Supporting Information for

Allenyl Azide Cycloaddition Chemistry: Application to the Total Synthesis of (±)-Meloscine

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General Experimental

Unless otherwise stated all, moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under a nitrogen atmosphere. Dry acetonitrile, dichloromethane, diethyl ether, tetrahydrofuran, toluene, and triethylamine were obtained by passing these solvents through activated alumina columns. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Thin layer chromatography was carried out on EMD 0.25 mm silica gel plates with UV visualization or by potassium permanganate or ceric ammonium molybdate stain. Purification of products via flash chromatography[1] was performed with 40-63 µm silica gel and the solvent system indicated. Melting points are uncorrected. High resolution mass spectra were obtained according to the specified technique and were performed at the Pennsylvania State University Proteomics and Mass Spectrometry Core Facility, University Park, PA. X-Ray data was obtained at Pennsylvania State University X-Ray Crystallography Facility, University Park, PA.

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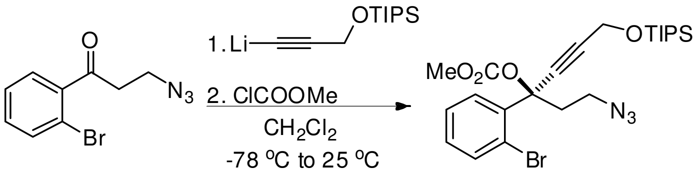
[1] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923-2925.



12 **13**

1-Azido-3-(2-bromophenyl)-6-(triisopropylsilyloxy)hex-4-yn-3-yl Methyl Carbonate (13). A solution of triisopropyl(prop-2-ynyloxy)silane[2] (9.78 g, 46.0 mmol) in CH_2Cl_2 (150 mL) was cooled to -78 °C and *n*-butyllithium (2.5 M in hexanes, 18.4 mL, 46.0 mmol) was added dropwise. The reaction mixture was stirred for 1.5 h at -78 °C, after which time a solution of 3-azido-1-(2-bromophenyl)propan-1-one[3] (**12**) (9.00 g, 35.4 mmol) in CH_2Cl_2 (150 mL) was added by canula. The mixture was stirred for 18 h, warming to 25 °C. The mixture was cooled to 0 °C and methyl chloroformate (11.7 g, 123 mmol, 9.58 mL) was added dropwise. The cooling bath was removed and the solution was allowed to stir for 18 h. Water (100 ml) was added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 150 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give a dark yellow oil which was purified by column chromatography on SiO_2 (5% ethyl acetate in hexanes) to give carbonate **13** as a pale yellow oil (14.0 g, 84%). IR (thin film) 2099, 1762 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.9, 1.7 Hz, 1H), 7.59 (dd, J = 7.9, 1.3 Hz, 1H), 7.33 (dt, J = 7.6, 1.3 Hz, 1H), 7.18 (td, J = 7.6, 1.7 Hz, 1H), 4.57 (s, 2H), 3.73 (s, 3H), 3.60 (m, 1H), 3.41 (m, 1H), 2.82 (m, 1H), 2.47 (m, 1H), 1.21-1.05 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.7, 137.0, 135.6, 130.4, 130.0, 127.3, 118.8, 89.1,

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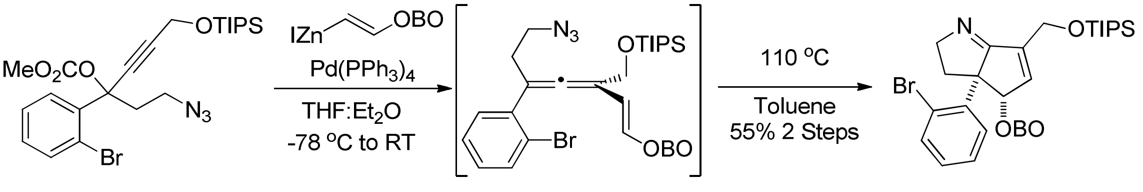
[2] Keck, D.; Vanderheiden, S.; Bräse, S. *Eur. J. Org. Chem.* **2006**, *21*, 4916-4923.

[3] Feldman, K. S.; Iyer, M. R.; López, C. S.; Faza, O. N. *J. Org. Chem.* **2008**, *73*, 5090-5099.

80.8, 80.0, 54.8, 52.0, 47.2, 38.9, 17.9, 11.9; HRMS (TOF MS ES+) [M+NH_4^+] calcd for $C_{23}H_{38}N_4O_4SiBr$ 541.1846, found 541.1866.



13 **10** **8**

3a-(2-Bromophenyl)-4-(4-methyl-2,6,7-trioxa-bicyclo[2.2.2]octan-1-yl)-6-((triisopropylsilyloxy)methyl)-2,3,3a,4-tetrahydrocyclopenta[b]pyrrole (8). A solution of 1-[(*E*)-2-iodoethenyl]-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane[4] (0.200 g, 0.709 mmol) in Et_2O (3 mL) was cooled to -78 °C and *tert*-butyllithium (1.7 M in *n*-pentane, 2.0 mL, 2.0 mmol) was added dropwise. The reaction mixture was stirred for 1 h, at which time a solution of zinc chloride (0.106 g, 0.780 mmol) in THF (3 mL) was added via cannula. The cooling bath was removed and the solution was allowed to warm to 25 °C and then stirred for 1 h. A solution of $Pd(PPh_3)_4$ (0.041 g, 0.036 mmol) in THF (1 mL) and carbonate **13** in THF (1 mL) were added sequentially via cannula. The reaction mixture was stirred at 25 °C until TLC (10:90 ethyl acetate:hexanes) indicated that the starting material was consumed. The reaction mixture was poured into a separatory funnel containing ice and saturated aqueous ammonium chloride (10 ml). The organic layer was drawn off and the aqueous layer was extracted with Et_2O (3 x 5 ml), washed with brine (1 x 10 ml) and dried over Na_2SO_4. The solution was filtered and concentrated in *vacuo* at a bath temperature not exceeding 40 °C to give crude unstable allene **10**.

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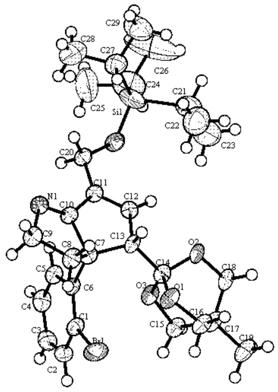
[4] Su, Y.; Jung, Y.; Seo, S.; Min, K.; Shin, D.; Lee, Y.; Kim, S.; Park, H. *J. Org. Chem.* **2002**, *67*, 4127-4137.

The crude allene mixture was dissolved in toluene (75 mL, 0.003 M) and sparged with a stream of nitrogen for 30 minutes. The solution was heated to 110 °C for 1.5 h and then concentrated *in vacuo*. The residue was purified by column chromatography on SiO_2 (5% to 10% to 20 % EtOAc/3% triethylamine/hexanes) to give a yellow solid. The solid was triturated with hexanes and the crystals were collected by vacuum filtration to give 0.069 g (55%) of **8** as a white solid. Conducting the above reaction on the following scale: 1-[(*E*)-2-iodoethenyl]-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (3.10 g, 11.0 mmol), *tert*-butyllithium (1.7 M in *n*-pentane, 17.1 mL, 29 mmol), zinc chloride (1.94 g, 14.3 mmol), $Pd(PPh_3)_4$ (0.63 g, 0.55 mmol), **13** (3.75 g, 7.15 mmol) gave **8** (0.98 g, 43%). mp 159-163 °C; IR (thin film) 1639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J*= 7.9 Hz, 1H), 7.39 (br s, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.94 (td, *J* = 7.5, 1.3, 1H), 6.70 (s, 1H), 4.74 (s, 2H), 3.94 (dd, *J* = 14.6, 6.7 Hz, 1H), 3.64-3.51 (m, 7H), 3.32 (br s, 1H), 3.05 (s, 1H), 1.93 (td, *J*=11.4, 6.8 Hz, 1H), 1.19-1.07 (m, 21H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 143.2, 141.9, 139.5, 135.0, 134.1, 128.0, 126.0, 123.5, 108.7, 72.5, 66.7, 63.9, 60.2, 59.5, 43.5, 30.7, 18.4, 14.9, 12.3; HRMS (TOF MS ES+) $[M+NH_4^+]$ calcd for $C_{29}H_{43}NO_4BrSi$ 576.2145, found 576.2128.

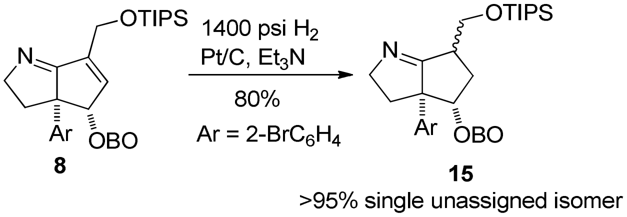
X-Ray Analysis of 8.



A colorless plate shaped crystal of **8** ($C_{29}H_{42}BrNO_4Si$) with approximate dimensions 0.10 x 0.33 x 0.50 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 123(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

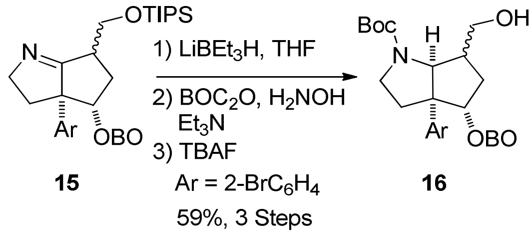
A total of 1950 frames were collected with a scan width of 0.3° in ω and an exposure time of 5 seconds/frame. The total data collection time was about 6 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 21654 reflections to a maximum θ angle of 28.27° (0.90 Å resolution), of which 7066 were independent, completeness = 98.8%, R_{int} = 0.0437, R_{sig} = 0.0601 and 4654 were greater than 2σ(I). The final cell constants: a = 8.533(4)Å, b = 12.505(5)Å, c = 14.664(6)Å, α = 72.580(7)°, β = 77.245(6)°, γ = 78.328(6)°, volume = 1440.3(11)Å^3, are based upon the refinement of the XYZ-centroids of 2022 reflections above 20σ(I) with 2.474° <θ <24.214°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.5071.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, C29 H42 Br N O4 Si . The final anisotropic full-matrix least-squares refinement on F^2 with 332 variables converged at R1 = 8.09%, for the observed data and wR2 = 26.17% for all data. The goodness-of-fit was 1.096 . The largest peak on the final difference map was 2.075 $e^-/Å^3$ and the largest hole was -1.763 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.330 g/cm^3 and F(000) amounts to 608 electrons.



3a-(2-Bromophenyl)-4-(4-methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)-6-(((triisopropylsilyl)oxy)methyl)-2,3,3a,4,5,6-hexahydrocyclopenta[b]pyrrole (15). A Parr bomb was charged with **8** (0.700 g, 1.21 mmol), 1,4-dioxane (12.0 mL), triethylamine (0.085 mL, 0.61g, 0.61 mmol), and 5% platinum on carbon (0.311 g, 0.061 mmol, 5 mol%). The bomb was sealed, purged with hydrogen gas three times, and then pressurized with hydrogen gas (1400 psi), and stirred at 40 °C for 18 hours. The gas was vented and an additional 0.05 equivalents of 5% platinum on carbon were added. The bomb was then resealed, purged with hydrogen gas three times, pressurized to 1400 psi of hydrogen gas, and stirred at 40 °C for 18 hours. This sequence was repeated until TLC

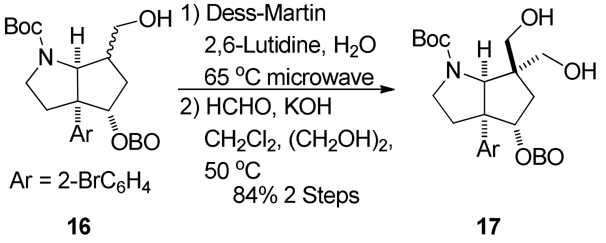
(10:90 ethyl acetate:hexanes) indicated that the starting material was completely consumed. The reaction mixture was filtered through Celite, rinsing with EtOAc, and concentrated in *vacuo* to give a light yellow oil, which was purified by column chromatography on SiO_2 (5% EtOAc/3% triethylamine/hexanes) to give **15** (0.566 g, 80%) as a clear oil. IR (thin film) 2246, 2215, 1667cm^{-1}; ^{1}H NMR (major isomer, 300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.32 (d, *J* = 8.0, 1.5 Hz, 1H), 7.17 (app td, *J* = 7.6, 1.4 Hz, 1H), 7.01 (app td, *J* = 7.6, 1.6 Hz, 1H), 4.07 (dd, *J* = 9.7, 4.3 Hz, 1H), 3.96 (dd, *J* = 14.4, 7.6 Hz, 1H), 3.79-3.60 (m, 8H), 3.21 (app dd, *J* = 12.8, 3.2 Hz, 2H), 2.12-2.35 (m, 3H), 2.05 (m, 1H), 1.12-1.04 (m, 21H), 0.73 (s, 3H); ^{13}C (major isomer, 75 MHz, $CDCl_3$) δ 191.1, 138.5, 134.9, 132.3, 127.8, 125.7, 124.2, 108.7, 72.2, 66.8, 65.0, 64.2, 53.4, 41.9, 41.7, 31.0, 29.9, 18.0, 14.6, 12.0; HRMS (TOF MS ES+) [M+H^{+}] calcd for $C_{29}H_{45}NO_4BrSi$ 578.2301, found 578.2298.



***tert*-Butyl-3a-(2-bromophenyl)-6-(hydroxymethyl)-4-(4-methyl-2,6,7-trioxabicyclo [2.2.2] octan-1-yl)hexahydrocyclopenta[b]pyrrole-1(2H)-carboxylate (16)**. A solution of Super Hydride (1.0 M in THF, 10 mL, 10 mmol) was added dropwise to a solution of **15** (0.586 g, 1.01 mmol) in THF (10.1 mL). There was an initial vigorous evolution of gas that subsided quickly. The mixture was heated at reflux for 72 h and then cooled to 0 °C, and the excess hydride was destroyed by the slow addition of ice. Saturated ammonium chloride solution (10 mL) was added and the biphasic solution was stirred for 1 h. Ethyl acetate (10 ml) was added and the organic layer was drawn off.

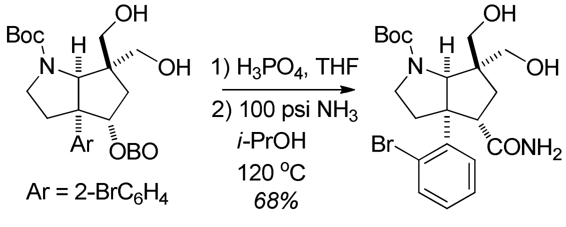
The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were washed with brine (1 x 15 mL) and dried over Na_2SO_4. The solution was filtered and concentrated in *vacuo*. The crude amine was dissolved in CH_2Cl_2 (10.0 mL) and triethylamine (0.706 mL, 0.512 g, 5.06 mmol), Boc_2O (0.442 g, 2.03 mmol), and hydroxylamine hydrochloride (0.035 g, 0.506 mmol) were added sequentially. The reaction mixture was stirred for 24 h at 25 °C and an additional portion of Boc_2O (0.111 g, 0.506 mmol) was added. The solution was stirred for an additional 48 h and then concentrated in *vacuo* to give a white oil. This crude mixture was dissolved in acetonitrile (10 mL) and extracted with hexanes (5 x 10 mL). The combined hexanes extracts were concentrated in *vacuo* to give a clear oil.

The crude oil was dissolved in THF (10.0 mL) and *n*-Bu_4NF solution (1.0 M in THF, 5.0 mL, 5.0 mmol) was added. The reaction mixture was stirred for 18 h at 25 °C and then was diluted with water (20.0 mL) and ethyl acetate (15.0 mL) was added. The layers were separated and the aqueous layer was extracted with ethyl acetate (1 x 10.0 mL) and dichloromethane (2 x 10.0 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude alcohol was purified by column chromatography on SiO_2 (1% to 4% to 10% ethyl acetate/3% triethylamine/hexanes) to give alcohol **16** (0.317 g, 59%) as white crystals. mp 82-86 °C; IR (thin film) 3441, 2244, 1667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.14 (app. t, *J* = 7.5 Hz, 1H), 6.99 (app t, *J* = 7.4 Hz, 1H), 5.17 (d, *J* = 9.5, 1H), 3.51-3.37 (m, 9H), 3.30 (d, *J* = 7.2 Hz, 1H), 3.21 (t, *J* = 9.5 Hz, 1H), 2.88-2.75 (m, 3H), 2.31 (dd, *J* = 8.8, 6.9 Hz, 1H), 1.94 (app. q, *J* = 11.7 Hz, 1H), 1.57 (m, 1H, overlapping with H_2O), 1.43 (s, 9H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 141.1, 134.1, 129.0, 127.1, 126.0, 125.8, 109.5, 80.3, 71.8, 65.3, 64.4, 61.4, 47.6, 45.1, 42.3, 34.8, 30.0, 28.3, 28.1, 14.2; HRMS (TOF MS ES+) [M+H$^+$] calcd for $C_{25}H_{35}NO_6Br$ 524.1648, found 524.1657.



***tert*-Butyl-3a-(2-bromophenyl)-6,6-bis(hydroxymethyl)-4-(4-methyl-2,6,7-trioxa-bicyclo[2.2.2]octan-1-yl)-hexahydrocyclopenta[b]pyrrole-1(2H)-carboxylate (17)**. A microwave reaction tube was charged with alcohol **16** (0.167 g, 0.318 mmol), water saturated dichloromethane (3.20 mL) and 2,6-lutidine (0.184 mL, 0.171 g, 1.59 mmol). Dess-Martin periodinane (0.405 g, 0.955 mmol) was added in a single portion and the tube was flushed with nitrogen and then sealed with a Teflon cap. The reaction mixture was heated via microwave irradiation to 65 °C for 30 min and then cooled to 25 °C. A 1:1 solution (3 mL) of saturated aqueous $NaHCO_3$: saturated aqueous $Na_2S_2O_3$ was added and the biphasic mixture was stirred until all of the solids had dissolved and the mixture was clear. The mixture was poured into a separatory funnel and the organic layer was drawn off. The aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo* to give a pale yellow oil.

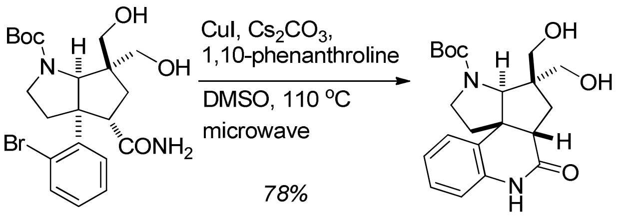
The oil was dissolved in ethylene glycol (3.18 mL) and dichloromethane (0.100 mL). Aqueous formaldehyde (37% w/w, 1.43 mL, 1.56 g, 19.1 mmol) and potassium hydroxide (0.371 g, 5.62 mmol) were added sequentially. The reaction solution was heated to 50 °C and stirred at that temperature for 48 h. The reaction solution was cooled to 25 °C, diluted with brine (15.0 mL), and extracted with dichloromethane (4x10.0 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo* to give a white foam. The foam was purified by column chromatography (1% to 5% to 10% $MeOH/CH_2Cl_2$) to give diol **17** (0.149 g, 84%, mixture of rotamers) as a white solid. mp 208-212 °C; IR (thin film) 3492, 1659 cm^{-1}; ^1H NMR (major rotamer, 300 MHz $CDCl_3$) δ 7.54 (app dd, *J* = 7.8, 1.0 Hz, 1H), 7.21-7.11 (m, 2H), 7.01 (app dt, *J* = 7.3, 2.0 Hz, 1H), 4.9 (s, 1H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.82 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.61 (app t, *J* = 11.1 Hz, 1H), 3.48-3.38 (m, 7H), 3.32 (dd, *J* = 6.7, 3.0 Hz, 1H), 3.23 (app t, *J* = 9.9 Hz, 1H), 2.99 (dd, *J* = 13.1, 6.7 Hz, 1H) 2.88 (dt, *J* = 11.2, 7.0 Hz, 1H), 2.42 (t, *J* = 6.1 Hz, 1H), 2.14, (dt, *J* = 12.3, 9.5 Hz, 1H), 2.07-1.98 (m, 2H), 1.43 (s, 9H), 0.59 (s, 3H); ^{13}C NMR (major rotamer, 75 MHz, $CDCl_3$) δ 155.6, 140.6, 134.1, 129.1, 127.2, 126.1, 126.0, 109.3, 80.4, 71.8, 69.6, 68.1, 67.9, 61.7, 49.1, 47.1, 45.0, 34.3, 31.8, 30.1, 28.4, 14,3; HRMS (TOF MS ES+) [$M+H^+$] calc'd for $C_{26}H_{37}NO_7Br$ 554.1753, found 554.1773.



17 **18**

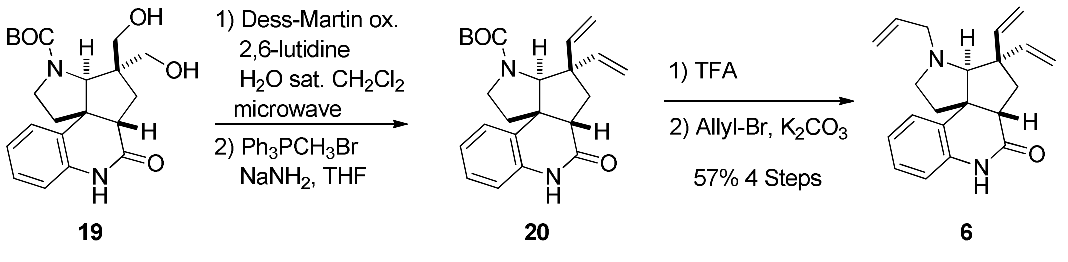
tert-Butyl-3a-(2-bromophenyl)-4-carbamoyl-6,6-bis(hydroxymethyl)-hexahydrocyclopenta[b]pyrrole-1(2H)-carboxylate (18). Orthoester **17** (0.119 g, 0.0214 mmol) was dissolved in 10% (v/v) H_3PO_4/THF (3.00 mL). The solution was stirred at 25 °C until consumption of the orthoester was indicated by TLC (10 $MeOH:CH_2Cl_2$). The solution was transferred to a Parr bomb and isopropyl alcohol (5.00

mL) was added. The bomb was purged with NH_3 gas three times, pressurized with 100 PSI NH_3 gas, and stirred for 30 min while connected to the NH_3 tank. The bomb was sealed and heated to 120 °C for 20 h. The bomb was cooled to 25 °C, the ammonia gas was vented, and the reaction solution in the bomb was allowed to sit for 1 h to give a milky suspension. The suspension was filtered through Celite and concentrated in *vacuo* to give a yellow solid. The solid was purified via column chromatography on SiO_2 (1%-5%-10% MeOH/CH_2Cl_2) to give **18** as a white solid, as a 2:1 mixture of rotamers (0.068 g, 68%). mp 206 °C (decomp); IR (solid) 3331, 2151, 1662 cm^{-1}; ^{1}H NMR (major rotamer, 300 MHz, CD_3OD) δ 7.59 (d, J = 8.0 Hz, 1H), 7.25 (m, 1H), 7.14-7.07 (m, 2H), 4.95 (s, 1H, overlapping with HOD), 4.17 (d, J = 8.9 Hz, 1H), 3.95 (m, 1H), 3.71 (d, J = 10.7 Hz, 1H), 3.61 (d, J = 10.7 Hz, 1H), 3.48 (m, 1H), 3.36 (m, 1H), 2.87 (m, 1H), 2.64-2.26 (m, 3H), 1.66 (d, J = 14.9 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (both rotamers, 75 MHz, CD_3OD) δ 179.6, 179.4, 157.1, 156.2, 143.1, 142.9, 136.4, 130.1, 130.0, 129.5, 129.4, 128.3, 128.2, 123.0, 122.9, 82.0, 81.9, 72.0, 71.3, 68.6, 67.9, 67.2, 66.3, 65.3, 63.2, 62.9, 51.4, 50.5, 50.4, 50.3, 46.5, 46.3, 36.4, 34.9, 34.1, 34.1, 28.9, 28.7; HRMS (TOF MS ES+) [M+H$^+$] calc'd for $C_{21}H_{30}N_2O_5Br$ 469.1361, found 469.1338.



18 **19**

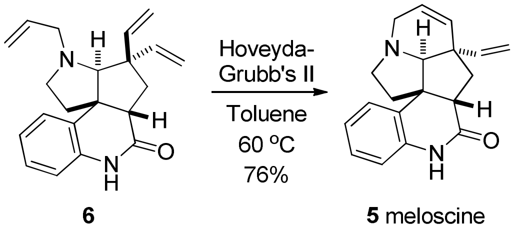
(3aR,5aS,11bR)-tert-Butyl 4,4-Bis(hydroxymethyl)-6-oxo-3a,4,5,5a,6,7-hexahydro-1H-pyrrolo[3',2':2,3]cyclopenta[1,2-c]quinoline-3(2H)-carboxylate (19). To a solution of primary amide **18** (0.008 g, 1.44x10^{-2} mmol) in DMSO (0.200 mL) in a microwave reactor tube was added Cs_2CO_3 (0.650 g, 0.198 mmol), copper (I) iodide (0.004 g, 1.98x10^{-2} mmol), and 1,10-phenanthroline (0.007 g, 3.97x10^{-2} mmol). The tube was flushed with N_2, sealed with a Teflon cap, and heated to 110 °C via microwave irradiation for 30 min. The solution was cooled to 25 °C, filtered through Celite, rinsing with CH_2Cl_2, and concentrated in *vacuo* to give a blue residue. The residue was purified by preparatory thin layer chromatography on SiO_2 (5% $MeOH/CH_2Cl_2$, applying the crude mixture to the TLC plate using no more than 10% $MeOH/CH_2Cl_2$) to give lactam **19** as a yellow solid (0.006 g, 78%, mixture of rotamers). mp 218-221 °C; IR (thin film) 3241, 1661 cm^{-1}; ^1H NMR (both rotamers, 500 MHz, CD_3OD) δ 7.30 (m, 1H), 7.19 (t, *J* = 6.9 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.46 (s, 0.6H, major rotamer), 4.42 (s, 0.4H, minor rotamer), 3.99 (t, *J* = 9.9 Hz, 1H), 3.59 (d, *J* = 12.8 Hz, 1H), 3.54-3.37 (m, 3H), 2.98 (dd, *J* = 12.0, 6.6 Hz, 1H), 2.30 (dd, *J* = 12.9, 6.6 Hz, 1H), 2.19-1.80 (m, 3H), 1.64 (t, *J* = 12.5 Hz, 1H), 1.51 (s, 6H), 1.28 (s, 3H); ^{13}C NMR (both rotamers, 125 MHz, CD_3OD) δ 173.6, 173.1, 156.7, 155.9, 136.8, 129.2, 129.0, 128.0, 127.6, 125.3, 125.1, 116.9, 116.8, 82.0, 81.9, 76.6, 75.0, 68.0, 67.2, 64.0, 62.0, 60.0, 58.9, 53.4, 52.6; 48.2, 47.9 (overlapping with CD_3OD), 40.5, 39.8, 37.2, 36.5, 30.8, 28.8, 28.6; HRMS (TOF MS ES+) [$M+H^+$] calc'd for $C_{21}H_{29}N_2O_5$ 389.2076, found 389.2103.



(3aS,5aS,11bR)-3-Allyl-4,4-divinyl-2,3,3a,4,5,5a-hexahydro-1H-pyrrolo[3',2':2,3] cyclopenta[1,2-c]quinolin-6(7H)-one (6). To a solution of lactam **19** (0.007 g, 1.80 x10^{-2} mmol) in water saturated CH_2Cl_2 (0.180 mL) in a microwave reactor tube was added Dess-Martin periodinane (0.076 g, 0.180 mmol). The tube was flushed with nitrogen, sealed with a Teflon cap, and heated to 65 °C via microwave irradiation for 30 min. The reaction mixture was cooled to 25 °C and 3.00 mL of a 1:1 mixture of saturated aqueous sodium bicarbonate:saturated aqueous $Na_2S_2O_3$ was added and the biphasic solution was stirred until all of the solids had dissolved and the mixture was clear. The mixture was poured into a separatory funnel and the organic layer was drawn off. The aqueous layer was extracted with CH_2Cl_2 (3 x 5.00 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give the unstable 1,3-dialdehyde as a pale yellow oil.

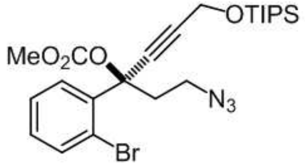
A suspension of methyltriphenylphosphonium bromide (0.129 g, 0.360 mmol) in THF (0.300 mL) was cooled to -78 °C and a solution of NaHMDS (1.0 M in THF, 0.34 mL, 0.34 mmol) was added dropwise. The suspension was stirred at -78 °C for 1.5 h. The previously prepared 1,3-dialdehyde was dissolved in 0.150 mL of THF and added via cannula to the ylide suspension, rinsing the flask with an additional 0.150 mL of THF. The reaction mixture was allowed to warm to 25 °C and stirred at that temperature for 72 h. Saturated aqueous ammonium chloride (5.00 mL) and ethyl acetate (5.00 mL) were added. The organic layer was drawn off and the aqueous layer was extracted with ethyl acetate (1 x 5.00 mL) and CH_2Cl_2 (2 x 5.00 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give **20** as a brown oil.

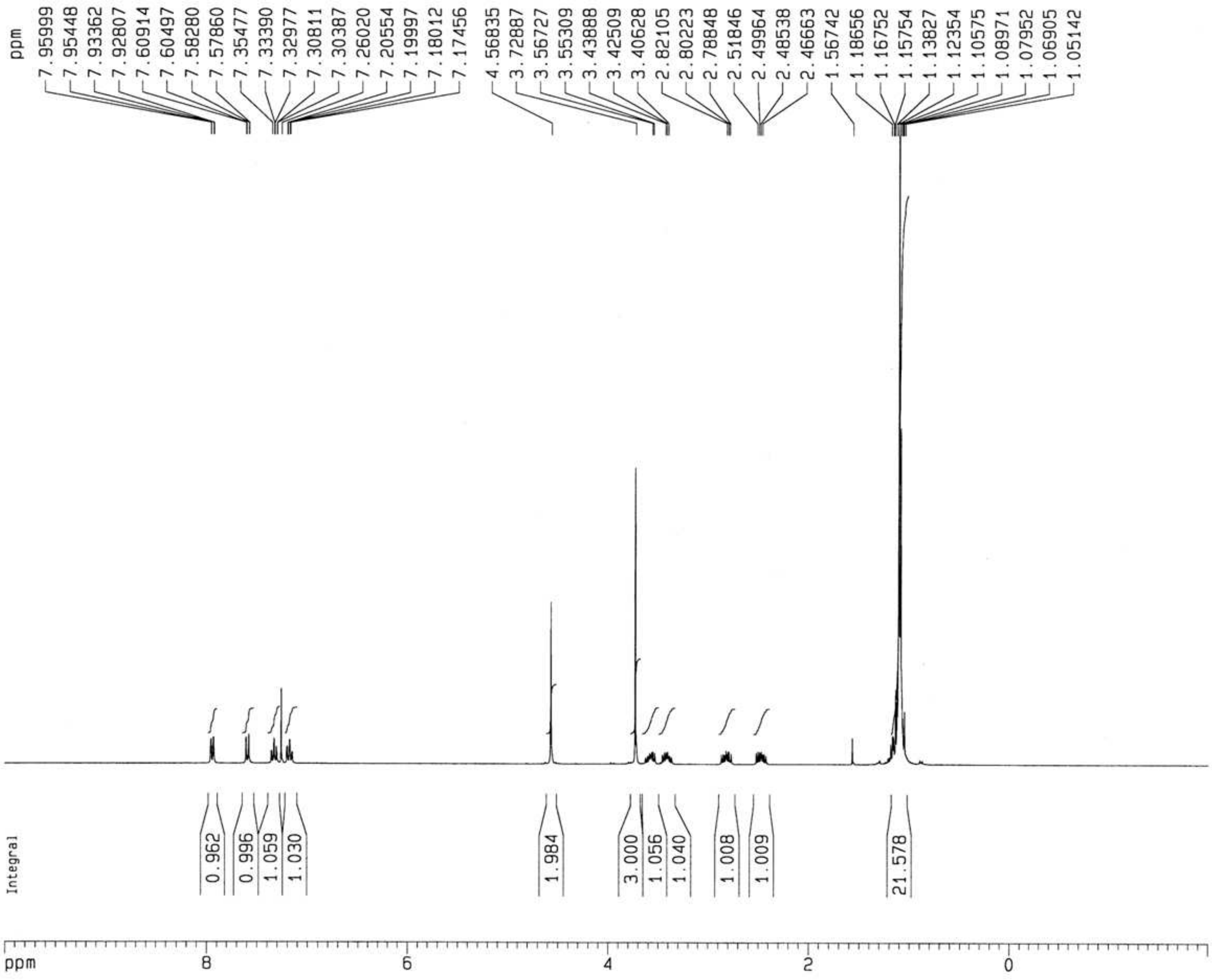
The crude oil was dissolved in 10% (v/v) TFA/CH_2Cl_2 (3.00 mL) and stirred for 4 h at 25 °C. The reaction solution was concentrated in *vacuo* and saturated aqueous sodium bicarbonate (3.00 mL) and CH_2Cl_2 (5.00 mL) were added. The organic layer was drawn off and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give the crude free amine as a brown oil. The oil was dissolved in MeCN (0.500 mL), and K_2CO_3 (0.015 g, 0.11 mmol) and allyl bromide (0.010 mL, 0.11 mmol) were added sequentially. The reaction mixture was stirred for 24 h at 25 °C, then water (3.00 mL) and CH_2Cl_2 (3.00 mL) were added. The mixture was transferred to a separatory funnel, the organic layer was drawn off, and the aqueous layer was extracted with CH_2Cl_2 (3 x 3.00 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give a brown residue. The residue was purified on SiO_2 (5% to 15% EtOAc/hexanes) to give **6** as a colorless oil (0.004 g, 57%). IR (thin film) 1674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (br s, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.15 (td, *J* = 7.6, 1.4 Hz, 1H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.24 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.93 (dddd, *J* = 17.4, 10.2, 7.5, 5.1 Hz, 1H), 5.74 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.30-5.09 (m, 4H), 4.94 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.88 (dd, *J* = 17.6, 0.8 Hz, 1H), 3.51 (m, 1H), 3.43 (s, 1H), 3.29 (dt, *J* = 10.1, 5.0 Hz, 1H), 3.04 (dd, *J* = 13.7, 7.5, 1H), 2.94 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.84 (dt, *J* = 10.0, 8.1 Hz, 1H), 2.41 (dd, *J* = 12.6, 6.9 Hz, 1H), 2.17 (dd, *J* = 12.6, 8.9 Hz, 1H), 2.02-1.97 (m, 2H); ^{13}C (150 Hz, $CDCl_3$) δ 171.5, 143.0, 140.6, 135.8, 134.4, 130.0, 127.7, 127.3, 123.7, 116.9, 115.3, 114.4, 113.7, 87.6, 58.6, 56.9, 55.6, 53.4, 50.5, 43.7, 41.4; HRMS (TOF MS ES+) $[M+H^+]$ calc'd for $C_{21}H_{25}N_2O$ 321.1967, found 321.1961.



(6bR,6b1S,12aS,13aS)-12a-vinyl-2,6b1,7,8,10,12a,13,13a-octahydro-1H-indolizino[1',8':2,3,4]cyclopenta[1,2-c]quinolin-1-one (±-Meloscine) (5). To a solution of **6** (0.0023g, 0.0072 mmol) in toluene (2.0 mL) was added Hoveyda-Grubb's 2nd generation catalyst (0.00023 g, 0.00036 mmol) in toluene (0.10 mL). The reaction mixture was heated to 60 °C for 24 h and then cooled to 25 °C and concentrated in *vacuo* to give a brown residue. The residue was purified via column chromatography on SiO_2 (hexanes -1%-2%-4% $MeOH/CH_2Cl_2$) to give **5** as a white solid (0.0014 g, 76%). mp 205-210 °C; IR (thin film) 1672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.01 (ddd, *J* = 10.0, 5.5, 2.2 Hz, 1H), 5.72 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.53 (dd, *J* = 17.4, 10.5 Hz, 1H), 4.91 (d, *J* = 17.3 Hz, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 3.51 (s, 1H), 3.30 (dd, *J* = 16.1, 5.5 Hz, 1H), 3.25 – 3.08 (m, 2H), 2.96 (t, *J* = 8.8 Hz, 1H), 2.88 (td, *J* = 8.0, 4.5 Hz, 1H), 2.31 (dd, *J* = 12.7, 8.3 Hz, 1H), 2.22 – 2.08 (m, 2H), 1.96 (dt, *J* = 12.8, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 143.2, 135.0, 132.4, 127.9, 127.7, 127.6, 127.0, 123.9, 115.1, 112.6, 82.5, 56.8, 53.0, 51.0, 48.1, 46.8, 43.4, 42.2; HRMS (TOF MS ES+) [$M+H^+$] calc'd for $C_{19}H_{21}N_2O$ 293.1654, found 293.1643.

13





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PROCNO                 1

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TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
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FIDRES          0.188380 Hz
AQ             2.6542580 sec
RG                   256
DW                81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

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PL1                 0.00 dB
SFO1         299.8718518 MHz

F2 - Processing parameters
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SF           299.8700101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
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F1               2998.70 Hz
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F2               -599.74 Hz
PPMCM            0.60000 ppm/cm
HZCM           179.92200 Hz/cm
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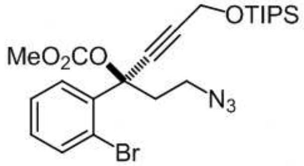
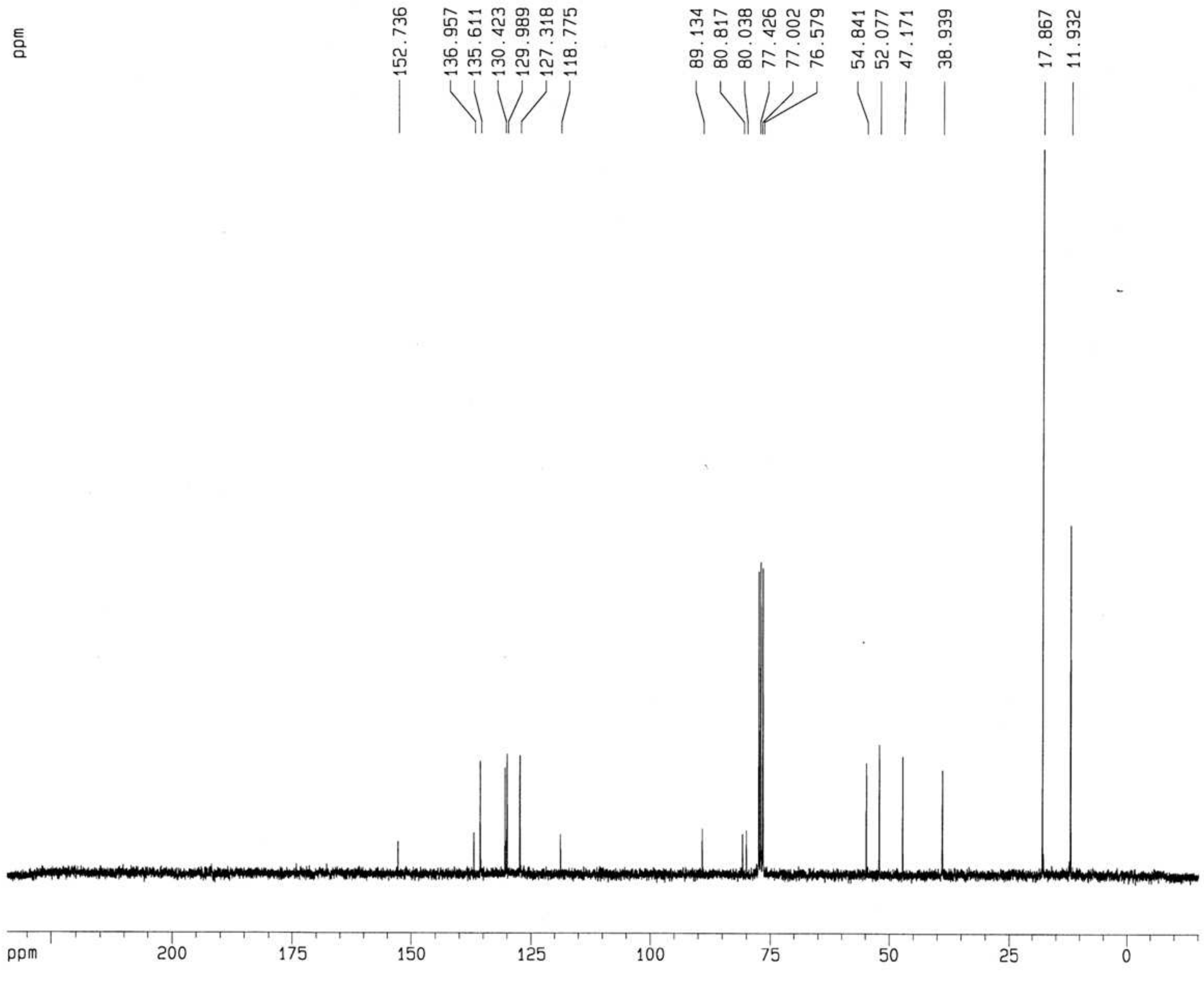
13





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NS                   1012
DS                      4
SWH           18796.992 Hz
FIDRES         0.764852 Hz
AQ            0.6537716 sec
RG                   1024
DW               26.600 usec
DE                 6.00 usec
TE                300.0 K
D1           0.50000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

============ CHANNEL f1 ===========
NUC1                  13C
P1                 5.25 usec
PL1               -6.00 dB
SFO1        75.4106357 MHz

============ CHANNEL f2 ===========
CPDPRG2           waltz16
NUC2                   1H
PCPD2            115.00 usec
PL2                0.00 dB
PL12              19.70 dB
PL13              19.70 dB
SFO2       299.8711995 MHz

F2 - Processing parameters
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SF          75.4023752 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
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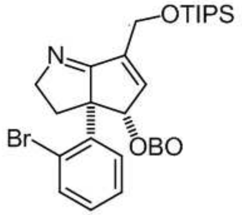
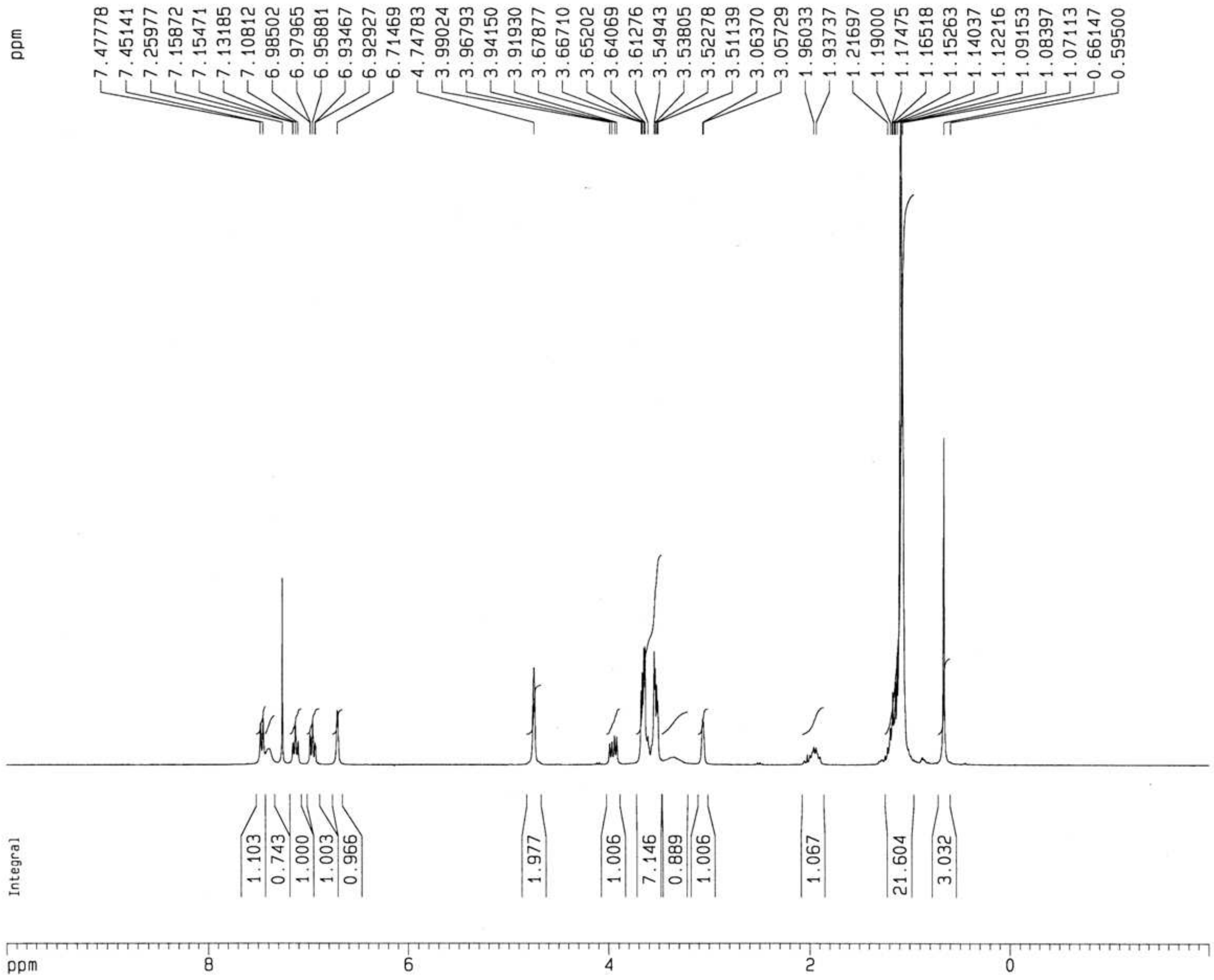
8





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PROCNO                 1

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INSTRUM            spect
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AG           5.3084660 sec
RG                  80.6
DW              81.000 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1               11.70 usec
PL1               0.00 dB
SFO1       299.8718518 MHz

F2 - Processing parameters
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SF         299.8700101 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              2998.70 Hz
F2P              -2.000 ppm
F2              -599.74 Hz
PPMCM           0.60000 ppm/cm
HZCM          179.92200 Hz/cm
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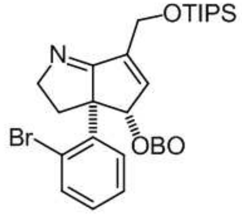
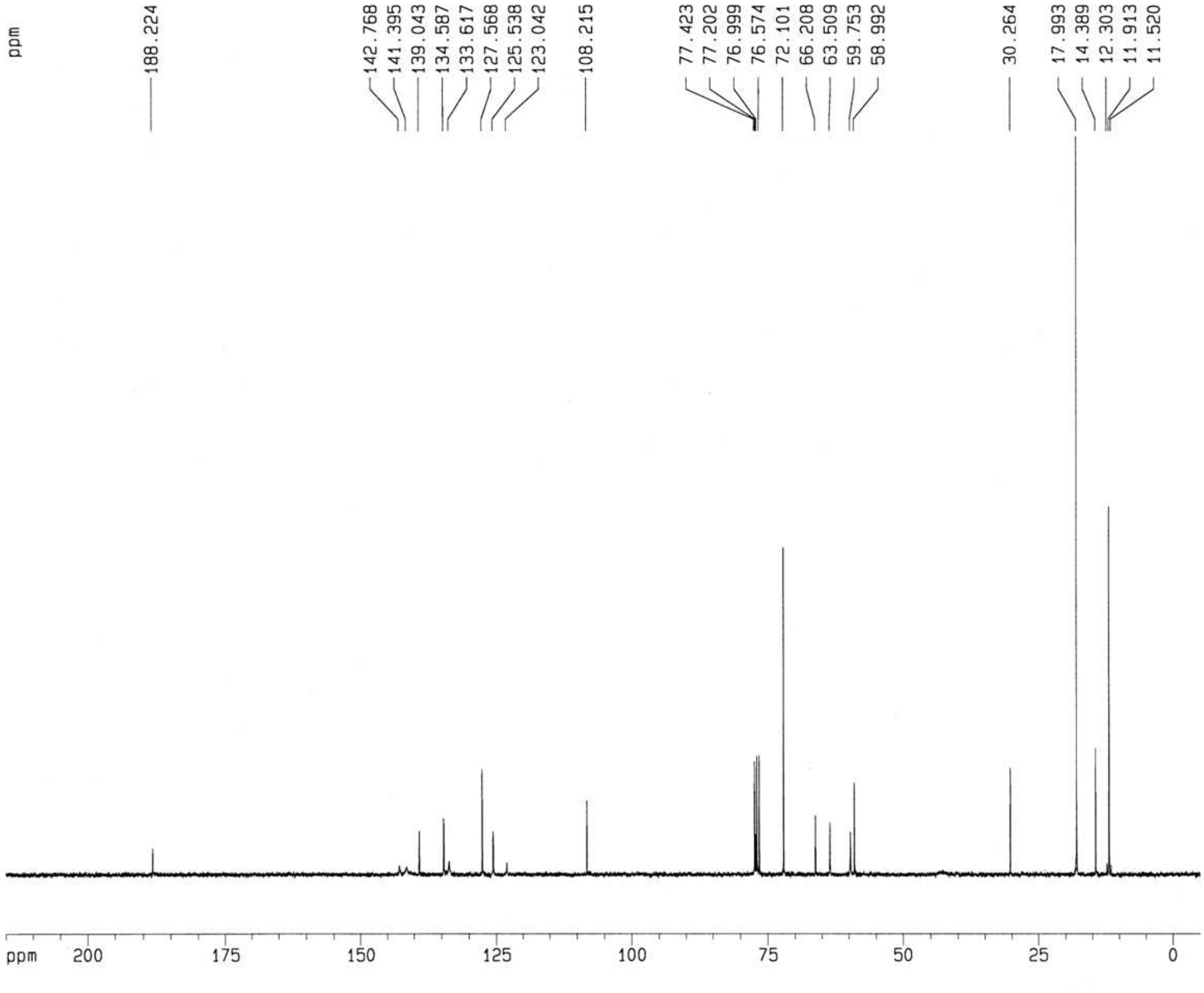
8

8





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EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
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INSTRUM              spect
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TD                   32768
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NS                     548
DS                       4
SWH             18796.992 Hz
FIDRES           0.573639 Hz
AQ              0.8716788 sec
RG                    2048
DW                  26.600 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec

============ CHANNEL f1 ============
NUC1                   13C
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PL1                  -6.00 dB
SFO1           75.4106357 MHz

============ CHANNEL f2 ============
CPDPRG2            waltz16
NUC2                    1H
PCPD2               115.00 usec
PL2                   0.00 dB
PL12                 20.00 dB
PL13                 20.00 dB
SFO2           299.8711995 MHz

F2 - Processing parameters
SI                   32768
SF             75.4023786 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                215.000 ppm
F1                16211.51 Hz
F2P                 -5.000 ppm
F2                 -377.01 Hz
PPMCM             11.00000 ppm/cm
HZCM             829.42621 Hz/cm
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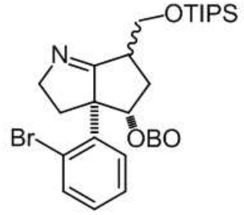
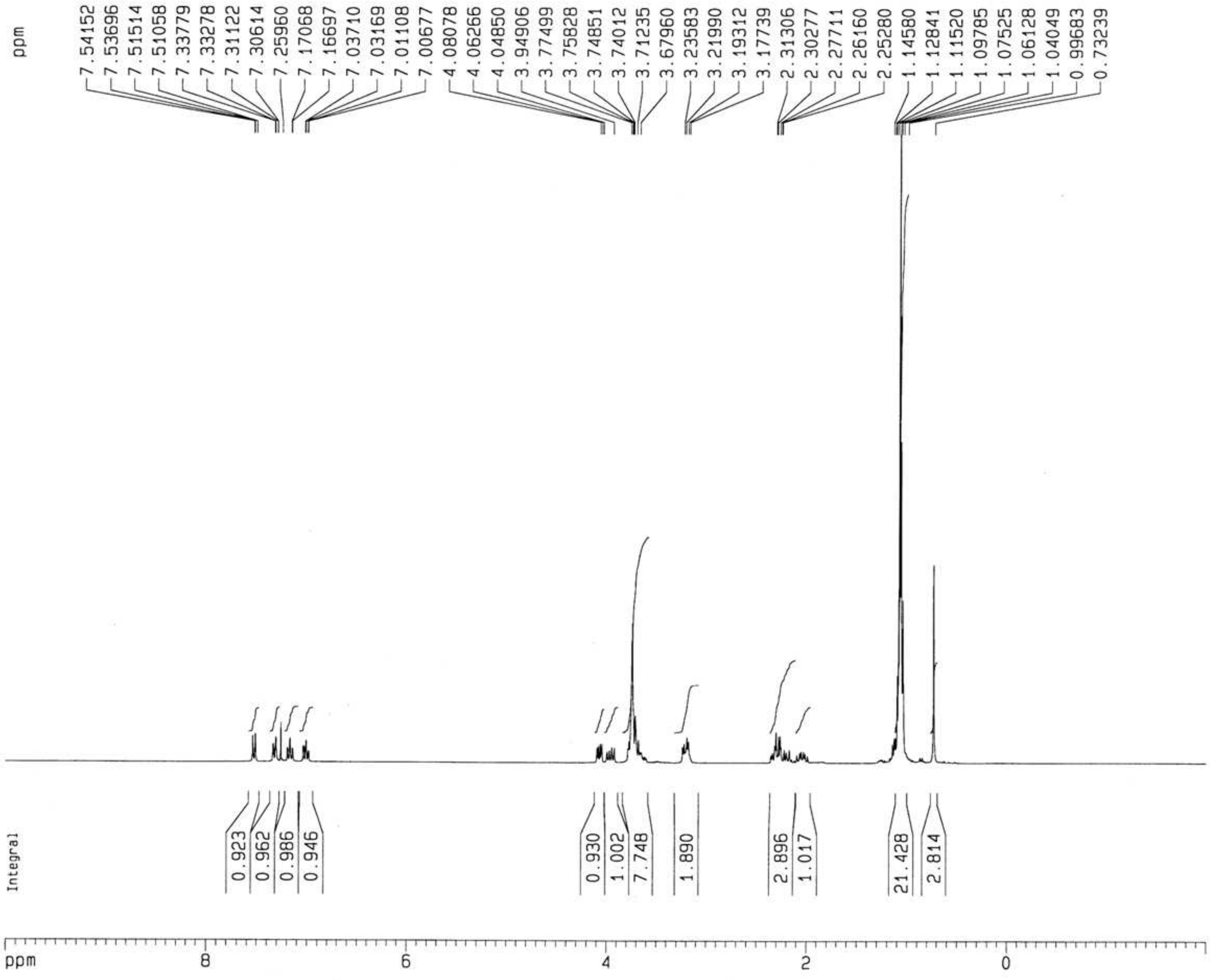
15





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PROCNO                 1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
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FIDRES        0.094190 Hz
AQ           5.3084660 sec
RG                   90.5
DW              81.000 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec

============ CHANNEL f1 ========
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P1               12.10 usec
PL1               0.00 dB
SFO1       299.8718518 MHz

F2 - Processing parameters
SI                  32768
SF         299.8700103 MHz
WDW                    EM
SSB                     0
LB                0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              2998.70 Hz
F2P              -2.000 ppm
F2              -599.74 Hz
PPMCM          0.60000 ppm/cm
HZCM         179.92200 Hz/cm
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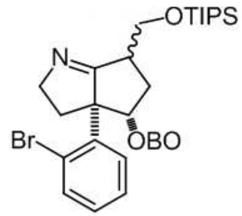
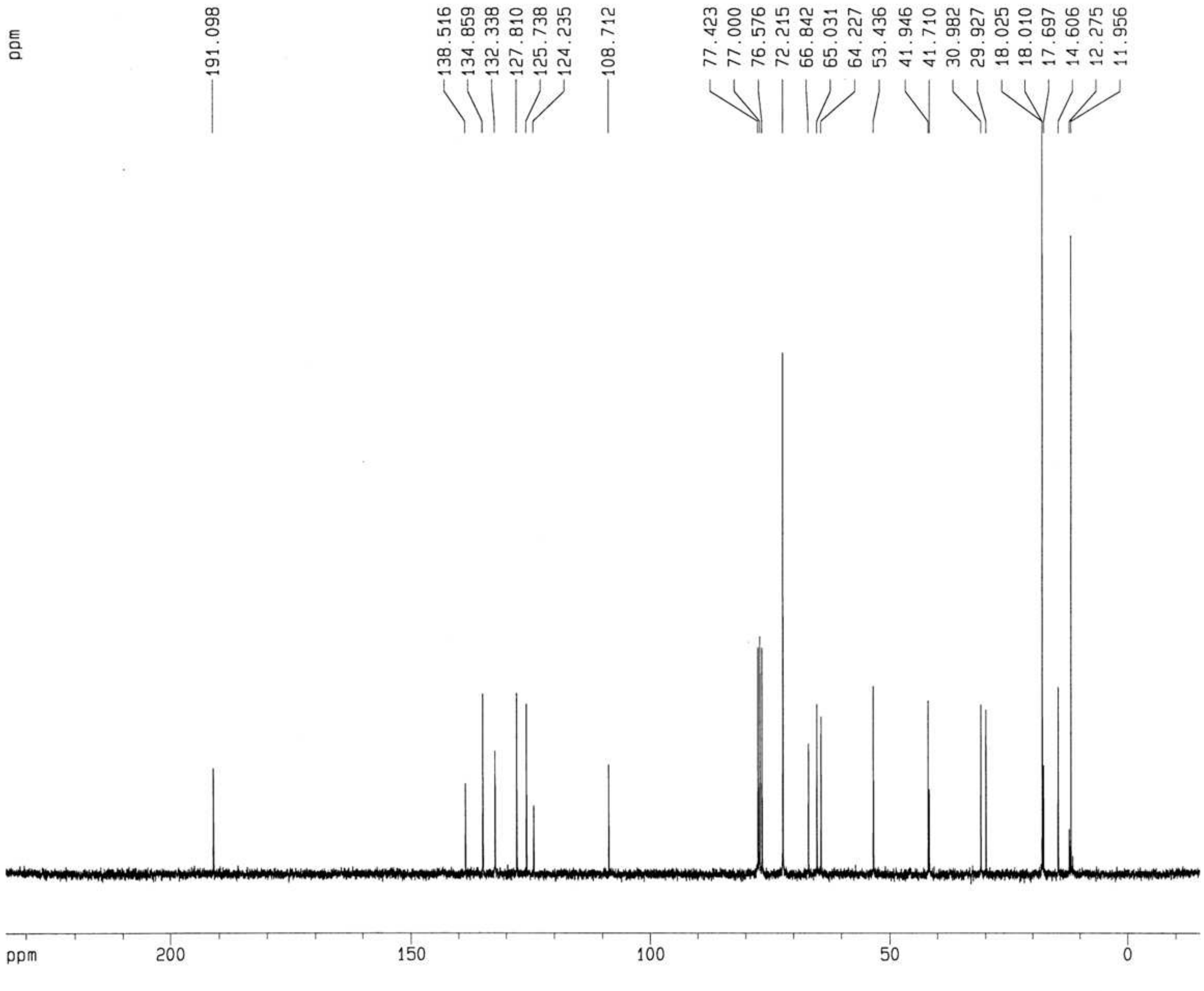
15





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PROCNO                 1

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TD                 24576
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NS                   722
DS                     4
SWH            18796.992 Hz
FIDRES          0.764852 Hz
AQ             0.6537716 sec
RG                   512
DW                26.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            0.50000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  5.25 usec
PL1                -6.00 dB
SFO1         75.4106357 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2             115.00 usec
PL2                 0.00 dB
PL12               19.70 dB
PL13               19.70 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF            75.4023763 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
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F1              17657.93 Hz
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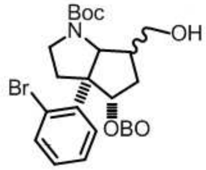
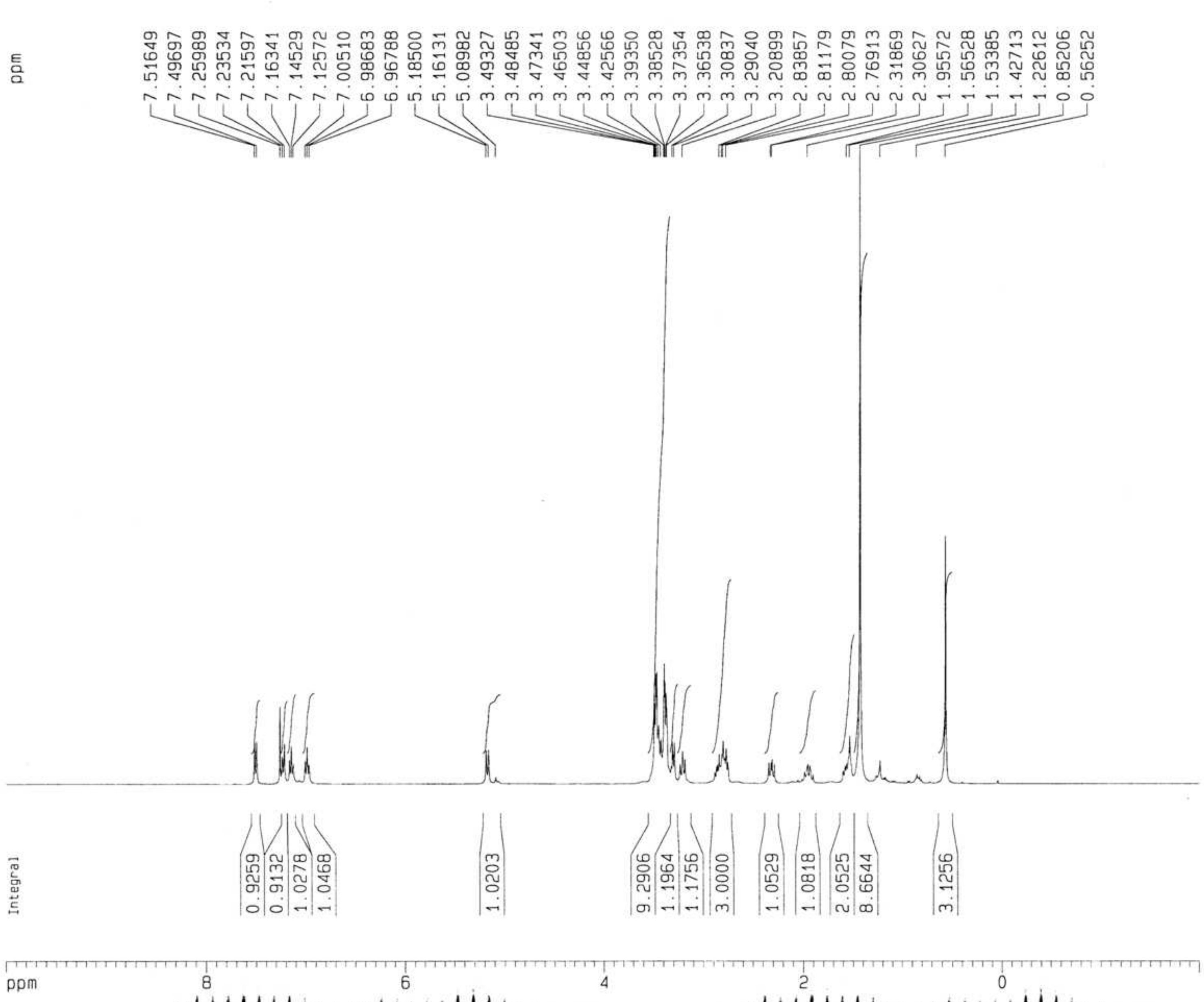
16





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PROCNO                 1

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INSTRUM            spect
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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8278.146 Hz
FIDRES         0.252629 Hz
AQ            1.9792372 sec
RG                  35.9
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ========
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PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
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SF           400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
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1D NMR plot parameters
CX                 20.00 cm
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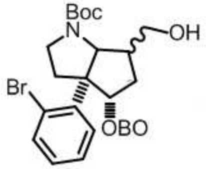
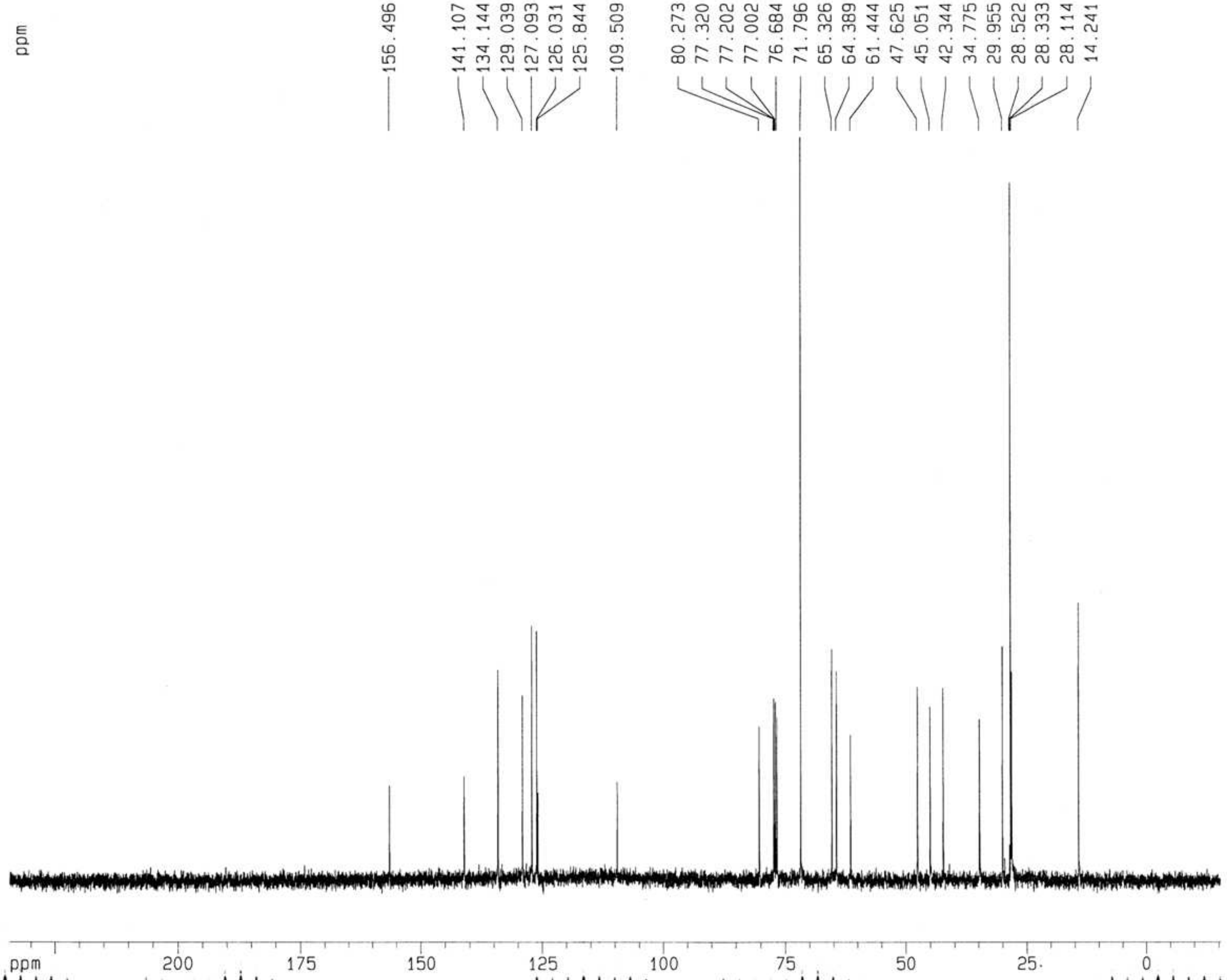
16





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PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  509
DS                    4
SWH           25125.629 Hz
FIDRES         0.766773 Hz
AQ            0.6521332 sec
RG               7298.2
DW               19.900 usec
DE                 6.00 usec
TE                300.0 K
D1           0.50000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

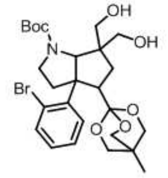
============ CHANNEL f1 ============
NUC1                13C
P1                16.35 usec
PL1               -6.00 dB
SFO1        100.6237959 MHz

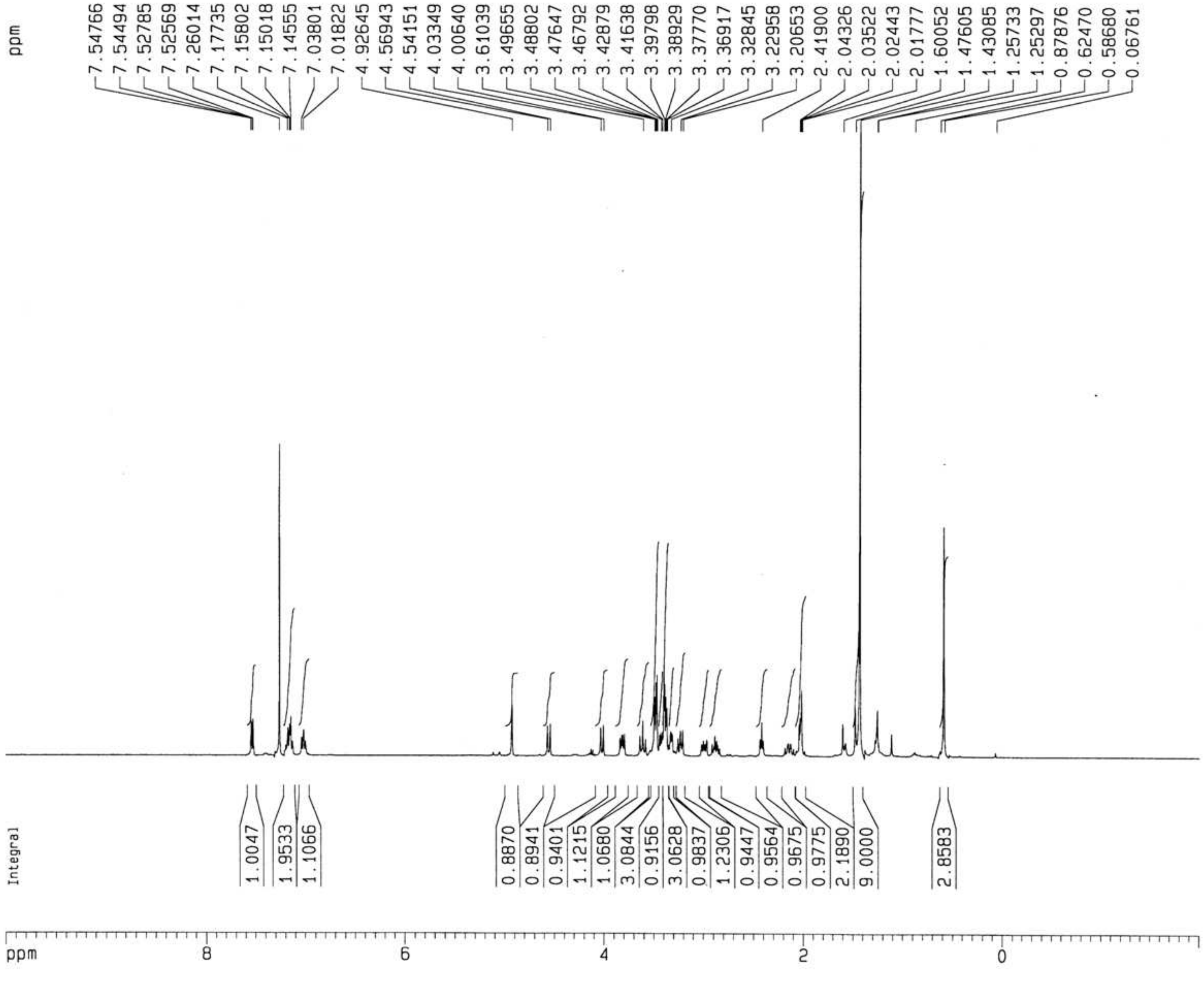
============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                 1H
PCPD2            114.00 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127761 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             234.390 ppm
F1             23582.59 Hz
F2P             -15.336 ppm
F2             -1543.04 Hz
PPMCM          12.48630 ppm/cm
HZCM         1256.28149 Hz/cm
```

17





```
Current Data Parameters
NAME       JFa-10-24-2011
EXPNO                   1
PROCNO                  1

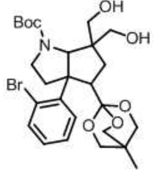
F2 - Acquisition Parameters
Date_            20111024
Time                14.10
INSTRUM             spect
PROBHD     5 mm BBI 1H-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.252629 Hz
AQ              1.9792372 sec
RG                  406.4
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

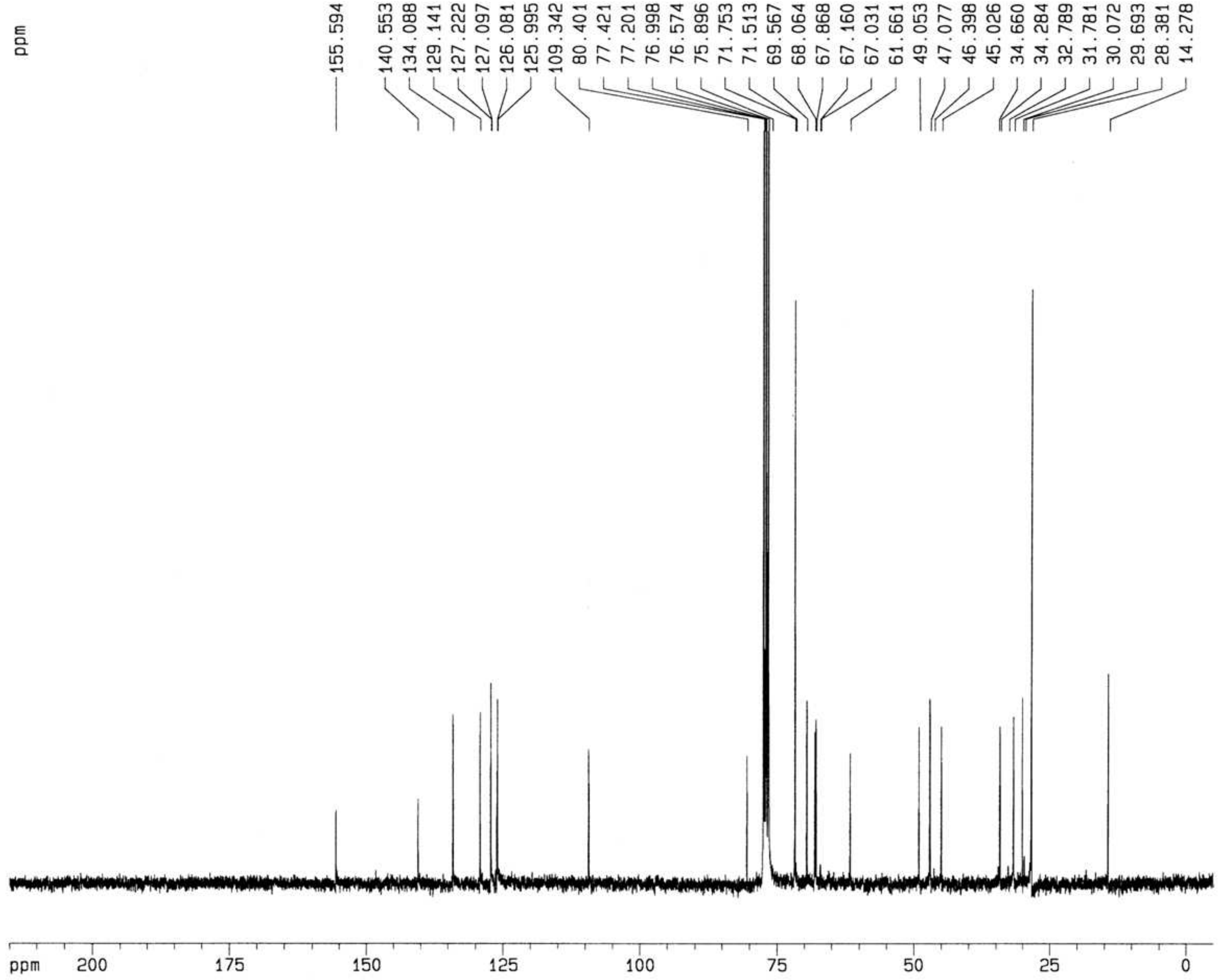
============ CHANNEL f1 ========
NUC1                   1H
P1                   6.45 usec
PL1                  0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF         400.1300091 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                10.000 ppm
F1                4001.30 Hz
F2P                -2.000 ppm
F2                -800.26 Hz
PPMCM             0.60000 ppm/cm
HZCM            240.07800 Hz/cm
```

17





```
Current Data Parameters
NAME      JFA-9-26-2011
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110927
Time               9.57
INSTRUM           spect
PROBHD   5 mm Multinu
PULPROG          zgpg30
TD                24576
SOLVENT           CDCl3
NS                52167
DS                    4
SWH           18832.393 Hz
FIDRES         0.766292 Hz
AQ            0.6525428 sec
RG                13004
DW               26.550 usec
DE                 6.00 usec
TE                300.0 K
D1           0.50000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

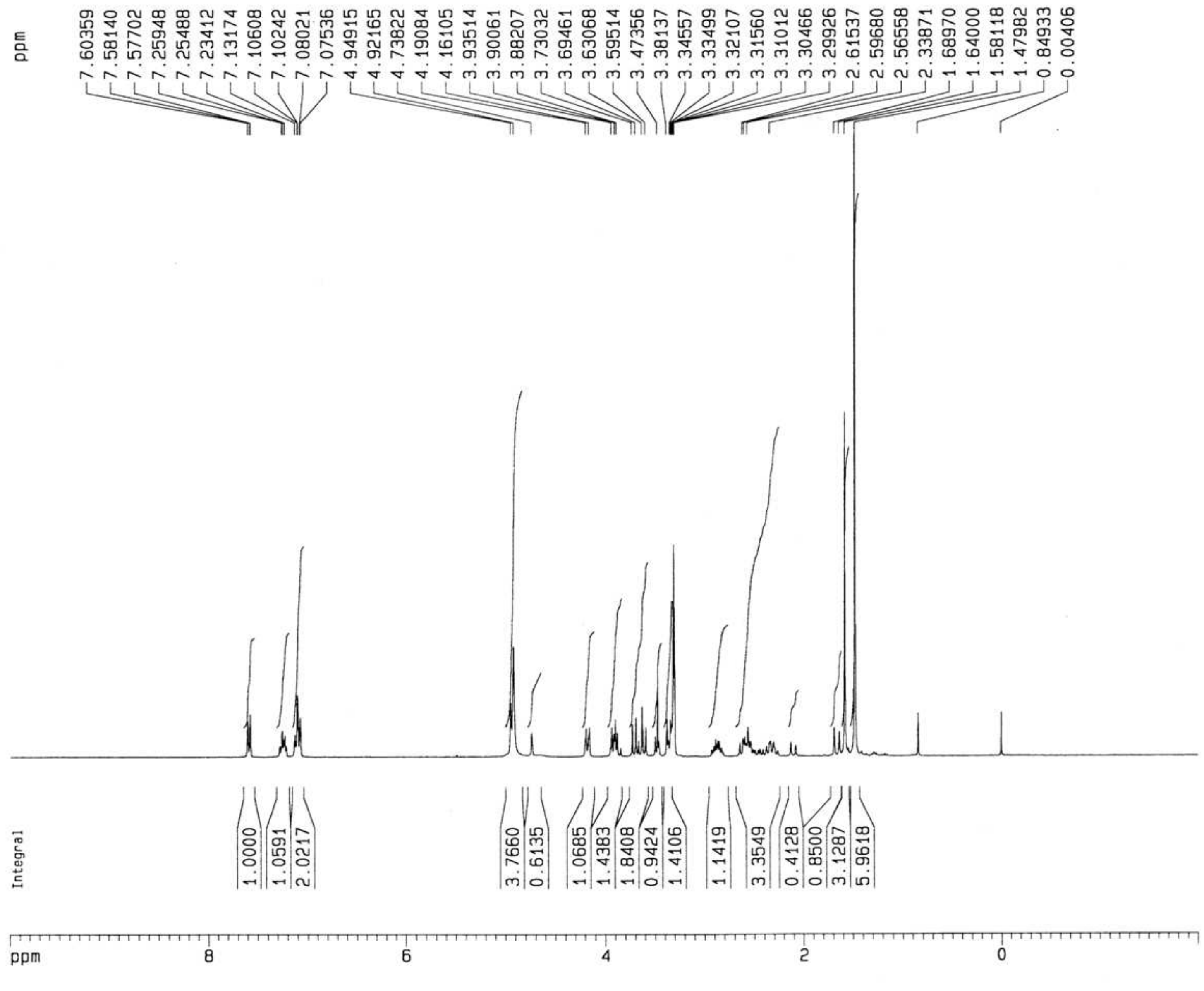
============ CHANNEL f1 ===========
NUC1                13C
P1                 9.75 usec
PL1                0.00 dB
SFO1        75.4760200 MHz

============ CHANNEL f2 ===========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            110.00 usec
PL2                0.00 dB
PL12              17.50 dB
PL13              17.50 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677503 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             215.000 ppm
F1             16225.57 Hz
F2P              -5.000 ppm
F2              -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14526 Hz/cm
```

18



```
Current Data Parameters
NAME         JFA-8-25-2011
EXPNO                    2
PROCNO                   1

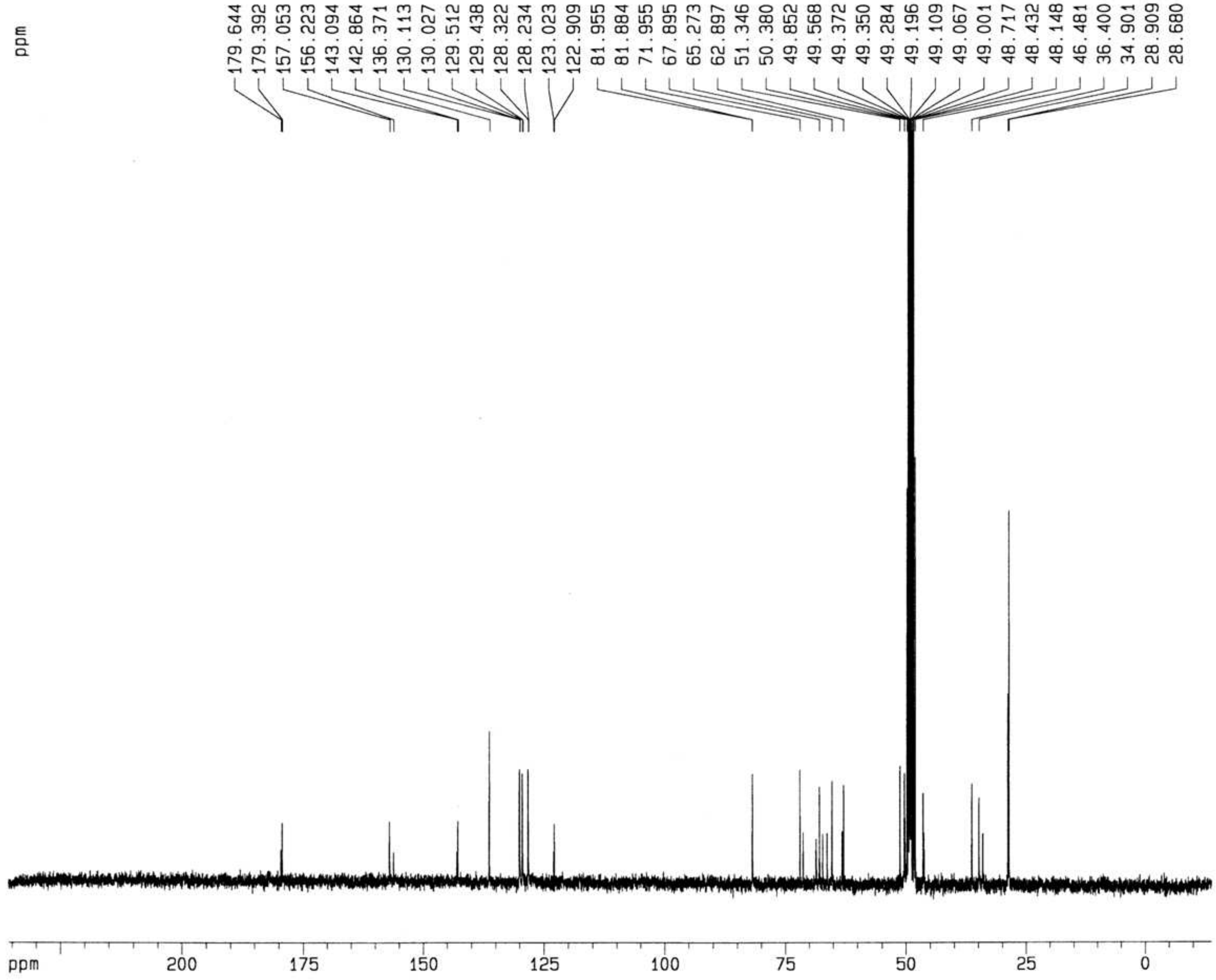
F2 - Acquisition Parameters
Date_             20110825
Time                 16.00
INSTRUM              spect
PROBHD     5 mm Multinu
PULPROG               zg30
TD                   32768
SOLVENT               MeOH
NS                      32
DS                       2
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542580 sec
RG                   456.1
DW               81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ========
NUC1                    1H
P1                10.10 usec
PL1               -6.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF          300.1300048 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              3001.30 Hz
F2P              -2.000 ppm
F2              -600.26 Hz
PPMCM           0.60000 ppm/cm
HZCM        180.07800 Hz/cm
```

18



```
Current Data Parameters
NAME      JFA-8-25-2011
EXPNO                 3
PROCNO                1

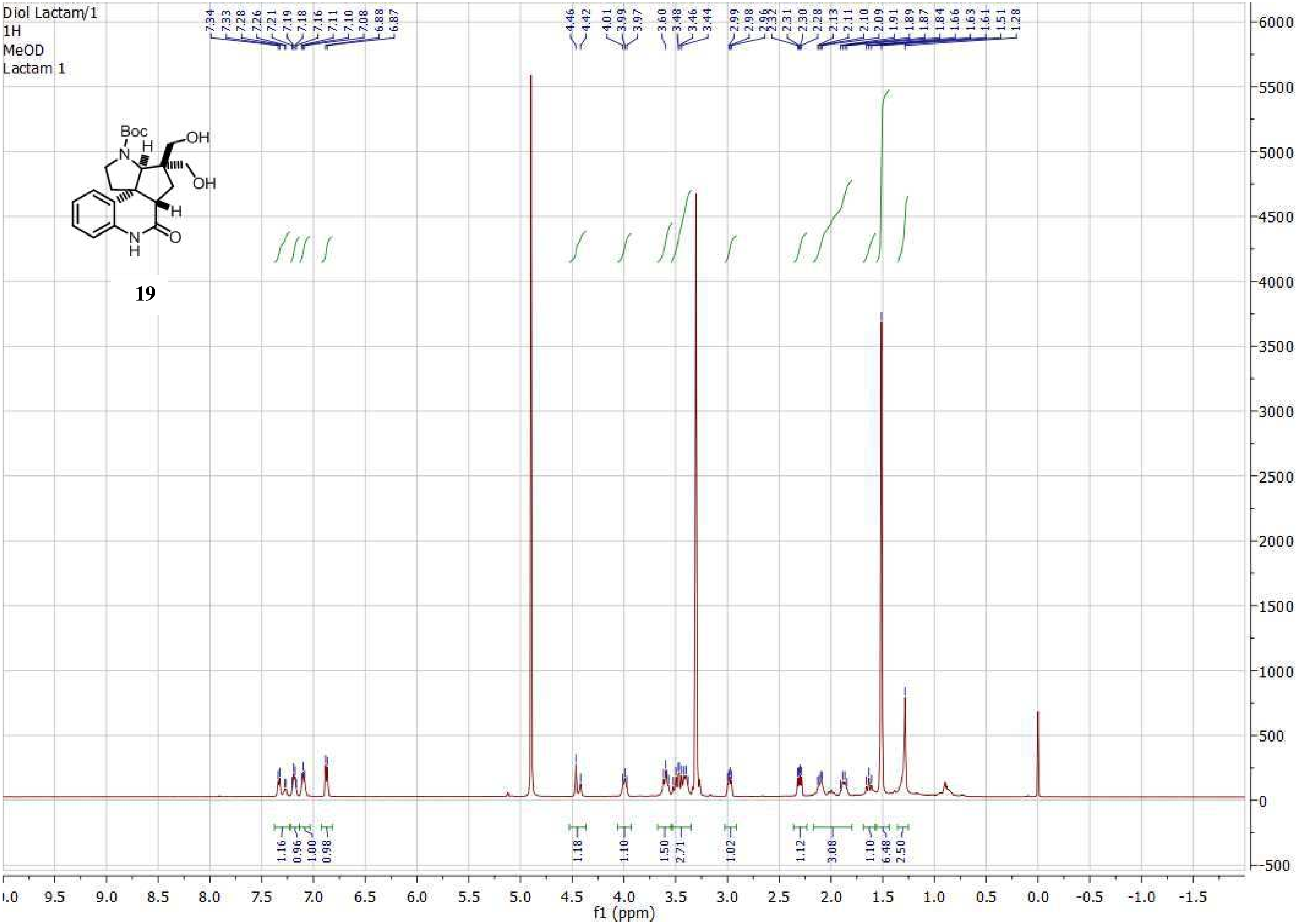
F2 - Acquisition Parameters
Date_          20110825
Time              16.06
INSTRUM           spect
PROBHD   5 mm Multinu
PULPROG          zgpg30
TD                24576
SOLVENT            MeOH
NS                11128
DS                    4
SWH           18832.393 Hz
FIDRES         0.766292 Hz
AQ            0.6525428 sec
RG                 8192
DW               26.550 usec
DE                 6.00 usec
TE                300.0 K
D1           0.50000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

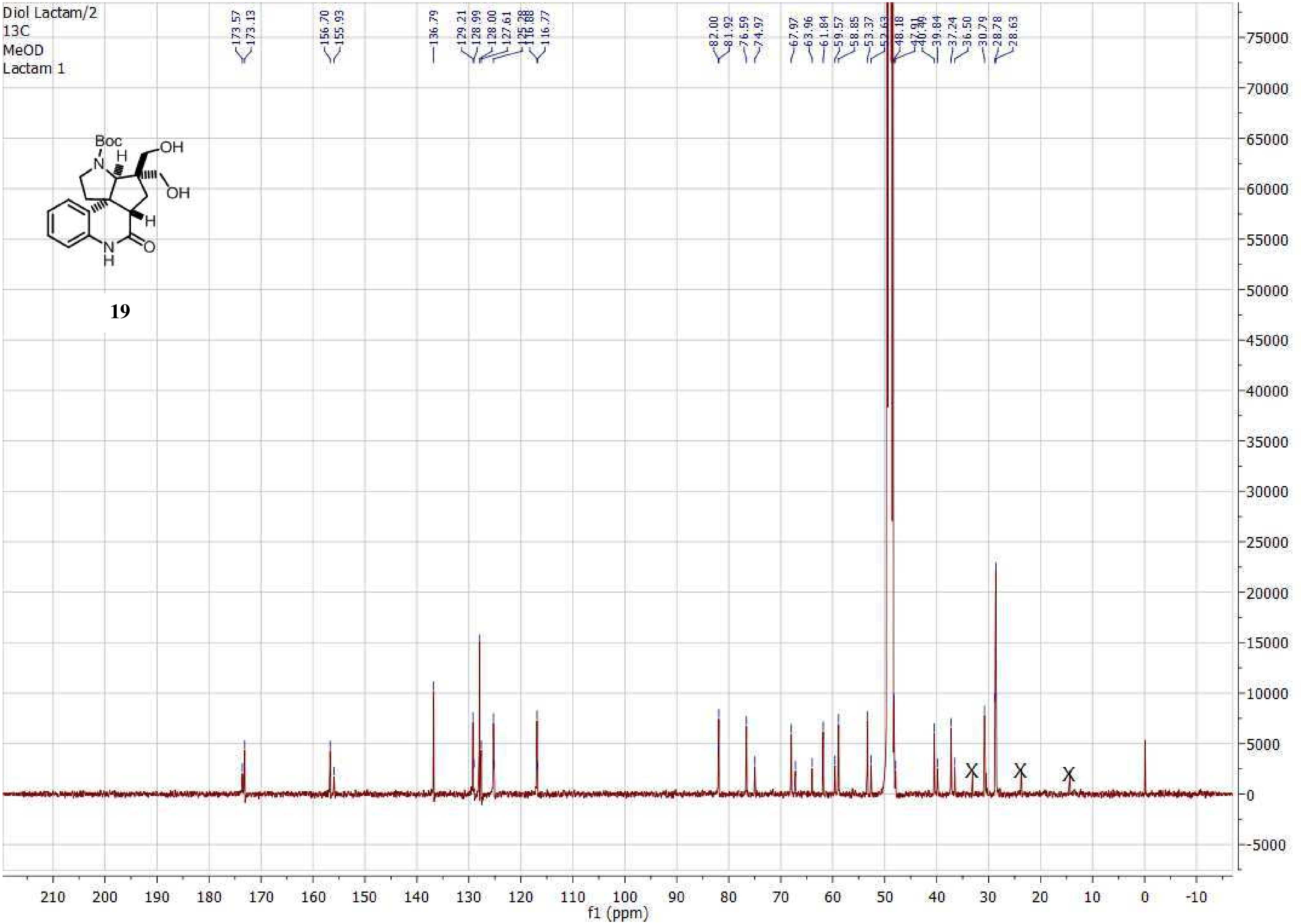
============ CHANNEL f1 ===========
NUC1                13C
P1                 9.75 usec
PL1                0.00 dB
SFO1         75.4760200 MHz

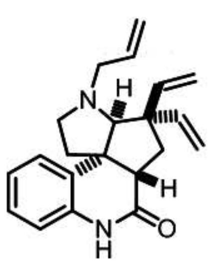
============ CHANNEL f2 ===========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            110.00 usec
PL2                0.00 dB
PL12              17.50 dB
PL13              17.50 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4676433 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

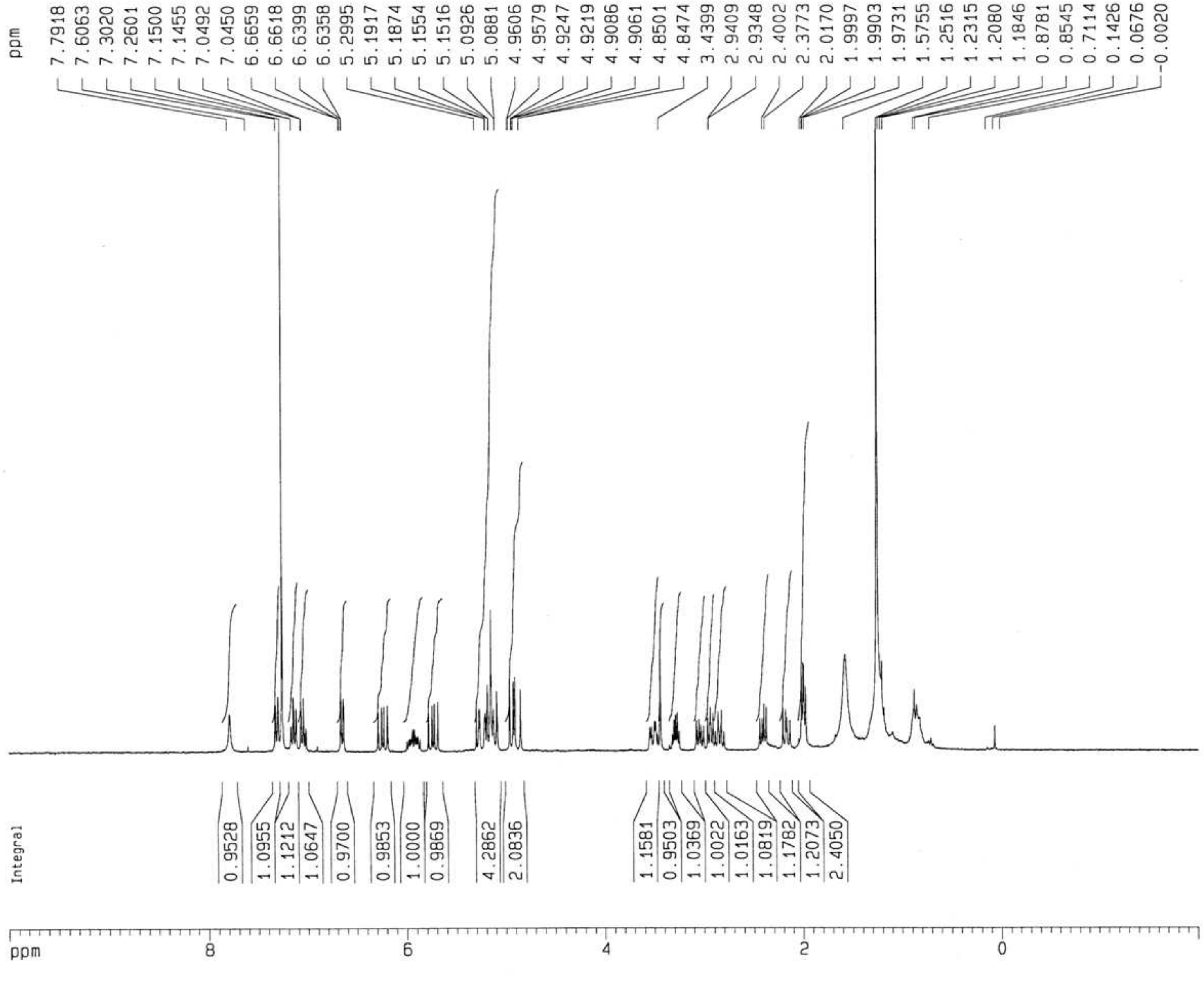
1D NMR plot parameters
CX                20.00 cm
F1P             235.769 ppm
F1             17792.90 Hz
F2P             -13.774 ppm
F2             -1039.49 Hz
PPMCM          12.47713 ppm/cm
HZCM          941.61963 Hz/cm
```


Diol Lactam/1
1H
MeOD
Lactam 1
Boc
N
H
OH
OH
H
N
H
O
19
7.34
7.33
7.28
7.26
7.21
7.19
7.18
7.16
7.11
7.10
7.08
6.88
6.87
4.46
4.42
4.01
3.99
3.97
3.60
3.48
3.46
3.44
2.99
2.98
2.96
2.32
2.31
2.30
2.28
2.13
2.11
2.10
2.09
1.91
1.89
1.87
1.84
1.66
1.63
1.61
1.51
1.28
1.16
0.96
1.00
0.98
1.18
1.10
1.50
2.71
1.02
1.12
3.08
1.10
6.48
2.50
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


Diol Lactam/2
13C
MeOD
Lactam 1
Boc
N
H
OH
OH
H
N
H
O
19
173.57
173.13
156.70
155.93
136.79
129.21
128.99
128.00
127.61
125.28
116.88
116.77
82.00
81.92
76.59
74.97
67.97
63.96
61.84
59.57
58.85
53.37
52.63
48.18
47.91
40.30
39.84
37.24
36.50
30.79
28.78
28.63
X
X
X
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



6



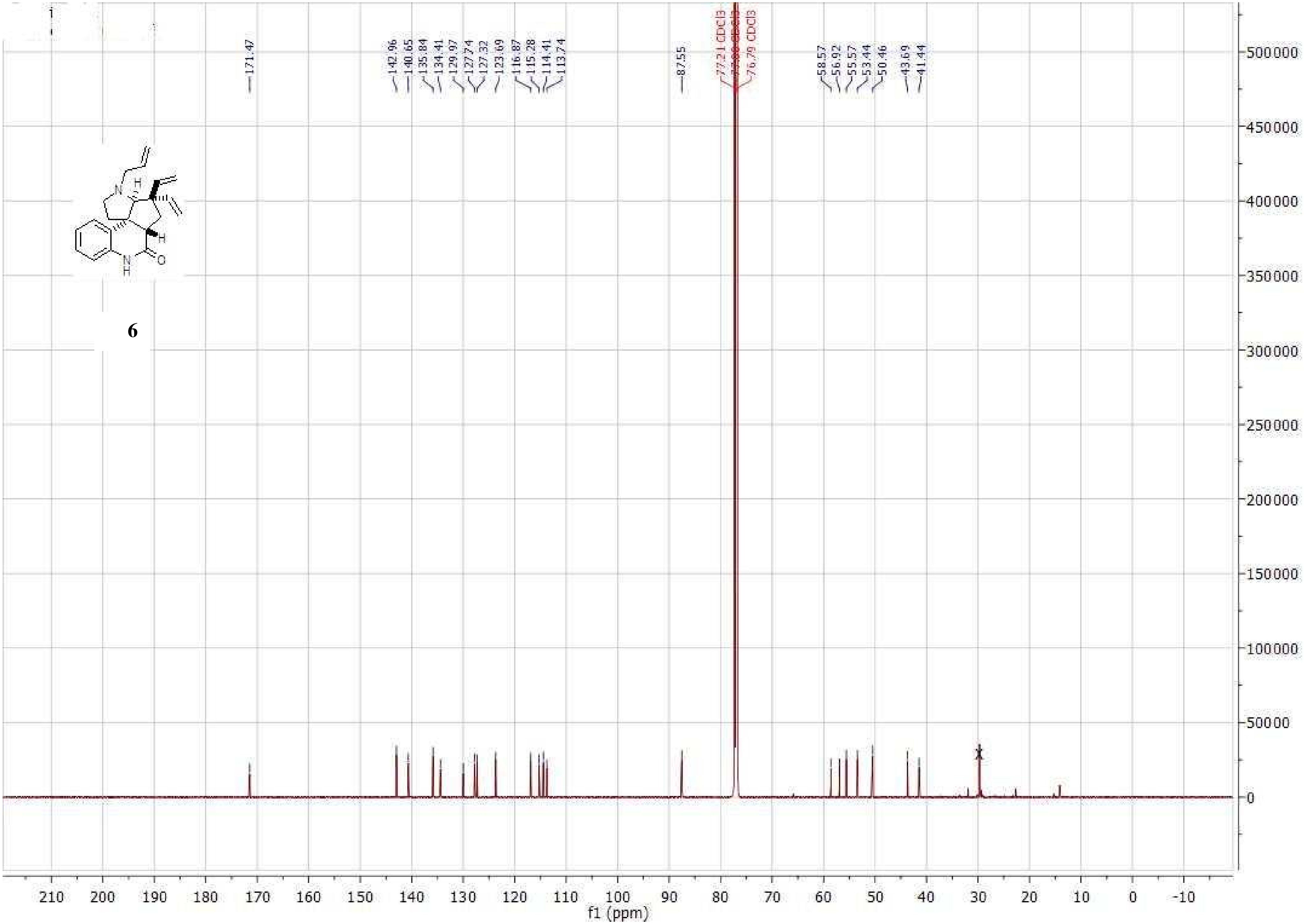
```
Current Data Parameters
NAME       JFA-11-1-2011
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20111101
Time               14.37
INSTRUM            spect
PROBHD   5 mm QNP 1H/1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ             2.6542580 sec
RG                  1024
DW                81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

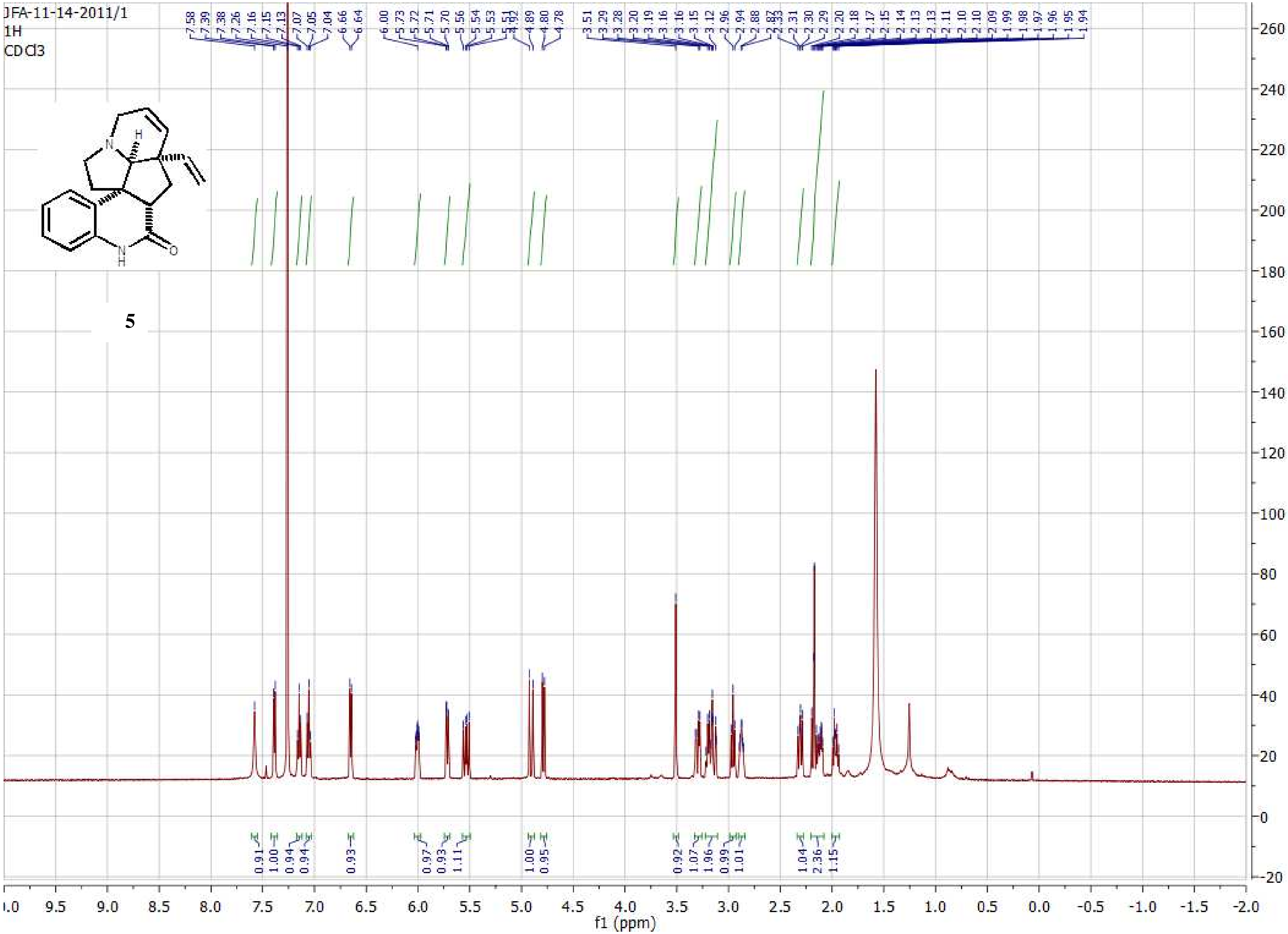
============ CHANNEL f1 ========
NUC1                  1H
P1                 12.10 usec
PL1                 0.00 dB
SFO1         299.8718518 MHz

F2 - Processing parameters
SI                 32768
SF           299.8700101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               2998.70 Hz
F2P               -2.000 ppm
F2               -599.74 Hz
PPMCM            0.60000 ppm/cm
HZCM           179.92200 Hz/cm
```


171.47
142.96
140.65
135.84
134.41
129.97
127.74
127.32
123.69
116.87
115.28
114.41
113.74
87.55
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
58.57
56.92
55.57
53.44
50.46
43.69
41.44
N
H
H
N
H
O
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6



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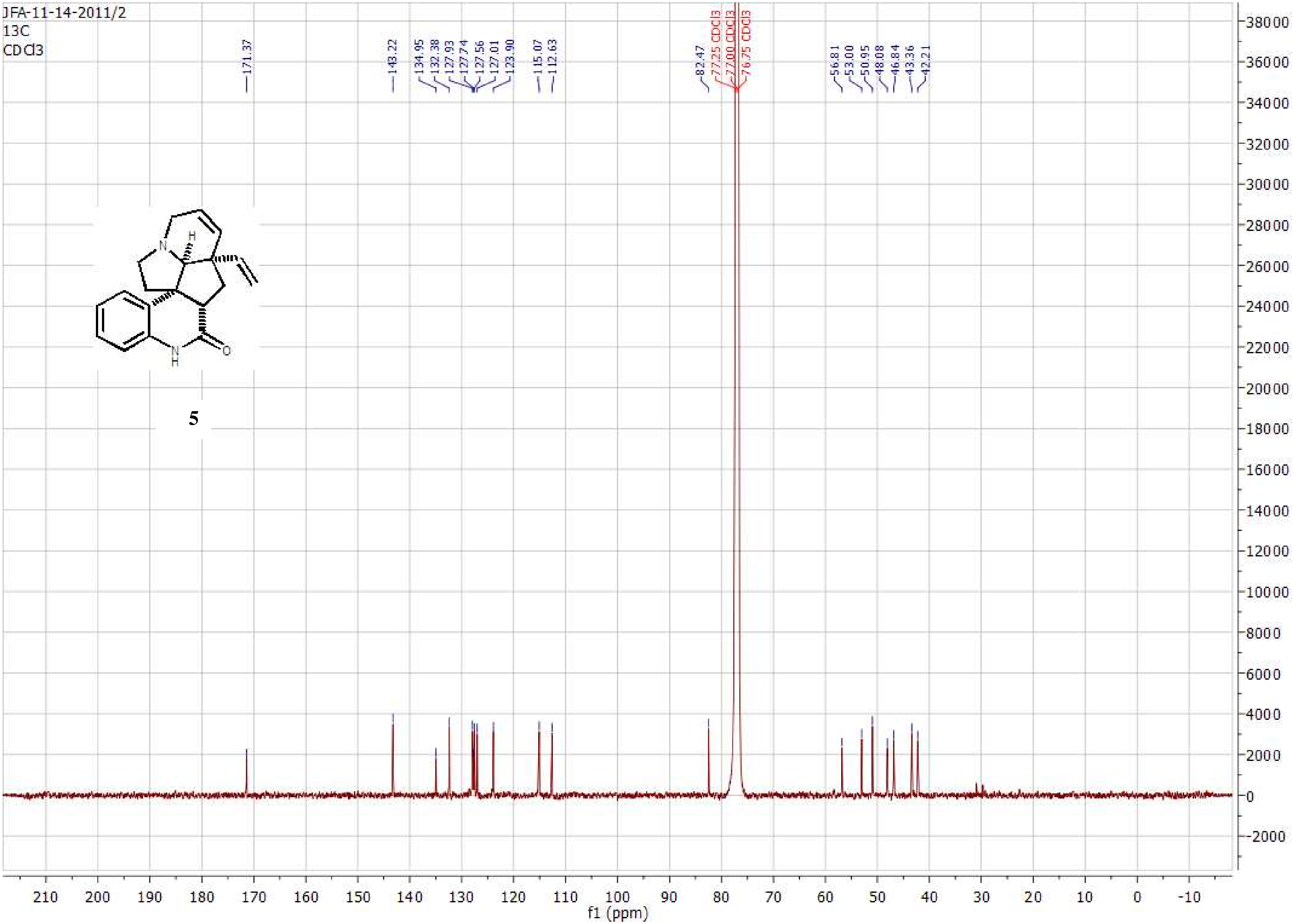
JFA-11-14-2011/1
1H
CDCl3
7.58
7.39
7.38
7.26
7.16
7.15
7.13
7.07
7.05
7.04
6.66
6.64
6.00
5.73
5.72
5.71
5.70
5.56
5.54
5.53
5.51
4.92
4.89
4.80
4.78
3.51
3.29
3.28
3.20
3.19
3.16
3.16
3.15
3.12
2.96
2.94
2.88
2.87
2.33
2.31
2.30
2.29
2.20
2.18
2.17
2.15
2.14
2.13
2.13
2.11
2.10
2.10
2.09
1.99
1.98
1.97
1.96
1.95
1.94
N
H
N
H
O
0.91
1.00
0.94
0.94
0.93
0.97
0.93
1.11
1.00
0.95
0.92
1.07
1.96
0.99
1.01
1.04
2.36
1.15
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


JFA-11-14-2011/2
13C
CDCl3
171.37
143.22
134.95
132.38
127.93
127.74
127.56
127.01
123.90
115.07
112.63
82.47
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
56.81
53.00
50.95
48.08
46.84
43.36
42.21
N
H
O
N
H
5
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)