Enantioselective Total Synthesis of (+)-Gliocladin C

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Supporting Information

(34 pages)

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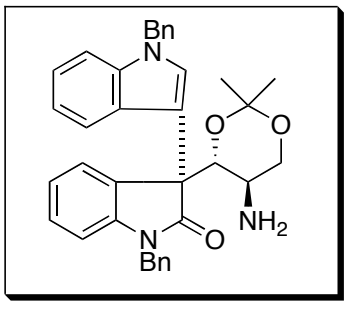
A. Experimental Procedures

General Details. Reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere. CH_2Cl_2 and THF were dried by passage through a bed of activated alumina. Commercial reagents were used without further purification. Thin-layer chromatography was performed on Merck 60 F_{254} precoated silica gel plate, which were visualized by exposure to UV (254 nm) or stained by submersion in *p*-anisaldehyde solution or ethanolic phosphomolybdic acid solution followed by heating on a hot plate. Flash column chromatography was performed in silica gel (230-400 mesh, Merck KGA). ^{1}H NMR spectra were recorded at 500 or 600 MHz and ^{13}C NMR spectra at 125 MHz or 150 MHz with Brucker Avance spectrometers. Infrared spectra were recorded using an ASI ReactIR™ 1000 spectrometer. Mass spectra were measured with a Micromass LCT spectrometer. Optical rotations were measured with a Jasco P-1010 polarimeter.

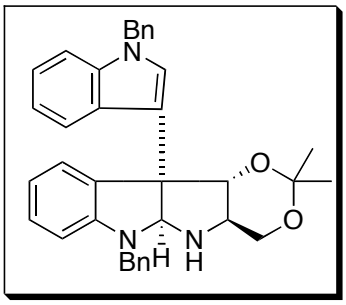


1,3-Dioxane 7. A methanol solution of HCl (3 M, 30 mL, prepared from AcCl and MeOH) was added at room temperature to Mukaiyama aldol product **6**[1] (2.57 g, 3.91 mmol). After the reaction was completed (usually 1.5 h, monitored by TLC), the solvent was removed on a rotary evaporator under reduced pressure keeping the bath temperature below 30 °C to suppress retroaldol reaction. Dichloromethane (20 mL) was added to the residue and this solution was concentrated under reduced pressure; this

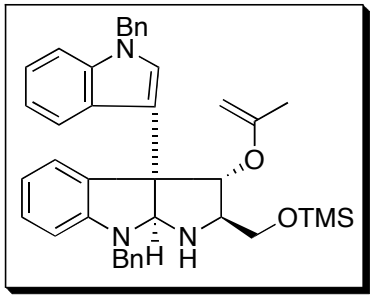
[1] Adhikari, S.; Caille, S.; Hanbauer, M.; Ngo, V. X.; Overman, L. E. *Org. Lett.* **2005**, *7*, 2795–2798.

procedure was repeated two times to remove all residual HCl–MeOH, which if present effects the next step. Diagnostic data for the amino diol intermedate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (br s, 1H), 7.45 (m, 1H), 7.41-7.28 (m, 4H), 7.25-7.01 (m, 10H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.86 (m, 1H), 6.81 (m, 1H), 6.76 (br d, *J* = 7.1 Hz, 1H), 6.51-5.74 (br, 2H), 5.37 (d, *J* = 3.7 Hz, 1H), 5.33 (m, 1H), 5.14 (d, *J* = 15.5 Hz, 1H), 5.08 (br s, 2H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.97 (br s, 1H), 4.64 (br s, 1H), 3.84 (br s, 1H), 3.73 (br s, 1H).

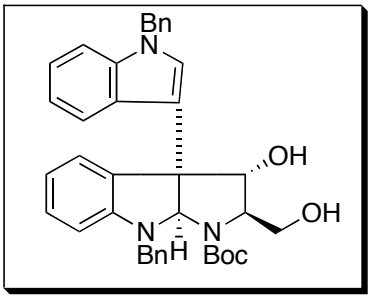
A solution of this residue, 2,2-dimethoxypropane (15 mL), camphorsulfonic acid (0.45 g) and benzene (15 mL) was heated at 50 °C for 3 h. After the reaction was completed, the reaction mixture was cooled to room temperature, and treated with saturated aqueous $NaHCO_3$ (5 mL). The phases were separated and the aqueous phase was extracted with EtOAc (10 mL). The combined organic layers were washed with brine, dried, and concentrated. Flash column chromatography (MeOH : CH_2Cl_2 = 1 : 9) of the crude residue yielded 1.85 g (85%) of **7** as a colorless foam: IR (film) 3382, 3054, 2939, 1713, 1611, 1466, 1366, 1181 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.25 (m, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.32-7.14 (m, 12H), 7.10 (dt, *J* = 1.0, 7.5 Hz, 1H), 7.03-6.98 (m, 2H), 6.92 (s, 1H), 6.69 (d, *J* = 7.3 Hz, 1H), 5.29 (d, *J* = 16.1 Hz, 1H), 5.23 (s, 2H), 5.16 (d, *J* = 8.3 Hz, 1H), 4.48 (d, *J* = 16.1 Hz, 1H), 3.81-3.73 (m, 1H), 3.52-3.46 (m, 2H), 1.57 (s, 3H), 1.35-1.02 (s, 2H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 144.1, 137.8, 137.3, 136.0, 128.9, 128.5, 127.9, 127.7, 127.4, 127.2, 126.6, 126.5, 125.9, 123.5, 122.7, 121.9, 120.2, 111.4, 110.5, 109.6, 99.5, 78.0, 65.9, 60.5, 56.9, 50.1, 48.5, 43.7, 28.1, 20.3; HRMS (CI) calcd for $C_{36}H_{35}O_3N_3$ 557.2678, found 557.2657; $[\alpha]^{23}_D$ –122.8 (*c* 5.0, CH_2Cl_2).



Pyrrolidinoindoline 8. A solution of aminodiol **7** (5.21 g, 9.35 mmol) in THF (20 mL) was added dropwise to a stirring suspension of $LiAlH_4$ (23.3 mL, 23.4 mmol, 1.0 M solution in THF) in THF (100 mL) at room temperature. The reaction mixture was then stirred at room temperature for 2 h, cooled to 0 °C and then carefully treated with H_2O (50 mL). The phases were separated and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried and concentrated. The residue was dissolved in MeOH (100 mL) and silica gel (10 g) was added to the resultant solution. The mixture was stirred at room temperature open to the air for 4 h, filtered, and the eluent was concentrated. Flash column chromatography (EtOAc : hexane = 1 : 3) of the crude product yielded 4.68 g (93%) of **8** as a colorless oil: IR (film) 3350, 3051, 3031, 2877, 1605, 1488, 1355, 1173, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.44-7.40 (m, 2H), 7.32-7.22 (m, 6H), 7.16-7.12 (m, 3H), 7.09 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.99 (dt, *J* = 6.9, 1.3 Hz, 1H), 6.87 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.73-6.65 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.52 (t, *J* = 7.3 Hz, 1H), 5.41 (s, 1H), 5.23 (s, 2H), 4.64 (d, *J* = 15.5 Hz, 1H), 4.41 (d, *J* = 15.5 Hz, 1H), 4.11-3.99 (m, 2H), 3.79 (t, *J* =10.3 Hz, 1H), 3.57 (dt, *J* = 10.3, 4.6 Hz, 1H), 2.11 (s, 1H), 1.51 (s, 3H), 1.39 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 138.4, 137.7, 136.7, 133.4, 129.1, 128.9, 128.6, 128.4, 128.0, 127.9, 127.7, 127.3, 124.5, 121.7, 120.6, 119.2, 117.5, 113.7, 109.9, 106.3, 100.8, 87.9, 82.7, 68.2, 60.7, 56.4, 54.7, 50.5, 49.2, 29.9, 19.7; HRMS (CI) calcd for $C_{36}H_{35}O_2N_3$ 541.2729, found 541.2725; $[\alpha]^{23}_D$ +137.6 (*c* 3.0, CH_2Cl_2).



Propenyl Ether 9. Following the general procedure of Rychnovsky,[2] TMSOTf (13.3 mL, 69.2 mmol) and *i*-Pr_2EtN (13.6 mL, 77.9 mmol) were added by syringe to a stirred solution of pyrrolidinoindoline **8** (4.68 g, 8.65 mmol) and CH_2Cl_2 (100 mL). The reaction mixture was stirred at room temperature for 48 h, and saturated aq. $NaHCO_3$ (40 mL) was added dropwise at a rate that minimized exothermic heating. The phases were separated and the aqueous phase was extracted with Et_2O (100 mL). The combined organic layers were washed with brine, dried, and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 15) of the crude product yielded 4.83 g (91%) of **9** as a colorless oil: IR (film) 3051, 2956, 1603, 1495, 1355, 1250, 1077, 872, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.34-7.18 (m, 9H), 7.16-7.12 (m, 1H), 7.09-6.98 (m, 5H), 6.83 (s, 1H), 6.61 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 1H), 5.46 (s, 1H), 5.18 (s, 2H), 5.10 (s, 1H), 4.50 (s, 2H), 4.24 (s, 1H), 3.83 (s, 1H), 3.66 (t, *J* = 7.8 Hz, 1H), 3.29-3.23 (m, 1H), 2.94 (t, *J* = 9.1 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 149.3, 139.1, 138.1,137.5, 133.4, 129.0, 128.9, 128.8, 128.2, 127.8, 127.4, 127.0, 126.8, 125.1, 122.1, 121.7, 119.1, 117.9, 117.0, 109.9, 107.2, 88.9, 85.2, 83.3, 67.2, 65.4, 60.8, 50.2, 49.2, 21.4, -0.3; HRMS (CI) calcd for $C_{39}H_{44}N_3O_2Si$ 614.3203 (M + H), found 614.3187; $[\alpha]^{23}_D$ +126.2 (*c* 2.0, CH_2Cl_2).

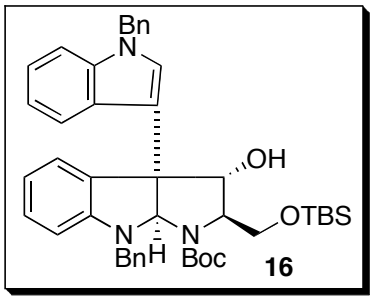


Diol 10. Aqueous Na_2CO_3 solution (10%, 20 mL) was added to a stirring solution of amine **9** (5.30 g, 8.64 mmol) in THF (20 mL). After stirring at room temperature for 10 min, Boc_2O (1.89 g, 8.67 mmol) was added. After 2 h, H_2O (50 mL) and Et_2O (50 mL) were added. The phases were separated and the aqueous phase was extracted twice with Et_2O (20 mL). The combined organic layers were washed with brine, dried, and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 5) of the crude residue yielded 6.20 g (quantitative yield) of the Boc derivative as a colorless oil: IR (film) 3029, 2991, 2931, 1696, 1604, 1467, 1374, 1216 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.38-7.22 (m, 8H), 7.19-7.08 (m, 2H), 7.09-7.03 (m, 4H), 6.83-6.68 (m, 2H), 6.32-6.19 (m, 2H), 5.45 (s, 1H), 5.21 (s, 2H), 5.15 (s, 1H), 4.51 (s, 2H), 4.29 (s, 1H), 3.87 (s, 1H), 3.75-3.67 (m, 1H), 3.25-3.21 (m, 1H), 2.93 (t, *J* = 9.8 Hz, 1H), 1.43 (s, 9H), 1.35 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 159.1, 149.4, 139.0, 138.1, 137.7, 133.2, 129.1, 128.8, 128.7, 128.5, 128.4, 128.1,

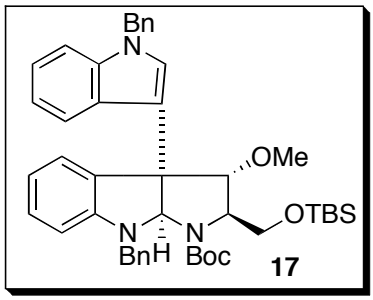
1. [2] Rychnovsky, S. D.; Kim, J. *Tetrahedron Lett.* **1991**, *32*, 7219.

127.9, 127.5, 126.9, 125.1, 122.3, 119.0, 117.8, 117.2, 109.9, 107.5, 88.7, 85.3, 83.5, 67.1, 65.4, 60.9, 50.5, 49.1, 28.6, 24.7, 21.3, 0.1; HRMS (CI) calcd for $C_{44}H_{52}N_3O_4Si$ 714.3728 (M + H), found 714.3731; $[\alpha]^{26}_D$ +46.8 (*c* 0.26, $CHCl_3$).

Oxalic acid (0.22 g, 1.75 mmol) was added to a stirred solution of this Boc-pyrrolidinoindoline intermediate (6.16 g, 8.64 mmol) in MeOH (48 mL) at room temperature. After stirring for 1 h at room temperature, saturated aqueous $NaHCO_3$ (10 mL) and EtOAc (50 mL) were added. The phases were separated and the aqueous phase was extracted twice with EtOAc (20 mL). The combined organic layers were washed with brine, dried, and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 2) of the crude material yielded 3.68 g (71%) of diol **10** as a colorless oil: IR (film) 3423, 3028, 2993, 2929, 1697, 1605, 1466, 1374, 1217 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82-7.66 (m, 1H), 7.35-7.12 (m, 12H), 7.12-7.03 (m, 3H), 6.74-6.62 (m, 1H), 6.42-6.28 (m, 1H), 6.15 (s, 1H), 5.14 (s, 2H), 5.03 (s, 1H), 4.93 (t, *J* = 16.0 Hz, 1H), 4.67 (s, 2H), 4.44-4.21 (m, 1H), 3.87-3.64 (m, 1H), 3.11-2.89 (m, 1H), 2.37 (br s, 1H), 1.83 (br s, 1H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 159.1, 149.4, 139.0, 138.1, 137.7, 133.2, 129.1, 128.8, 128.7, 128.5, 128.4, 128.1, 127.9, 127.5, 126.9, 125.1, 122.3, 119.0, 117.8, 117.2, 109.9, 88.7, 83.5, 67.1, 65.4, 60.9, 50.5, 49.1, 28.6, 24.7; HRMS (CI) calcd for $C_{38}H_{40}N_3O_4$ 602.3020 (M + H), found 602.3024; $[\alpha]^{25}_D$ +109.7 (*c* 0.75, $CHCl_3$).

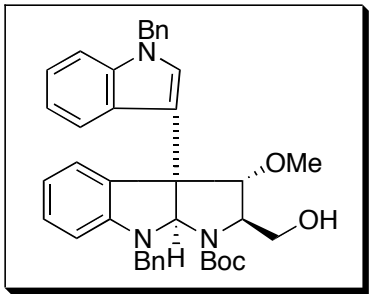


TBS Intermediate 16. NaH (60% dispersion in mineral oil, 0.49 g, 12.2 mmol) was added to a stirring solution of diol **10** (3.68 g, 6.11 mmol) in THF (100 mL) at room temperature. After stirring for 10 min, TBSCl (1.0 g, 6.63 mmol) was added and the reaction mixture was stirred for an additional 2 h at room temperature. Brine (50 mL) and Et_2O (100 mL) were added, the phases were separated, and the aqueous phase was extracted twice with Et_2O. The combined organic layers were dried and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 9) of the residue yielded 4.20 g (96%) of **16** as a colorless oil: IR (film) 3489, 3030, 2957, 2930, 1695, 1606, 1467, 1366, 1254 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82-7.67 (m, 1H), 7.36-7.11 (m, 12H), 7.12-7.04 (m, 3H), 6.76-6.62 (m, 1H), 6.42-6.28 (m, 1H), 6.17 (s, 1H), 5.16 (s, 2H), 5.02 (s, 1H), 4.92 (t, *J* = 15.6 Hz, 1H), 4.65 (s, 2H), 4.47-4.21 (m, 1H), 3.88-3.64 (m, 1H), 3.11-2.87 (m, 1H), 2.34 (br s, 1H), 1.43 (s, 9H), 0.86 (s, 9H), -0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 159.2, 149.7, 139.2, 138.0, 137.7, 133.4, 129.2, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 127.5, 126.7, 125.1, 122.5, 119.1, 117.9, 117.2, 109.8, 88.6, 83.5, 67.2, 65.6, 60.9, 50.7, 49.3, 28.8, 24.6, 14.5, -3.2, -4.9; HRMS (CI) calcd for $C_{44}H_{54}N_3O_4Si$ 716.3884 (M + H), found 716.3891; $[\alpha]^{25}_D$ +99.8 (*c* 1.2, $CHCl_3$).

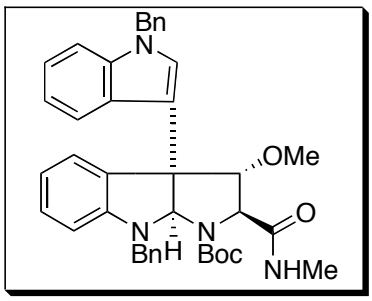


Methyl TBS Intermediate 17. NaH (60% dispersion in mineral oil, 36 mg, 0.92 mmol) was added to a stirring solution of alcohol **16** (101 mg, 0.14 mmol) in THF (2.8 mL) at 0 °C. After 10 min, MeI (0.088 mL, 1.4 mmol) was added dropwise and the reaction mixture was warmed to room temperature. After 2 h, the reaction mixture was quenched by adding H_2O (10 mL) and Et_2O (10 mL) was added. The phases were separated and the aqueous phase was extracted

twice with Et_2O (5 mL). The combined organic layers were washed with brine, dried and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 9) of the crude material yielded 79.2 mg (77%) of **17** as a colorless oil: IR (film) 2954, 2929, 2856, 1694, 1603, 1495, 1453, 1389, 1250, 1158, 1096, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.39-7.17 (m, 8H), 7.15-7.10 (m, 2H), 6.99 (s, 1H), 6.77 (m, 3H), 6.31 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 5.35-5.20 (m, 3H), 4.75-4.68 (m, 3H), 4.55 (m, 1H), 3.79 (m, 1H), 3.30 (s, 3H), 3.03 (m, 1H), 1.52-1.39 (m, 9H), 0.95-0.93 (m, 9H), 0.05-0.01 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 148.7, 139.2, 137.7, 137.5, 131.9, 128.8, 128.5, 128.3, 127.7, 127.5, 127.3, 126.9, 126.6, 126.0, 126.3, 124.8, 122.0, 121.6, 119.1, 117.8, 115.6, 109.9, 107.2, 88.5, 87.8, 80.7, 66.2, 62.4, 60.6, 57.7, 50.1, 29.8, 28.5, 28.3, 25.9, -5.4; HRMS (CI) calcd for $C_{45}H_{55}N_3O_4Si$ 752.3860 (M + Na), found 752.3864; $[\alpha]^{24}_D$ +36.4 (*c* 0.11, $CHCl_3$).



Alcohol Intermediate 11. TBAF (1.0 M solution in THF, 0.11 mL) was added dropwise to a stirred solution of TBS-protected alcohol **17** (79.2 mg, 0.11 mmol) in THF (5 mL) at room temperature. After 12 h at room temperature, the reaction was concentrated and the residue was purified by flash chromatography (EtOAc : hexane = 3 : 7) to yield 61.2 mg (92%) of alcohol **11** as a colorless foam: IR (film) 2981, 2954, 1677, 1603, 1391, 1368, 1266, 1177, 1138, 1096, 908, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.38-7.28 (m, 9H), 7.22 (m, 2H), 7.15 (m, 3H), 7.08 (m, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.44 (m, 1H), 6.15 (m, 1H), 5.37 (m, 2H), 4.80-4.63 (m, 2H), 4.57 (m, 1H), 4.28 (m, 1H), 3.83-3.60 (m, 3H), 3.41 (s, 3H), 1.48-1.32 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 148.9, 138.9, 137.7, 137.1, 128.8, 128.7, 128.3, 127.6, 126.9, 126.6, 124.8, 121.7, 121.5, 119.2, 118.2, 112.6, 110.0, 108.0, 90.5, 89.8, 81.7, 67.3, 65.7, 58.8, 51.0, 50.2, 28.1, 21.1; HRMS (CI) calcd for $C_{39}H_{41}N_3O_4Na$ 638.2995 (M + Na), found 638.2996; $[\alpha]^{24}_D$ +57.4 (*c* 0.2, $CHCl_3$).



Boc-Protected Carboxamide 12. Dess-Martin periodinane[3] (0.25 g, 0.60 mmol) and pyridine (0.097 mL) were added to a solution of alcohol **11** (61.2 mg, 0.10 mmol) and CH_2Cl_2 (2 mL) at room temperature. After 1 h, the mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and saturated aqueous $Na_2S_2O_3$ (10 mL). The resulting mixture was extracted with ethyl ether (10 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration provided the crude aldehyde intermediate as a pale yellow oil, which was used immediately in the next reaction without further purification.

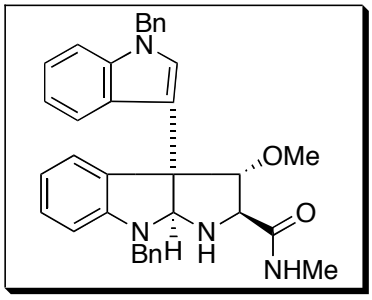
Following the general procedure of Pinnick,[4] a 2 M solution of 2-methyl-2-butene in THF (0.28 mL, 0.57 mmol), $NaH_2PO_4 \bullet H_2O$ (0.041 g, 0.30 mmol), and $NaClO_2$ (0.24 g, 0.30 mmol) were added successively at room temperature to a stirring mixture of this crude aldehyde, THF (0.5 mL) and H_2O (0.5 mL). The reaction mixture was then stirred for an

[3] (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155–4156. (b) Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549–7552.

[4] Bal, B. S.; Childers, W. E.; Pinnick, H. W. *Tetrahedron*, **1981**, *37*, 2091.

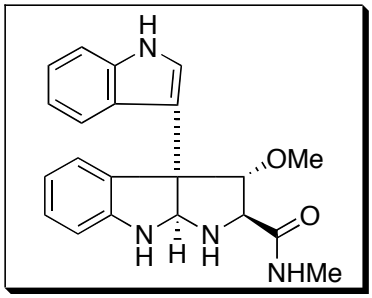
additional 2 h at room temperature, diluted with H_2O (10 mL), and extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, concentrated, and the residual crude acid was used for the next reaction without further purification.

Benzotriazole-1-yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (BOP, 48 mg, 0.11 mmol), $MeNH_3Cl$ (7.4 mg, 0.11 mmol), and Et_3N (0.021 mL, 0.15 mmol) were added successively at room temperature to a stirring solution of the crude acid in CH_2Cl_2 (1 mL). After 3h, the reaction was completed and the reaction was concentrated. The residue was purified by flash chromatography (hexane : EtOAc = 3 : 2) to yield 38.1 mg (60% for three steps) of amide product **12** as a pale yellow oil: IR (film) 3054, 2987, 1673, 1441, 1370,1266, 1144, 895 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.49-7.42 (m, 4H), 7.34-7.29 (m, 3H), 7.28-7.23 (m, 3H), 7.19-7.14 (m, 2H), 7.09-7.07 (m, 3H), 6.73 (m, 1H), 6.22 (s, 1H), 5.87 (br s, 1H), 5.24 (d, *J* = 16.4 Hz, 1H), 5.21(d, *J* = 16.3 Hz, 1H), 4.91 (m, 1H), 4.70 (m, 2H), 3.41 (m, 3H), 3.09 (d, *J* = 5.0 Hz, 3H), 2.37 (d, *J* = 4.9 Hz, 3H), 1.49 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 155.4, 148.7, 142.4, 139.9, 137.5, 131.2, 129.0, 128.7, 128.6, 128.33, 128.25, 127.5, 127.2, 126.6, 121.7, 119.3, 118.7, 110.0, 92.5, 68.2, 51.1, 50.1, 29.8, 28.3, 26.9, 26.0 ; HRMS (CI) calcd for $C_{40}H_{42}N_4O_4Na$ 665.3104 (M + Na), found 665.3103; $[\alpha]^{25}_D$ +52.1 (*c* 0.25, $CHCl_3$).

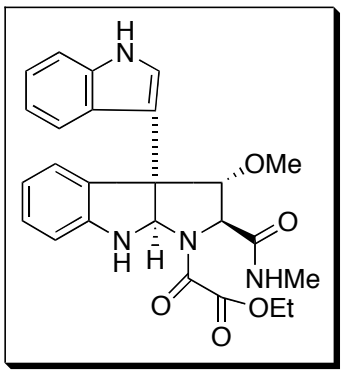


Aminocarboxamide 13. Following the general procedure Danishefsky,[5] Boc-protected amide **12** (49.8 mg, 77.5 μmol) was dissolved in dry MeCN (1.5 mL) and this solution was cooled to 0 °C under argon. TMSI (0.066 mL, 0.47 mmol) was then added dropwise over 10 min. After 30 min, the reaction mixture was poured into sat. aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine, dried, filtered, and concentrated. Flash column chromatography (EtOAc : hexane = 1 : 1) of the crude residue yielded 27.3 mg (65%) of aminocarboxamide **13** as a colorless oil: IR (film) 3369, 2925, 1733, 1665, 1603, 1530, 1482, 1453, 1353, 1245, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.37-7.31 (m, 7H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.21-7.16 (m, 3H), 7.13-7.10 (m, 1H), 7.08 (dt, *J* = 1.1, 7.6 Hz, 1H), 6.94 (m, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.42 (s, 1H), 5.26 (s, 2H), 4.94 (d, *J* = 2.0 Hz, 1H), 4.60 (d, *J* = 14.7 Hz, 1H), 4.48 (d, *J* = 14.6 Hz, 1H), 4.08 (s, 1H), 3.44 (s, 3H), 2.39 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 148.8, 138.1, 137.4, 137.2, 132.4, 128.77, 128.75, 128.67, 128.0, 127.6, 127.4, 127.1, 126.3, 125.0, 121.6, 121.0, 119.1, 118.5, 114.6, 109.9, 107.2, 90.7, 89.0, 67.6, 59.7, 58.1, 50.1, 49.9, 29.8, 25.5; HRMS (CI) calcd for $C_{35}H_{34}O_2N_4Na$ 565.2579, found 565.2580; $[\alpha]^{26}_D$ +66.3 (*c* 0.10, $CHCl_3$).

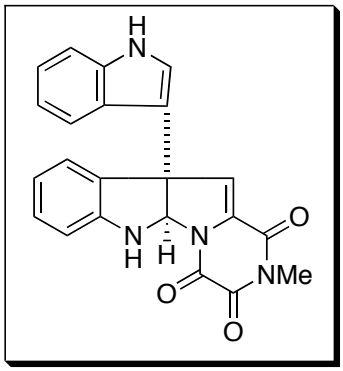
[5] Depew, K. M.; Marsden, S.P.; Zatorska, D.; Zatorski, A.; Bornmann, W. G.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 11953.



Triamine Carboxamide 14. Freshed cut Na (30 mg, 1.3 mmol) was added to a liquid ammonia (1.6 mL) in a 10 mL two-necked flask cooled to –78 °C. After 5 min, a solution of *t*-BuOH (0.061 mL) in THF (0.5 mL) was added to the blue ammonia solution, followed by a solution of amide **13** (17.3 mg, 31.9 μmol) in THF (1 mL). The reaction mixture was stirred at –78 °C for 30 min at which the blue color had disappeared. The reaction mixture then was quenched with solid NH_4Cl (0.2 g), and ammonia was allowed to evaporate by replacing the cooling bath with a water bath. The residue was dissolved in CH_2Cl_2 (4 mL) and filtered through a cotton-plugged pippet. After concentration of the filtrate, flash column chromatography (MeOH: CH_2Cl_2 = 1 : 9) of the crude residue yielded 10.0 mg (87%) of amine **14** as a colorless oil: IR (film) 3330, 2927, 1648, 1605,1538, 1484, 1461, 1410, 1241,1100, 1081, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 10.4, 8.1 Hz, 1H), 7.16-7.12 (m, 3H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.13-7.10 (m, 2H), 7.02 (dt, *J* = 1.0, 7.6 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 4.89 (s, 1H), 4.02 (s, 1H), 3.37 (s, 3H), 2.32 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 148.0, 137.0, 131.4, 128.8, 126.5, 125.4, 122.5, 121.8, 121.1, 119.6, 119.4, 115.9, 111.4, 109.8, 90.7, 84.5, 68.3, 61.4, 57.8, 25.4; HRMS (CI) calcd for $C_{21}H_{22}O_2N_4Na$ 385.1640, found 385.1641; $[\alpha]^{23}_D$ +23.5 (*c* 0.19, $CHCl_3$).



Oxalyl Amide 15. Ethyl chlorooxoacetate (5.0 μL, 44 μmol) and Et_3N (6 μL, 44 μmol) were added at room temperature to a solution of triamine amide **14** (10.7 mg, 30.0 μmol) in dry CH_2Cl_2 (0.6 mL). After 30 min, the solvent was evaporated under reduced pressure, and the resulting residue was subjected to a flash column chromatography (EtOAc : hexane = 7 : 3) to give 11.8 mg (87%) of **15** as a colorless oil: IR (film) 3357, 2927, 1737, 1656, 1542, 1466, 1414, 1250, 1218, 1162, 1102, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.19 (m, 1H), 7.15-7.07 (m, 2H), 7.03 (s, 1H), 6.79-6.76 (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.14 (s, 1H), 5.55 (s, 1H), 5.03 (s, 1H), 4.90 (s, 1H), 4.25 (m, 2H), 3.38 (s, 3H), 2.34 (d, *J* = 4.9 Hz, 3H), 1.43 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 162.0, 160.5, 146.8, 136.9, 129.9, 129.5, 126.2, 125.7, 123.1, 122.2, 121.0, 120.0, 119.7, 114.2, 111.5, 109.5, 87.8, 83.4, 67.6, 63.4, 61.4, 58.0, 26.1, 14.0; HRMS (CI) calcd for $C_{25}H_{26}O_5N_4Na$ 485.1801, found 485.1788; $[\alpha]^{23}_D$ +63.0 (*c* 0.26, $CHCl_3$).

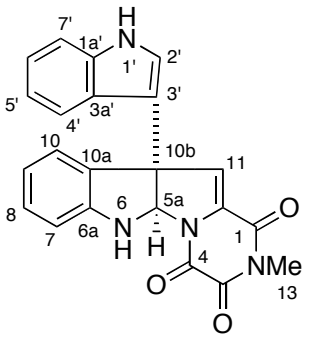


(+)-Gliocladin C (1). Following the general procedure of Mulliez,[6] 1,1,1,3,3,3-hexamethyldisilasane (1 mL) was added to caroxamide ester ester **15** (2.8 mg) in sealed tube and the reaction mixture was placed in a 140 °C oil bath. After 20 min, the tube was removed from the bath, allowed to cool to room temperature, and volatile components were removed under high vacuum. Flash column chromatography (EtOAc : hexane = 1 : 1) of the crude residue yielded 1.7 mg (73%) of (+)-gliocladin C (**1**) as a yellow powder: IR (film) 3351, 1679, 1470, 1318 cm^{-1}; ^1H NMR (600 MHz, Acetone-d_6) δ 10.33 (br s, 1H), 7.43 (br d *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 0.7, 8.2 Hz, 1H), 7.23 (d, *J* = 2.6 Hz, 1H), 7.18 (br d, *J* = 7.4 Hz, 1H), 7.13 (ddd, *J* = 8.7, 7.5, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.96 (s, 1H), 6.90 (ddd, *J* = 8.0, 7.1, 0.8 Hz, 1H), 6.86 (br d, *J* = 7.9 Hz, 1H), 6.72 (ddd, *J* = 7.4, 7.3, 1.0 Hz, 1H), 6.61 (br d, *J* = 1.9 Hz, 1H), 6.24 (d, *J* = 2.6 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 158.62, 158.01, 150.70, 149.93, 138.47, 133.08, 131.11, 129.68, 126.94, 126.29, 125.47, 123.70, 122.76, 120.13, 120.11, 119.65, 116.66, 112.63, 110.58, 84.69, 60.97, 27.09; HRMS (CI) calcd for $C_{22}H_{16}N_4O_3Na$ 407.1120 (M + Na), found 407.1118; $[\alpha]^{27}_D$ +116.4 (*c* 0.02, $CHCl_3$), reported[7] $[\alpha]_D$ +131.4 (*c* 0.07, $CHCl_3$).

[6] Mulliez, M.; Royer, J. *Tetrahedron* **1984**, *40*, 5143–5151.

[7] Usami, Y.; Yamaguchi, J.; Numata, A. *Heterocycles* **2004**, *63*, 1123–1129.

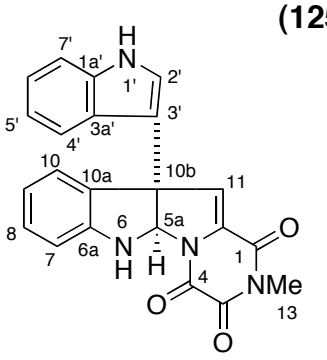
B. Tabulated ^{1}H and ^{13}C NMR spectra of natural and synthetic (+)-gliocladin C



	LITERATURE (500 MHz, acetone-d_6)	**SYNTHETIC (600 MHz, acetone-d_6)**
1		
3		
4		
5a	6.24 (d, 3.2)	6.24 (d, 2.6)
6	6.61 (br d, 3.2)	6.61 (br d, 1.9)
7	6.86 (br d, 8.2)	6.86 (br d, 7.9)
8	7.13 (br dd, 8.2, 7.6)	7.13 (ddd, 8.7, 7.5, 1.1)
9	6.72 (dddd, 7.6, 7.3, 1.6, 1.1)	6.72 (ddd, 7.4, 7.3, 1.0)
10	7.18 (br d, 7.3)	7.18 (br d, 7.4)
10a		
10b		
11a	6.96 (s)	6.96 (s)
11b		
12		
13	3.25 (s)	3.26 (s)
1'	10.3 (brd, 1.6)	10.33 (br s)
1a'		
2'	7.23 (d, 1.6)	7.23 (d, 2.6)
3a'		
4'	7.33 (br d, 8.2)	7.33 (dd, 8.2, 0.7)
5'	6.90 (ddd, 8.0, 7.1, 0.9)	6.90 (ddd, 8.0, 7.1, 0.8)
6'	7.10 (ddd, 8.2, 7.1, 1.1)	7.11 (ddd, 8.1, 7.1, 1.0)
7'	7.43 (br d, 8.2)	7.43 (br d, 8.2)

Source : *Heterocycles* **2004**, *63*, 1123

LITERATURE
(125 MHz, acetone-d_6)



SYNTHETIC
(125 MHz, acetone-d_6)

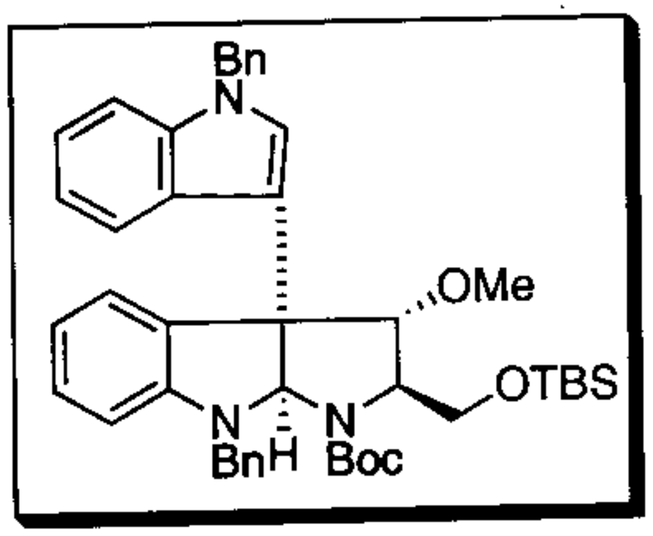
1	158.62
3	158.01
4	150.71
5a	84.72
6a	149.94
7	110.59
8	129.68
9	119.66
10	125.47
10a	131.12
10b	61.00
11a	126.97
11b	
12	133.08
13	27.10
1'	
1a'	138.49
2'	123.71
3'	122.75
3a'	123.55
4'	119.71
5'	119.71
6'	120.12
7'	112.64

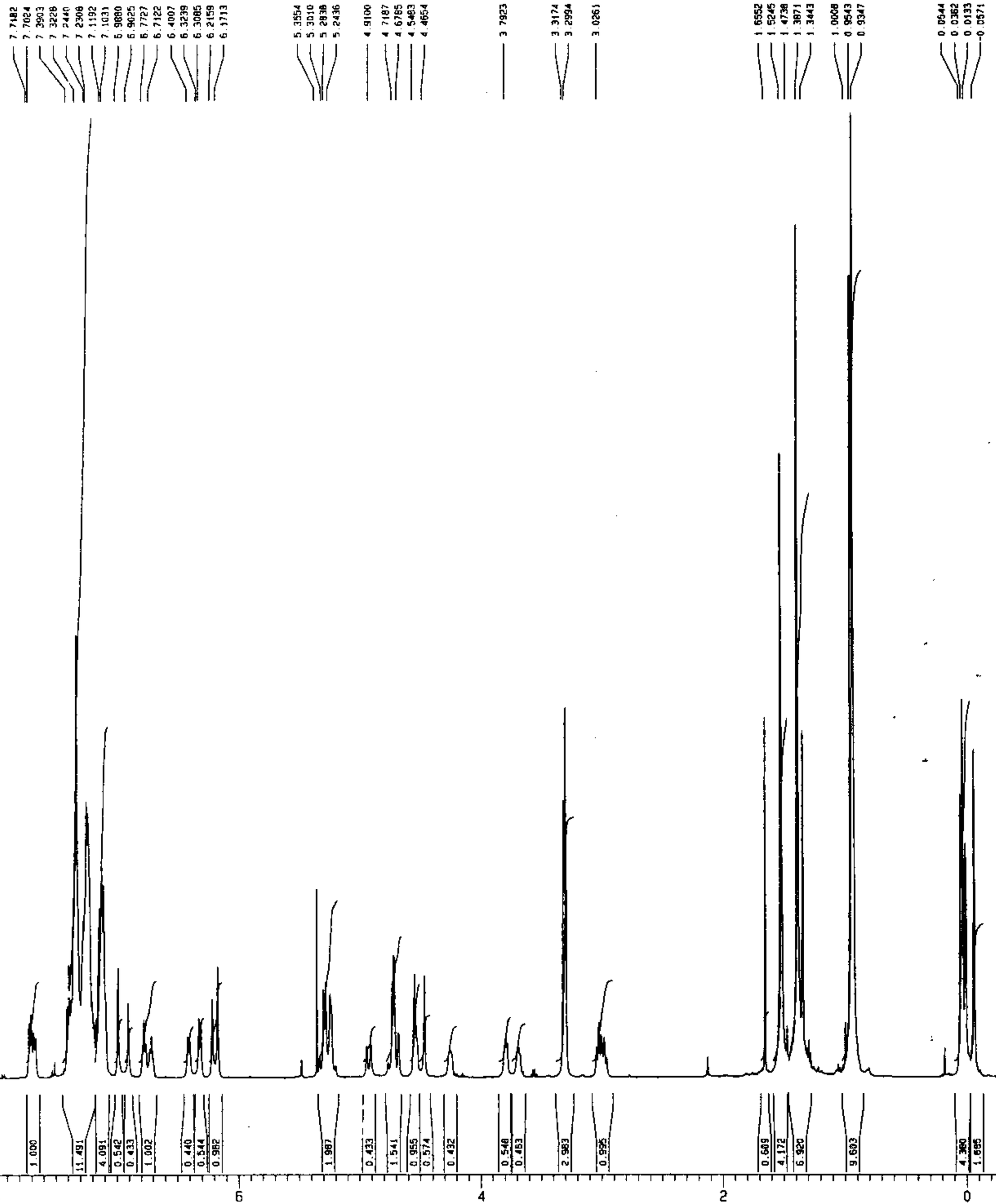
1	158.62
3	158.01
4	150.70
5a	84.69
6a	149.93
7	110.58
8	129.68
9	119.65
10	125.47
10a	131.11
10b	60.97
11a	126.94
11b	
12	133.08
13	27.09
1'	
1a'	138.47
2'	123.70
3'	**116.66**
3a'	**126.29**
4'	**120.11**
5'	**120.13**
6'	**122.76**
7'	112.63

Source : *Heterocycles* **2004**, *63*, 1123

confirmed by HMQC, HMBC

1H spectrum





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F2 - Processing parameters

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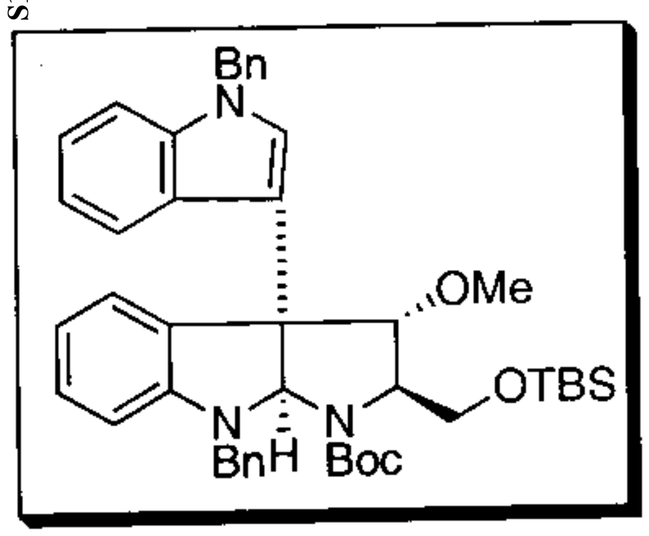
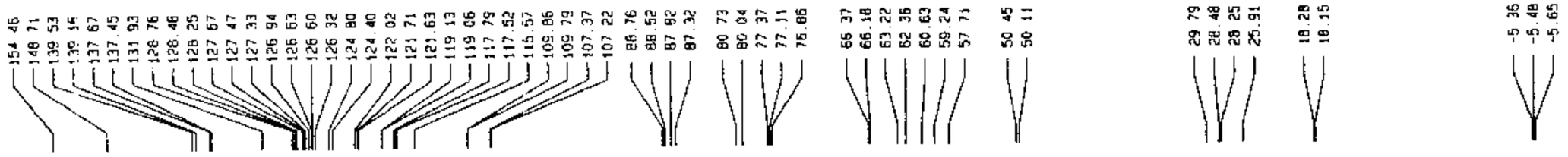
HZCM	263.27368 Hz/cm

13C spectrum with 1H decoupling

S12





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1D NMR plot parameters

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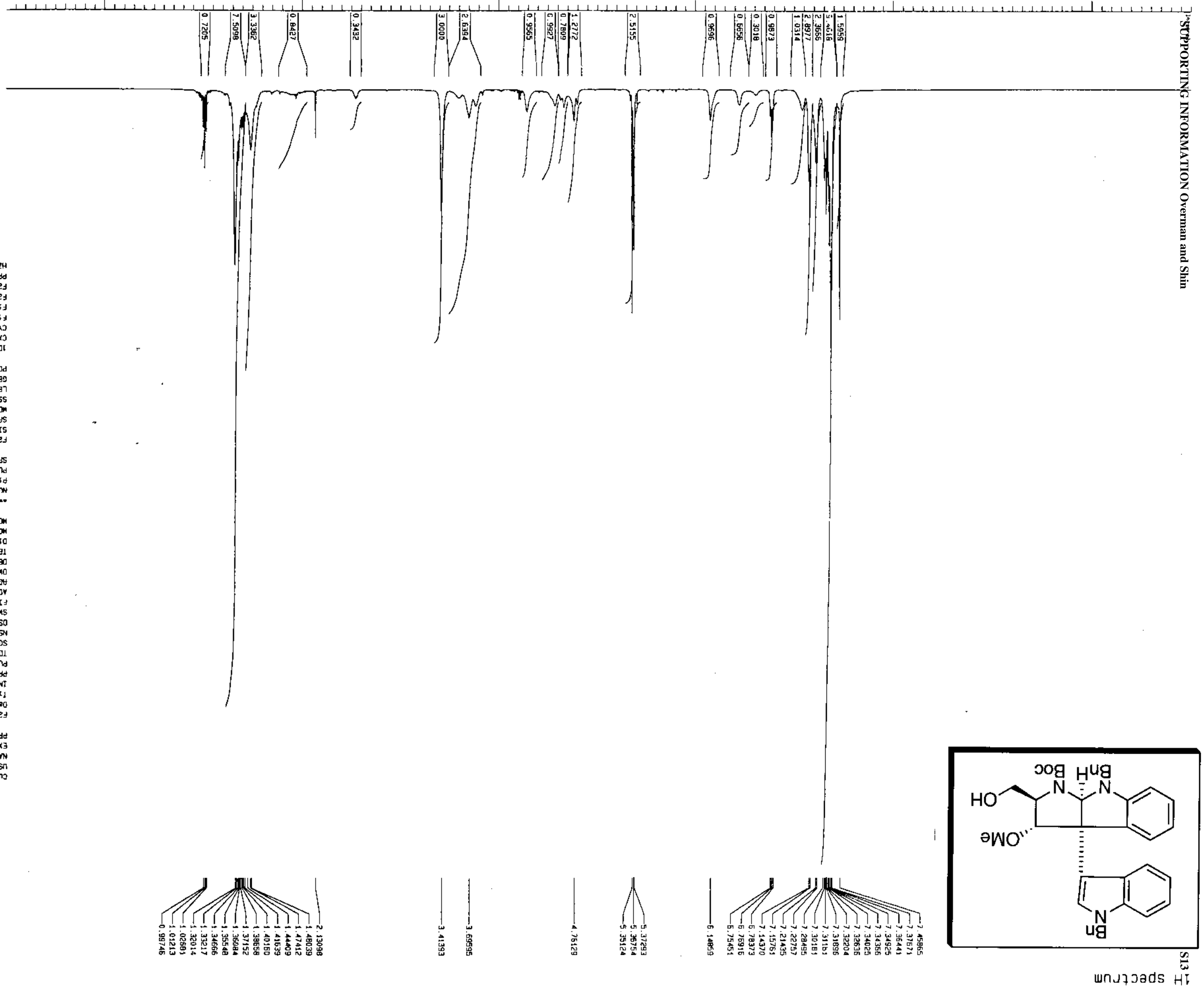

¹H spectrum


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1D NMR plot parameters
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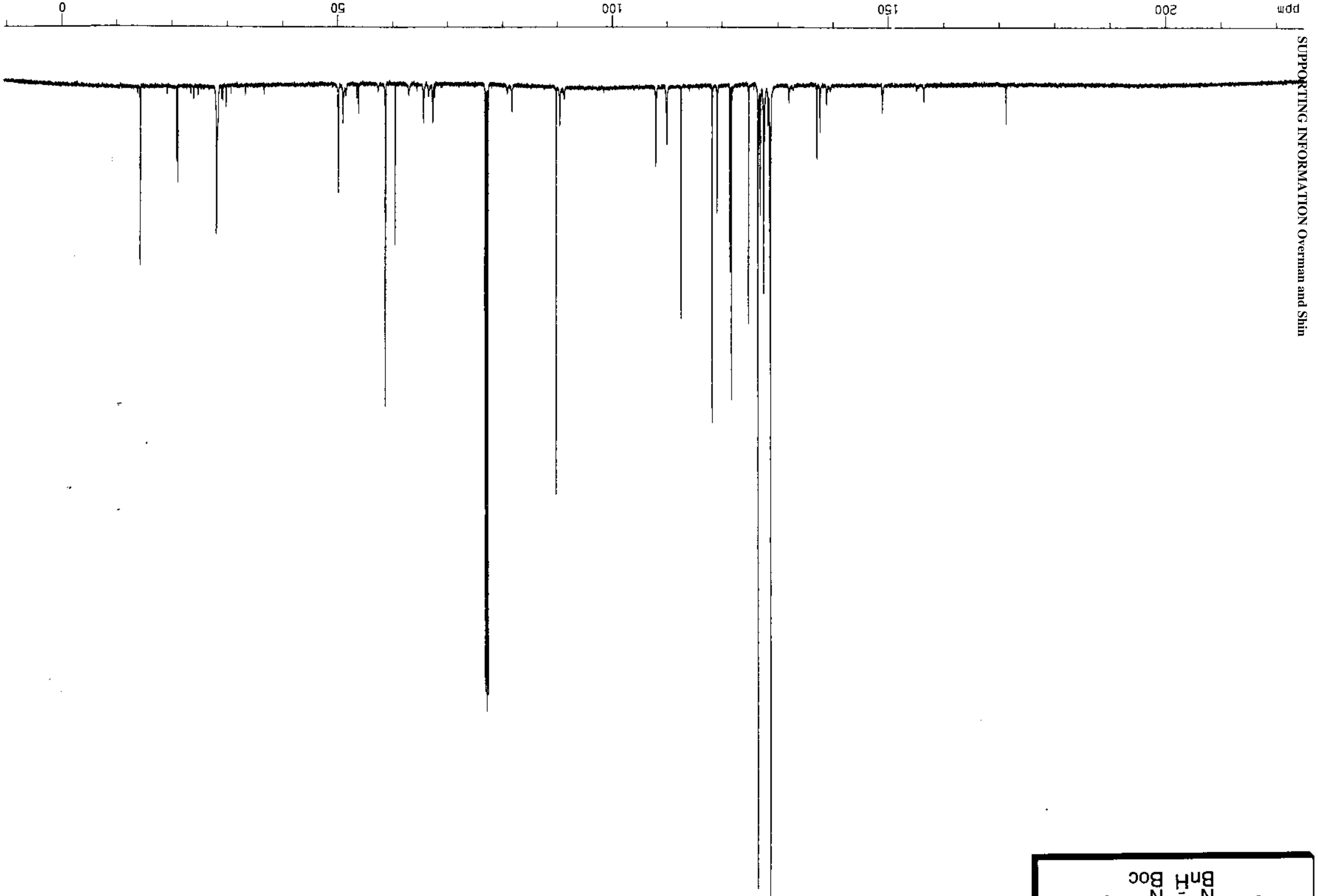

^{13}C spectrum with ^{1}H decoupling

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F2 - Processing parameters
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GB 0
PC 2.00

1D NMR plot parameters
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CY 15.55 cm
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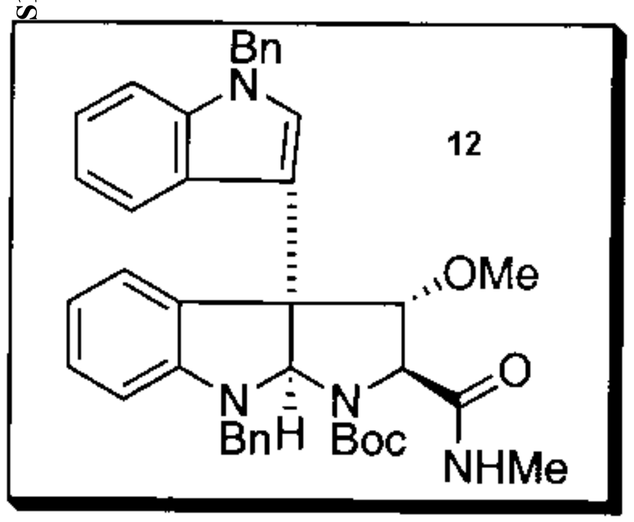
HZCM 1324.00439 Hz/cm

1H spectrum

S15

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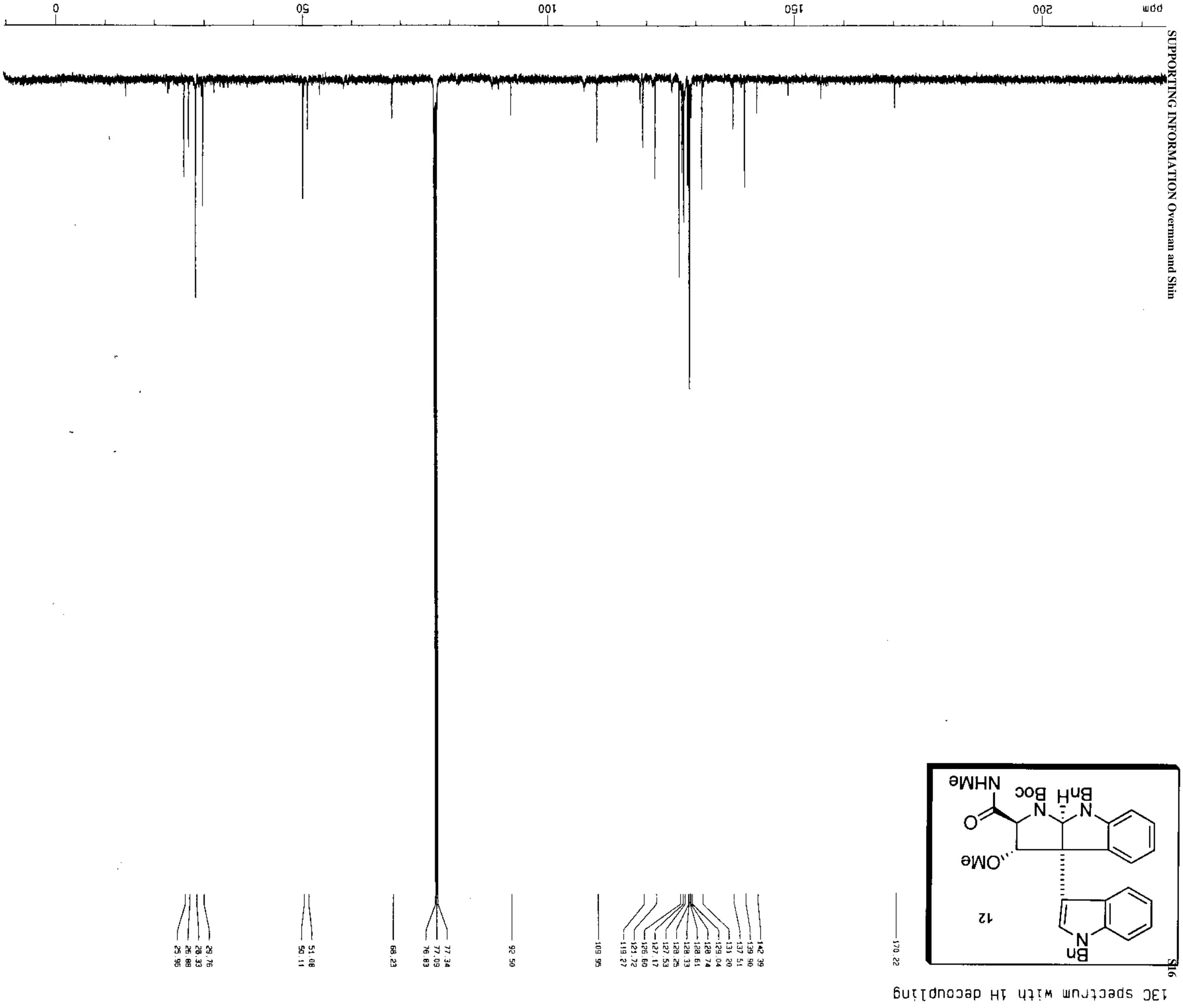
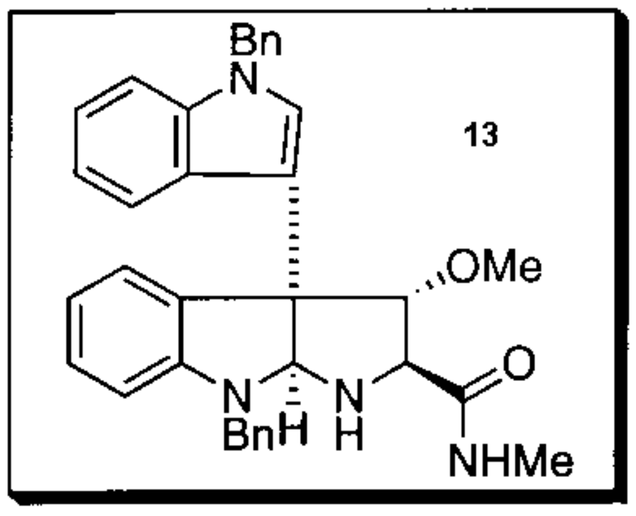
GB                          0
PC                       4.00

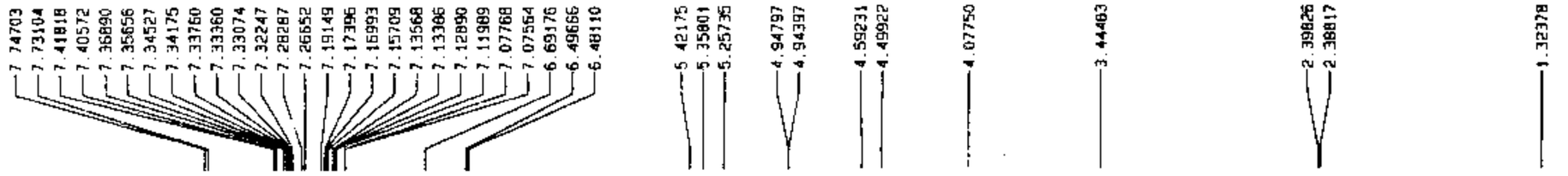
1D NMR plot parameters
CX                  22.80 cm
CY                   3.00 cm
F1P                11.000 ppm
F1                 5502.42 Hz
F2P                -1.000 ppm
F2                 -500.22 Hz
PPMCM             0.52632 ppm/cm
HZCM            263.27368 Hz/cm
```

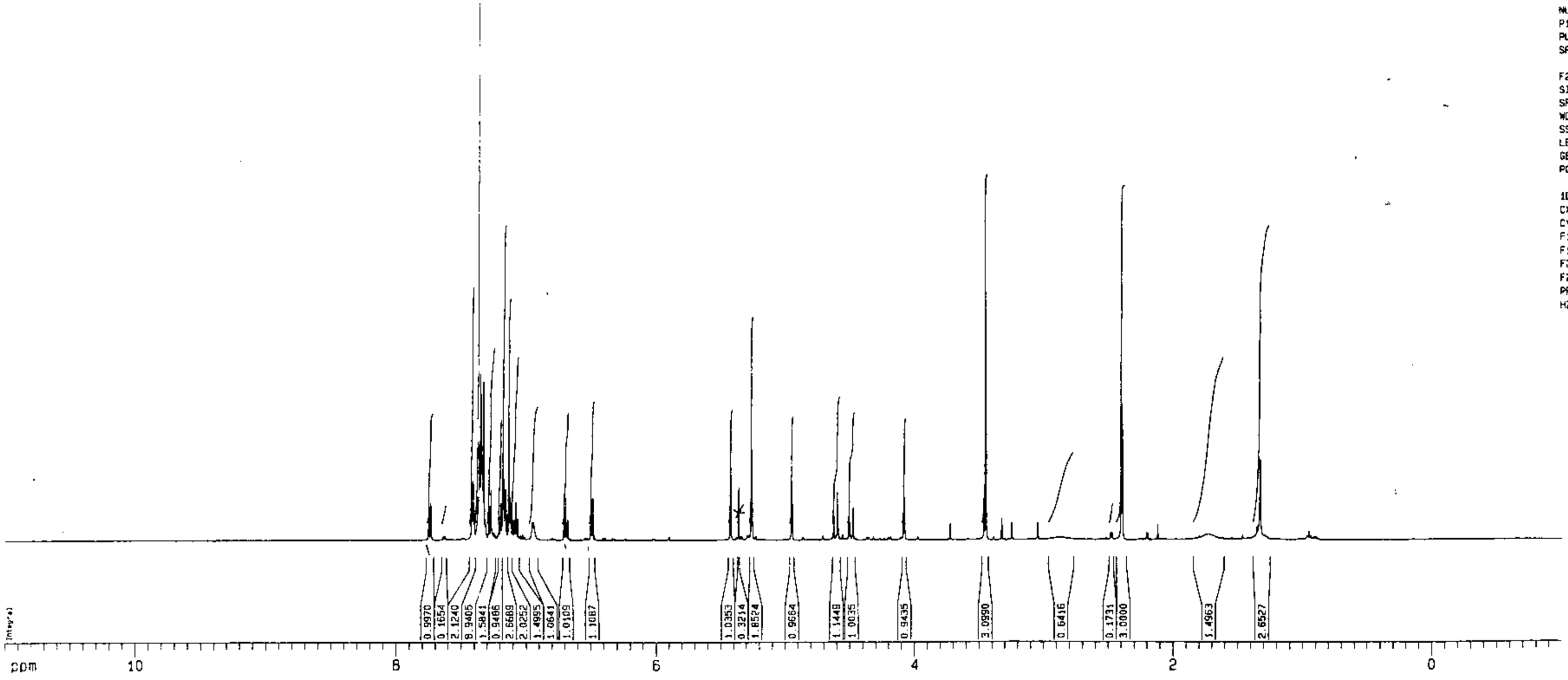


13C spectrum with 1H decoupling

1H spectrum







Current Data Parameters

USER	ysshin
NAME	yss082106
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

Date_	20060821
Time	17.45
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	81728
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.098043 Hz
AQ	5.0999398 sec
RG	5
DW	62.400 usec
DE	6.00 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	1H
P1	8.00 usec
PL1	1.60 dB
SFO1	500.2235015 MHz

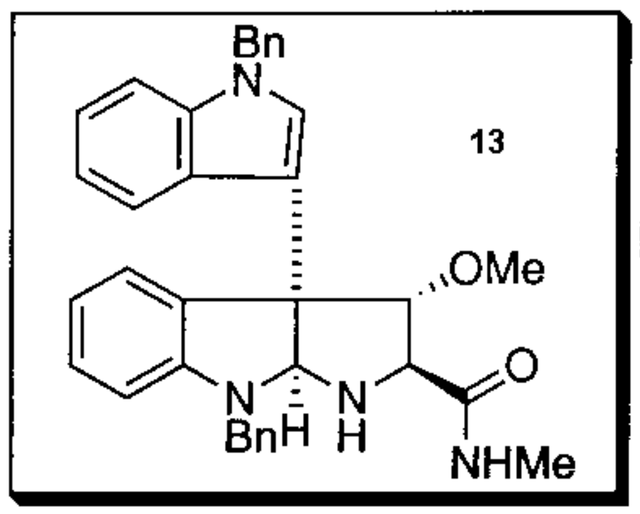
F2 - Processing parameters

SI	65536
SF	500.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	4.00

1D NMR plot parameters

CX	22.80 cm
CY	5.00 cm
F1P	11.000 ppm
F1	5502.42 Hz
F2P	-1.000 ppm
F2	-500.22 Hz
PPMCM	0.52632 ppm/cm
HZCM	263.27368 Hz/cm

13C spectrum with 1H decoupling



172.59
148.84
138.11
137.41
137.15
132.36
128.84
128.77
128.75
128.67
127.99
127.63
127.41
127.07
126.32
125.02
121.57
121.03
119.13
118.54
114.55
109.87
107.22
90.71
89.01
77.35
77.08
76.84
67.56
59.68
58.07
50.10
49.89
29.77
25.52

Current Data Parameters
USER ysshin
NAME yss082106
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060821
Time 18.18
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zgdc30
TD 65418
SOLVENT CDCl3
NS 1158
DS 4
SWH 30303.031 Hz
FIDRES 0.463222 Hz
AQ 1.0794635 sec
RG 13004
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 15.00 usec
PL1 -1.00 dB
SFO1 125.7942548 MHz

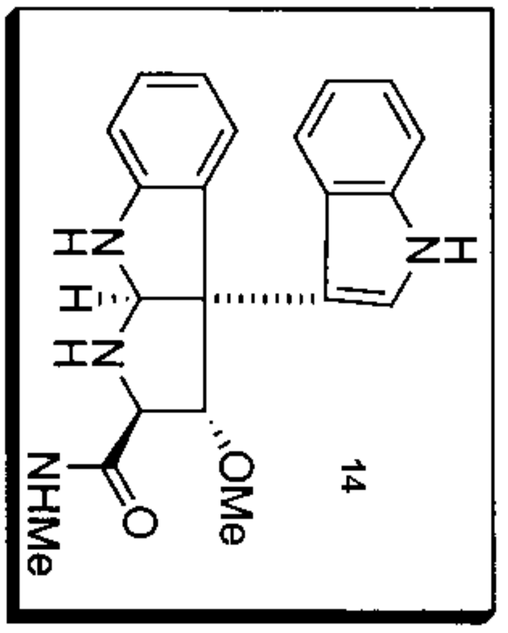
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 225.000 ppm
F1 28300.59 Hz
F2P -15.000 ppm
F2 -1886.71 Hz
PPMCM 10.52632 ppm/cm
HZCM 1324.00439 Hz/cm

ppm 200 150 100 50 0

1H spectrum



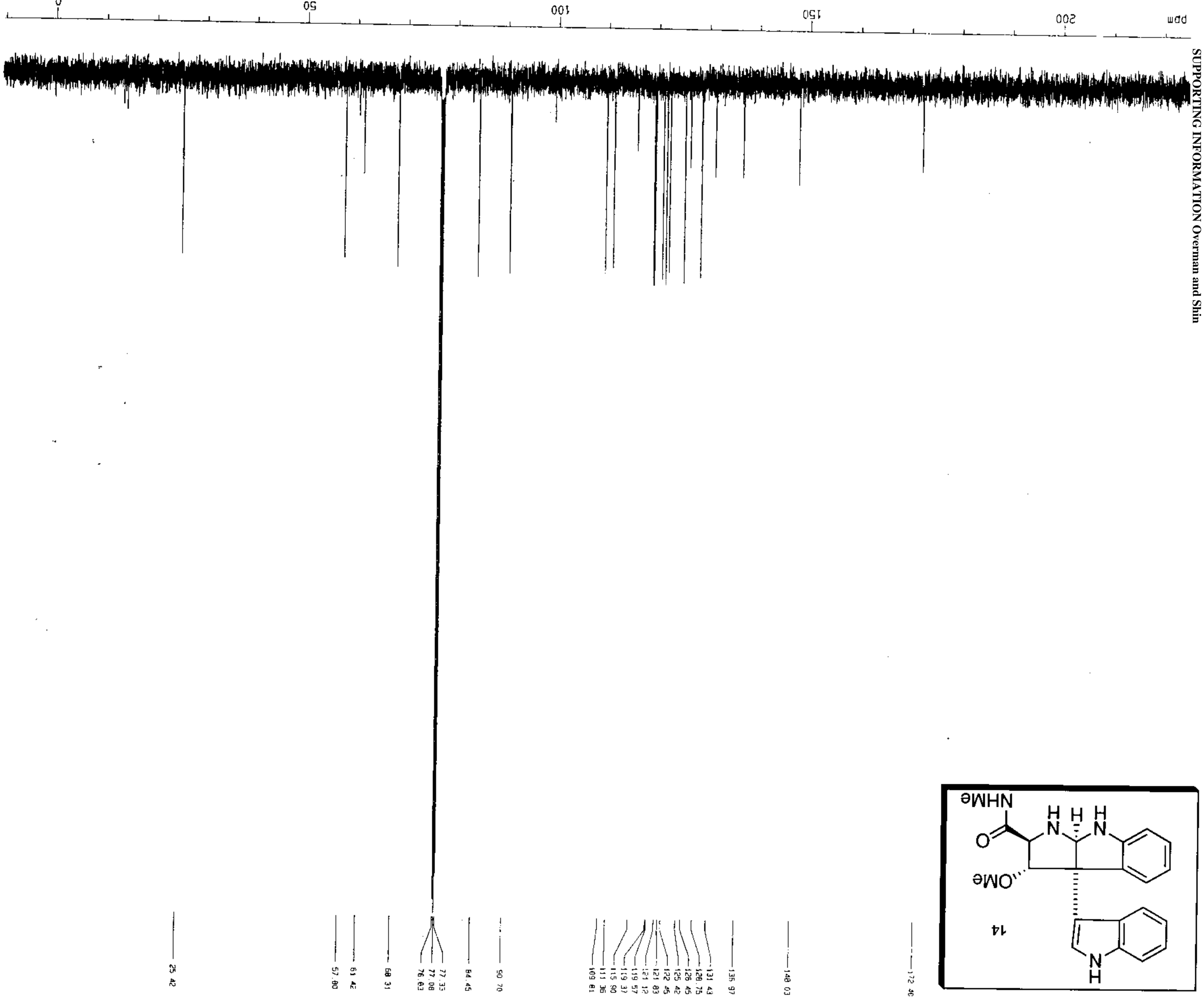
Current Data Parameters
USER1 vss8in
NAME vss080AE
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060804
Time 17.35
INSTRUM qnp500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0964544 sec
RG 256
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.0000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

----------- CHANNEL f1 ----------
NUC1 1H
P1 11.50 usec
PL1 3.00 dB
SFO1 499.9339955 MHz

F2 - Processing parameters
SI 65536
SF 499.9302003 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

ID NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 11.000 ppm
F1 5499.24 Hz
F2P 1.000 ppm
F2 -499.93 Hz
PPMCM 0.52632 ppm/cm
HZCM 263.12106 Hz/cm



13C spectrum with 1H decoupling


```
Current Data Parameters
USER            ysshin
NAME            ys508040б
EXPNO           2
PROCNO          1

F2 - Acquisition Parameters

Date_           20060804
Time            17.40
INSTRUM         gn500
PROBHD     5 mm broadband
PULPROG         zgdc30
TD              65536
SOLVENT         CDCl3
NS              207
DS              4
SWH             30303.031 Hz
FIDRES          0.462386 Hz
AQ              1.0814105 sec
RG              6502
DW              16.500 usec
DE              4.50 usec
TE              298.0 K
D1              0.25000000 sec
D11             0.03000000 sec
MCREST          0 000000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1            13C
P1              7.00 usec
PL1             0.00 dB
SF01            125 7213258 MHz

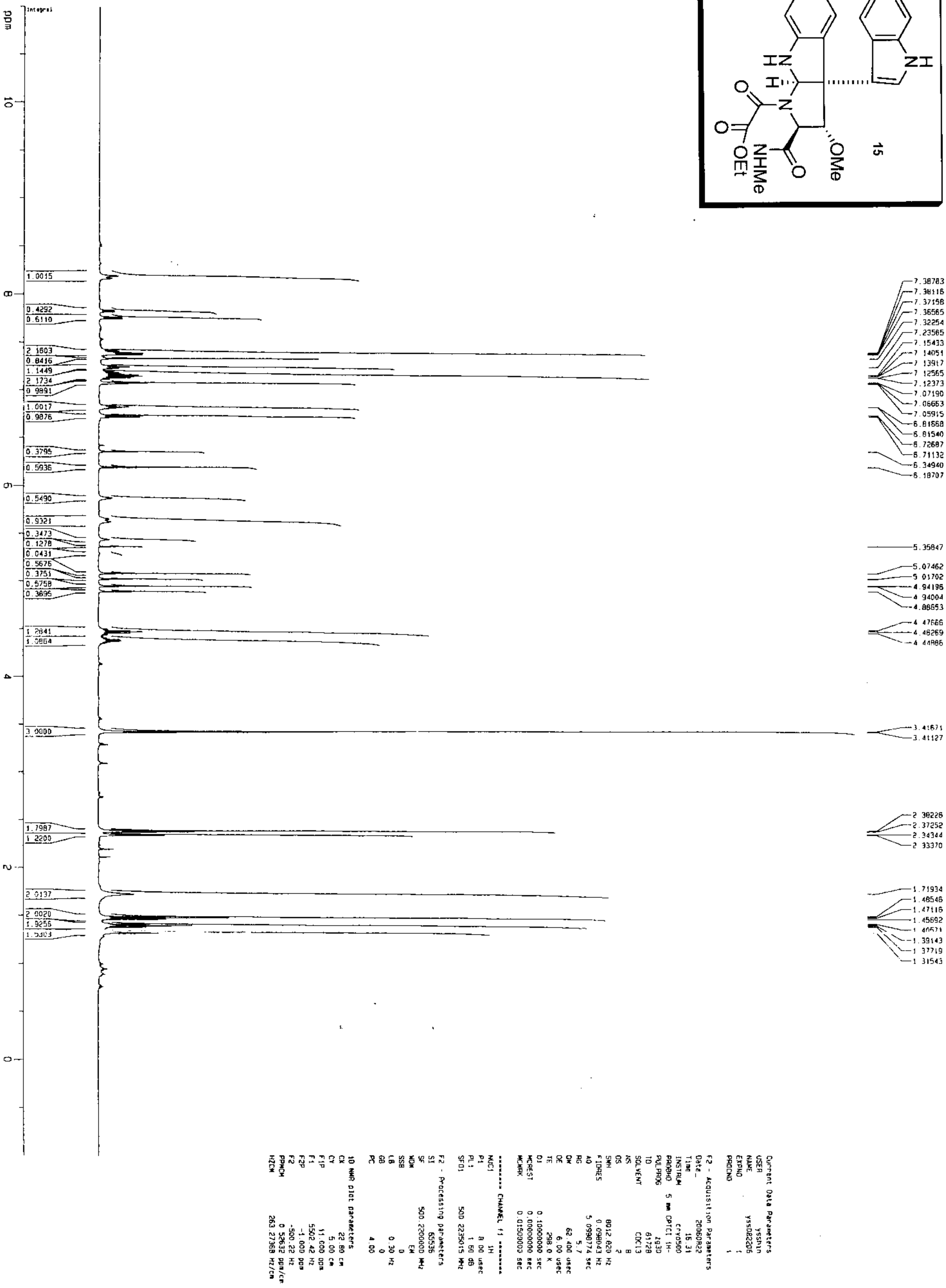
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2            1H
PCPD2           80.00 usec
PL2             15.00 dB
PL12            -3.00 dB
SF02            499.9324997 MHz

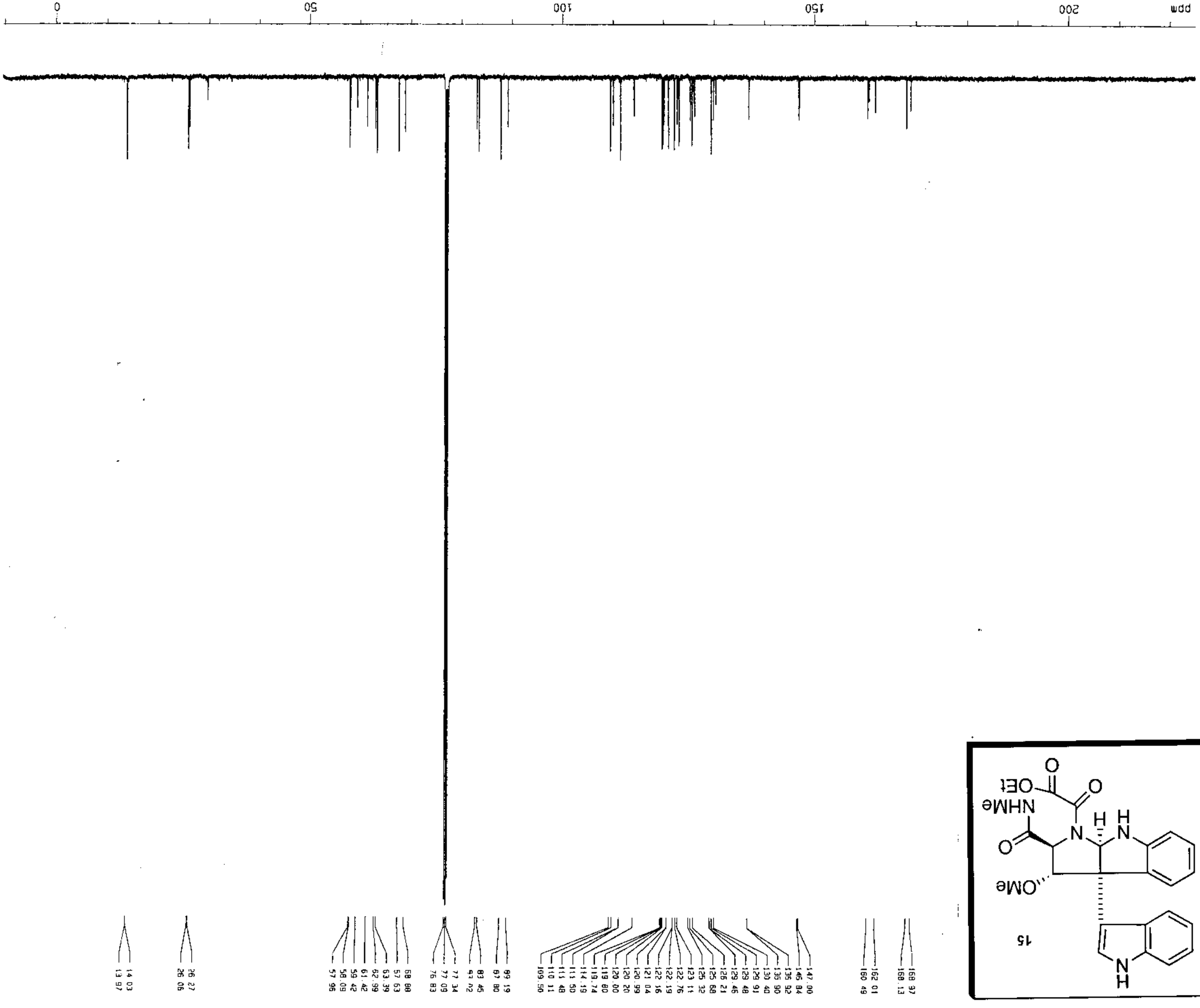
F2 - Processing parameters

SI              65536
SF              125.7074980 MHz
WDW             EM
SSB             0
LB              1.00 Hz
GB              0
PC              2.00

10 NMR plot parameters

CX              22.80 cm
CY              15.65 cm
F1P             225.000 ppm
F1              28284.19 Hz
F2P             -15.000 ppm
F2              -1885.61 Hz
PPMCM           10.52632 ppm/cm
HZCM            1323.23682 Hz/cm
```


1H spectrum
15
OMe
NHMe
OEt
7.38783
7.38116
7.37158
7.36565
7.32254
7.23565
7.15433
7.14051
7.13917
7.12565
7.12373
7.07190
7.06653
7.05915
6.81868
6.81540
6.72687
6.71132
6.34940
6.18707
5.35847
5.07462
5.01702
4.94195
4.94004
4.88653
4.47666
4.46269
4.44886
3.41671
3.41127
2.38226
2.37252
2.34344
2.33370
1.71934
1.48546
1.47116
1.45692
1.40571
1.39143
1.37719
1.31543
1.0015
0.4292
0.6110
2.1603
0.8416
1.1449
2.1734
0.9891
1.0017
0.9876
0.3795
0.5936
0.5490
0.9321
0.3473
0.1278
0.0431
0.5676
0.3751
0.5758
0.3896
1.2841
1.0864
3.0000
1.7987
1.2200
2.0137
2.0020
1.9256
1.5403
Current Data Parameters
USER yssnin
NAME yss082205
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060822
Time 15.31
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0980774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 1.50 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
CY 5.00 cm
F1P 11.000 ppm
F1 5502.42 Hz
F2P -1.000 ppm
F2 -500.22 Hz
PPMCM 0.52632 ppm/cm
HZCM 263.27368 Hz/cm



13C spectrum with 1H decoupling


```
Current Data Parameters
USER      yssnin
NAME      yss082206
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters

Date_     20060822
Time      16.53
INSTRUM   cry0500
PROBHD    5 mm CPTCI 1H-
PULPROG   zgdc30
TD        65418
SOLVENT   CDCl3
NS        1170
DS        4
SWH       30303.031 Hz
FIDRES    0.463252 Hz
AQ        1.0794470 sec
RG        11585.2
DW        16.500 usec
DE        6.00 usec
TE        298.0 K
D1        0.25000000 sec
D11       0.03000000 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

------- CHANNEL f1 --------

NUC1      13C
P1        15.00 usec
PL1       -1.00 dB
SFO1      125.7942548 MHz

------- CHANNEL f2 --------

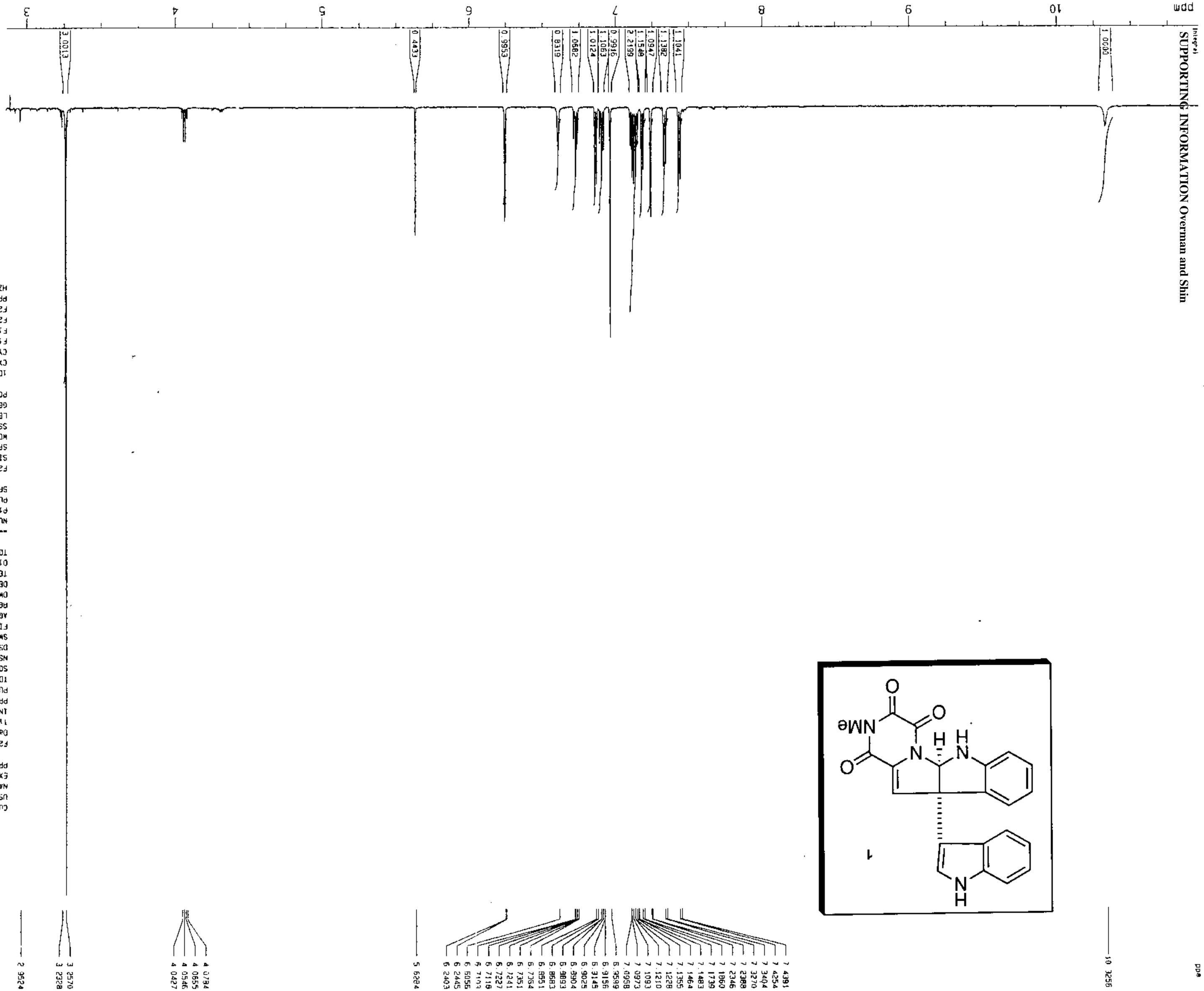
CPDPRG2   waltz16
NUC2      1H
PCPD2     100.00 usec
PL2       1.60 dB
PL12      23.54 dB
SFO2      500.22250311 MHz

F2 - Processing parameters

SI        65536
SF        125.78041.90 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        2.00

1D NMR plot parameters

CX        22.80 cm
CY        15.55 cm
F1P       225.000 ppm
F1        28300.59 Hz
F2P       -15.000 ppm
F2        -1886.71 Hz
PPMCM     10.52632 ppm/cm
HZCM      1324.00439 Hz/cm
```



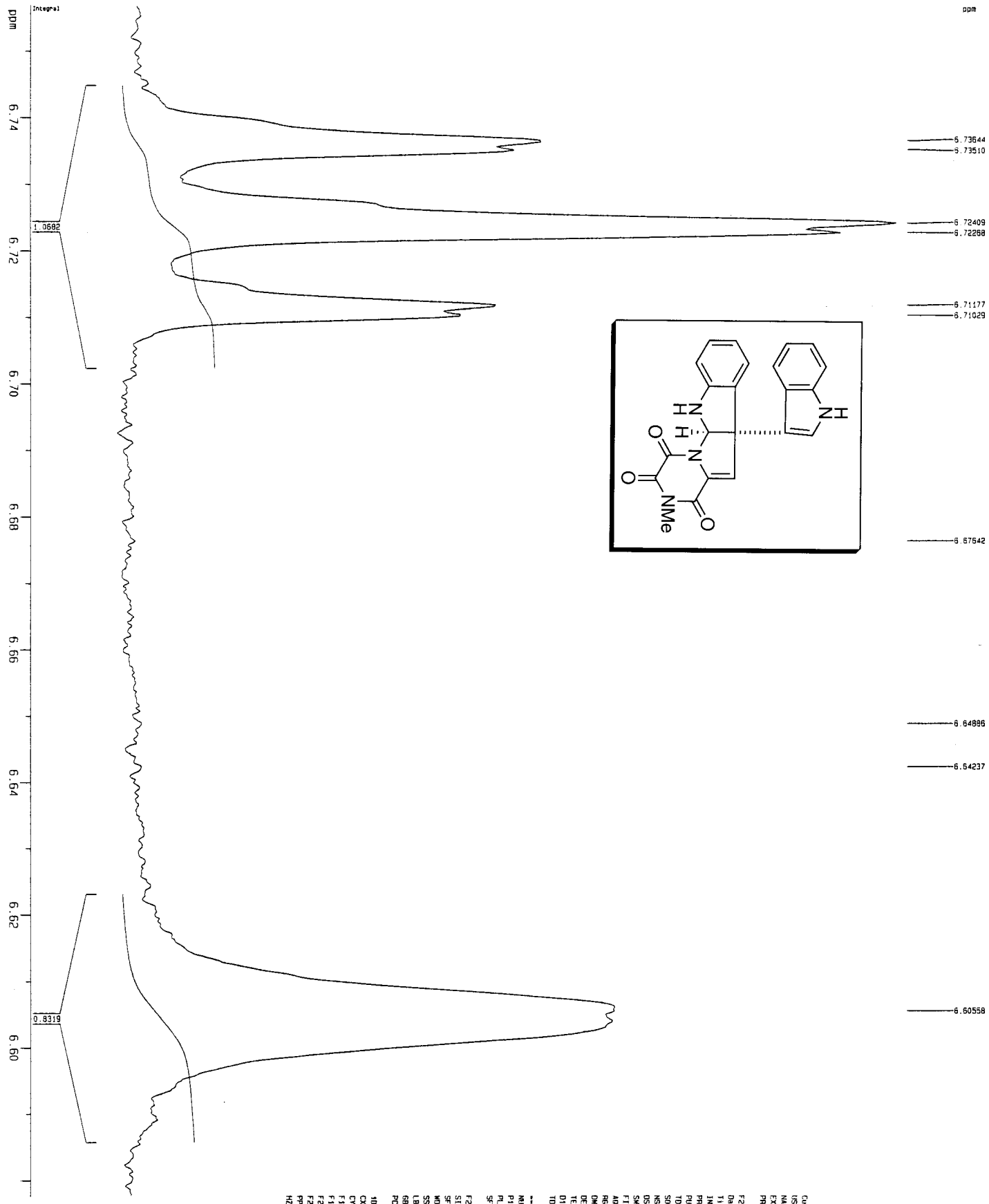

```
Current Data Parameters
USER      gtan15
NAME      ys5449
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_          20060818
Time           13.11
INSTRUM        av600
PROBHD     5 mm TBI 1H/13
PULPROG        zg30
TD             97598
SOLVENT        Acetone
NS             8
DS             2
SWH        9615.385 Hz
FIDRES     0.058178 Hz
AQ         5.0928259 sec
RG             456
DW         52.000 usec
DE         6.00 usec
TE         298.0 K
D1         0.10000000 sec
TD1            1

======== CHANNEL f1 ========
NUC1           1H
P1         8.00 usec
PL1        -1.00 dB
SFO1       600.1342009 MHz

F2 - Processing parameters
SI             65536
SF         600.1300134 MHz
WDW            EM
SSB            0
LB         0.30 Hz
GB             0
PC         1.00

1D NMR plot parameters
CX         22.80 cm
CY         15.00 cm
F1P        10.965 ppm
F1         6580.38 Hz
F2P        2.856 ppm
F2         1713.97 Hz
PPMCM      0.35565 ppm/cm
HZCM       213.43910 Hz/cm
```



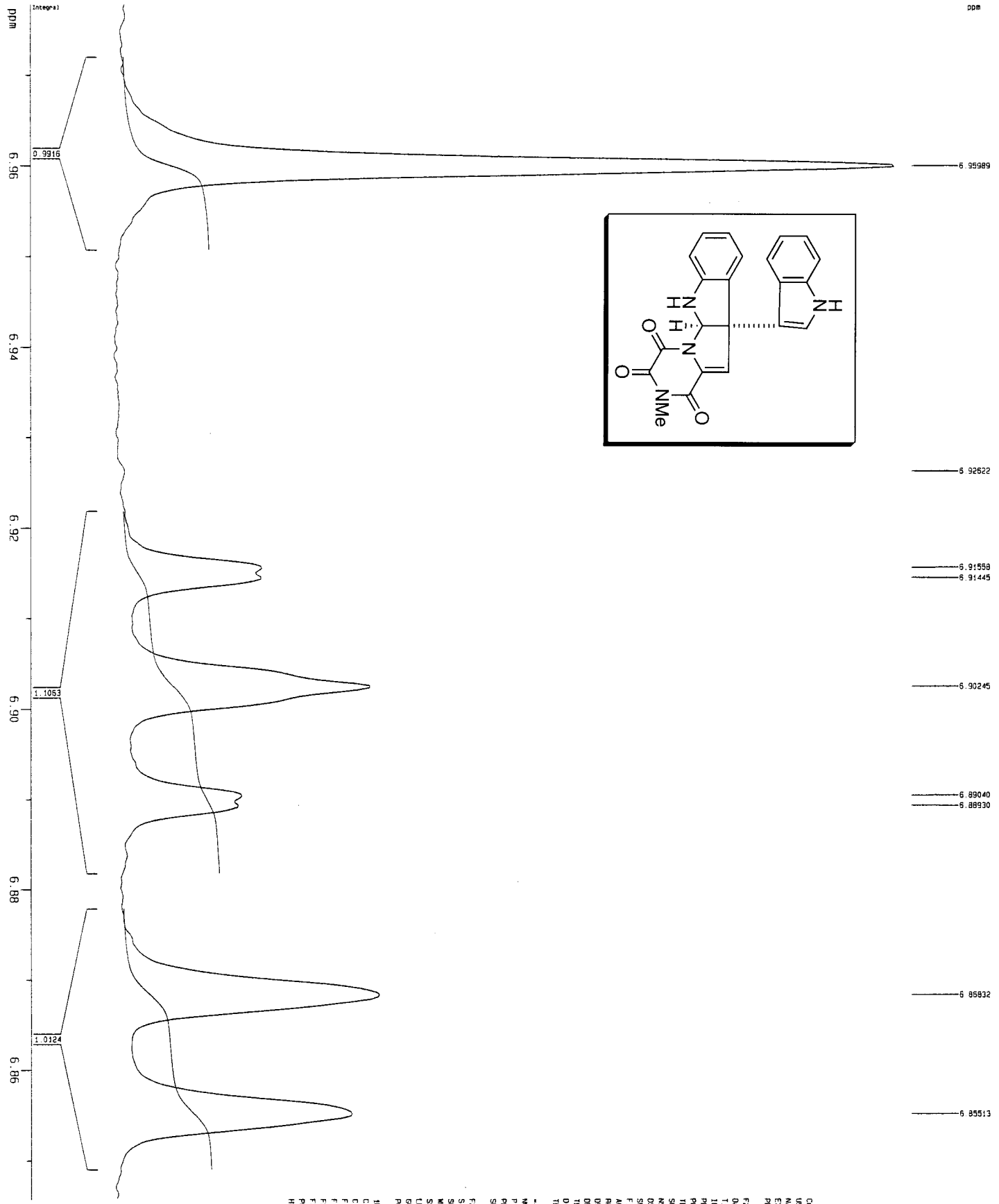

```
Current Data Parameters
USER                 ptanis
NAME                 yss449
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060818
Time                 13.11
INSTRUM              av600
PROBHD     5 mm TBI 1H/13
PULPROG              zg30
TD                   97938
SOLVENT              Acetone
NS                       8
DS                       2
SWH              9615.385 Hz
FIDRES           0.098176 Hz
AQ               5.0928259 sec
RG                     456
DW                52.000 usec
DE                 6.00 usec
TE                 298.0 K
D1                 0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.00 usec
PL1                -1.00 dB
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                   65536
SF           600.1300134 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                6.757 ppm
F1                 4055.04 Hz
F2P                6.578 ppm
F2                 3947.38 Hz
PPMCM           0.00787 ppm/cm
HZCM            4.72225 Hz/cm
```




```
Current Data Parameters
USER                ptanis
NAME                ys5449
EXPNO                    2
PROCNO                   1

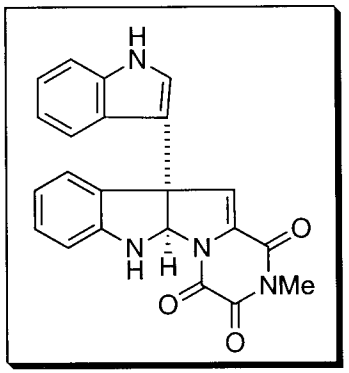
F2 - Acquisition Parameters
Date_            20060818
Time                13.11
INSTRUM             av600
PROBHD  5 mm TBI 1H/13
PULPROG             zg30
TD                 97930
SOLVENT           Acetone
NS                       8
DS                       2
SWH              9615.385 Hz
FIDRES           0.098178 Hz
AQ               5.0928259 sec
RG                     456
DW                52.000 usec
DE                 6.00 usec
TE                298.0 K
D1                 0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -1.00 dB
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                   65536
SF           600.1300134 MHz
WDW                      EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  6.978 ppm
F1                4187.64 Hz
F2P                  6.846 ppm
F2                4108.28 Hz
PPMCM             0.00580 ppm/cm
HZCM              3.48077 Hz/cm
```

gliocladin c



ppm

7.18537
7.17389
7.13547
7.12275
7.12102
7.10928
7.09731
7.09581

Current Data Parameters
USER ptanis
NAME yss449
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060818
Time 13.11
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 97938
SOLVENT Acetone
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098178 Hz
AQ 5.0928259 sec
RG 456
DW 52.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -1.00 dB
SF01 600.1342009 MHz

F2 - Processing parameters
SI 65536
SF 600.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

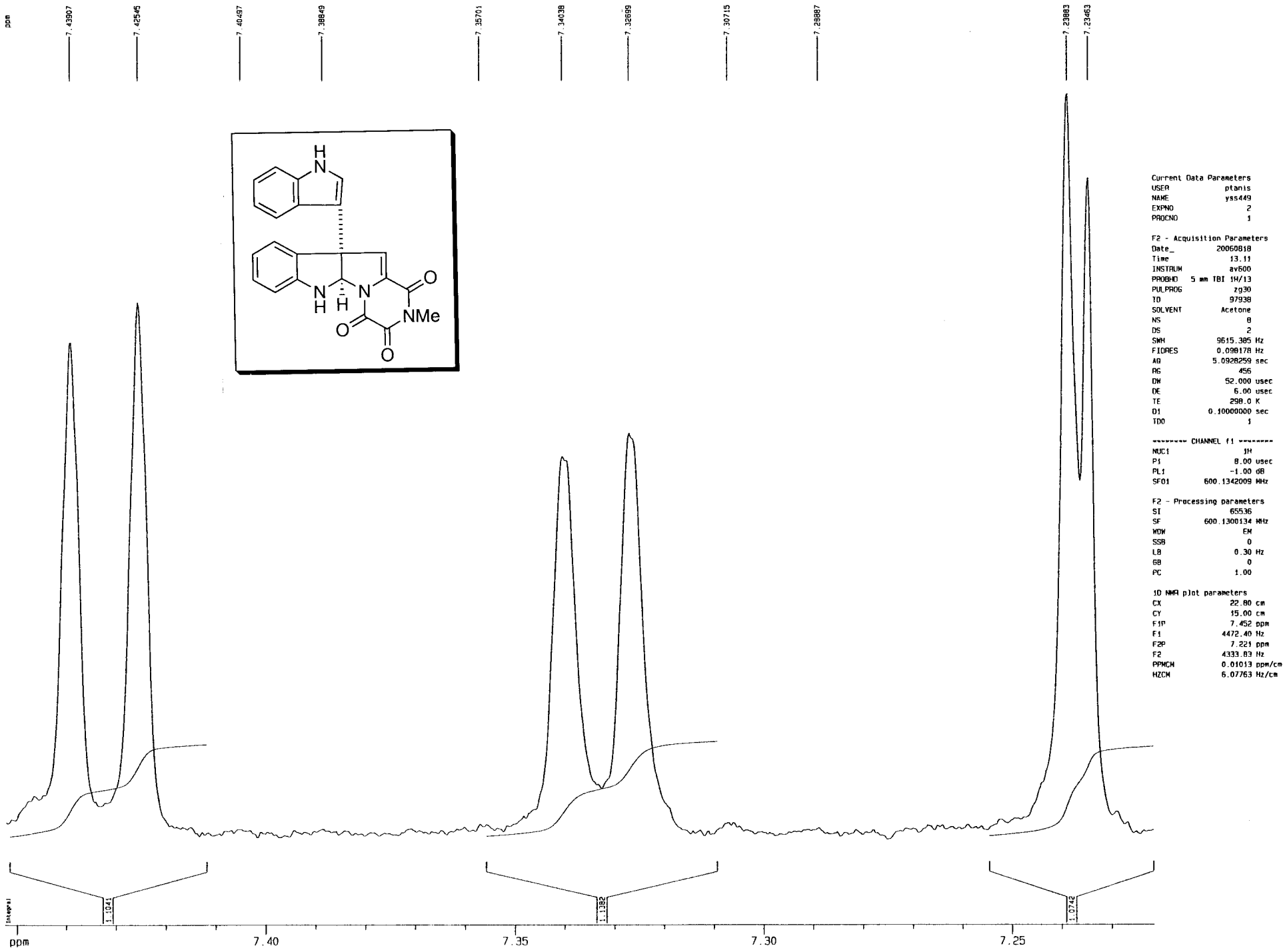
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 7.204 ppm
F1 4323.58 Hz
F2P 7.082 ppm
F2 4250.17 Hz
PPMCM 0.00537 ppm/cm
HZCM 3.21994 Hz/cm

Integral

1.1548
2.2199

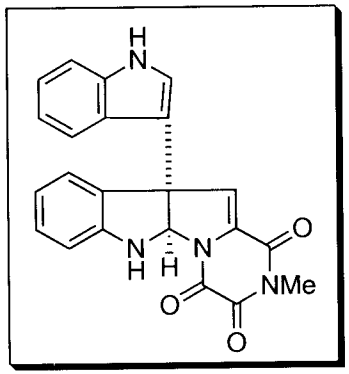
ppm
7.18
7.16
7.14
7.12
7.10

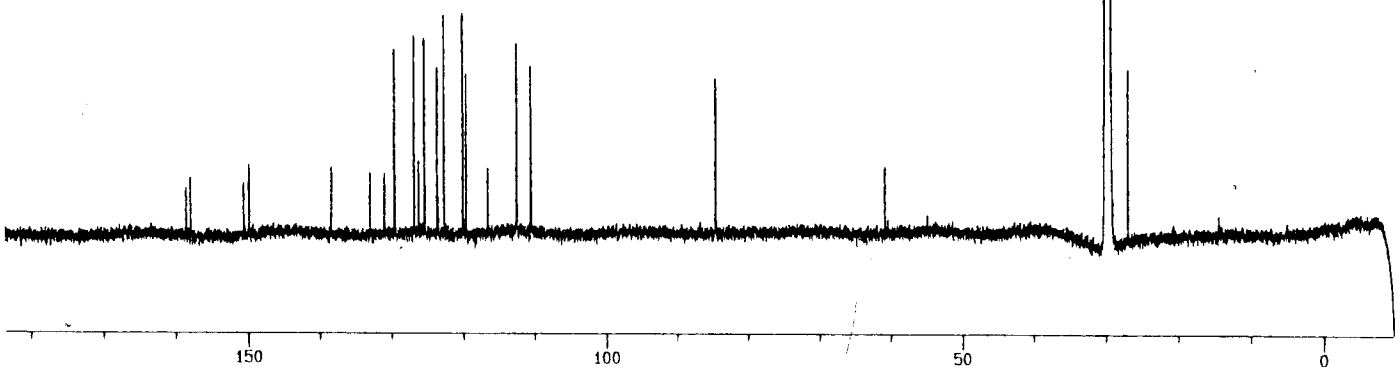
gliocladin c



YSS 447

13C spectrum with 1H decoupling






```
Current Data Parameters
USER            ysshin
NAME            yss081506
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20060815
Time               8.37
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          zgdc30
TD                65418
SOLVENT             CDCl3
NS                20314
DS                   4
SWH          30303.031 Hz
FIDRES        0.463222 Hz
AQ            1.0794470 sec
RG               5160.6
DW              16.500 usec
DE               6.00 usec
TE              298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

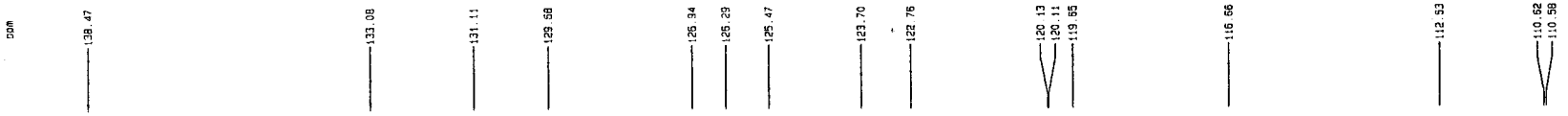
======== CHANNEL f1 ========
NUC1               13C
P1               15.00 usec
PL1              -1.00 dB
SF01        125.7942548 MHz

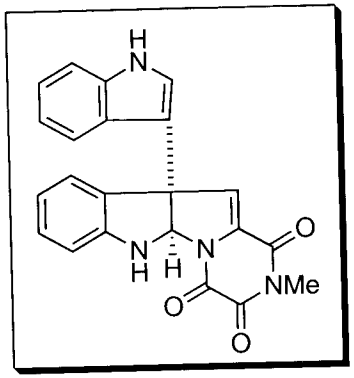
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           100.00 usec
PL2              1.60 dB
PL12            23.54 dB
SF02        500.2225011 MHz

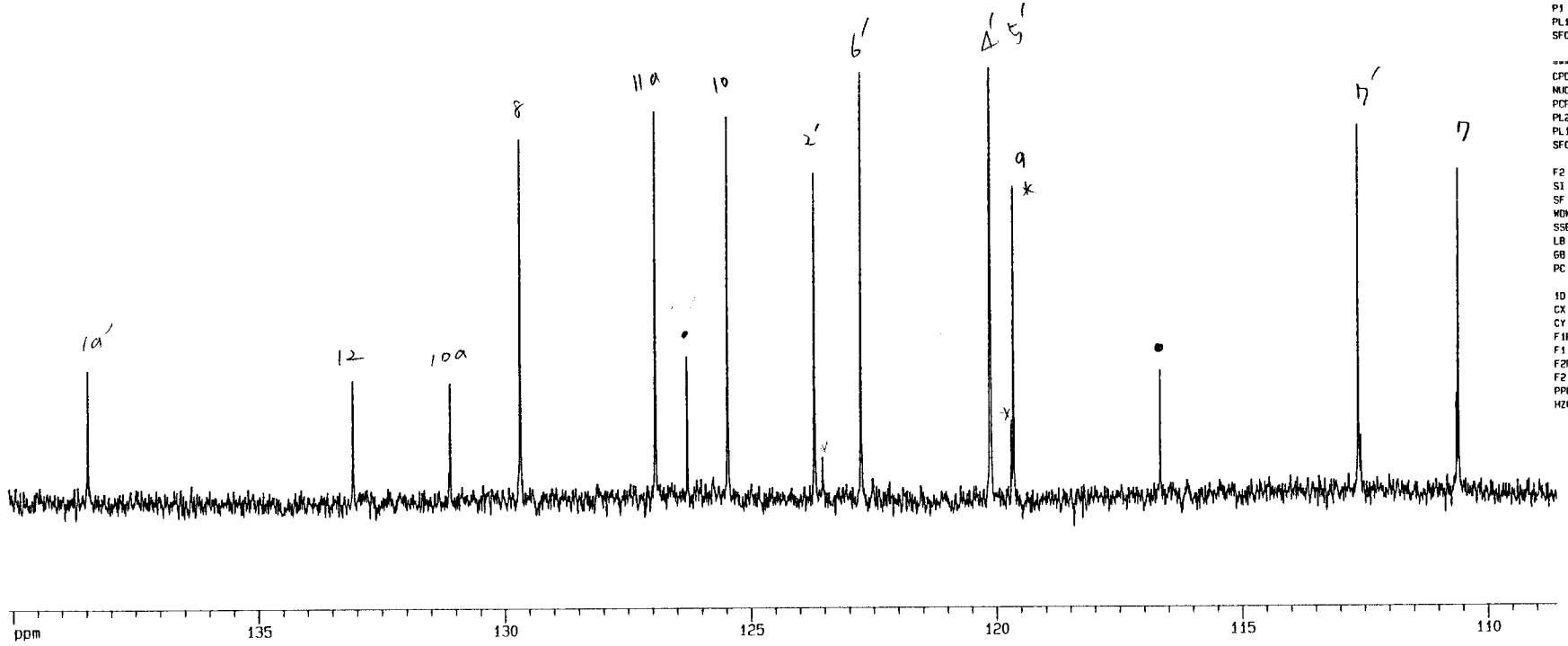
F2 - Processing parameters
SI                65536
SF          125.7803105 MHz
WDW                EM
SSB                0
LB              1.00 Hz
GB                 0
PC              2.00

1D NMR plot parameters
CX              22.80 cm
CY             700.00 cm
F1P            225.000 ppm
F1           28300.57 Hz
F2P            -15.000 ppm
F2           -1886.70 Hz
PPMCM          10.52632 ppm/cm
HZCM         1324.00330 Hz/cm
```

13C spectrum with 1H decoupling








```
Current Data Parameters
USER                ysshin
NAME             yss081506
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060815
Time                 0.37
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zgdc30
TD                 65410
SOLVENT             CDCl3
NS                  20314
DS                      4
SWH           30303.031 Hz
FIDRES        0.463222 Hz
AQ            1.0794470 sec
RG                5160.6
DW               16.500 usec
DE                6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

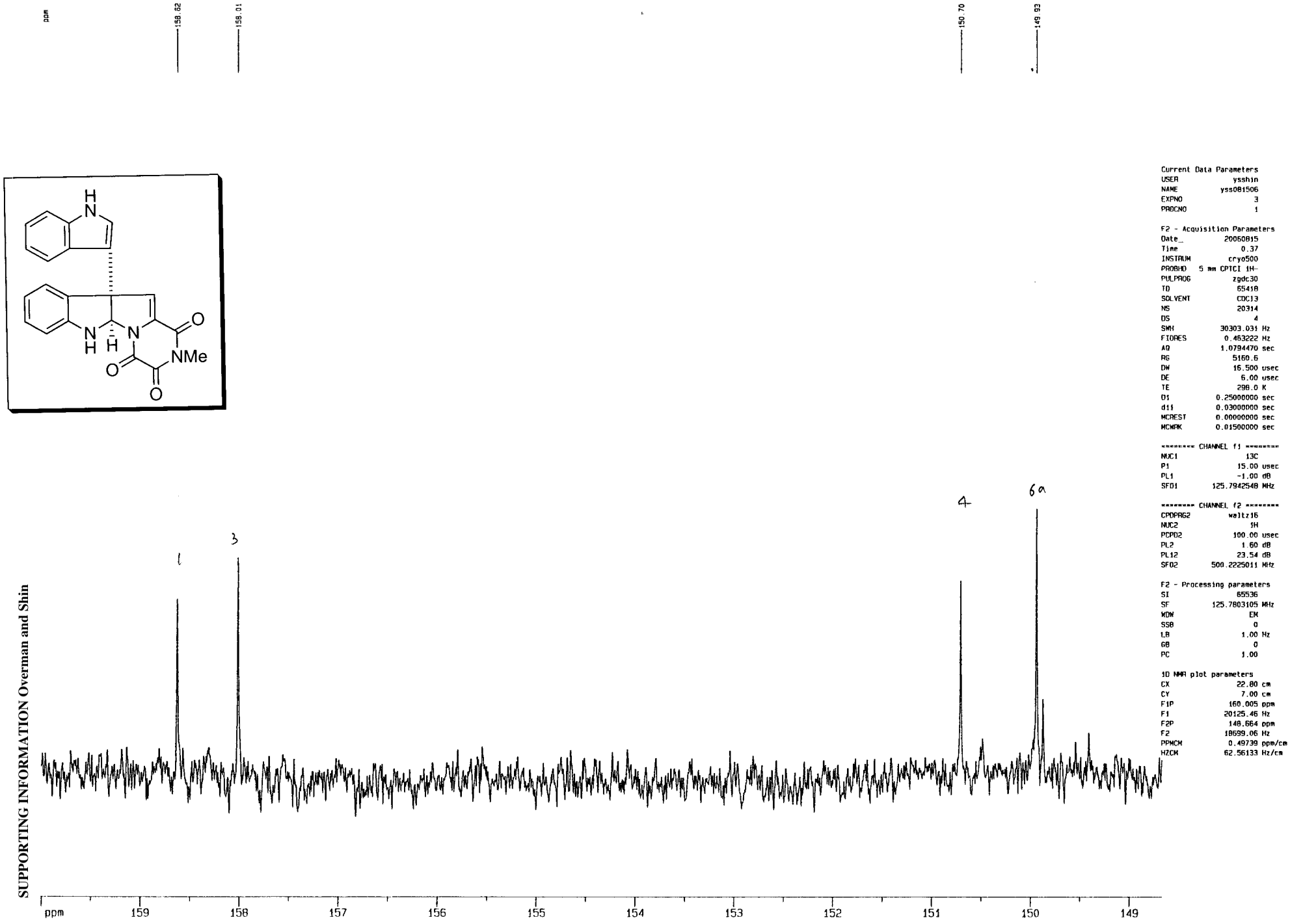
======== CHANNEL f1 ========
NUC1                 13C
P1                15.00 usec
PL1                -1.00 dB
SFO1         125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2         500.2225011 MHz

F2 - Processing parameters
SI                  65536
SF           125.7803105 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  7.00 cm
F1P               140.100 ppm
F1                17621.80 Hz
F2P               108.593 ppm
F2                13658.92 Hz
PPMCM              1.38186 ppm/cm
HZCM             173.81053 Hz/cm
```

13C spectrum with 1H decoupling

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Current Data Parameters
USER                ysshin
NAME             yss081506
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20060815
Time                 0.37
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zgdc30
TD                  65418
SOLVENT             CDCl3
NS                  20314
DS                      4
SWH           30303.031 Hz
FIDRES         0.463222 Hz
AQ             1.0794470 sec
RG                5160.6
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                15.00 usec
PL1               -1.00 dB
SFO1         125.7942548 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2         500.2225011 MHz

F2 - Processing parameters
SI                  65536
SF           125.7803105 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  7.00 cm
F1P              160.005 ppm
F1             20125.46 Hz
F2P              148.664 ppm
F2             18599.06 Hz
PPMCM           0.49739 ppm/cm
HZCM           62.56133 Hz/cm
```
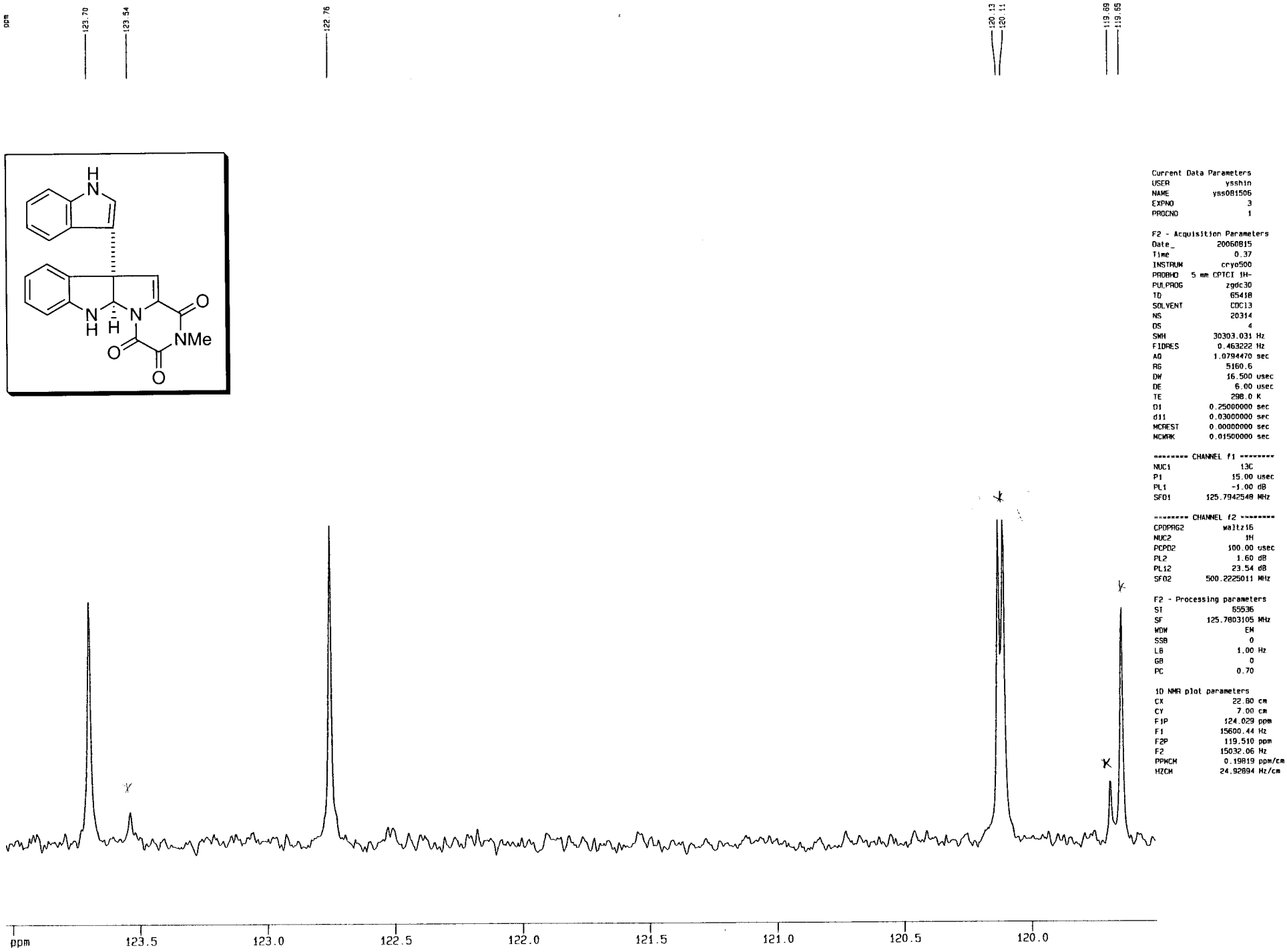
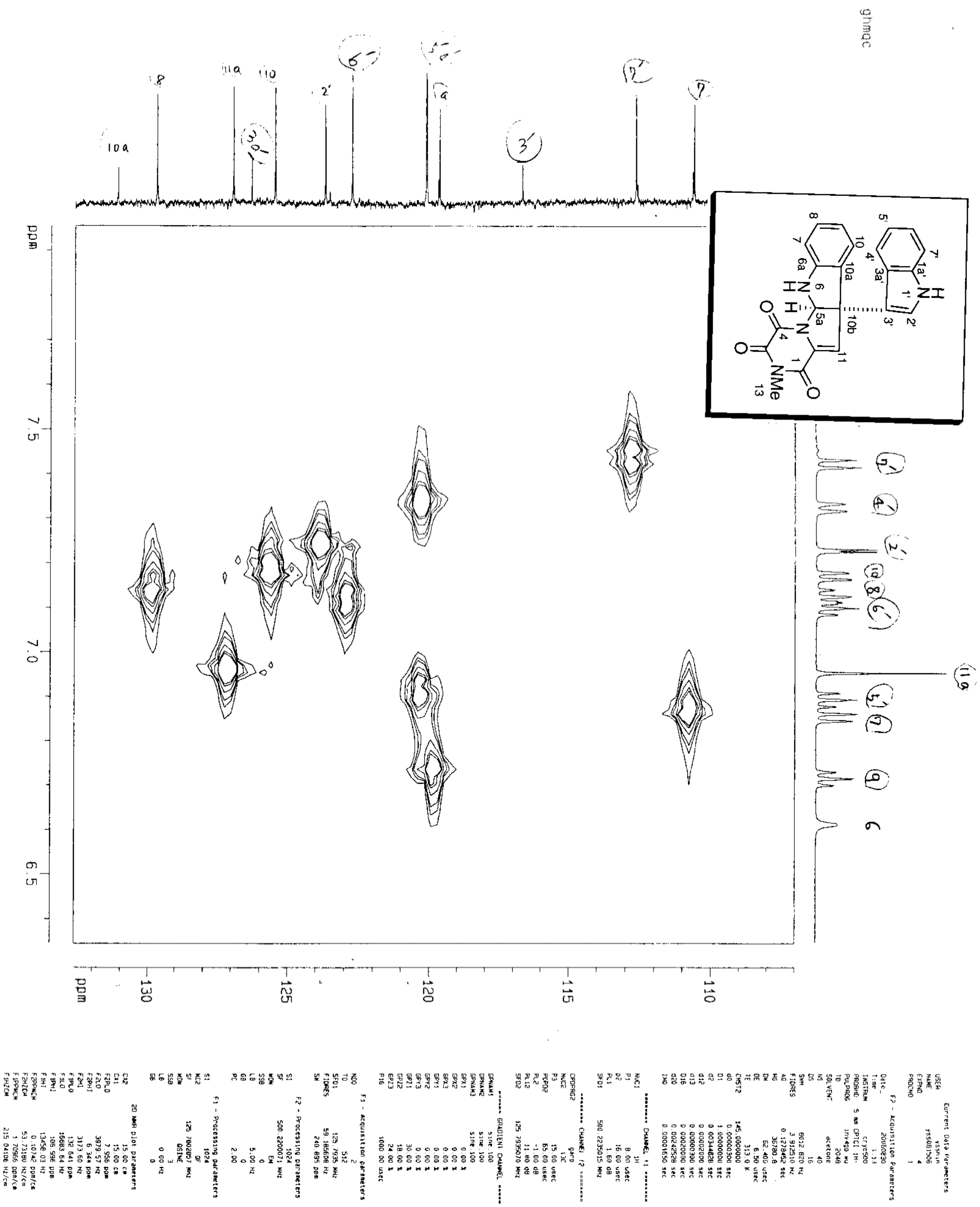
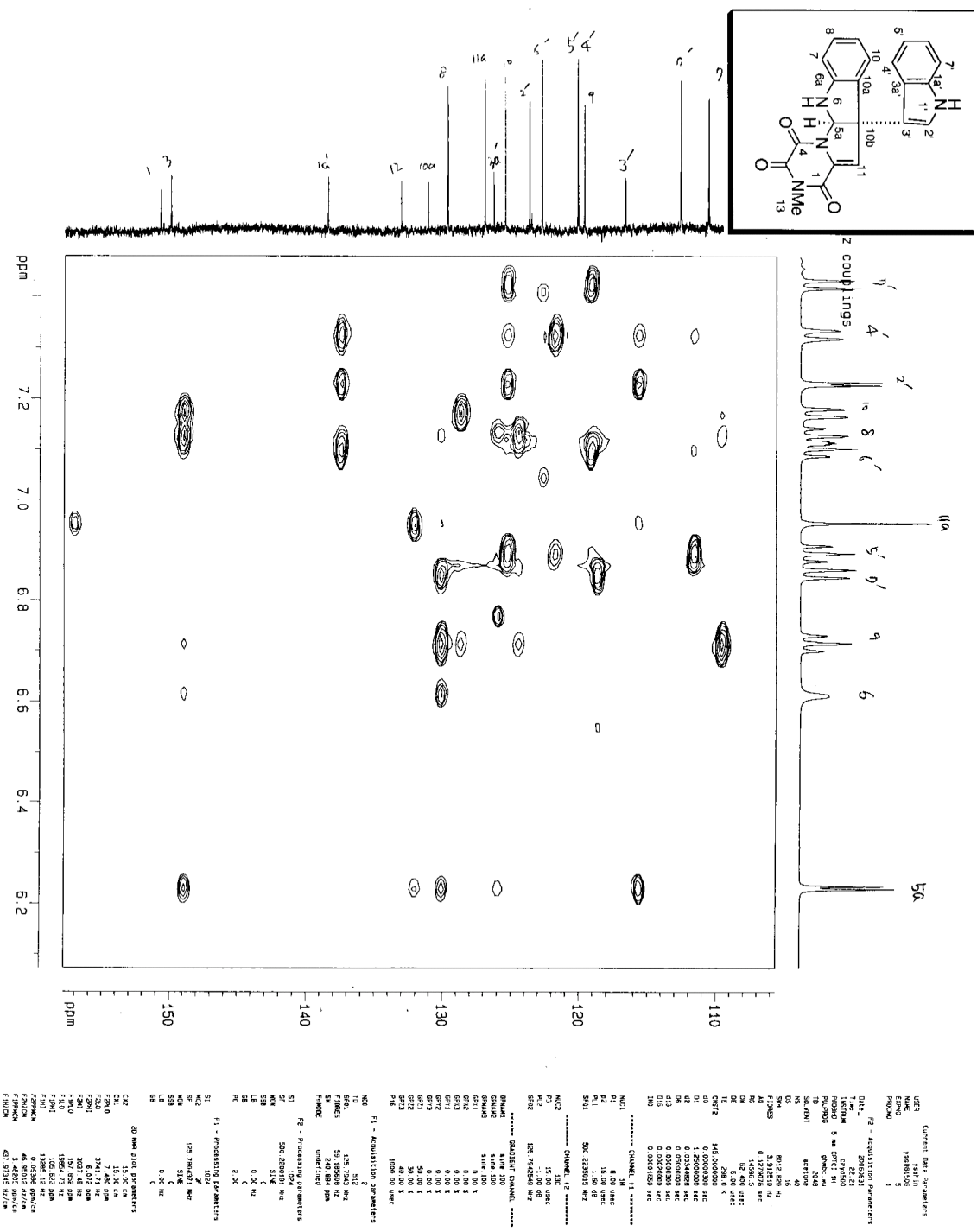
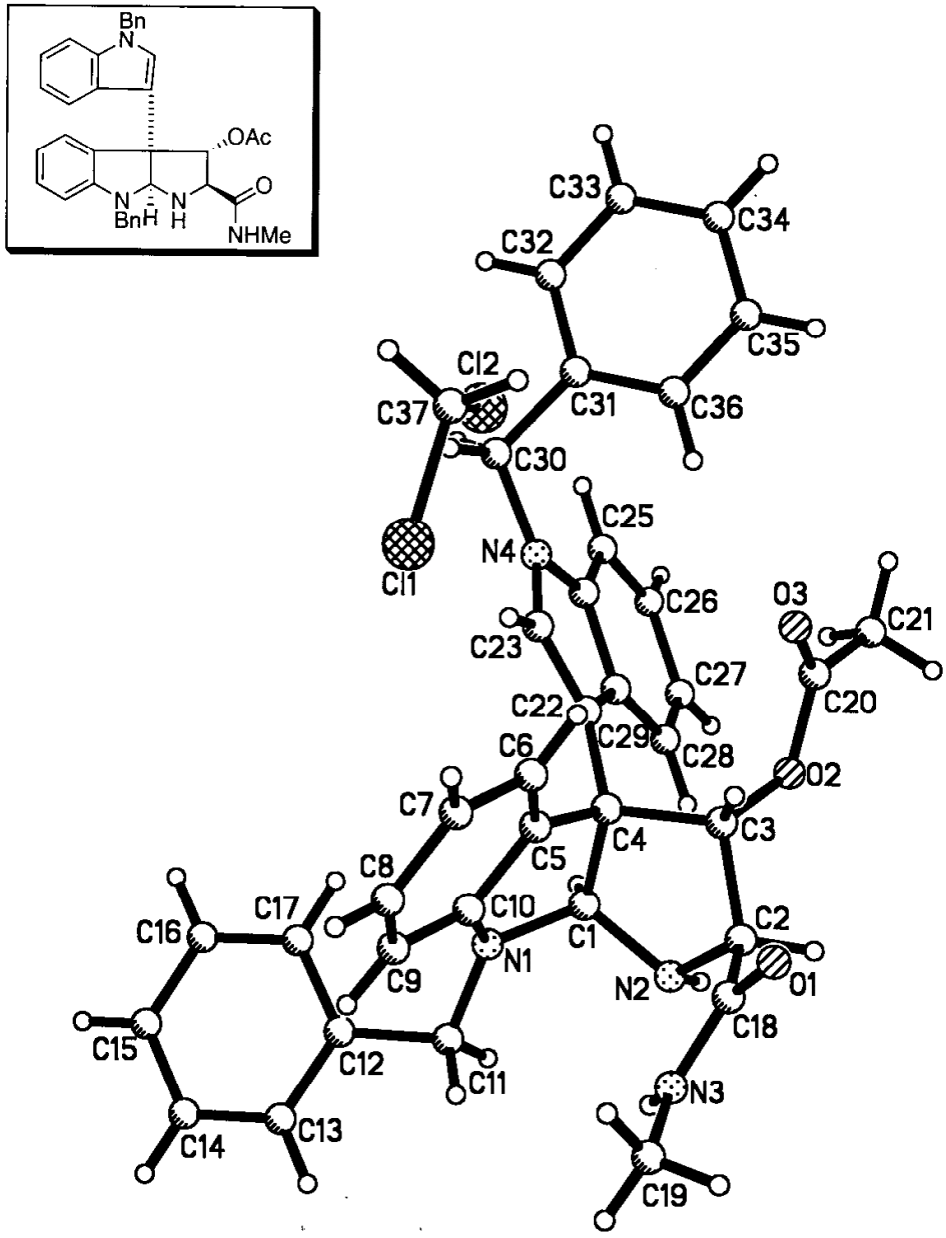

13C spectrum with 1H decoupling




ghmqc
ppm
130
125
120
115
110
7.5
7.0
6.5


ppm
7.2
7.0
6.8
6.6
6.4
6.2
150
140
130
120
110
z couplings
NMe
13


Bn
N
OAc
N
BnH
N
H
O
NHMe
C33
C34
C32
C35
Cl2
C37
C31
C36
C30
C25
N4
Cl1
C26
O3
C21
C23
C27
C20
C22
C29
C28
C6
O2
C7
C4
C3
C5
C8
C17
C10
C1
C2
C16
C9
N1
N2
O1
C18
C15
C12
C11
N3
C13
C14
C19