
RG                  32768
DW                 13.200 usec
DE                  6.00 usec
TE                290.0 K
D1           8.00000000 sec
D3           0.00100000 sec

============ CHANNEL f1 ======
NUC1                13C
P1                13.50 usec
PL1                0.00 dB
SFO1        151.0953827 MHz

============ CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                1H
PCPD2          100.00 usec
PL2                0.00 dB
PL12              12.00 dB
SFO2        600.8336050 MHz

F2 - Processing parameters
SI                  65536
SF          151.0788321 MHz
WDW                    EM
SSB                     0
LB                1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               200.000 ppm
F1              30215.77 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM         10.00000 ppm/cm
HZCM          1510.78833 Hz/cm
```

xjb-5-272, cdc13, rt, 500MHZ

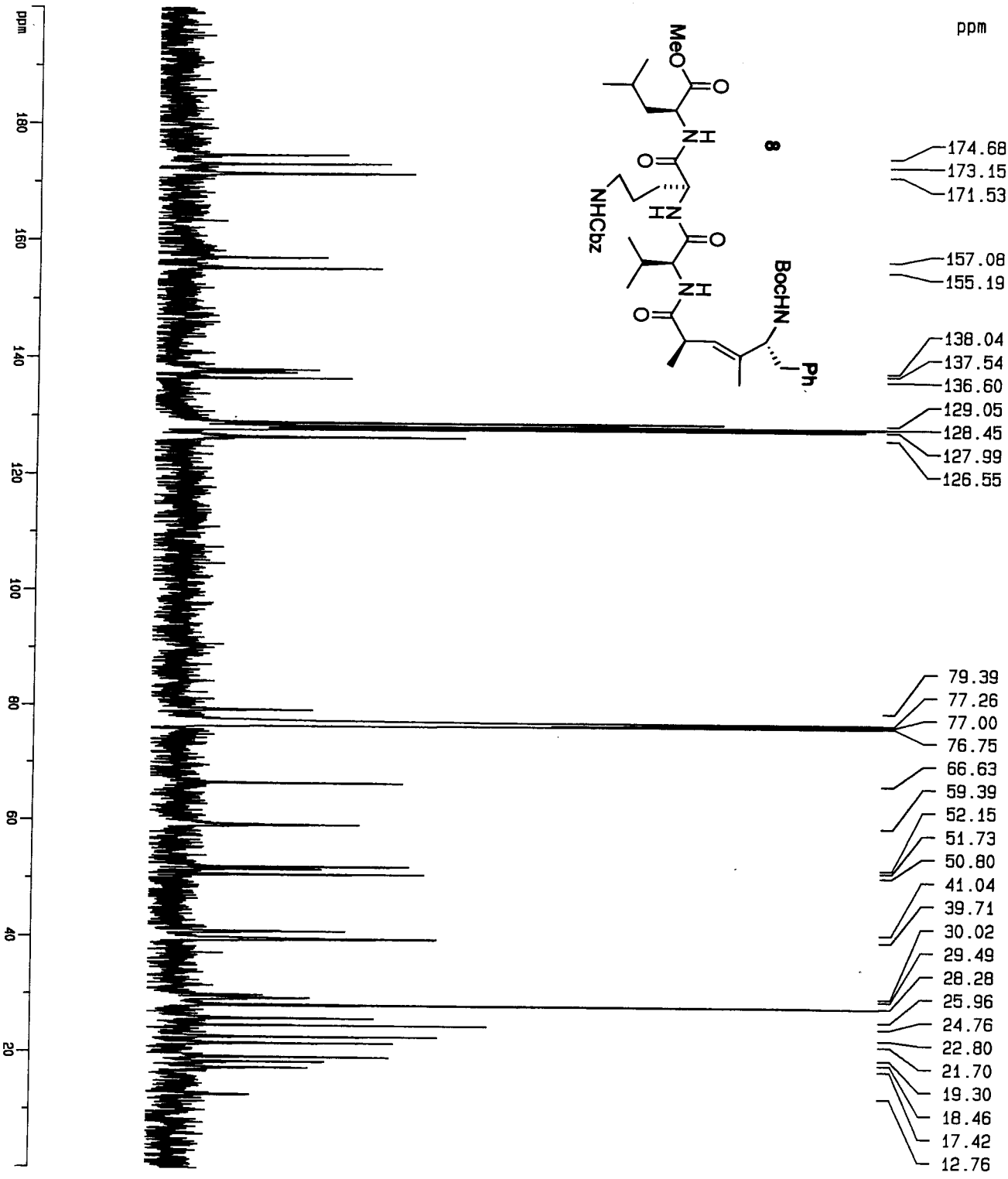


Current Data Parameters
NAME xjb-5-272-500
EXPNO 1
PROCNO 1

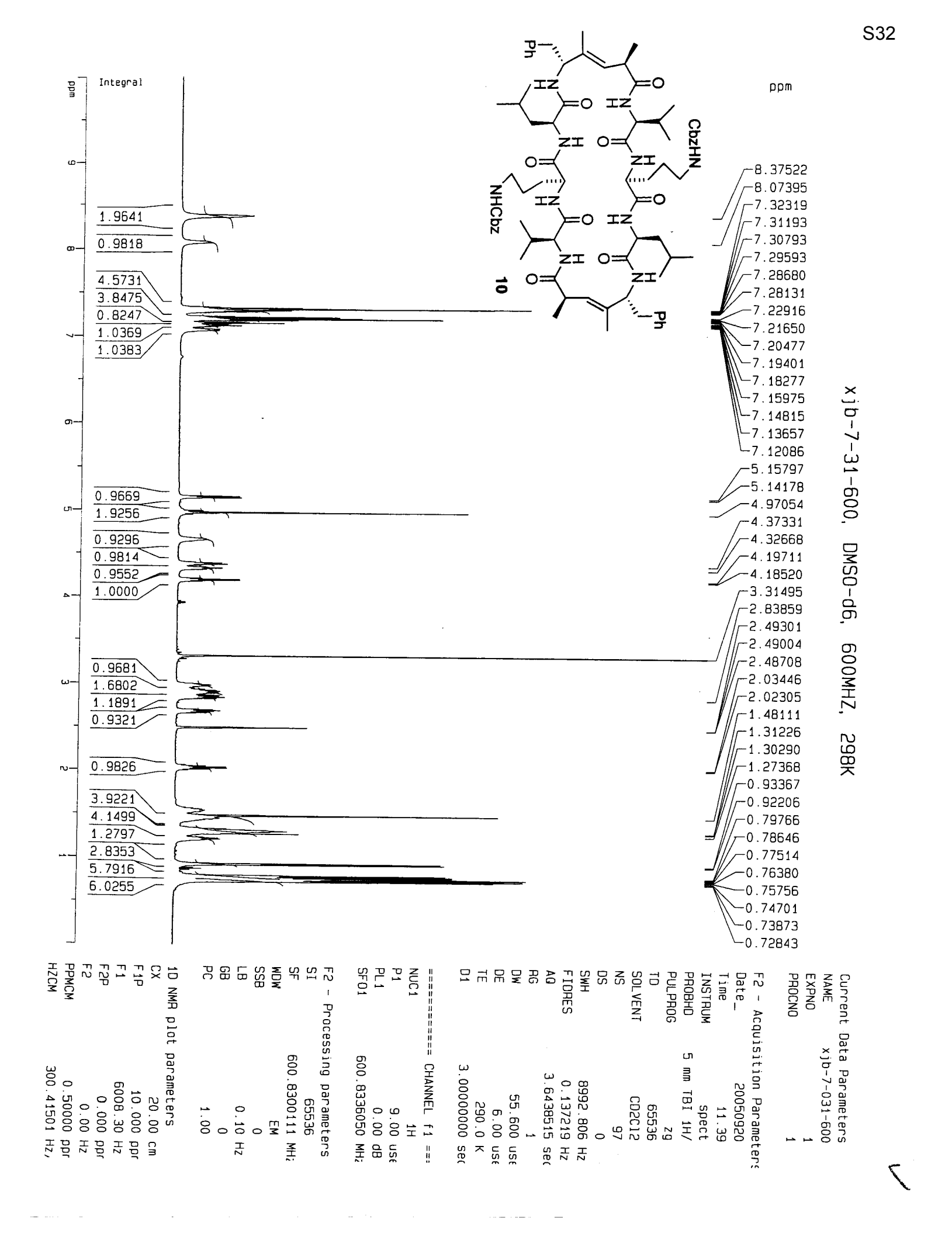
F2 - Acquisition Parameters
Date_ 500000
Time 18.24
INSTRUM spect
PROBHD 5 mm TXI 13C
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 40
DS 0
SWH 7507.507 Hz
FIDRES 0.229111 Hz
AQ 2.1823988 sec
RG 2
DW 66.600 usec
DE 6.00 usec
TE 290.0 K
D1 6.00000000 sec
P1 10.60 usec
DE 6.00 usec
SFO1 500.1330008 MHz
NUC1 1H
PL1 0.00 dB

F2 - Processing parameters
SI 32768
SF 500.1300228 MHz
WDW EM
SSB 0
LB 0.40 Hz
GB 0
PC 1.00

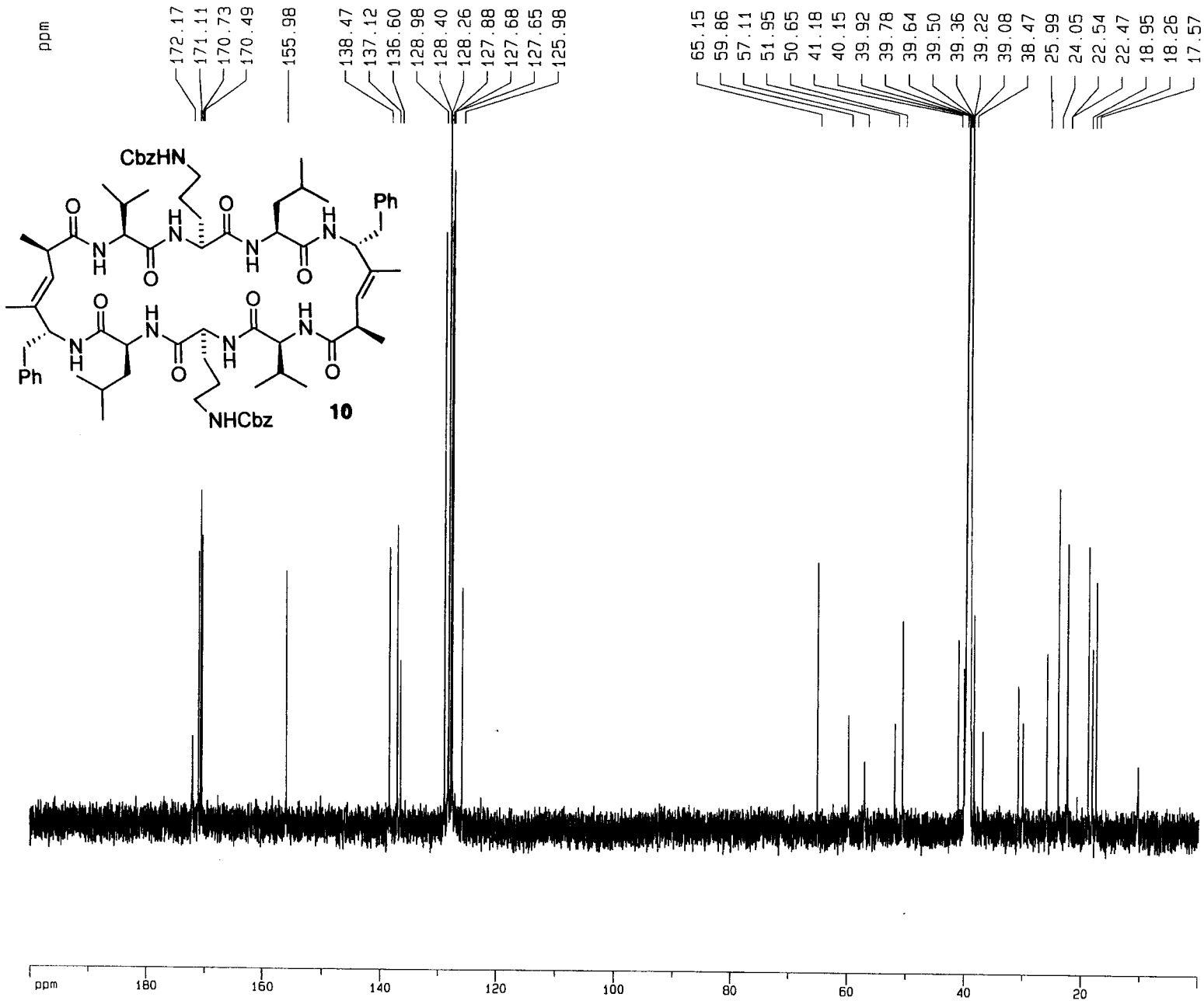
1D NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05852 Hz/cm




```
Current Data Parameters
NAME                  xjb-5-272-500
EXPNO                            14
PROCNO                            1

F2 - Acquisition Parameters
Date_                        500000
Time                          15.33
INSTRUM                        spect
PROBHD                5 mm TXI 13C
PULPROG                    c13wonoe
TD                            32768
SOLVENT                      CDCl3
NS                             2935
DS                                0
SWH                     32679.738 Hz
FIDRES                      0.997306 Hz
AQ                          0.5014004 sec
RG                             32768
DW                            15.300 usec
DE                             6.00 usec
TE                           290.0 K
D3                      0.00100000 sec
PL12                          6.00 dB
D1                      8.00000000 sec
CPDPRG2                     waltz16
PCPD2                       100.00 usec
SFO2                    500.1330008 MHz
NUC2                            1H
PL2                          120.00 dB
P1                            21.60 usec
DE                             6.00 usec
SFO1                    125.7715724 MHz
NUC1                            13C
PL1                           0.00 dB

F2 - Processing parameters
SI                             8192
SF                      125.7577961 MHz
WDW                              EM
SSB                               0
LB                             4.00 Hz
GB                                0
PC                             1.00

1D NMR plot parameters
CX                            20.00 cm
F1P                          200.000 ppm
F1                         25151.56 Hz
F2P                          0.000 ppm
F2                           0.00 Hz
PPMCM                     10.00000 ppm/cm
HZCM                    1257.57800 Hz/cm
```


xjb-7-31-600, DMSO-d6, 600MHZ, 298K
ppm
Integral
CbzHN
NHCbz
Ph
Ph
10
8.37522
8.07395
7.32319
7.31193
7.30793
7.29593
7.28680
7.28131
7.22916
7.21650
7.20477
7.19401
7.18277
7.15975
7.14815
7.13657
7.12086
5.15797
5.14178
4.97054
4.37331
4.32668
4.19711
4.18520
3.31495
2.83859
2.49301
2.49004
2.48708
2.03446
2.02305
1.48111
1.31226
1.30290
1.27368
0.93367
0.92206
0.79766
0.78646
0.77514
0.76380
0.75756
0.74701
0.73873
0.72843
1.9641
0.9818
4.5731
3.8475
0.8247
1.0369
1.0383
0.9669
1.9256
0.9296
0.9814
0.9552
1.0000
0.9681
1.6802
1.1891
0.9321
0.9826
3.9221
4.1499
1.2797
2.8353
5.7916
6.0255
Current Data Parameters
NAME xjb-7-031-600
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050920
Time 11.39
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CD2Cl2
NS 97
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.643515 sec
RG 1
DW 55.600 use
DE 6.00 use
TE 290.0 K
D1 3.00000000 sec
========== CHANNEL f1 ===
NUC1 1H
P1 9.00 use
PL1 0.00 dB
SFO1 600.8336050 MHz
F2 - Processing parameters
SI 65536
SF 600.8300111 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm/
HZCM 300.41501 Hz/

xjb-7-031-600, DMSO-d6, 298K, 150MHZ



Current Data Parameters

NAME	xjb-7-031-600
EXPNO	13
PROCNO	1

F2 - Acquisition Parameters

Date_	20050920
Time	11.51
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	c13wonoe
TD	65536
SOLVENT	CDCl3
NS	2192
DS	0
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ======

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ======

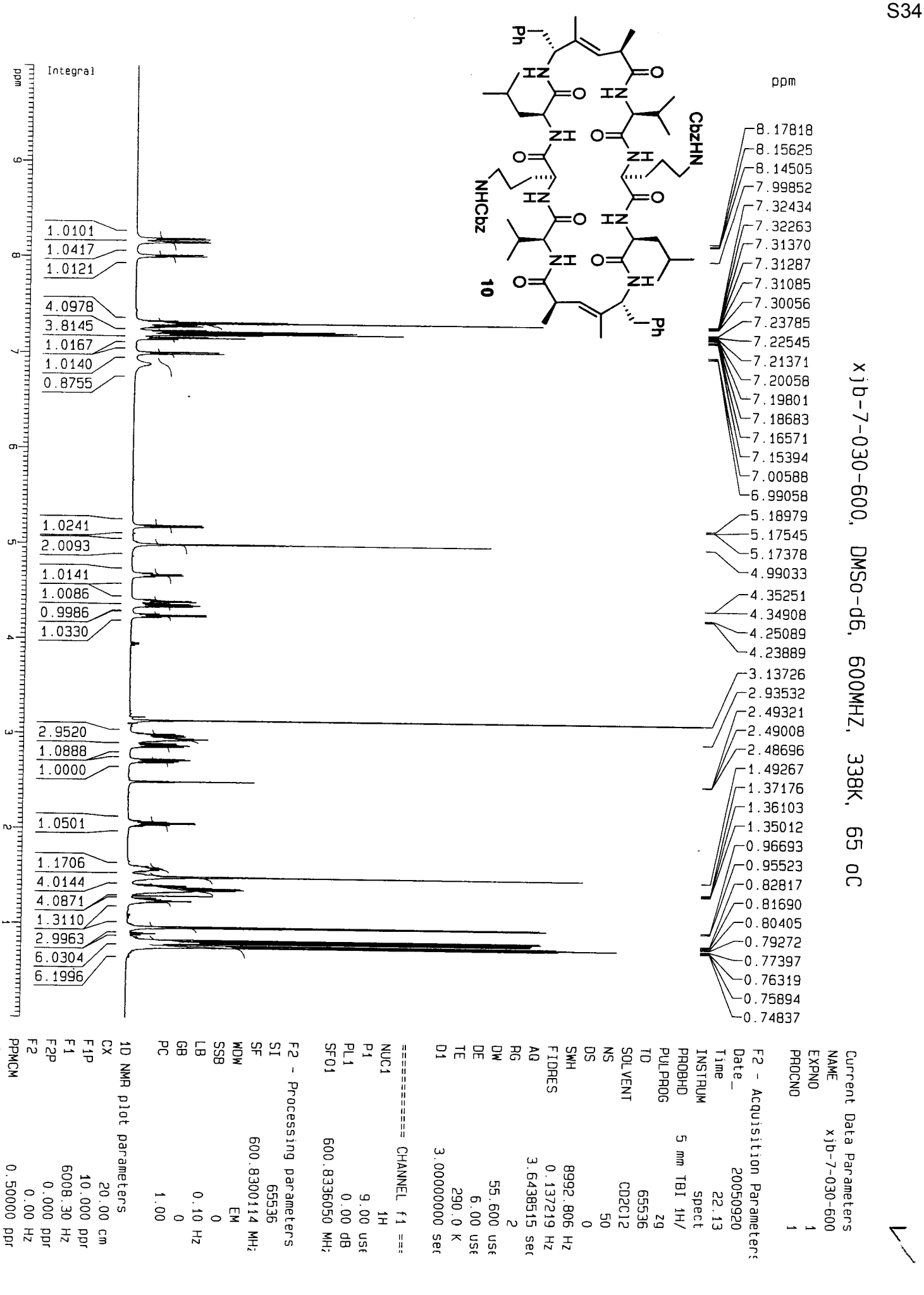
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

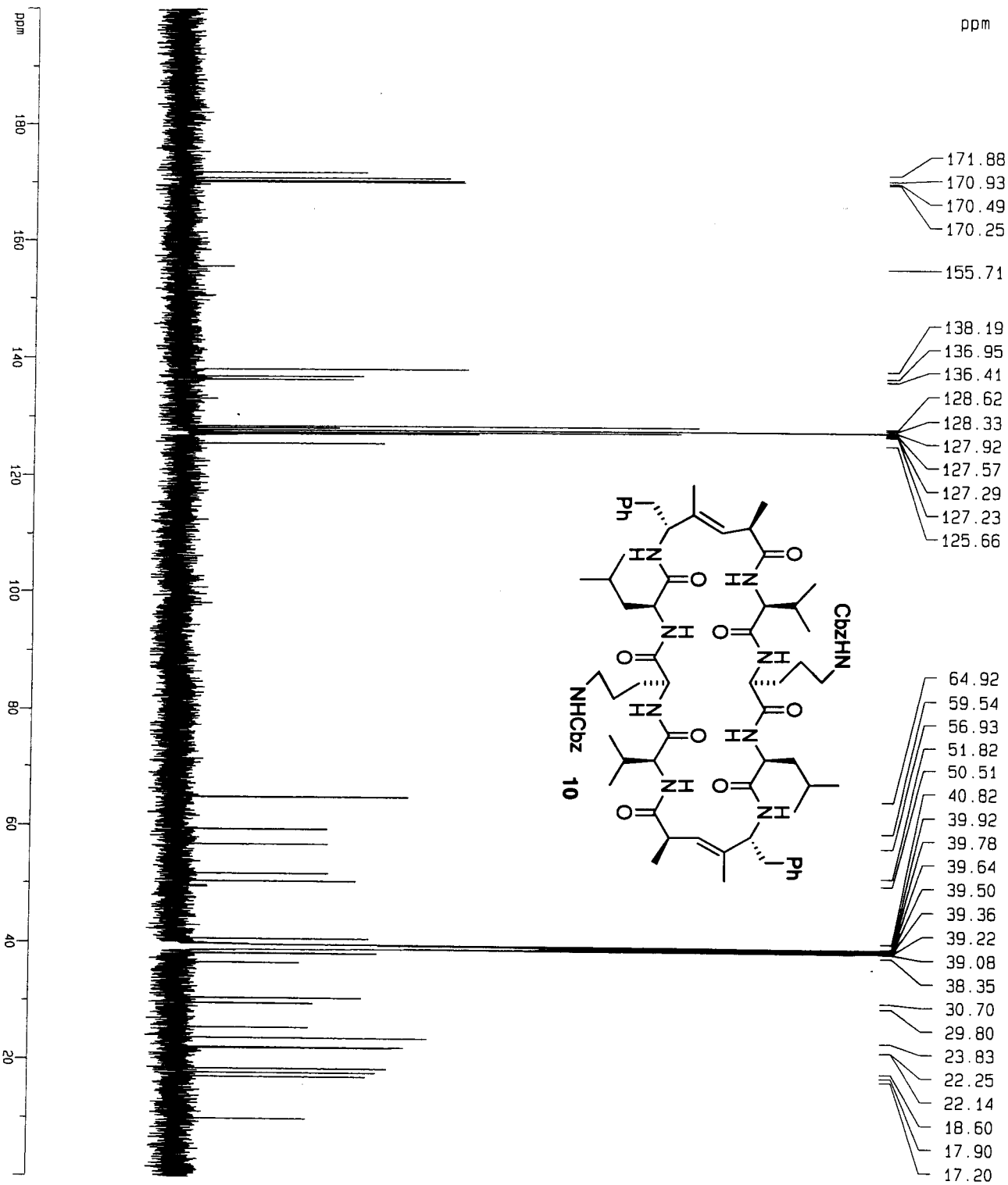
F2 - Processing parameters

SI	65536
SF	151.0789003 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

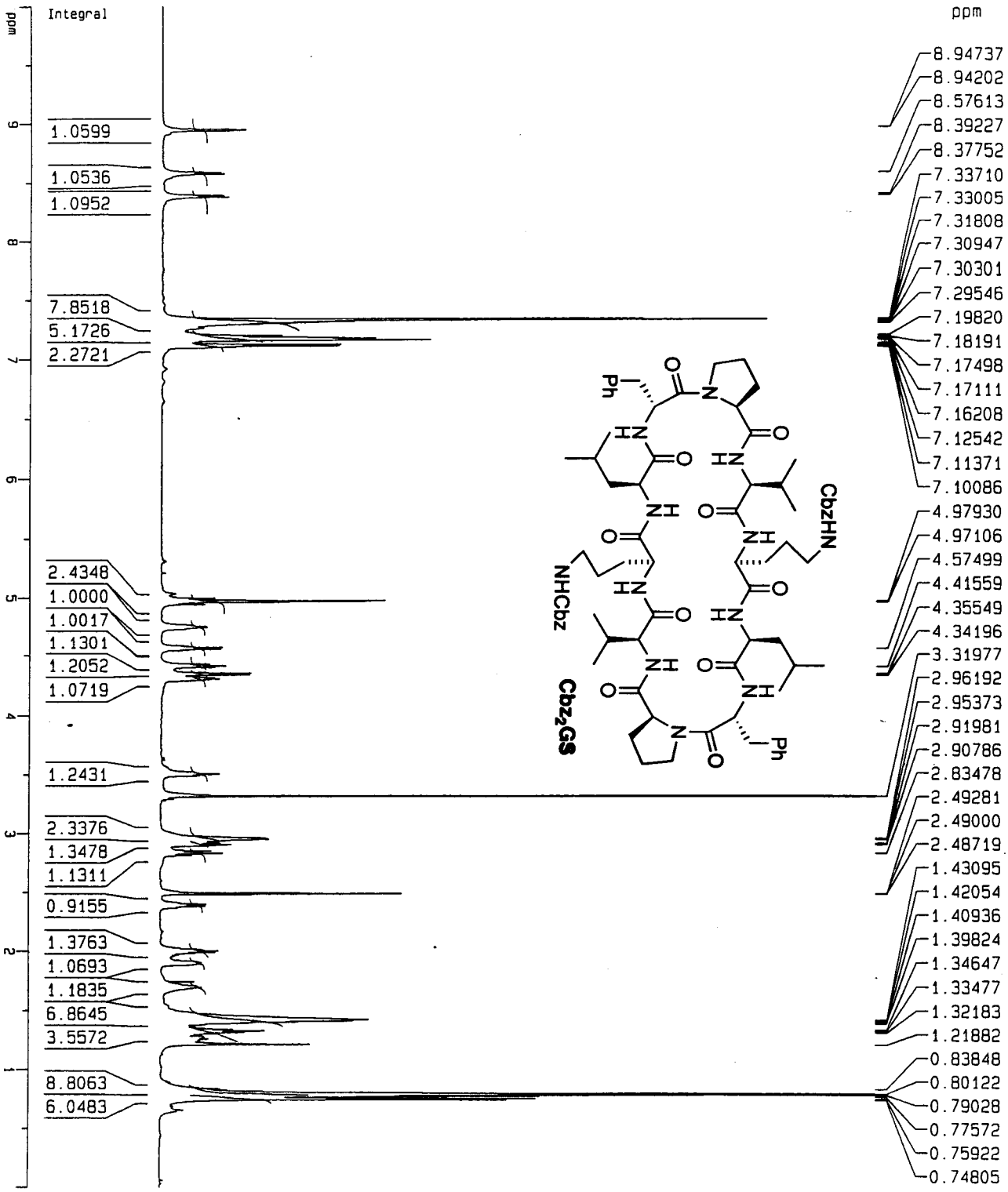
1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	30215.78 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	1510.78906 Hz/cm


xjb-7-030-600, DMSo-d6, 600MHZ, 338K, 65 oC
ppm
Integral
8.17818
8.15625
8.14505
7.99852
7.32434
7.32263
7.31370
7.31287
7.31085
7.30056
7.23785
7.22545
7.21371
7.20058
7.19801
7.18683
7.16571
7.15394
7.00588
6.99058
5.18979
5.17545
5.17378
4.99033
4.35251
4.34908
4.25089
4.23889
3.13726
2.93532
2.49321
2.49008
2.48696
1.49267
1.37176
1.36103
1.35012
0.96693
0.95523
0.82817
0.81690
0.80405
0.79272
0.77397
0.76319
0.75894
0.74837
1.0101
1.0417
1.0121
4.0978
3.8145
1.0167
1.0140
0.8755
1.0241
2.0093
1.0141
1.0086
0.9986
1.0330
2.9520
1.0888
1.0000
1.0501
1.1706
4.0144
4.0871
1.3110
2.9963
6.0304
6.1996
CbzHN
NHCbz
Ph
Ph
10
Current Data Parameters
NAME xjb-7-030-600
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20050920
Time 22.13
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CD2Cl2
NS 50
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 2
DW 55.600 use
DE 6.00 use
TE 290.0 K
D1 3.00000000 sec
========== CHANNEL f1 ===
NUC1 1H
P1 9.00 use
PL1 0.00 dB
SFO1 600.8336050 MHz
F2 - Processing parameters
SI 65536
SF 600.8300114 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm
HZCM 300.41501 Hz




```
Current Data Parameters
NAME                  xjb-7-030-600
EXPNO                            2
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20050921
Time                          9.40
INSTRUM                       spect
PROBHD     5 mm TBI 1H/
PULPROG                   c13wonoe
TD                           65536
SOLVENT                     CDCl3
NS                            1267
DS                               0
SWH                      37878.789 Hz
FIDRES                    0.577984 Hz
AQ                        0.8651252 sec
RG                           32768
DW                          13.200 usec
DE                           6.00 usec
TE                          290.0 K
D1                       8.00000000 sec
D3                       0.00100000 sec

========== CHANNEL f1 ======
NUC1                           13C
P1                           13.50 usec
PL1                           0.00 dB
SFO1                151.0953827 MHz

========== CHANNEL f2 ======
CPDPRG2                     waltz16
NUC2                            1H
PCPD2                       100.00 usec
PL2                           0.00 dB
PL12                         12.00 dB
SFO2                600.8336050 MHz

F2 - Processing parameters
SI                           65536
SF                151.0789437 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.00

1D NMR plot parameters
CX                           20.00 cm
F1P                         200.000 ppm
F1                        30215.79 Hz
F2P                         0.000 ppm
F2                          0.00 Hz
PPMCM                    10.00000 ppm/cm
HZCM                  1510.78955 Hz/cm
```



Current Data Parameters
NAME xjb-4-235-600
EXPNO 3
PROCNO 1

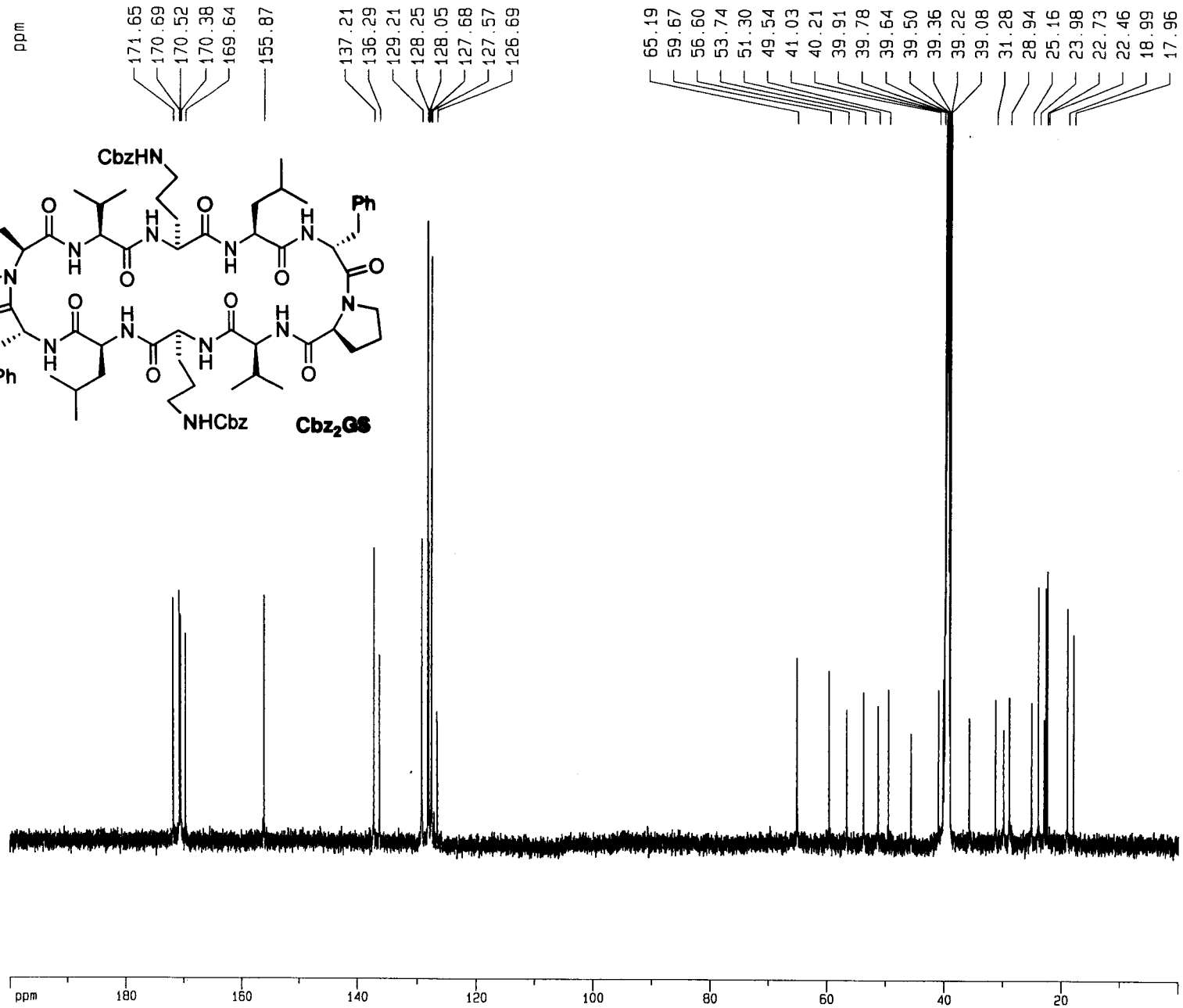
F2 - Acquisition Parameters
Date_ 20040303
Time 17.09
INSTRUM spect
PROBHD 5 mm TBI 1H/
PULPROG zg
TD 65536
SOLVENT CD2Cl2
NS 100
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.643515 sec
RG 2
DW 55.600 use
DE 6.00 use
TE 290.0 K
D1 6.00000000 sec

========== CHANNEL f1 ==
NUC1 1H
P1 9.00 use
PL1 0.00 dB
SFO1 600.8336050 MHz

F2 - Processing parameters
SI 65536
SF 600.8300108 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 6008.30 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.50000 ppm
HZCM 300.41501 Hz

xjb-4-235, DMSO-d6, 150MHz, C13, Z-GS



Current Data Parameters

NAME	xjb-4-235-600
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20040303
Time	8.36
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	c13wonoe
TD	65536
SOLVENT	CDCl3
NS	3533
DS	0
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ======

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ======

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	151.0789009 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

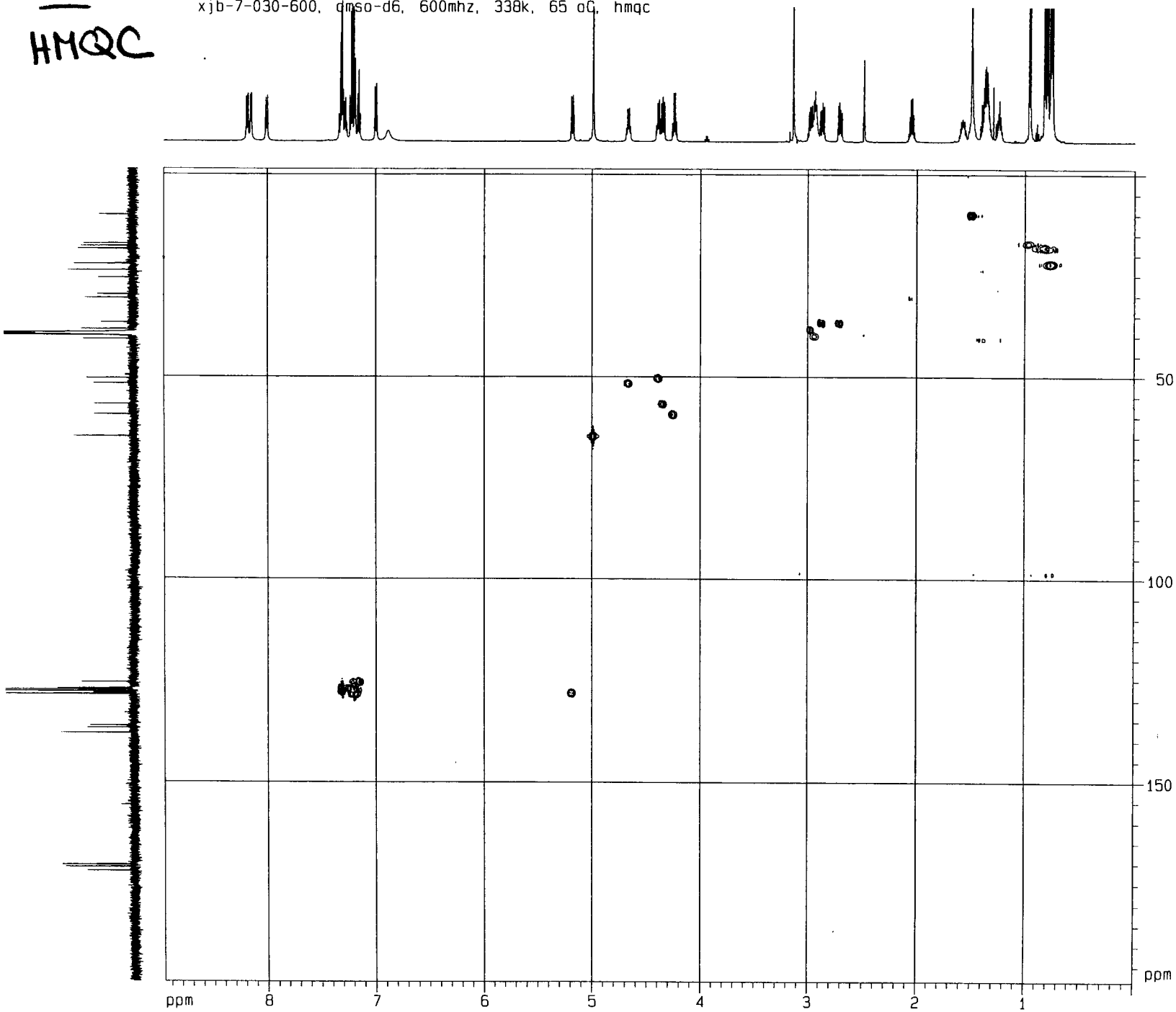
1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	30215.78 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	1510.78906 Hz/cm

S38

10

HMQC



Current Data Parame

NAME	xjb-7-030-600
EXPNO	12
PROCNO	1

F2 - Acquisition Para

Date_	20050921
Time	12.12
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	inv4gs
TD	2048
SOLVENT	CDCl3
NS	35
DS	4
SWH	5387.931 Hz
FIDRES	2.630826 Hz
AQ	0.1901044 se
RG	32768
DW	92.800 us
DE	6.00 us
TE	310.0 K
CNST2	145.0000000
d0	0.00000300 se
D1	1.50000000 se
d2	0.00344828 se
d12	0.00002000 se
d13	0.00000300 se
D16	0.00050000 se
d20	0.00242528 se
IN0	0.00001655 se

========== CHANNEL f1 ==

NUC1	1H
P1	9.60 us
p2	19.20 us
PL1	0.00 dB
SFO1	600.8327037 MH

========== CHANNEL f2 ==

CPDPRG2	garp
NUC2	13C
P3	13.50 us
PCPD2	100.00 us
PL2	0.00 dB
PL12	12.00 dB
SFO2	151.0938719 MH

========== GRADIENT CHANN

P16	1000.00 us

F1 - Acquisition para

NDO	2
TD	256
SFO1	151.0939 MH
FIDRES	118.013596 Hz
SW	199.952 ppi

F2 - Processing para

SI	1024
SF	600.8300110 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing para

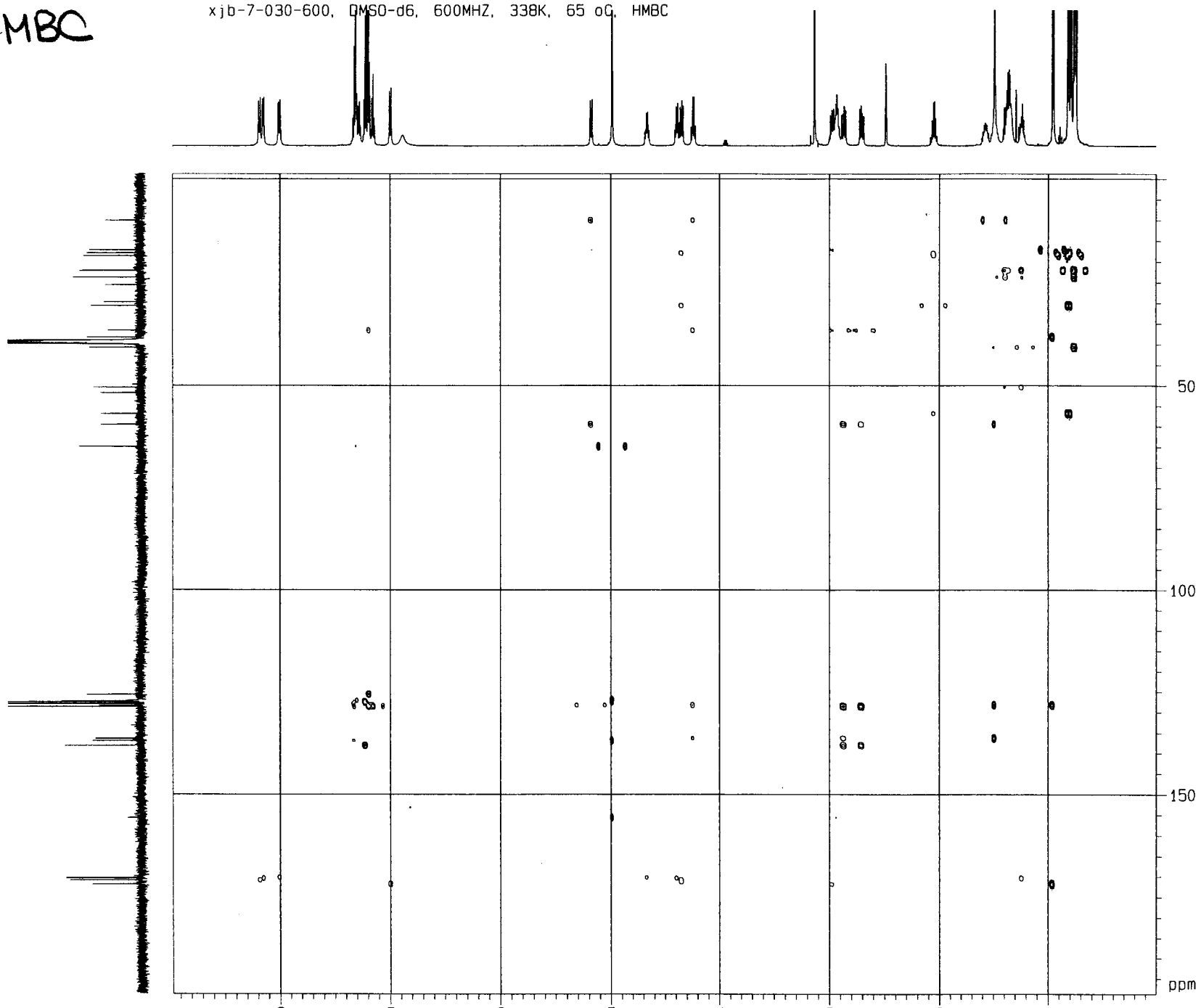
SI	1024
MC2	QF
SF	151.0789673 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parame

CX2	18.00 cm
CX1	15.00 cm
F2PLO	8.965 ppi
F2LO	5386.71 Hz
F2PHI	-0.002 ppi
F2HI	-1.22 Hz
F1PLO	198.640 ppi
F1LO	30010.34 Hz
F1PHI	-1.332 ppi
F1HI	-201.17 Hz
F2PPMCM	0.49819 ppi
F2HZCM	299.32950 Hz
F1PPMCM	13.33145 ppi
F1HZCM	2014.10095 Hz

S39 10

HMBC



Current Data Parameters

NAME	xjb-7-030-600
EXPNO	1122
PROCNO	1

F2 - Acquisition Parameter

Date_	20050921
Time	0.54
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	inv4gslrnd
TD	4096
SOLVENT	CDCl3
NS	80
DS	4
SWH	5387.931 Hz
FIDRES	1.315413 Hz
AQ	0.3801588 sec
RG	32768
DW	92.800 usec
DE	6.00 usec
TE	310.0 K
d0	0.00000300 sec
D1	1.00000000 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00050000 sec
IN0	0.00001655 sec

========== CHANNEL f1 ======

NUC1	1H
P1	9.60 usec
p2	19.20 usec
PL1	0.00 dB
SFO1	600.8327037 MHz

========== CHANNEL f2 ======

NUC2	13C
P3	13.50 usec
PL2	0.00 dB
SFO2	151.0938719 MHz

========== GRADIENT CHANNEL =

P16	1000.00 usec

F1 - Acquisition parameter

ND0	2
TD	256
SFO1	151.0939 MHz
FIDRES	118.013596 Hz
SW	199.952 ppm

F2 - Processing parameter

SI	1024
SF	600.8300094 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameter

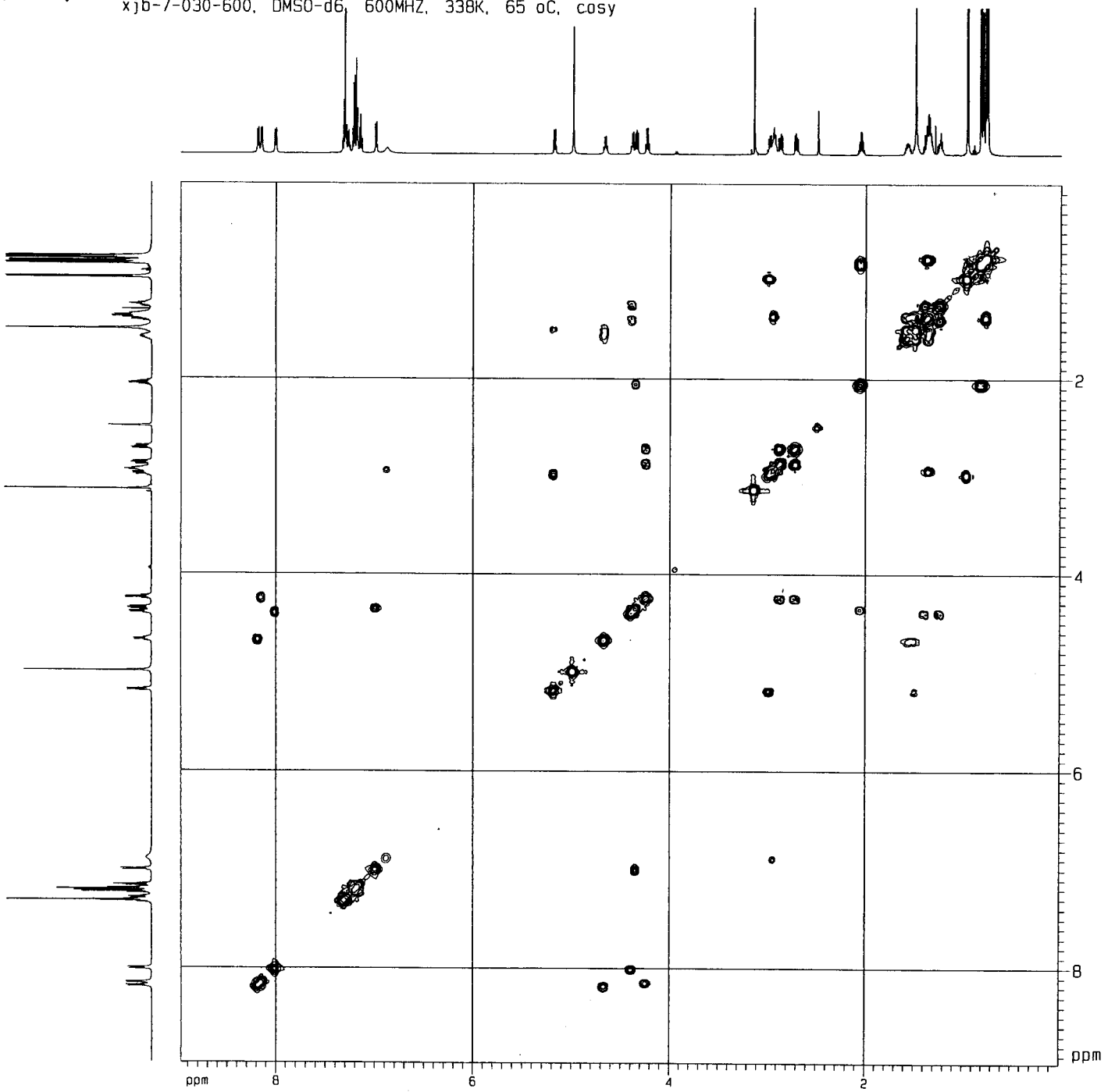
SI	2048
MC2	QF
SF	151.0789546 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	8.968 ppm
F2LO	5388.33 Hz
F2PHI	0.001 ppm
F2HI	0.40 Hz
F1PLO	198.724 ppm
F1LO	30022.97 Hz
F1PHI	-1.248 ppm
F1HI	-188.51 Hz
F2PPMCM	0.49819 ppm/cm
F2HZCM	299.32950 Hz/cm
F1PPMCM	13.33143 ppm/cm
F1HZCM	2014.09863 Hz/cm

S40 10 cosy

xjb-7-030-600, DMSO-d6, 600MHZ, 338K, 65 oC, cosy



Current Data Parameters

NAME	xjb-7-030-600
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20050920
Time	22.28
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	cosy
TD	1024
SOLVENT	CDCl3
NS	30
DS	16
SWH	5387.931 Hz
FIDRES	5.261652 Hz
AQ	0.0950772 sec
RG	100
DW	92.800 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
IN0	0.00018560 sec

========== CHANNEL f1 ==========

NUC1	1H
P0	8.20 usec
P1	9.60 usec
PL1	0.00 dB
SFO1	600.8327037 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.8327 MHz
FIDRES	21.046606 Hz
SW	8.967 ppm

F2 - Processing parameters

SI	512
SF	600.8300081 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	512
MC2	QF
SF	600.8300080 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

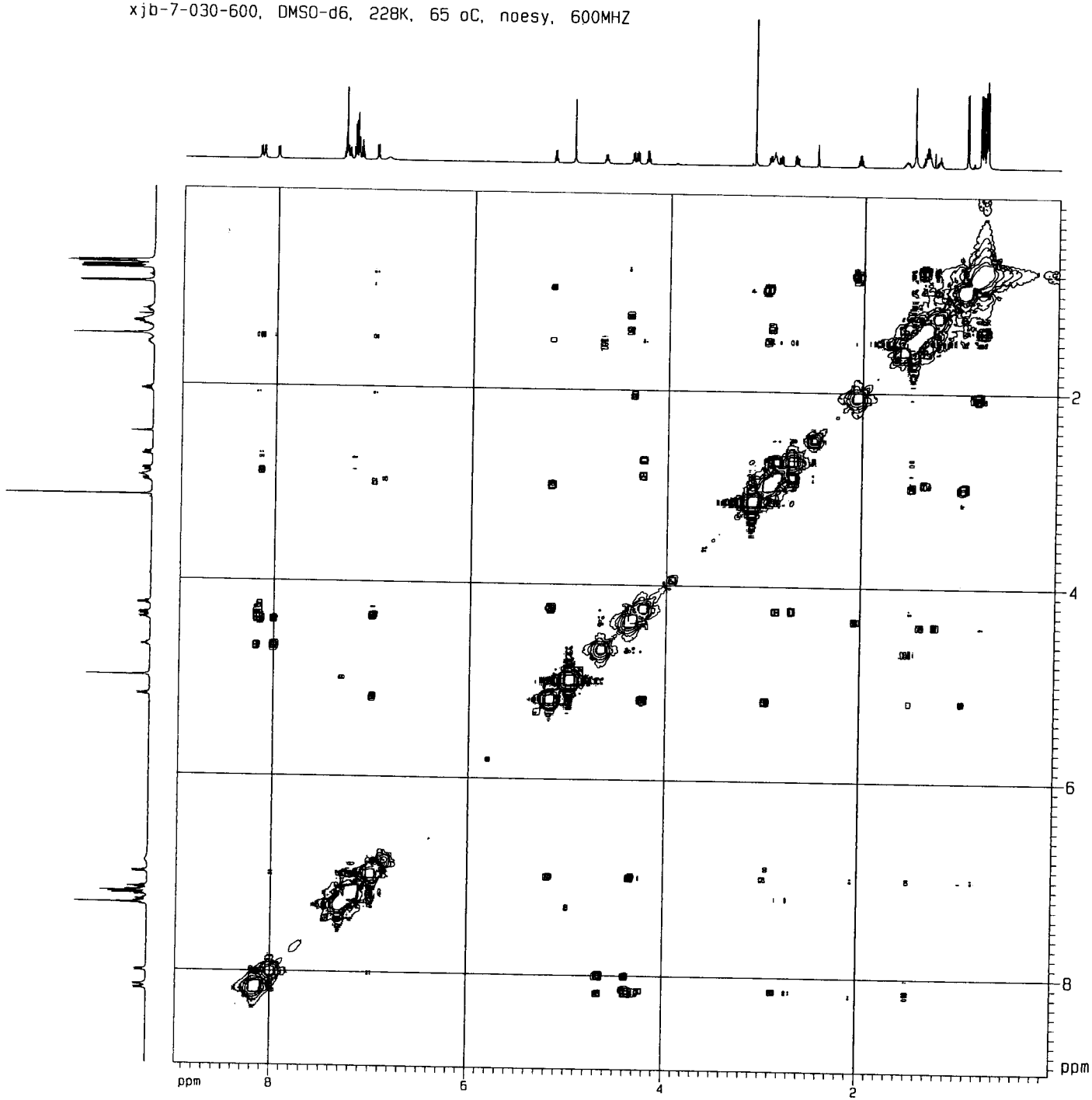
2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.970 ppm
F2LO	5389.59 Hz
F2PHI	0.003 ppm
F2HI	1.66 Hz
F1PLO	8.970 ppm
F1LO	5389.69 Hz
F1PHI	0.003 ppm
F1HI	1.76 Hz
F2PPMCM	0.59783 ppm/cm
F2HZCM	359.19540 Hz/cm
F1PPMCM	0.59783 ppm/cm
F1HZCM	359.19540 Hz/cm

S41 10

NOESY

xjb-7-030-600, DMSO-d6, 228K, 65 oC, noesy, 600MHZ



Current Data Parameters

NAME	xjb-7-030-600
EXPNO	1111
PROCNO	1

F2 - Acquisition Parameters

Date_	20050921
Time	18.32
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	noesytp
TD	1024
SOLVENT	CDCl3
NS	70
DS	16
SWH	5387.931 Hz
FIDRES	5.261652 Hz
AQ	0.0950772 sec
RG	60
DW	92.800 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
D8	0.34999999 sec
INO	0.00009280 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	13.50 usec
PL1	0.00 dB
SFO1	600.8327037 MHz

F1 - Acquisition parameters

NDO	2
TD	256
SFO1	600.8327 MHz
FIDRES	21.046606 Hz
SW	8.967 ppm

F2 - Processing parameters

SI	1024
SF	600.8300080 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	0.10

F1 - Processing parameters

SI	1024
MC2	TPPI
SF	600.8300076 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

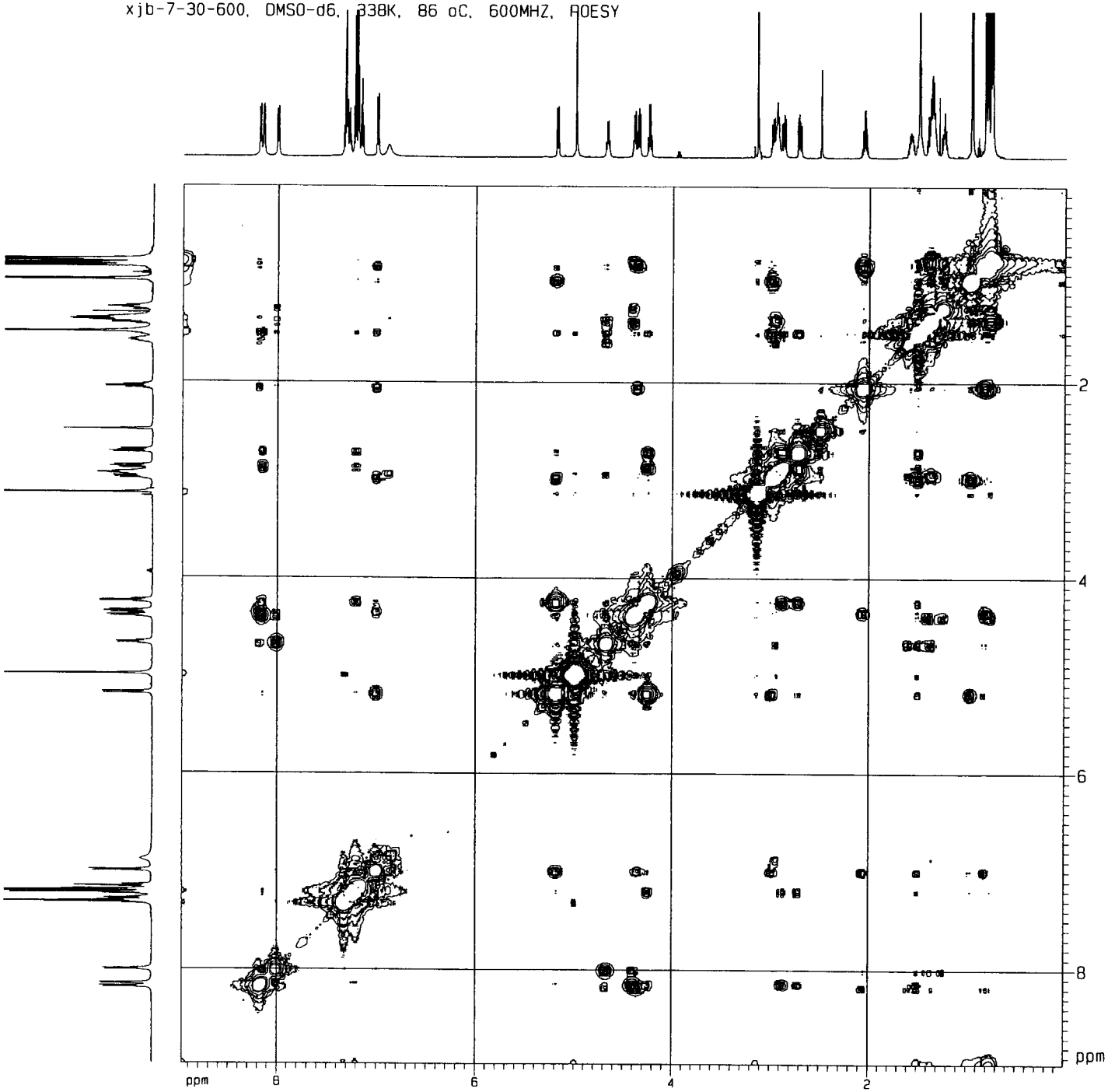
2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.970 ppm
F2LO	5389.71 Hz
F2PHI	0.003 ppm
F2HI	1.77 Hz
F1PLO	8.971 ppm
F1LO	5390.06 Hz
F1PHI	0.004 ppm
F1HI	2.13 Hz
F2PPMCM	0.59783 ppm/cm
F2HZCM	359.19540 Hz/cm
F1PPMCM	0.59783 ppm/cm
F1HZCM	359.19540 Hz/cm

S42 10

ROESY

xjb-7-30-600, DMSO-d6, 338K, 86 oC, 600MHZ, ROESY



Current Data Parameters

NAME	xjb-7-030-600
EXPNO	2222
PROCNO	1

F2 - Acquisition Parameters

Date_	20050922
Time	1.48
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	roesytp
TD	1024
SOLVENT	CDCl3
NS	70
DS	16
SWH	5387.931 Hz
FIDRES	5.261652 Hz
AQ	0.0950772 sec
RG	60
DW	92.800 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d12	0.00002000 sec
INO	0.00009280 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	9.00 usec
P15	250000.00 usec
PL1	0.00 dB
PL11	24.00 dB
SFO1	600.8327037 MHz

F1 - Acquisition parameters

NDO	2
TD	256
SFO1	600.8327 MHz
FIDRES	21.046606 Hz
SW	8.967 ppm

F2 - Processing parameters

SI	1024
SF	600.8300082 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	0.10

F1 - Processing parameters

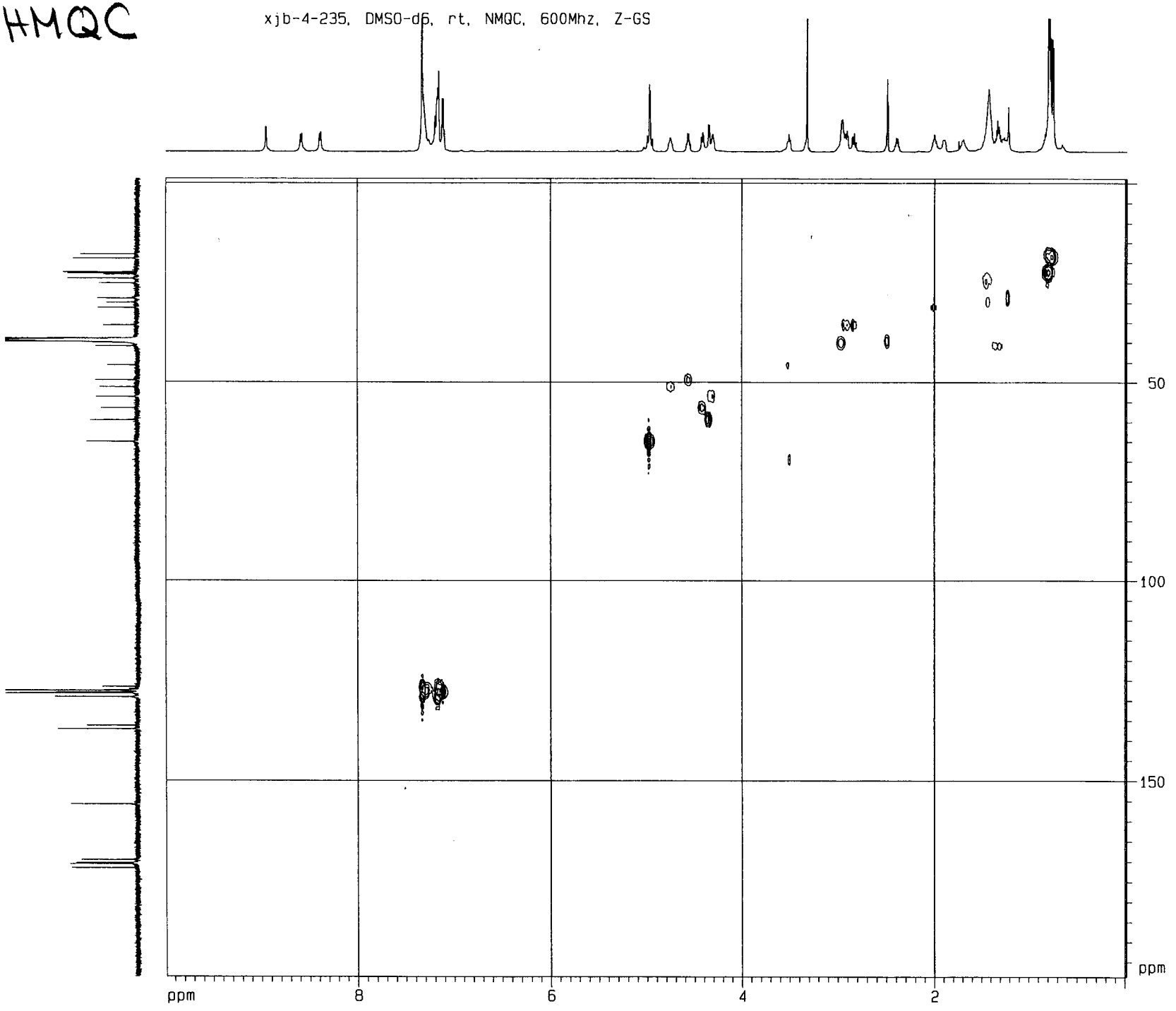
SI	1024
MC2	TPPI
SF	600.8300088 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.970 ppm
F2LO	5389.45 Hz
F2PHI	0.003 ppm
F2HI	1.52 Hz
F1PLO	8.969 ppm
F1LO	5388.88 Hz
F1PHI	0.002 ppm
F1HI	0.95 Hz
F2PPMCM	0.59783 ppm/cm
F2HZCM	359.19540 Hz/cm
F1PPMCM	0.59783 ppm/cm
F1HZCM	359.19540 Hz/cm

S43 Cbz_2 GS

HMQC



Current Data Parame

NAME	xjb-4-235-600
EXPNO	12
PROCNO	1

F2 - Acquisition Para

Date_	20040302
Time	20.46
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	inv4gs
TD	2048
SOLVENT	CDCl3
NS	30
DS	4
SWH	6009.615 Hz
FIDRES	2.934382 Hz
AQ	0.1704436 se
RG	32768
DW	83.200 us
DE	6.00 us
TE	310.0 K
CNST2	145.0000000
d0	0.00000300 se
D1	1.50000000 se
d2	0.00344828 se
d12	0.00002000 se
d13	0.00000300 se
D16	0.00050000 se
d20	0.00242528 se
IN0	0.00001655 se

========== CHANNEL f1 ==

NUC1	1H
P1	9.60 us
p2	19.20 us
PL1	0.00 dB
SFO1	600.8330041 MH

========== CHANNEL f2 ==

CPDPRG2	garp
NUC2	13C
P3	13.50 us
PCPD2	100.00 us
PL2	0.00 dB
PL12	12.00 dB
SFO2	151.0938719 MH

========== GRADIENT CHANN

P16	1000.00 us

F1 - Acquisition para

NDO	2
TD	256
SFO1	151.0939 MH
FIDRES	118.013596 Hz
SW	199.952 ppm

F2 - Processing para

SI	1024
SF	600.8300097 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

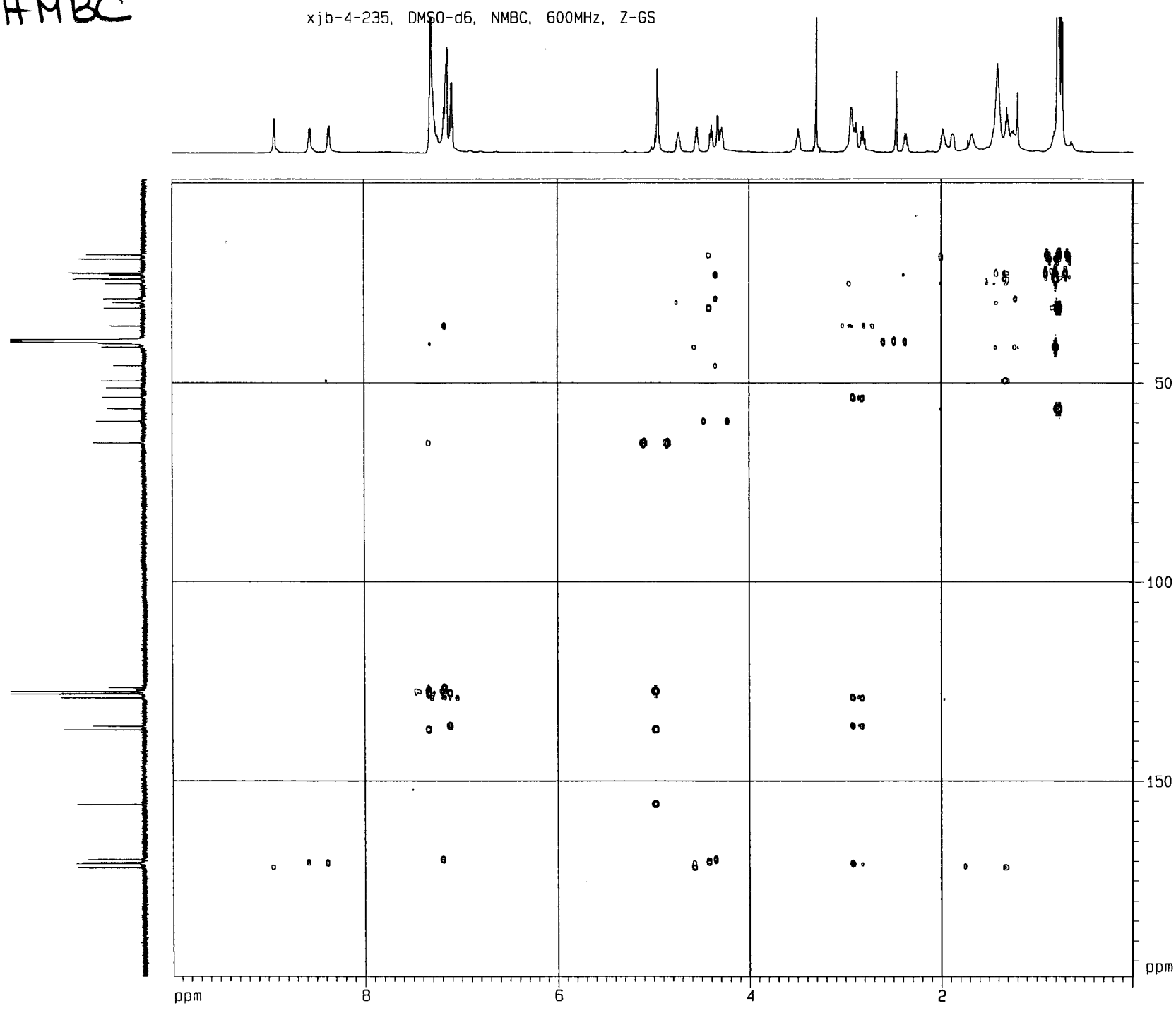
F1 - Processing para

SI	1024
MC2	QF
SF	151.0789366 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parame

CX2	18.00 cm
CX1	15.00 cm
F2PLO	9.985 ppm
F2LO	5999.29 Hz
F2PHI	-0.017 ppm
F2HI	-10.32 Hz
F1PLO	198.843 ppm
F1LO	30041.04 Hz
F1PHI	-1.128 ppm
F1HI	-170.47 Hz
F2PPMCM	0.55568 ppm
F2HZCM	333.86752 Hz
F1PPMCM	13.33145 ppm
F1HZCM	2014.10059 Hz

S44 Cbz_2 GS HMBC



Current Data Parameters

NAME	xjb-4-235-600
EXPNO	1122
PROCNO	1

F2 - Acquisition Parameter

Date_	20040303
Time	0.23
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	inv4gslrnd
TD	4096
SOLVENT	CDCl3
NS	80
DS	4
SWH	6009.615 Hz
FIDRES	1.467191 Hz
AQ	0.3408372 sec
RG	32768
DW	83.200 usec
DE	6.00 usec
TE	310.0 K
d0	0.00000300 sec
D1	1.00000000 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00050000 sec
IN0	0.00001655 sec

========== CHANNEL f1 ======

NUC1	1H
P1	9.60 usec
p2	19.20 usec
PL1	0.00 dB
SFO1	600.8330041 MHz

========== CHANNEL f2 ======

NUC2	13C
P3	13.50 usec
PL2	0.00 dB
SFO2	151.0938719 MHz

========== GRADIENT CHANNEL =

P16	1000.00 usec

F1 - Acquisition parameter

ND0	2
TD	256
SFO1	151.0939 MHz
FIDRES	118.013596 Hz
SW	199.952 ppm

F2 - Processing parameter

SI	1024
SF	600.8300066 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

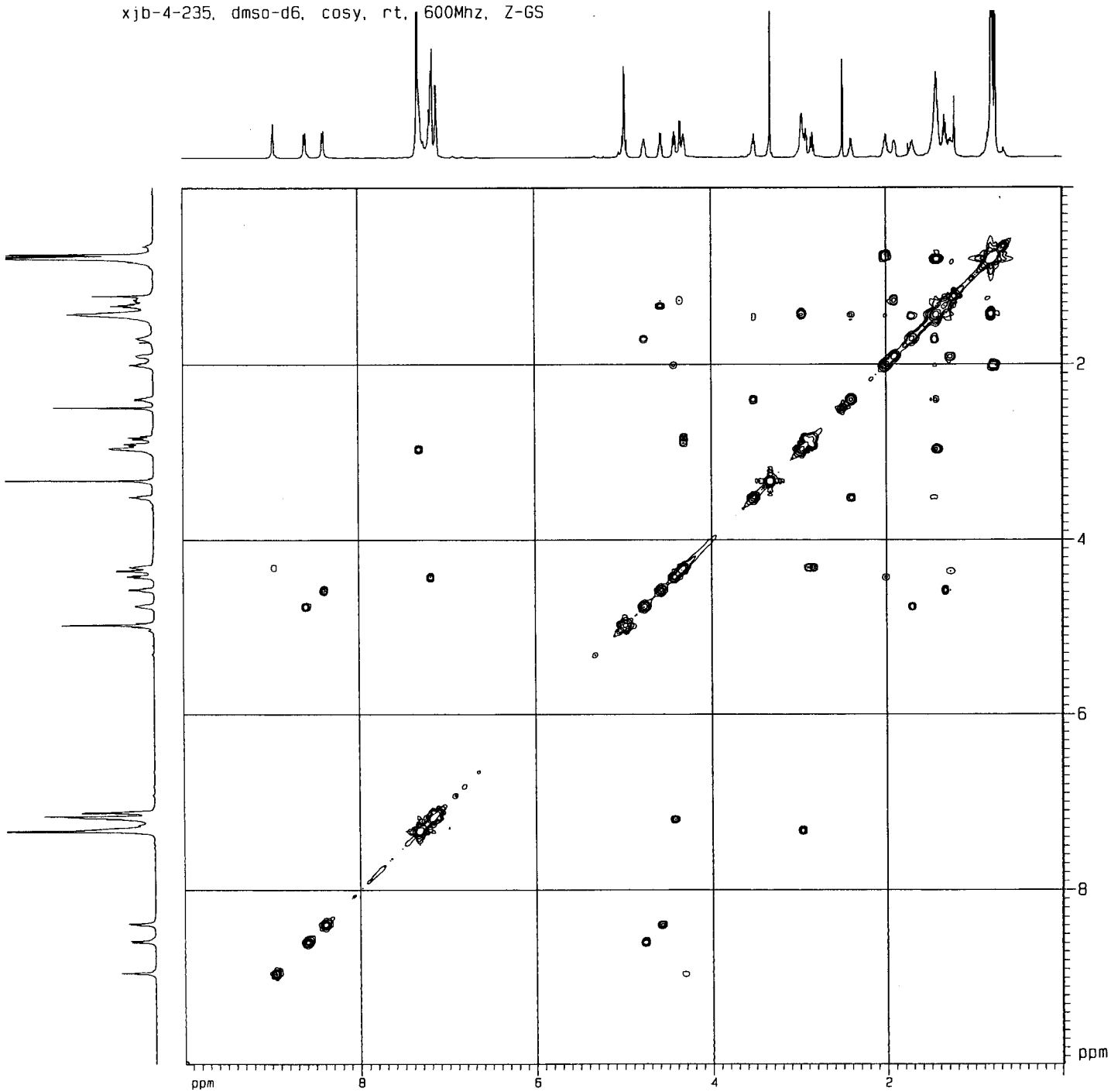
F1 - Processing parameter

SI	2048
MC2	QF
SF	151.0789062 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	9.990 ppm
F2LO	6002.32 Hz
F2PHI	-0.012 ppm
F2HI	-7.30 Hz
F1PLO	199.044 ppm
F1LO	30071.40 Hz
F1PHI	-0.927 ppm
F1HI	-140.11 Hz
F2PPMCM	0.55568 ppm/cm
F2HZCM	333.86752 Hz/cm
F1PPMCM	13.33145 ppm/cm
F1HZCM	2014.10059 Hz/cm

S45 Cbz_2 GS
COSY



Current Data Parameters

NAME	xjb-4-235-600
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20040302
Time	19.29
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	cosy
TD	1024
SOLVENT	CDCl3
NS	16
DS	16
SWH	6009.615 Hz
FIDRES	5.868765 Hz
AQ	0.0852468 sec
RG	100
DW	83.200 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
IN0	0.00016640 sec

========== CHANNEL f1 ==========

NUC1	1H
P0	8.20 usec
P1	8.20 usec
PL1	0.00 dB
SFO1	600.8330041 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.833 MHz
FIDRES	23.475060 Hz
SW	10.002 ppm

F2 - Processing parameters

SI	512
SF	600.8300060 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

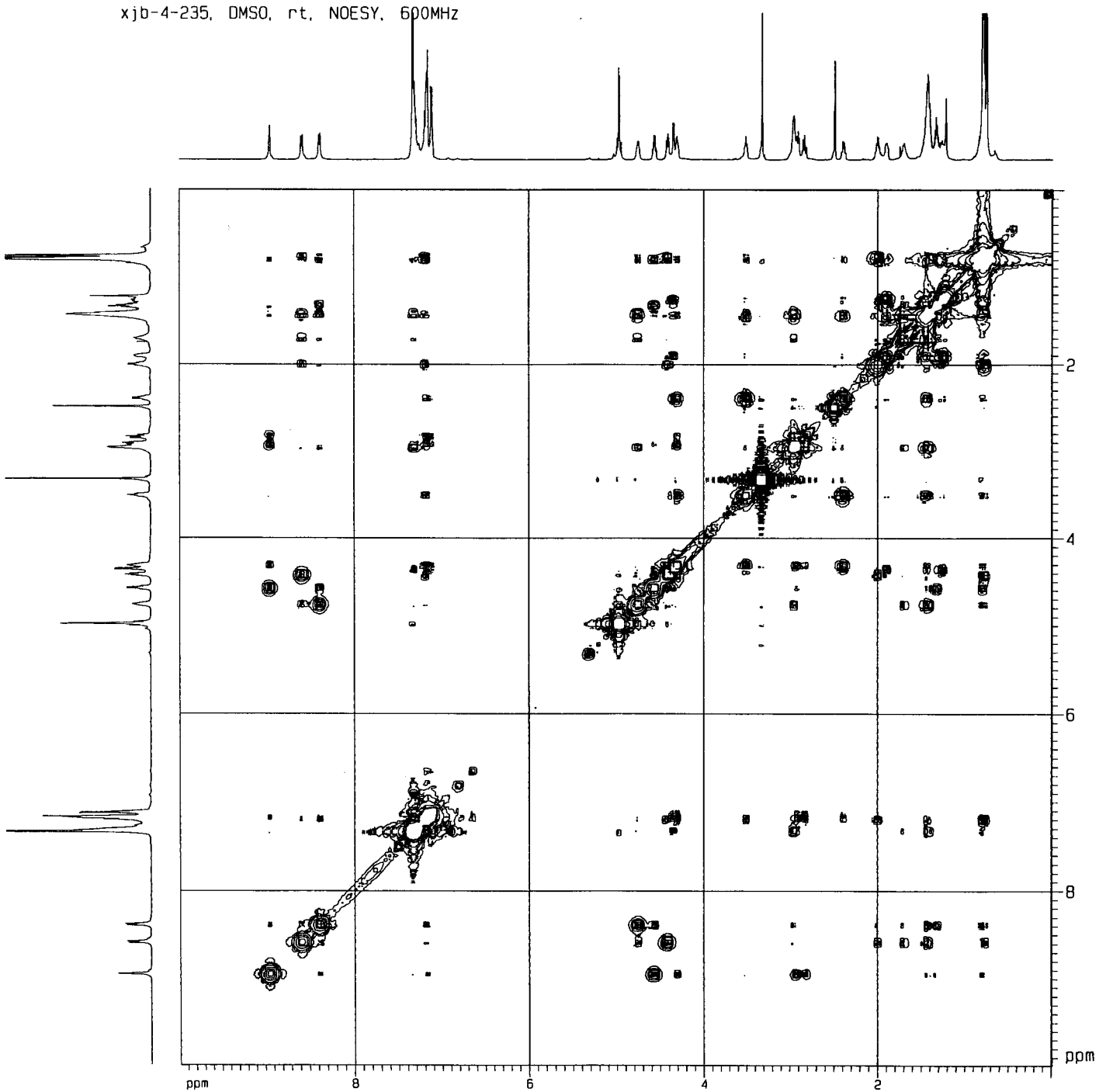
F1 - Processing parameters

SI	512
MC2	QF
SF	600.8300055 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	9.991 ppm
F2LO	6002.96 Hz
F2PHI	-0.011 ppm
F2HI	-6.66 Hz
F1PLO	9.992 ppm
F1LO	6003.42 Hz
F1PHI	-0.010 ppm
F1HI	-6.19 Hz
F2PPMCM	0.66681 ppm/cm
F2HZCM	400.64105 Hz/cm
F1PPMCM	0.66681 ppm/cm
F1HZCM	400.64105 Hz/cm

S46 Cbz_2GS NOESY



Current Data Parameters

NAME	xjb-4-235-600
EXPNO	1111
PROCNO	1

F2 - Acquisition Parameters

Date_	20040303
Time	18.01
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	noesytp
TD	1024
SOLVENT	CDCl3
NS	80
DS	16
SWH	6009.615 Hz
FIDRES	5.868765 Hz
AQ	0.0852468 sec
RG	300
DW	83.200 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
DB	0.34999999 sec
INO	0.00008320 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	600.8330041 MHz

F1 - Acquisition parameters

NDO	2
TD	256
SFO1	600.833 MHz
FIDRES	23.475060 Hz
SW	10.002 ppm

F2 - Processing parameters

SI	1024
SF	600.8300055 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

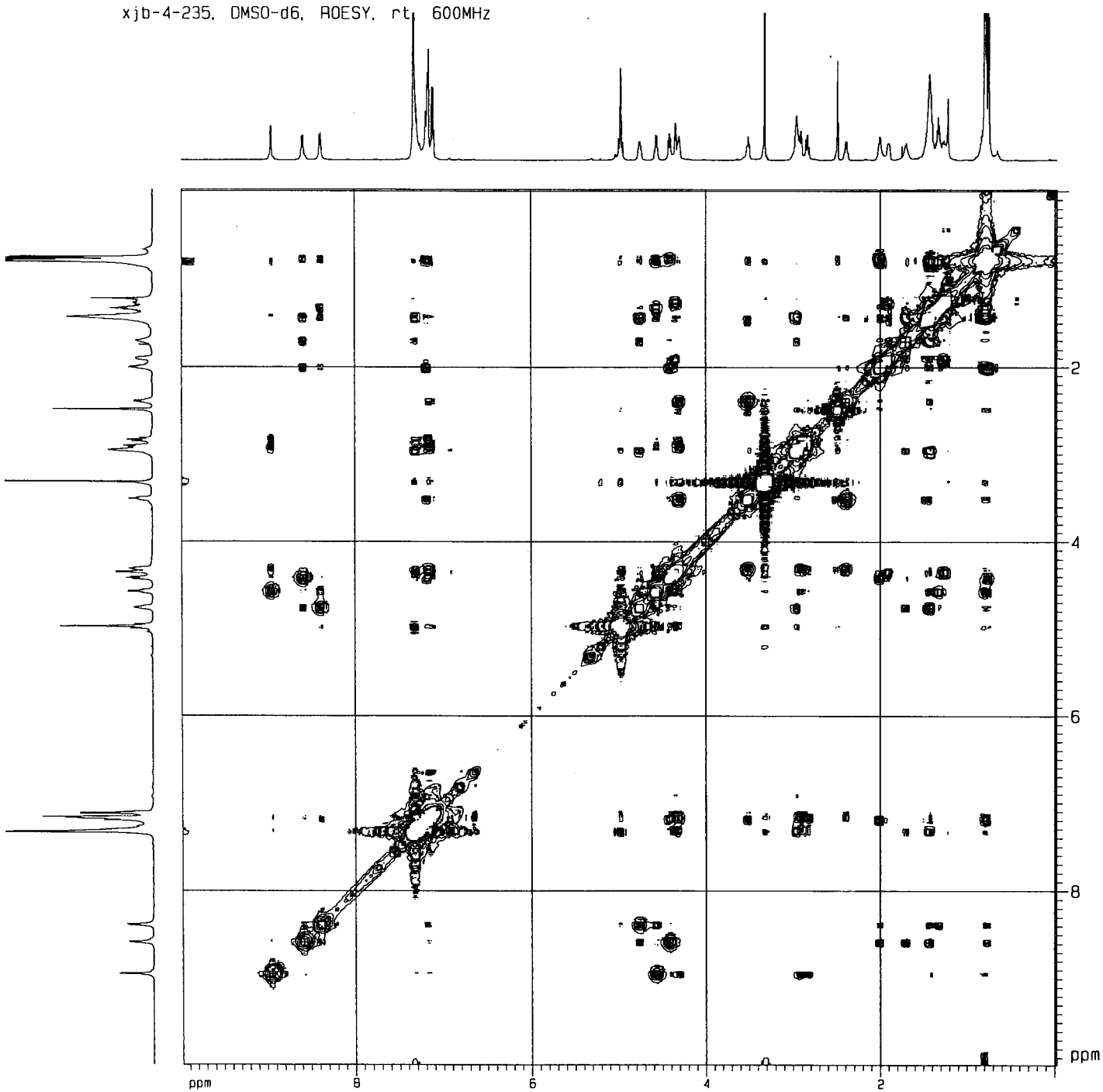
SI	1024
MC2	TPPI
SF	600.8300058 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	9.992 ppm
F2LO	6003.46 Hz
F2PHI	-0.010 ppm
F2HI	-6.16 Hz
F1PLO	9.992 ppm
F1LO	6003.21 Hz
F1PHI	-0.011 ppm
F1HI	-6.41 Hz
F2PPMCM	0.66681 ppm/cm
F2HZCM	400.64105 Hz/cm
F1PPMCM	0.66681 ppm/cm
F1HZCM	400.64105 Hz/cm

S47

Cbz_2GS ROESY



Current Data Parameters

NAME	xjb-4-235-600
EXPNO	2222
PROCNO	1

F2 - Acquisition Parameters

Date_	20040304
Time	2.16
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	roesytp
TD	1024
SOLVENT	CDCl3
NS	80
DS	16
SWH	6009.615 Hz
FIDRES	5.868765 Hz
AQ	0.0852468 sec
RG	300
DW	83.200 usec
DE	6.00 usec
TE	290.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d12	0.00002000 sec
IN0	0.00008320 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	9.00 usec
P15	250000.00 usec
PL1	0.00 dB
PL11	24.00 dB
SFO1	600.8330041 MHz

F1 - Acquisition parameters

NDO	2
TD	256
SFO1	600.833 MHz
FIDRES	23.475060 Hz
SW	10.002 ppm

F2 - Processing parameters

SI	1024
SF	600.8300115 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	0.10

F1 - Processing parameters

SI	1024
MC2	TPPI
SF	600.8300119 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	9.982 ppm
F2LO	5997.49 Hz
F2PHI	-0.020 ppm
F2HI	-12.13 Hz
F1PLO	9.981 ppm
F1LO	5997.10 Hz
F1PHI	-0.021 ppm
F1HI	-12.51 Hz
F2PPMCM	0.66681 ppm/cm
F2HZCM	400.64105 Hz/cm
F1PPMCM	0.66681 ppm/cm
F1HZCM	400.64105 Hz/cm

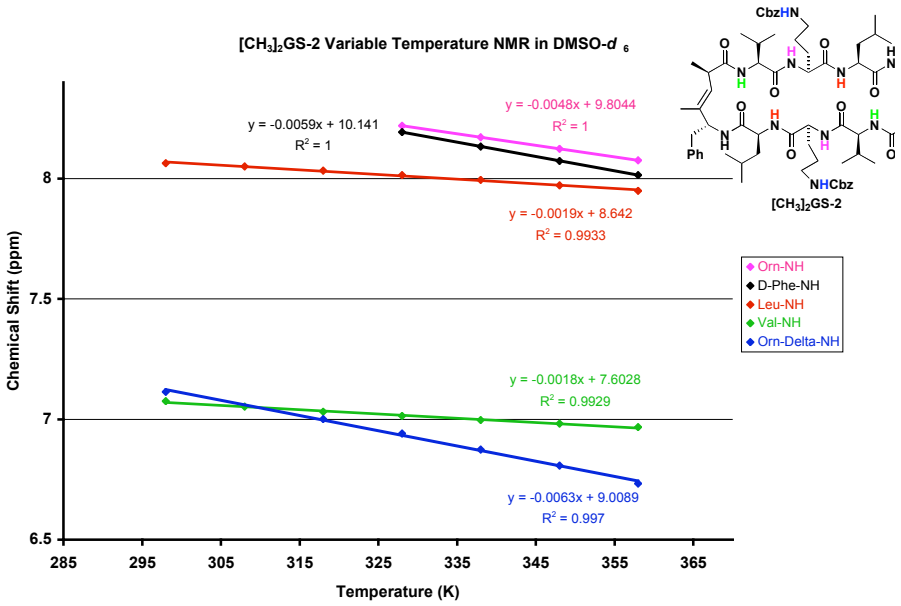


Figure 1. Amide proton chemical shift dependence on temperature for a solution of **10** in DMSO-d_6

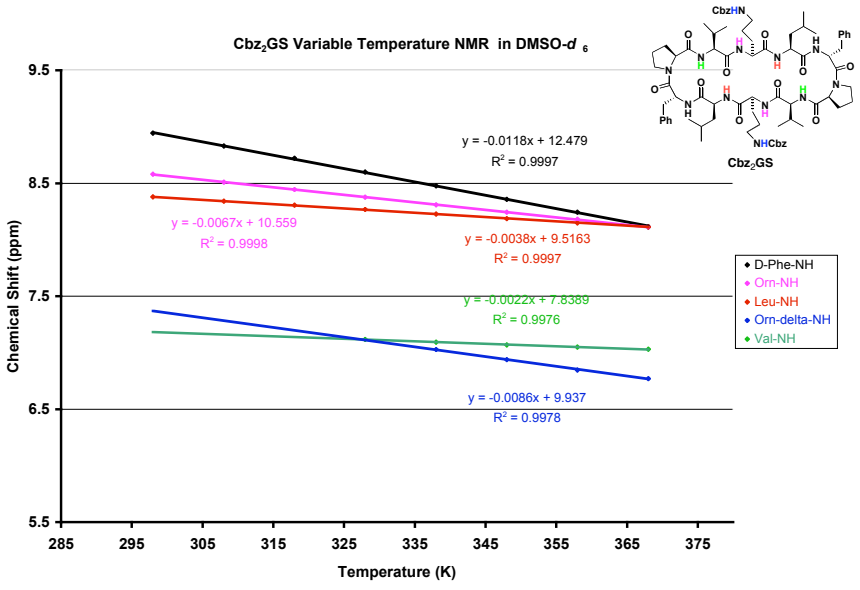


Figure 2. Amide proton chemical shift dependence on temperature for a solution of **Cbz_2GS** in DMSO-d_6.