Total Syntheses of Clausamines A-C and Clausevatine D

Supporting Information

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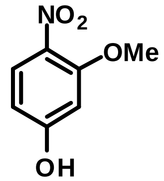
Experimental

General

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were obtained as thin films on NaCl plates using a Bruker Vector 33 FT-IR instrument. NMR experiments were performed on Varian Mercury 400, Varian Inova 600 and Inova 400 instruments and samples were obtained in $CDCl_3$ (referenced to 7.26 ppm for ^1H and 77.0 for ^{13}C), acetone-d_6 (referenced to 2.05 ppm for ^1H and 29.8 for ^{13}C), or DMSO-d_6 (referenced to 2.50 for ^1H and 29.8 for ^{13}C) . Coupling constants (J) are in Hz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 8200 spectrometer at 70 eV. Optical rotations were recorded in cells of 10 cm path length using a Perkin-Elmer 241 digital polarimeter in either $CHCl_3$ or MeOH at 23 °C.

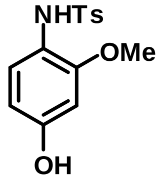
Tetrahydrofuran (THF), dioxane, and dichloromethane (DCM) were dried and deoxygenated by passing the nitrogen purged solvents through activated alumina columns. All other reagents and solvents were used as purchased from Aldrich, Strem, Caledon or VWR. Reaction progress was followed by thin layer chromatography (TLC) (EM Science, silica gel 60 F_{254}) visualizing with UV light, and the plates developed using acidic anisaldehyde. Flash chromatography was performed using silica gel purchased from Silicycle Chemical Division Inc. (230-400 mesh).



Intermediate A

Fluoro compound **10** (7.100 g, 41.490 mmol) was dissolved in DMSO (60 ml). NaOH (8.123 g, 203.075 mmol) dissolved in H_2O (20 ml) was then added and the solution vigorously stirred for 20.5 hours, after which TLC showed complete consumption of the starting material. The reaction was cooled to 0 °C and acidified with 6 M HCl and then poured into 5 % HCl solution and extracted 4 times with ether. The combined organics were washed with 5 % HCl three times, then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield nitro phenol intermediate **A** (5.972 g, 35.309 mmol, 85 %) as a bright yellow solid: m.p. = 143-145 °C; R_f = 0.44, 50 % EtOAc in hexanes; ^1H-NMR (400 MHz, Acetone-d_6): δ = 7.88 (d, J = 9.2 Hz, 1H), 6.67 (d, J = 2.2 Hz, 1H), 6.54 (dd, J = 9.2, 2.2 Hz, 1H), 3.93 (s, 3H), 3.02 (br.s., 1H); ^{13}C NMR (100 MHz, Acetone-d_6) δ = 164.2, 156.7, 128.9, 108.0, 105.4, 101.2, 56.7; IR (thin film): 3358, 3094, 3076, 3055, 3030, 2999, 2955, 1628, 1582, 1516, 1492, 1459, 1432, 1371, 1347, 1313, 1278, 1248, 1210, 1199, 1177, 1168, 1099, 1024, 963, 912, 854, 822, 755; HRMS calc'd for $C_7H_7NO_4$ = 169.0375, found = 169.0369.

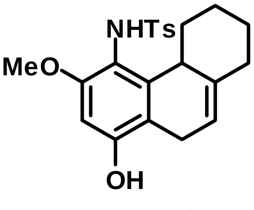
The tosylated amino phenol **11** was prepared in two steps from nitro phenol intermediate **A** without purification of the aniline intermediate.



Compound 11

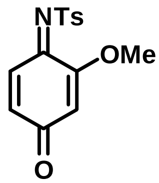
Nitro phenol intermediate **A** (500 mg, 2.956 mmol) was dissolved in THF (4 ml) and MeOH (16 ml). 10 % Pd/C (50 mg) was added and the reaction put over an atmosphere of H_2 and allowed to stir for 4 hours after which TLC showed complete consumption of the starting material. The reaction was filtered through a plug of celite washing with EtOAc and THF. The solvent was removed under reduced pressure to give the crude amine as a purple-blue crystalline solid which was dissolved in pyridine (20 ml) and cooled to 0 °C. TsCl (592 mg, 3.105 mmol) was then added and the reaction stirred for 14 hours after which TLC showed complete consumption of the starting material. The solvent was removed under reduced pressure to give a crude mixture that was dissolved in EtOAc and poured into 5 % HCl solution and extracted 3 times with EtOAc. The combined organics were washed with 5 % HCl two times, water, then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (methanol / DCM as eluent) to yield tosylated amino phenol **11** (829 mg, 2.826 mmol, 96 % over two steps) as a light grey solid: m.p. = 144-145 °C; R_f = 0.49, 5 % methanol in DCM; ^{1}H-NMR (600 MHz, Acetone-d_6): δ = 8.33 (br.s, 1H), 7.67 (br.s, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 9.0 Hz, 1H), 6.38 (dd, J = 9.0, 3.0 Hz, 1H), 6.31 (d, J = 3.0 Hz, 1H), 3.42 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ = 157.5, 154.3, 143.8, 138.5, 129.8, 128.1, 127.3, 118.4, 107.6, 100.1, 55.7, 21.3; IR (thin film): 3425, 3255, 2969, 2940, 2841, 1608, 1511, 1481, 1457, 1443, 1399, 1328, 1306, 1199, 1158, 1118, 1091, 1033, 955, 906, 836, 813, 668; HRMS calc'd for $C_{14}H_{15}NO_4S$ = 293.0722, found = 293.0731.

Phenol **12** was prepared in two steps from tosylated amino phenol **11** without purification of the imine quinone **8** as it was of sufficient purity to be used in the following Diels-Alder reaction. However, for authenticative purposes a small amount of imine quinone **8** was recrystallized from benzene to allow full characterization.



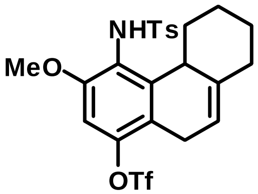
Compound 12

Amino phenol **11** (828 mg) was dissolved in DCM (40ml). $NaIO_4/SiO_2$ (6.199 g of 0.683 mmol/g $NaIO_4/SiO_2$, 4.234 mmol) was added and the mixture stirred for 1 hour, after which TLC (5% MeOH in DCM) showed complete consumption of the starting material. The reaction mixture was then filtered through a cintered glass funnel to remove the $NaIO_4/SiO_2$ washing with EtOAc. The solvent was removed under reduced pressure to give the crude imine quinone **8** as an orange-red solid (842 mg). The crude imine quinone **8** and excess diene **7** were dissolved in DCM (30 ml) and the reaction brought to reflux. The reaction was monitored by H^1 NMR and upon dissapearance of the imine quinone [peaks monitored for dissapearance: ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.10 (d, J = 10.2 Hz, 1H), 6.57 (dd, J = 10.2, 1.8 Hz, 1H)] the reaction was cooled to room temperature and 30 drops of DBU were added. After 15 minutes of stirring at room temperature NMR showed that all of the Diels-Alder adduct had aromatized [peak monitored for dissapearance: ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H)]. The reaction mixture was then poured into 5% HCl solution and extracted 3 times with DCM The combined organics were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield phenol **12** (913 mg, 2.285 mmol, 81 % over the two steps) as a very light tan solid: m.p. = 207-209 °C; R_f = 0.50, 50 % EtOAc in hexane; ^{1}H-NMR (600 MHz, Acetone-d_6): δ = 8.27 (br.s, 1H), 7.53 (d, J = 7.5 Hz, 2H), 7.42 (br.s, 1H), 7.31 (d, J = 7.5 Hz, 2H), 6.20 (s, 1H), 5.52 (br.s, 1H), 3.97-3.92 (m, 1H), 3.24-3.10 (m, 2H), 3.07 (s, 3H), 2.51-2.46 (m, 1H), 2.40 (s, 3H), 2.32 (br.d, J = 12.0 Hz, 1H), 2.03-2.00 (m, 1H), 1.87 (br.d, J = 12.0 Hz, 1H), 1.78 (br.d, 12.6 Hz, 1H), 1.61 (tq, J = 13.2, 3.6 Hz, 1H), 1.34 (tq, J = 13.2, 4.2 Hz, 1H), 1.02 (dq, J = 13.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 155.0, 154.6, 141.8, 139.9, 139.7, 139.2, 128.7, 126.6, 113.8, 112.9, 112.5, 96.3, 54.2, 38.7, 36.2, 35.9, 29.0, 27.0, 24.4, 20.9; IR (thin film): 3420, 3286, 2926, 2853, 1596, 1497, 1447, 1375, 1341, 1316, 1305, 1222, 1157, 1121, 1092, 1070, 1058, 1032, 1009, 960, 918, 871, 812; HRMS calc'd for $C_{22}H_{25}NO_4S$ = 399.1504, found = 399.1499.



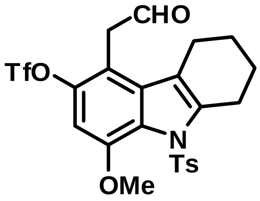
Compound 8

golden orange solid: m.p. = 141-144 ^{0}C; R_f = 0.75, 5 % methanol in DCM; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.10 (d, J = 10.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 6.57 (dd, J = 10.2, 1.8 Hz, 1H), 5.90 (s, 1H), 3.77 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.2, 161.3, 159.5, 144.7, 136.9, 134.6, 129.7, 128.7, 127.7, 107.6, 56.4, 21.7; IR (thin film): 3069, 3042, 2990, 1651, 1627, 1582, 1552, 1450, 1365, 1324, 1308, 1232, 1225, 1179, 1156, 1127, 1091, 994, 862, 816, 701, 689; HRMS calc'd for $C_{14}H_{13}NO_4S$ = 291.0565, found = 291.0555.



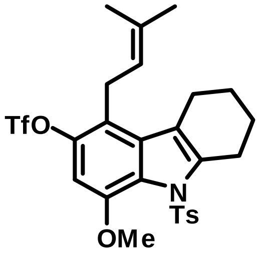
Compound 13

A slurry of phenol **12** (694 mg, 1.737 mmol), pyridine (0.23 ml, 2.844 mmol) and DCM (30 ml) was cooled to 0 °C. Tf_2O (0.30 ml, 1.783 mmol) was added dropwise and the mixture stirred for 30 minutes after which all solid had dissolved and TLC showed complete consumption of the starting material. The reaction was quenched with 5 % HCl solution and the mixture poured into 5 % HCl solution and extracted 3 times with DCM. The combined organics were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield the crude triflate which was purified by column chromatography on silica gel (EtOAc / hexanes as eluent) to yield triflate **13** (0.829 mg, 1.556 mmol, 90 %) as a very pale yellow solid: m.p. = 152-154 °C; R_f = 0.77, 50 % EtOAc in hexane; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53-7.49 and 7.23-7.20 (m, AA'BB', 4H), 6.46 (s, 1H), 6.09 (s, 1H), 5.49 (t, J = 3.2 Hz, 1H), 4.60 (dq, J = 12.0, 5.4 Hz, 1H), 3.35-3.31 (m, 2H), 3.18 (s, 3H), 2.44-2.37 (m, 4H), 2.36-2.30 (m, 1H), 2.13-2.03 (m, 1H), 1.91-1.77 (m, 2H), 1.65 (tq, J = 12.8, 3.6 Hz, 1H), 1.33 (tq, J = 12.8, 4.4 Hz, 1H), 1.06 (dq, J = 12.8, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.7, 146.7, 143.6, 142.0, 139.7, 136.6, 128.9, 127.6, 122.1, 120.3, 120.1, 116.9, 111.8, 101.9, 55.1, 38.8, 36.1, 36.0, 29.2, 27.2, 24.6, 21.4; IR (thin film): 3249, 2931, 2854, 1617, 1577, 1480, 1442, 1420, 1336, 1307, 1246, 1214, 1164, 1141, 1108, 1092, 1040, 1015, 999, 959, 918, 895, 854, 841, 814, 761, 734; HRMS calc'd for $C_{23}H_{24}F_3NO_6S_2$ = 531.0997, found = 531.0999.



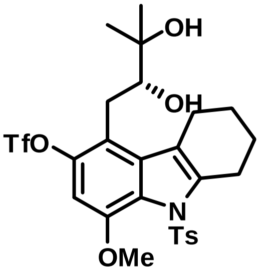
Compound 14

Triflate **13** (1.540 g, 2.897 mmol) and NMO (407 mg, 3.474 mmol) were dissolved in THF (20 ml) and H_2O (5 ml). A catalytic amount of OsO_4 (a few crystals) was then added and the reaction stirred at room temperature until TLC indicated the complete consumption of the starting material. Na_2SO_3 (1.825 g, 14.480 mmol) dissolved in H_2O (10 ml) was then added and the solution stirred for 3.5 hours after which the reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield the crude diol as a light tan solid (1.678 g). The diol (1.678 g) was redissolved in DCM (50 ml) and $NaIO_4/SiO_2$ (7.124 g of 0.61 mmol/g $NaIO_4/SiO_2$, 4.346 mmol) was added and the mixture stirred for 23 hours, after which TLC showed complete consumption of the diol (R_f of dihydroxyaled product = 0.34, 50 % ethyl acetate in hexanes). The reaction mixture was then filtered through a cintered glass funnel, to remove the $NaIO_4/SiO_2$, washing with EtOAc. The solvent was removed under reduced pressure to give a crude residue which was redissolved in THF (25 ml). Concentrated sulfuric acid (6 drops) was then added and the reaction stirred for 2 hours, after which TLC showed only one spot corresponding to aldehyde **14**. The solution was then neutralized with Na_2CO_3 and $MgSO_4$ was added to remove any water. The reaction mixture was then filtered, washing with EtOAc, and the solvent removed under reduced pressure to yield an off-white foam that was purified by column chromatography on silica gel (EtOAc / hexanes as eluent) to yield aldehyde **14** (1.507 g, 2.762 mmol, 95 % over 3 steps) as an off-white solid: m.p. = 134-136 °C; R_f = 0.56, 33 % EtOAc in hexane; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, J = 1.2 Hz, 1H), 7.74-7.10 and 7.33-7.29 (m, AA'BB', 4H), 6.59 (s, 1H), 4.07 (d, J = 1.2 Hz, 2H), 3.60 (s, 3H), 3.18-3.13 (m, 2H), 2.75-2.71 (m, 2H), 2.43 (s, 3H), 1.89-1.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.8, 147.2, 144.1, 143.9, 141.8, 138.8, 132.2, 129.3, 126.3, 125.7, 119.5, 117.4, 109.8, 100.6, 55.7, 41.0, 26.4, 24.1, 22.7, 22.3, 21.5; IR (thin film): 2942, 2847, 2729, 1729, 1621, 1583, 1499, 1419, 1368, 1339, 1316, 1276, 1243, 1214, 1187, 1175, 1140, 1092, 1044, 1003, 980, 964, 932, 875, 830, 733, 663; HRMS calc'd for $C_{23}H_{22}F_3NO_7S_2$ = 545.0790, found = 545.0773.



Compound 15

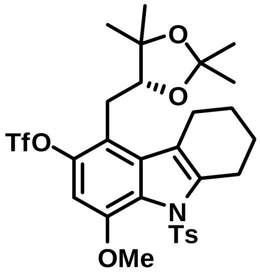
A slurry of isopropyltriphenyl-phosphonium iodide (1.791 g, 4.143 mmol) in THF (15 ml) was cooled to 0 °C. nBuLi (1.55 ml of 2.5 M solution in hexanes, 3.875 mmol) was added dropwise and the solution allowed to stir for 10 minutes producing a dark orange-red solution. Aldehyde **14** (1.507 g, 2.762 mmol) was then transferred dropwise to the ylide solution in THF (10 ml). To ensure complete transfer the flask containing the aldehyde was washed once more with THF (2 ml) and the contents added to the ylide solution. After 10 minutes TLC showed complete consumption of the starting material and water was added to quench the reaction. The reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to produce the crude alkene which was purified by column chromatography on silica gel (EtOAc / hexanes as eluent) to yield alkene **15** (1.149 g, 2.010 mmol, 73 %) as a white solid: m.p. = 123-125 °C; R_f = 0.68, 33 % EtOAc in hexane; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 5.01 (br.t, J = 6.0 Hz, 1H), 3.62 (d, J = 6.0 Hz, 2H), 3.57 (s, 3H), 3.18-3.14 (m, 2H), 2.90-2.87 (m, 2H), 2.43 (s, 3H), 1.88-1.82 (m, 4H), 1.74 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 143.9, 143.6, 140.7, 138.9, 132.3, 131.6, 129.2, 126.2, 125.7, 122.5, 120.2, 119.4, 118.4, 117.0, 100.7, 55.6, 26.5, 25.5, 25.0, 23.9, 22.9, 22.5, 21.5, 18.0; IR (thin film): 2940, 2860, 1620, 1582, 1496, 1418, 1368, 1313, 1242, 1213, 1177, 1141, 1094, 1031, 960, 906, 874, 830, 775, 666; HRMS calc'd for $C_{26}H_{28}F_3NO_6S_2$ = 571.1310, found = 571.1306.



Intermediate B

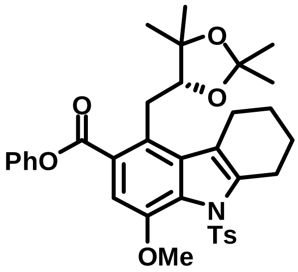
K_2CO_3 (943 mg, 6.823 mmol), $K_3Fe(CN)_6$ (2.246 g, 6.821 mmol), $K_2OsO_2(OH)_4$ (32 mg, 0.0563 mmol), and $(DHQD)_2PHAL$ (267 mg, 0.228 mmol) were dissolved in tBuOH (12.5 ml) and H_2O (12.5 ml). Methanesulfonamide (433 mg, 4.552 mmol) and alkene **15** (1.300 g, 2.274 mmol) were then added and the reaction vigorously stirred for 44 hours after which TLC showed complete consumption of the starting material. Na_2SO_3 (1.433 g, 11.369 mmol) was then added and the solution stirred for 1 hour after which the reaction was poured into water and extracted 3 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield the crude diol as an off-white foam that was purified by column chromatography on silica gel (EtOAc / hexanes as eluent) to yield diol intermediate **B** (1.331 g, 2.198 mmol, 98 %) as a white solid: R_f = 0.25, 33 % EtOAc in hexanes; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.75-7.72 and 7.32-7.29 (m, AA'BB', 4H), 6.57 (s, 1H), 3.64 (br.d, J = 11.2 Hz, 1H), 3.58 (s, 3H), 3.22-3.06 (m, 5H), 2.82-2.73 (m, 1H), 2.43 (s, 3H), 2.16 (br.s, 1H), 1.94-1.76 (m, 5H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 144.8, 143.7, 141.1, 138.9, 132.5, 129.2, 126.2, 125.7, 123.2, 120.0, 118.6, 116.8, 116.7, 113.7, 100.7, 78.0, 72.7, 55.6, 27.8, 26.5, 26.3, 24.8, 23.6, 22.8, 22.5, 21.5; IR (thin film): 3545, 3422, 2974, 2943, 2863, 1621, 1597, 1582, 1496, 1441, 1418, 1367, 1313, 1276, 1242, 1214, 1175, 1141, 1122, 1092, 1066, 1042, 1011, 980, 965, 935, 906, 861, 832, 815, 767, 734, 669, 636; HRMS calc'd for $C_{26}H_{30}F_3NO_8S_2$ = 605.1365, found = 605.1354; $[\alpha]_D$ = +11.9° (*c* = 0.536, MeOH).

The enantiomeric excess was determined to be 45% by chiral shift reagent (Europium tris[3-(heptafluoro-propylhydroxymethylene)-(+)-camphorate]). Peak monitored is at 6.57 ppm (s, 1H). Upon addition of the chiral shift reagent the (-) enantiomer is shifted downfield with respect to the (+) enantiomer.



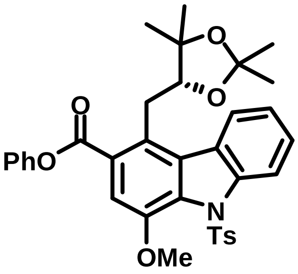
Compound 16

Diol intermediate **B** (1.793 g, 2.960 mmol) and paratoluenesulfonic acid (169 mg, 0.888 mmol) were dissolved in DMF (20 ml) and cooled to 0 °C. 2-methoxypropene (1.42 ml, 14.828 mmol) was then added and the solution allowed to warm to room temperature over 12 hours, after which TLC showed complete consumption of the starting material. The reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield acetonide **16** (1.866 g, 2.900 mol, 98 %) as a white solid: R_f = 0.65, 33 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.57 (s, 1H), 3.89 (d, J = 9 Hz, 1H), 3.59 (s, 3H), 3.30-3.22 (m, 2H), 3.17 (br.s, 2H), 2.93 (d, J = 14.4 Hz, 1H), 2.77-2.71 (m, 1H), 2.43 (s, 3H), 1.93-1.78 (m, 4H), 1.40 (s, 3H), 1.31 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 144.3, 143.7, 141.0, 139.1, 132.4, 129.3, 126.3, 125.8, 120.1, 118.7, 116.9, 116.6, 107.0, 100.7, 83.3, 80.2, 55.6, 28.2, 26.7, 26.6, 25.9, 25.8, 24.7, 23.1, 22.9, 22.5, 21.6; IR (thin film): 2981, 2939, 2863, 1620, 1582, 1496, 1418, 1370, 1338, 1314, 1270, 1243, 1215, 1188, 1176, 1141, 1119, 1104, 1093, 1051, 1017, 1000, 980, 965, 932, 889, 874, 841, 814, 776, 766, 734, 704, 670, 609, 574 ; HRMS calc'd for $C_{29}H_{34}F_3NO_8S_2$ = 645.1678, found = 645.1671.



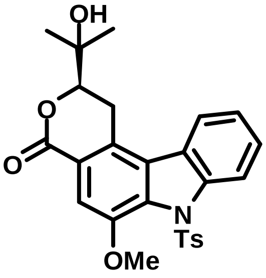
Intermediate C

Acetonide **16** (1.238 g, 1.917 mmol), phenol (1.804 g, 19.169 mmol), and $Pd(PPh_3)_4$ (665 mg, 0.575 mmol) were dissolved in NEt_3 (3 ml) and dioxane (17 ml). CO was bubbled through the solution for 20 minutes and while maintaining an atmosphere of CO the reaction mixture was heated to 95 °C for 4 days after which TLC showed that some starting material still remained. Regardless, the reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield ester intermediate **C** (703 mg, 1.138 mmol, 59 %) as a white solid along with recovered acetonide **16** (471 mg, 0.729 mmol). The recovered acetonide was resubjected to the reaction conditions. Acetonide **16** (471 mg, 0.729 mmol), phenol (686 mg, 7.289 mmol), and Pd(PPh$_3$)$_4$ (253 mg, 0.219 mmol) were dissolved in NEt$_3$ (1.5 ml) and dioxane (10 ml). CO was bubbled through the solution for 20 minutes and while maintaining an atmosphere of CO the reaction mixture was heated to 95 °C for 4 days after which TLC showed that some starting material still remained. Regardless, the reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with MgSO$_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield ester intermediate **C** (140 mg, 0.227 mmol, 31 %) as a white solid along with recovered starting material acetonide **16** (318 mg, 0.675 mmol). Therefore, two cycles yielded ester intermediate **C** (843 mg, 1.364, 71 % over 2 cycles, or 96 % BRSM) along with unreacted starting material (318 mg, 0.675 mmol): R$_f$ = 0.57, 33 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, CDCl$_3$): δ = 7.77 (d, J = 8.7 Hz, 2H), 7.45 (s, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 3.94 (dd, J = 9.6, 3.0 Hz, 1H), 3.65 (s, 3H), 3.60-3.53 (m, 2H), 3.49-3.44 (m, 1H), 3.19 (br.s, 2H), 2.82-2.76 (m, 1H), 2.43 (s, 3H), 1.95-1.78 (m, 4H), 1.40 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 166.2, 151.0, 145.5, 143.5, 140.0, 139.3, 133.0, 129.6, 129.4, 129.2, 128.9, 126.2, 125.7, 124.9, 121.8, 119.2, 110.0, 106.6, 84.8, 80.4, 55.5, 28.3, 27.7, 26.7, 26.1, 25.6, 23.4, 23.0, 22.7, 21.6; IR (thin film): 3098, 3063, 3043, 2979, 2935, 2859, 1734, 1594, 1494, 1479, 1457, 1403, 1369, 1337, 1315, 1271, 1216, 1188, 1176, 1159, 1112, 1093, 1031, 1016, 999, 965, 921, 839, 813, 772, 738, 670, 667; HRMS calc'd for C$_{39}$H$_{39}$NO$_7$S = 617.2447, found = 617.2443.



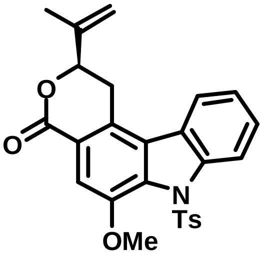
Compound 17

Ester intermediate **C** (201 mg, 0.325 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (221 mg, 0.974 mmol) were dissolved in benzene (5 ml) and added to a 2-5 ml microwave vial. The head space was purged with Ar and the vial capped and heated to 100 °C for 2 hours , after which TLC showed complete consumption of the starting material. The reaction was transferred to a round bottom flask and the solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield carbazole **17** (187 mg, 0.305 mmol, 94 %) as a very pale yellow solid: R$_f$ = 0.51, 33 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, CDCl$_3$): δ = 8.43 (t, J = 8.4 Hz, 2H), 7.84-7.82 and 7.25-7.22 (m, AA'BB', 4H), 7.67 (s, 1H), 7.55 (dt, J = 8.4, 1.2 Hz, 1H), 7.47-7.43 (m, 2H), 7.41 (dt, J = 8.4, 1.2 Hz, 1H), 7.31-7.28 (m, 3H), 4.13 (X of ABX system, J = 10.3, 3.3 Hz, 1H), 3.94 (B of ABX system, J = 14.3, 10.3 Hz, 1H), 3.78 (s, 3H), 3.75 (A of ABX system, J = 14.3, 3.3 Hz, 1H), 2.43 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 165.9, 150.9, 146.4, 143.9, 141.4, 138.5, 131.9, 130.3, 129.5, 129.3, 128.9, 127.2, 126.7, 126.3, 125.9, 123.8, 123.5, 121.7, 116.9, 113.1, 106.8, 83.8, 80.5, 55.7, 28.4, 26.7. 26.1, 23.5, 21.6; IR (thin film): 3047, 2980, 2935, 2872, 1735, 1595, 1496, 1457, 1369, 1338, 1280, 1219, 1189, 1154, 1114, 1093, 1019, 1000, 957, 921, 811, 771, 742, 690, 668, 657; HRMS calc'd for C$_{35}$H$_{35}$NO$_7$S = 613.2134, found = 613.2126.



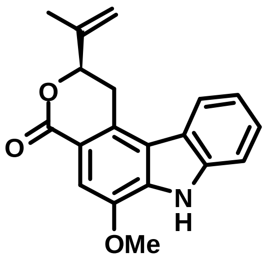
Compound 18

Carbazole **17** (123 mg, 0.200 mmol) and paratoluenesulfonic acid (40 mg g, 0.210 mmol) were dissolved in THF (8 ml) and ethylene glycol (2 ml) and the mixture was brought to reflux for 7 hours, after which TLC showed complete consumption of the starting material. The reaction was poured into water and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield alcohol **18** (95 mg, 0.198 mmol, 99 %) as a white solid: R_f = 0.24, 50 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.62 (s, 1H), 7.58 (t, J = 8.4 Hz, 1H), 7.46 (t, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 4.41 (X of ABX system, J = 12.6, 3.6 Hz, 1H), 3.74 (s, 3H), 3.60 (B of ABX system, J = 16.2, 3.6 Hz, 1H), 3.41 (A of ABX system, J = 16.2, 12.6 Hz, 1H), 2.43 (s, 3H), 2.24 (s, 1H), 1.48 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.3, 147.2, 144.2, 141.3, 138.3, 132.3, 129.4, 127.6, 127.2, 126.3, 125.63, 125.56, 124.1, 121.9, 120.9, 117.1, 110.8, 83.9, 71.3, 55.7, 25.8, 25.2, 25.1, 21.6; IR (thin film): 3447, 3076, 2975, 2934, 2853, 1718, 1601, 1499, 1451, 1362, 1321, 1280, 1213, 1176, 1118, 1092,1067, 1023, 962, 914, 813, 777, 732, 684, 656; HRMS calc'd for $C_{26}H_{25}NO_6S$ = 479.1403, found = 479.1377.



Intermediate D

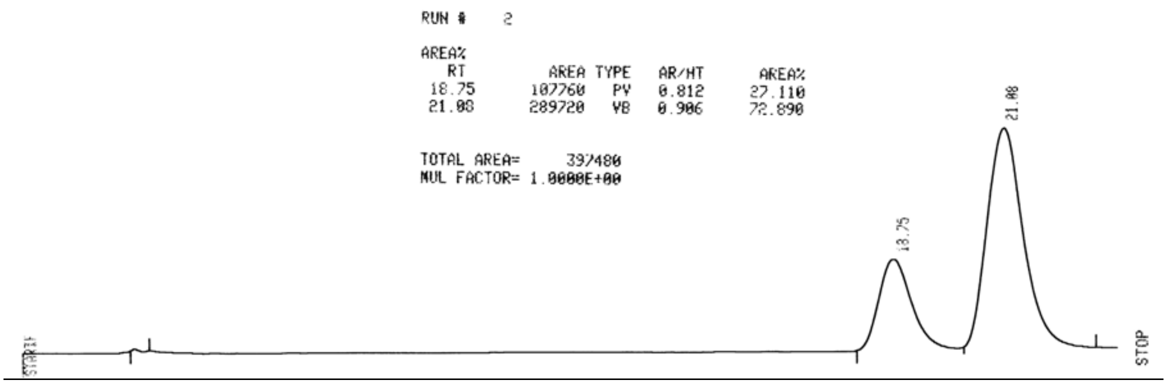
Alcohol **18** (68 mg, 0.142 mmol) and Martin's sulfurane (143 mg, 0.213 mmol) were added to a schlenk tube and the vessel was evacuated and filled with N_2. DCM (5 ml) was then added and the reaction allowed to stir for 20 minutes, after which TLC showed complete consumption of the starting material. The reaction mixture was then transferred to a round bottom flask and the solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield alkene intermediate **D** (51 mg, 0.111 mmol, 77 %) as a white solid: R_f = 0.63, 50 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.65 (s, 1H), 7.56 (t, J = 8.1 Hz, 1H), 7.45 (t, J = 8.1 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 5.22 (s, 1H), 5.11 (s, 1H), 5.04 (X of ABX system, J = 11.5, 3.5 Hz, 1H), 3.75 (s, 3H), 3.59 (B of ABX system, J = 16.2, 3.5 Hz, 1H), 3.47 (A of ABX system, J = 16.2, 11.5 Hz, 1H), 2.43 (s, 3H), 1.97 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.3, 147.3, 144.2, 141.8, 141.5, 138.4, 132.3, 129.4, 127.6, 126.9, 126.4, 125.7, 125.5, 124.1, 121.8, 121.3, 117.2, 114.4, 111.1, 80.8, 55.7, 29.5, 21.6, 18.3; IR (thin film): 3061, 2974, 2922, 2850, 1718, 1599, 1499, 1451, 1357, 1321, 1279, 1222, 1175, 1155, 1117, 1091, 1066, 1043, 1023, 1003, 961, 930, 872, 831, 812, 778, 747, 704, 681, 656; HRMS calc'd for $C_{26}H_{23}NO_5S$ = 461.1297, found = 461.1298.



Clausamine B

Alkene intermediate **D** (34 mg, 0.0737 mmol) was dissolved in THF (5 ml) and added to a 2-5 ml microwave vial. TBAF (0.15 ml of 1.0 M solution in THF, 0.150 mmol) was then added dropwise. The head space was purged with Ar and the vial capped and heated to 60 °C for 20 minutes in the microwave, after which TLC showed complete consumption of the starting material. The reaction was poured into saturated NH_4Cl solution and extracted 3 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield Clausamine B as a white solid along with a minor impurity. The solid was resubjected to column chromatography (DCM as eluent) to afford pure Clausamine B (19 mg, 0.0618 mmol, 84 %) as a white solid. The spectroscopic data for synthetic Clausamine B is in agreement with literature[1], with the exception of the optical rotation: R_f = 0.66, 50 % EtOAc in hexanes; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.67 (br.s, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.64 (s, 1H) 7.54 (d, J = 7.8 Hz, 1H), 7.48 (dt, J = 7.8, 1.2 Hz, 1H), 7.30 (dt, J = 7.8, 1.8 Hz, 1H), 5.24 (s, 1H), 5.10 (s, 1H), 5.08 (X of ABX system, J = 11.7, 3.9 Hz, 1H), 4.04 (s, 3H), 3.62 (B of ABX system, J = 16.2, 3.9 Hz, 1H), 3.48 (A of ABX system, J = 16.2, 11.7 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.6, 144.5, 142.3, 139.5, 133.5, 128.7, 126.1, 123.3, 121.8, 120.5, 120.2, 116.2, 114.0, 111.6, 106.4, 80.8, 55.9, 29.5, 18.4; IR (thin film): 3311, 3076, 2920, 2837, 1690, 1587, 1507, 1457, 1357, 1310, 1253, 1228, 1162, 1148, 1115, 1083, 1064, 1042, 1004, 900, 849, 733; HRMS calc'd for $C_{19}H_{17}NO_3$ = 307.1208, found = 307.1211; $[\alpha]_D$ = +62.8° (c = 0.083, $CHCl_3$), $[\alpha]_D$ = +63.0° (c = 0.276, $CHCl_3$), literature $[\alpha]_D$ = 0° (c = 0.082, $CHCl_3$).[1]

The enantiomeric excess was determined to be 46% by chiral HPLC, Chiralcel OD-H, 250 x 4.6 mm[2], Diacel Chemical Industries; 96:3:1 Hexanes / MeOH / EtOH at 1.5 mL/min; 220 nm; The retention time for the enantiomers were r_t (-) = 18.75 min, r_t(+) = 21.08 min.



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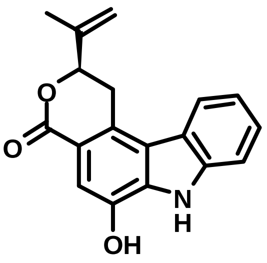
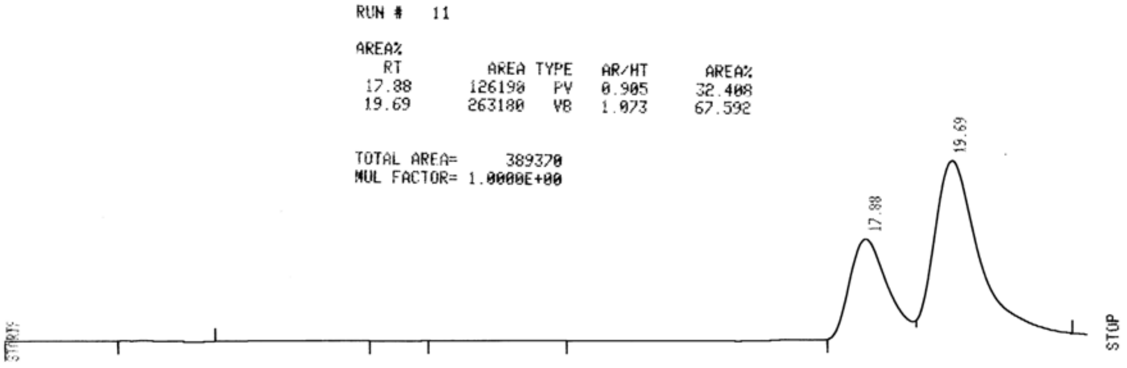


Clausamine A

Clausamine B (29 mg, 0.0944 mmol) was dissolved in DCM (5 ml). BBr_3 (0.50 ml of 1.0 M solution in DCM, 0.500 mmol) was added dropwise and the solution allowed to stir for 2 hours at which point a second addition of BBr_3 (0.50 ml of 1.0 M solution in DCM, 0.500 mmol) was added. The solution was stirred for an additional hour, after which TLC showed complete consumption of the starting material. Saturated $NaHCO_3$ solution (10 ml) and EtOAc (10 ml) was added to quench the excess BBr_3 (cautiously at first) and the mixture was stirred for 4.5 hours. The reaction was poured into 5% HCl solution and extracted 3 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) followed by a second column (acetone / hexanes as eluent) to yield Clausamine A (21 mg, 0.0716 mmol, 75 %) as a pale yellow solid. The spectroscopic data for synthetic Clausamine A is in agreement with literature[1], with the exception of the optical rotation: R_f = 0.59, 50 % acetone in hexanes; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 10.82 (br.s, 1H), 9.17 (br.s, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.66 (ddd, J = 8.0, 1.2, 0.8 Hz, 1H), 7.57 (s, 1H), 7.45 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.25 (ddd, 8.2, 7.2, 0.8 Hz, 1H), 5.27-5.25 (m, 1H), 5.12 (X of ABX system, J = 11.7, 3.5, 1H), 5.08-5.06 (m, 1H), 3.70 (B of ABX system, J = 16.4, 3.5, 1H), 3.51 (A of ABX system, J = 16.4, 11.4 Hz, 1H) 1.97 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ = 166.1, 144.2, 142.8, 141.4, 134.4, 128.6, 126.6, 124.3, 122.9, 121.5, 120.7, 117.0, 113.6, 112.6, 110.9, 81.2, 30.2, 18.6; IR (thin film): 3320, 3101, 3056, 2976, 2922, 1696, 1670, 1628, 1589, 1508, 1457, 1367, 1313, 1262, 1231, 1142, 1113, 1084, 1064, 902, 856, 779, 730; HRMS calc'd for $C_{18}H_{15}NO_3$ = 293.1052, found = 293.1054; $[\alpha]_D$ = +33.2° (*c* = 0.063, $CHCl_3$), $[\alpha]_D$ = +34.6° (*c* = 0.211, $CHCl_3$), literature $[\alpha]_D$ = 0° (*c* = 0.072, $CHCl_3$).[1]

The enantiomeric excess was determined to be 35% by chiral HPLC, Chiralcel OD-H, 250 x 4.6 mm^2, Diacel Chemical Industries; 96:3:1 Hexanes / MeOH / EtOH at 1.5 mL/min; 220 nm; The retention time for the enantiomers were $r_t(-)$ = 17.88 min, $r_t(+)$ = 19.69 min.



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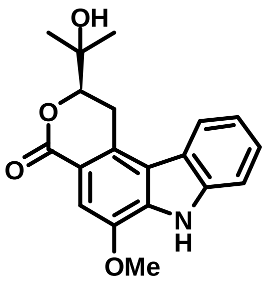
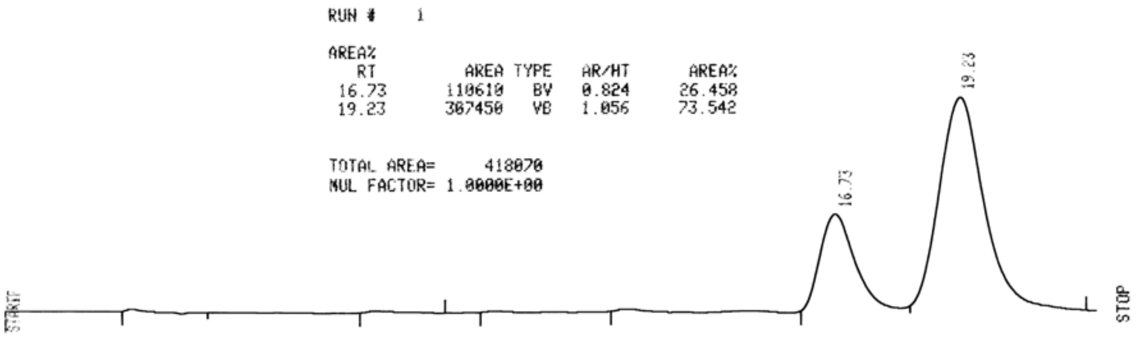


Clausamine C

Alcohol intermediate **D** (75 mg, 0.156 mmol) was dissolved in THF (5 ml) and added to a 2-5 ml microwave vial. TBAF (0.32 ml of 1.0 M solution in THF, 0.320 mmol) was then added dropwise. The head space was purged with Ar and the vial capped and heated to 60 °C for 2 hours in the microwave, after which TLC showed complete consumption of the starting material. The reaction was poured into saturated NH_4Cl solution and extracted 4 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (ethyl acetate / hexanes as eluent) to yield Clausamine C (42 mg, 0.129 mmol, 82 %) as a white solid The spectroscopic data for synthetic Clausamine C is in agreement with literature[1], with the exception of the optical rotation: R_f = 0.53, 80 % EtOAc in hexanes; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.74 (br.s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 4.44 (X of ABX system, J = 13.5, 3.3 Hz, 1H), 4.03 (s, 3H), 3.62 (B of ABX system, J = 16.2, 3.3 Hz, 1H), 3.41 (A of ABX system, J = 16.2, 13.5 Hz, 1H), 2.41 (br.s, 1H), 1.49 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.5, 144.6, 139.5, 133.6, 128.9, 126.2, 123.4, 121.9, 120.6, 120.4, 115.9, 111.6, 106.4, 84.0, 71.4, 55.9, 26.0, 25.4, 24.9; IR (thin film): 3352, 3091, 3059, 2976, 2936, 2837, 1685, 1587, 1507, 1457, 1430. 1358, 1310, 1253, 1226, 1162, 1148, 1116, 1094, 1064, 1037, 1013, 909, 852, 777, 733; HRMS calc'd for $C_{19}H_{19}NO_4$ = 325.1314, found = 325.1319; $[\alpha]_D$ = +50.0° (*c* = 0.036, $CHCl_3$), $[\alpha]_D$ = +53.8° (*c* = 0.950, $CHCl_3$), literature $[\alpha]_D$ = 0° (*c* = 0.037, $CHCl_3$). [1]

The enantiomeric excess was determined to be 47% by chiral HPLC, Chiralcel OD-H, 250 x 4.6 mm^2, Diacel Chemical Industries; 94:4.5:1.5 Hexanes / MeOH / EtOH at 1.5 mL/min; 220 nm; The retention time for the enantiomers were r_t(-) = 16.73 min, r_t (+) = 19.23 min.



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AREA%
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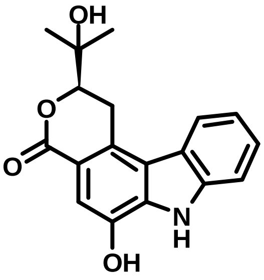
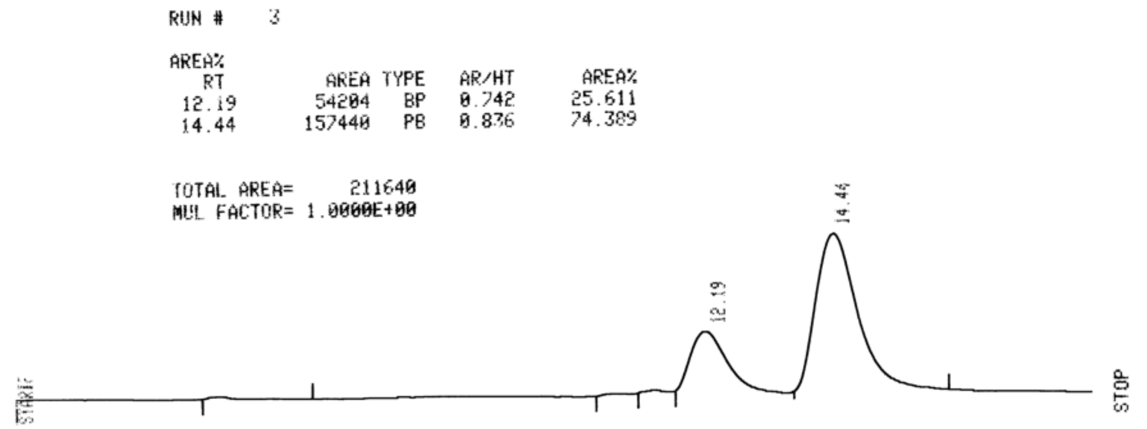


Clausevatine D

Clausamine C (26 mg, 0.0799 mmol) was dissolved in DCM (5 ml). BBr_3 (0.50 ml of 1.0 M solution in DCM, 0.500 mmol) was added dropwise and the solution allowed to stir for 2 hours at which point a second addition of BBr_3 (0.50 ml of 1.0 M solution in DCM, 0.500 mmol) was added. The solution was stirred for an additional 2.5 hours, after which TLC showed complete consumption of the starting material. Saturated $NaHCO_3$ solution (10 ml) and EtOAc (10 ml) was added to quench the excess BBr_3 (cautiously at first) and the mixture was stirred for 3 hours. The reaction was poured into 5% HCl solution and extracted 3 times with ethyl acetate. The combined organics were washed with water then brine, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a crude mixture that was purified by column chromatography on silica gel (acetone / hexanes as eluent) to yield Clausevatine D (18 mg, 0.0578 mmol, 72 %) as a colourless oil. The spectroscopic data for synthetic Clausevatine D is in agreement with literature[2], with the exception of the optical rotation: R_f = 0.38, 50 % acetone in hexanes; ^{1}H-NMR (600 MHz, Acetone-d_6): δ = 10.83 (br.s, 1H), 9.15 (br.s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.56 (s, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 4.45 (dd, J = 12.6, 3.3 Hz, 1H), 3.99 (br.s, 1H), 3.78 (dd, J = 16.5, 3.3 Hz, 1H), 3.43 (dd, J = 16.5, 12.6 Hz, 1H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ = 166.3, 142.7, 141.4, 134.4, 129.1, 126.6, 124.4, 122.9, 121.7, 120.7, 116.9, 112.7, 110.8, 84.8, 71.3, 26.8, 26.0, 25.4; IR (thin film): 3323, 2982, 2938, 1692, 1588, 1509, 1455, 1423, 1361, 1313, 1275, 1228, 1210, 1158, 1142, 1114, 1094, 1062, 1018, 998, 956, 918, 856, 779, 750, 735; HRMS calc'd for $C_{18}H_{17}NO_4$ = 311.1158, found = 311.1149; $[\alpha]_D$ = +55.0° (*c* = 0.433, MeOH), $[\alpha]_D$ = +50.7° (*c* = 1.380, MeOH), literature $[\alpha]_D$ = -5.7° (*c* = 0.932, MeOH).[2]

The enantiomeric excess was determined to be 49% by chiral HPLC, Chiralcel OD-H, 250 x 4.6 mm[2], Diacel Chemical Industries; 90:7.5:2.5 Hexanes / MeOH / EtOH at 1.5 mL/min; 220 nm; The retention time for the enantiomers were r_t(-) = 12.19 min, r_t (+) = 14.44 min.



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AREA%
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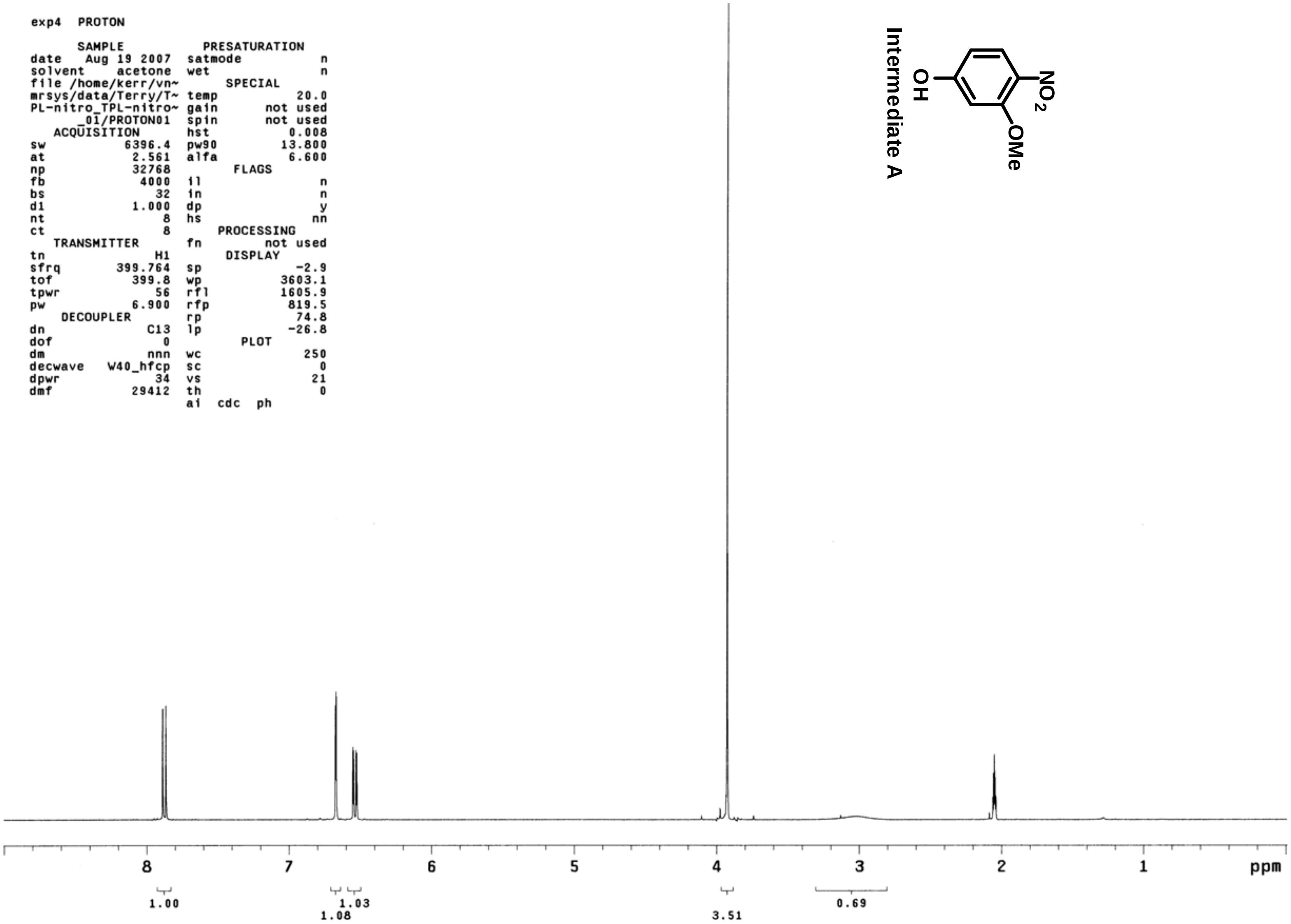
MUL FACTOR= 1.0000E+00
```

References

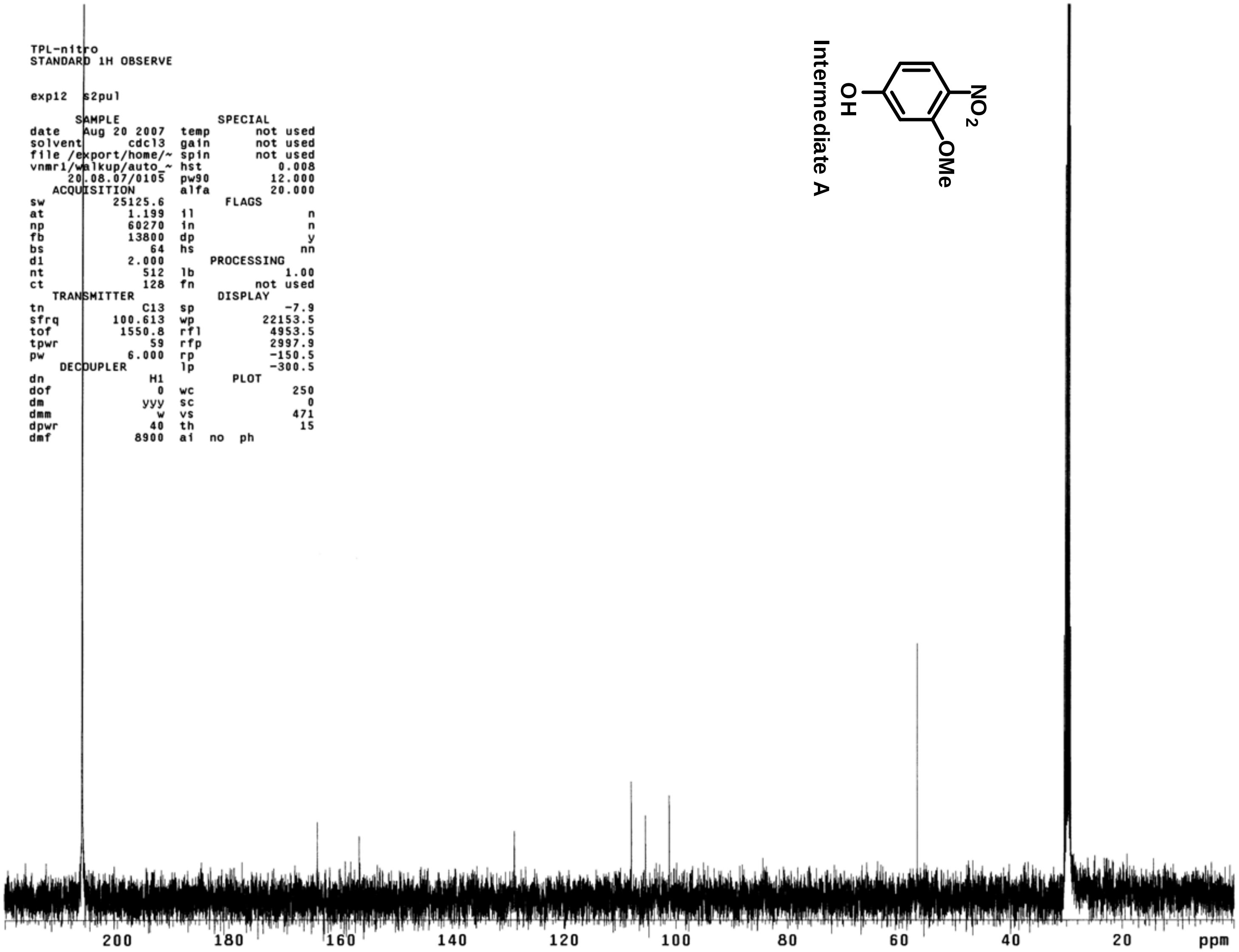
1) Ito, C.; Katsuno, S.; Ruangrungsi, N.; Furukawa, H. *Chem. Pharm. Bull.* **1998**, 46, 344.
2) Wu, T.-S.; Huang, S.-C.; Wu, P.-L. *Chem. Pharm. Bull.* **1998**, 46, 1459



Intermediate A

```
exp4  PROTON

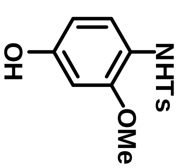
      SAMPLE             PRESATURATION
date   Aug 19 2007   satmode            n
solvent     acetone  wet                n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~  temp            20.0
PL-nitro_TPL-nitro~  gain        not used
      _01/PROTON01   spin        not used
   ACQUISITION       hst            0.008
sw           6396.4  pw90          13.800
at            2.561  alfa           6.600
np            32768        FLAGS
fb             4000  il                 n
bs               32  in                 n
d1            1.000  dp                 y
nt                8  hs                nn
ct                8       PROCESSING
   TRANSMITTER       fn          not used
tn               H1        DISPLAY
sfrq        399.764  sp              -2.9
tof           399.8  wp            3603.1
tpwr             56  rfl           1605.9
pw            6.900  rfp            819.5
    DECOUPLER        rp              74.8
dn              C13  lp             -26.8
dof               0          PLOT
dm              nnn  wc               250
decwave   W40_hfcp   sc                 0
dpwr             34  vs                21
dmf           29412  th                 0
                     ai   cdc  ph
```


Intermediate A

```
TPL-nitro
STANDARD 1H OBSERVE


exp12  s2pul

      SAMPLE              SPECIAL
date   Aug 20 2007  temp      not used
solvent      cdcl3  gain      not used
file /export/home/~ spin      not used
vnmr1/walkup/auto_~ hst          0.008
     20.08.07/0105  pw90        12.000
   ACQUISITION      alfa        20.000
sw         25125.6          FLAGS
at           1.199  il               n
np           60270  in               n
fb           13800  dp               y
bs              64  hs              nn
d1           2.000        PROCESSING
nt             512  lb            1.00
ct             128  fn        not used
   TRANSMITTER            DISPLAY
tn             C13  sp            -7.9
sfrq       100.613  wp         22153.5
tof         1550.8  rfl         4953.5
tpwr            59  rfp         2997.9
pw           6.000  rp          -150.5
    DECOUPLER       lp          -300.5
dn              H1          PLOT
dof              0  wc             250
dm             yyy  sc               0
dmm              w  vs             471
dpwr            40  th              15
dmf           8900  ai  no  ph
```

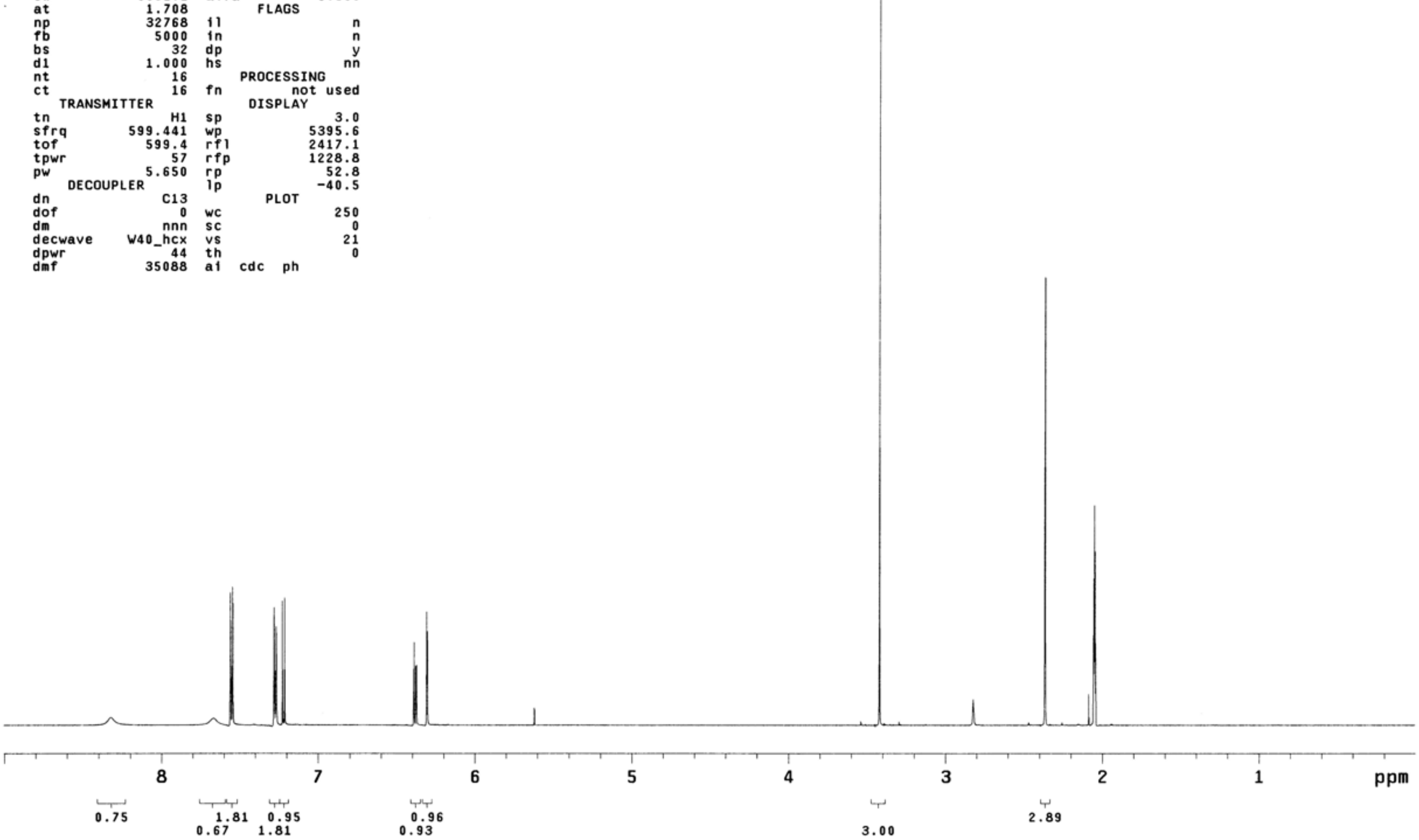


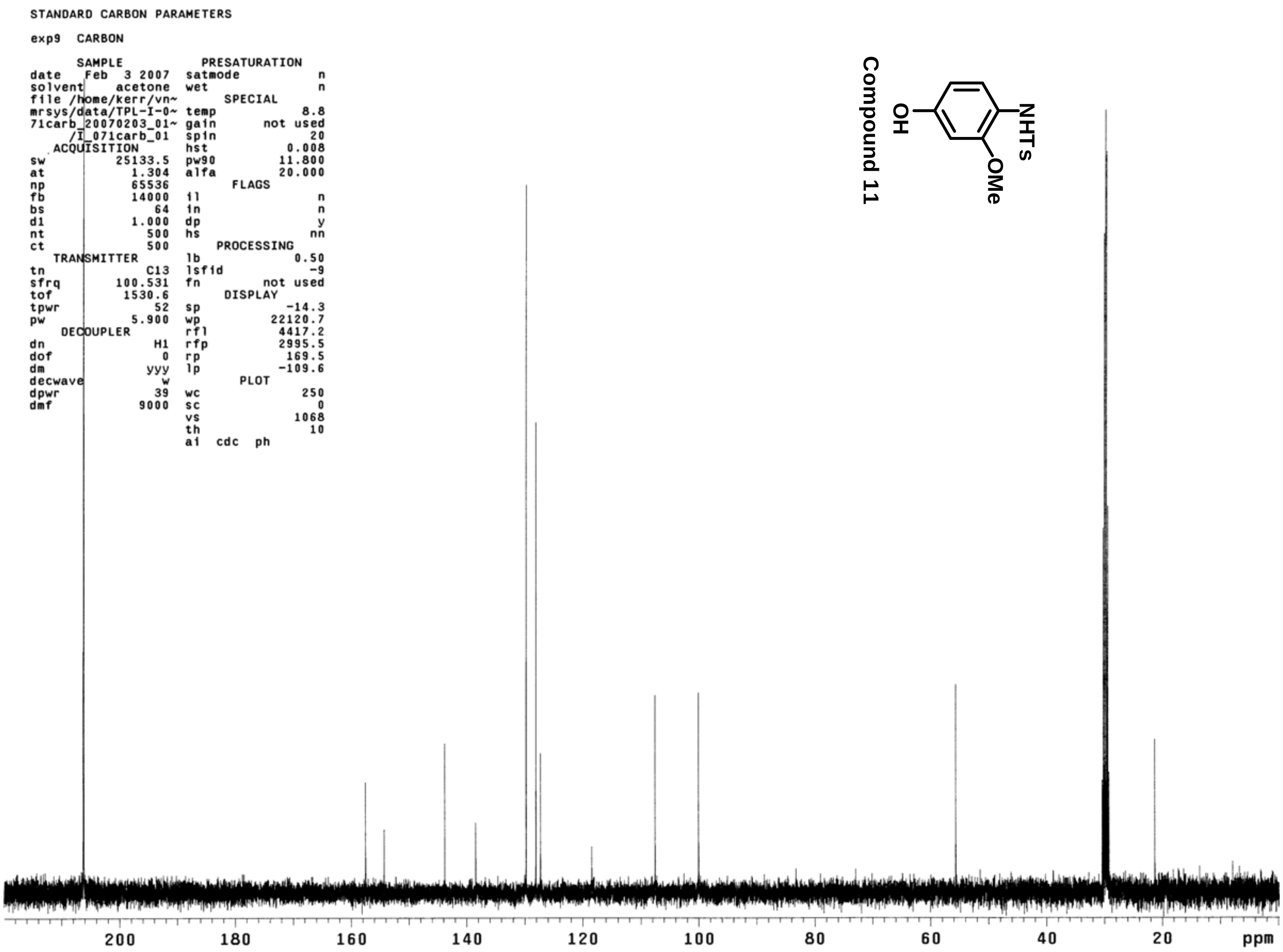
Compound 11

```
STANDARD PROTON PARAMETERS

exp2  PROTON

      SAMPLE             PRESATURATION
date   Feb  3 2007  satmode            n
solvent    Acetone  wet                n
file /export/home/~        SPECIAL
kerr/vnmrsys/data/~ temp            25.0
TPL-I-071colag/I_0~ gain        not used
71colag_01/PROTON_~ spin              20
                01  hst            0.008
    ACQUISITION     pw90          11.300
sw          9591.2  alfa           6.600
at           1.708          FLAGS
np           32768  il                 n
fb            5000  in                 n
bs              32  dp                 y
d1           1.000  hs                nn
nt              16       PROCESSING
ct              16  fn          not used
   TRANSMITTER            DISPLAY
tn              H1  sp               3.0
sfrq       599.441  wp            5395.6
tof          599.4  rfl           2417.1
tpwr            57  rfp           1228.8
pw           5.650  rp              52.8
    DECOUPLER       lp             -40.5
dn             C13          PLOT
dof              0  wc               250
dm             nnn  sc                 0
decwave    W40_hcx  vs                21
dpwr            44  th                 0
dmf          35088  ai  cdc  ph
```





Compound 11

```
STANDARD CARBON PARAMETERS

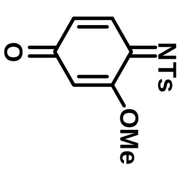
exp9  CARBON

      SAMPLE           PRESATURATION
date   Feb  3 2007  satmode            n
solvent    acetone  wet                n
file /home/kerr/vn~       SPECIAL
mrsys/data/TPL-I-0~ temp             8.8
71carb_20070203_01~ gain        not used
    /I_071carb_01   spin              20
   ACQUISITION      hst            0.008
sw         25133.5  pw90          11.800
at           1.304  alfa          20.000
np           65536         FLAGS
fb           14000  il                 n
bs              64  in                 n
d1           1.000  dp                 y
nt             500  hs                nn
ct             500      PROCESSING
   TRANSMITTER      lb              0.50
tn             C13  lsfid             -9
sfrq       100.531  fn          not used
tof         1530.6       DISPLAY
tpwr            52  sp             -14.3
pw           5.900  wp           22120.7
    DECOUPLER       rfl           4417.2
dn              H1  rfp           2995.5
dof              0  rp             169.5
dm             yyy  lp            -109.6
decwave          w         PLOT
dpwr            39  wc               250
dmf           9000  sc                 0
                    vs              1068
                    th                10
                    ai   cdc  ph
```

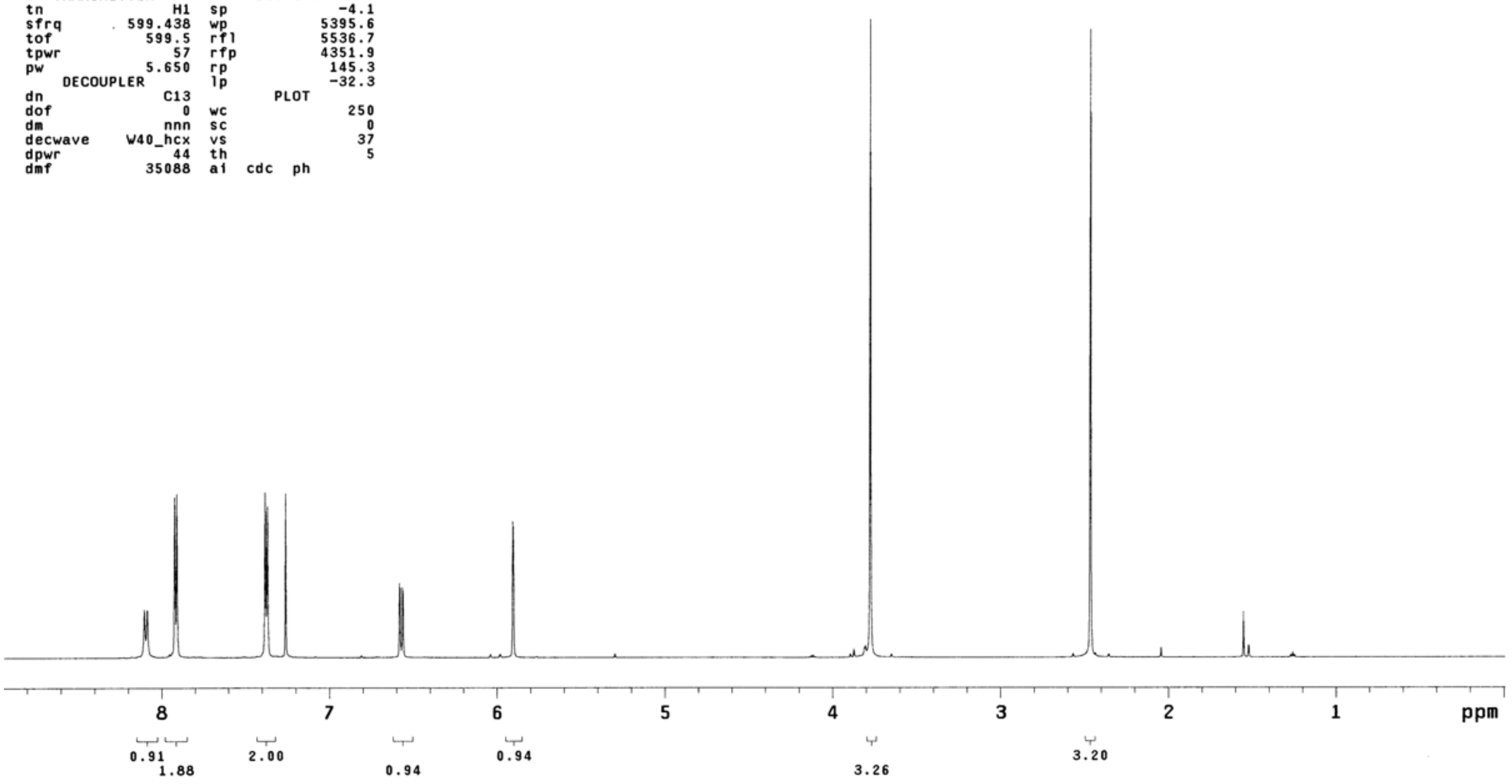
```
STANDARD PROTON PARAMETERS

exp1  PROTON

      SAMPLE              PRESATURATION
date   Feb  7 2007  satmode              n
solvent      CDCl3  wet                  n
file /export/home/~        SPECIAL
kerr/vnmrsys/data/~ temp              25.0
TPL-I-083recryst/I~ gain          not used
_083recryst_01/PRO~ spin          not used
            TON_01  hst              0.008
   ACQUISITION      pw90            11.300
sw          9591.2  alfa             6.600
at           1.708           FLAGS
np           32768  il                   n
fb            5000  in                   n
bs              32  dp                   y
d1           1.000  hs                  nn
nt              32        PROCESSING
ct              32  fn            not used
   TRANSMITTER             DISPLAY
tn              H1  sp                -4.1
sfrq     . 599.438  wp              5395.6
tof          599.5  rfl             5536.7
tpwr            57  rfp             4351.9
pw           5.650  rp               145.3
    DECOUPLER       lp               -32.3
dn             C13           PLOT
dof              0  wc                 250
dm             nnn  sc                   0
decwave    W40_hcx  vs                  37
dpwr            44  th                   5
dmf          35088  ai   cdc   ph
```



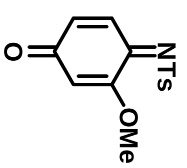
Compound 8



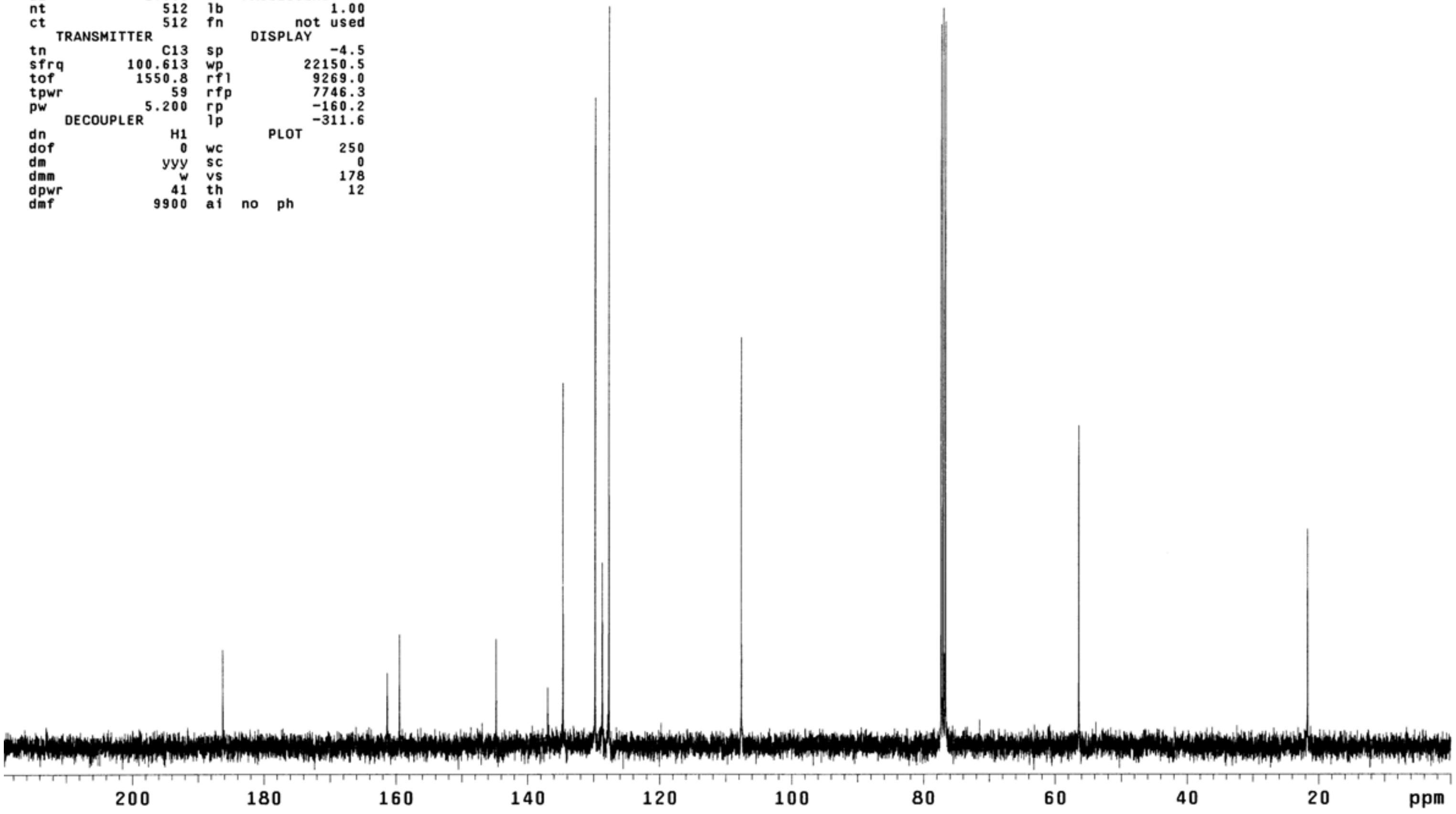
```
TPL-I-083CARBON
STANDARD 1H OBSERVE

exp1  s2pul

      SAMPLE              SPECIAL
date   Feb  7 2007  temp       not used
solvent       cdcl3  gain       not used
file /export/home/~ spin       not used
vnmr1/walkup/auto_~ hst           0.008
    07.02.07/0218  pw90         10.400
   ACQUISITION      alfa         20.000
sw          25125.6            FLAGS
at            1.199  il               n
np            60270  in               n
fb            13800  dp               y
bs               64  hs              nn
d1            1.000          PROCESSING
nt              512  lb            1.00
ct              512  fn        not used
   TRANSMITTER               DISPLAY
tn              C13  sp            -4.5
sfrq        100.613  wp         22150.5
tof          1550.8  rfl         9269.0
tpwr             59  rfp         7746.3
pw            5.200  rp          -160.2
    DECOUPLER        lp          -311.6
dn               H1            PLOT
dof               0  wc             250
dm              yyy  sc               0
dmm               w  vs             178
dpwr             41  th              12
dmf            9900  ai  no  ph
```



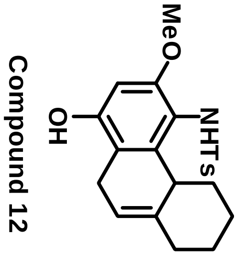
Compound 8



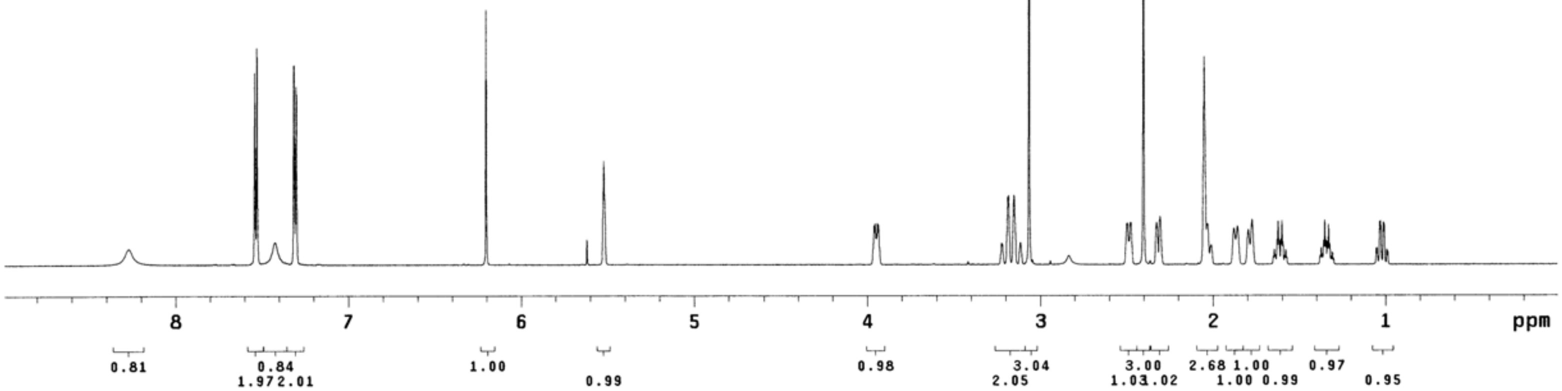
```
STANDARD PROTON PARAMETERS

exp1  PROTON

      SAMPLE            PRESATURATION
date   Feb  8 2007  satmode             n
solvent    Acetone  wet                 n
file /export/home/~       SPECIAL
kerr/vnmrsys/data/~ temp             25.0
TPL-I-061prod/I_06~ gain         not used
1prod_01/PROTON_02~ spin         not used
              .fid  hst             0.008
   ACQUISITION      pw90           11.300
sw          9591.2  alfa            6.600
at           1.708         FLAGS
np           32768  il                  n
fb            5000  in                  n
bs              32  dp                  y
d1           1.000  hs                 nn
nt              16        PROCESSING
ct              16  fn           not used
   TRANSMITTER             DISPLAY
tn              H1  sp                4.3
sfrq       599.441  wp             5385.1
tof          599.5  rfl            2415.9
tpwr            57  rfp            1228.8
pw           5.650  rp             -124.6
    DECOUPLER       lp              -29.8
dn             C13         PLOT
dof              0  wc                250
dm             nnn  sc                  0
decwave    W40_hcx  vs                 45
dpwr            44  th                  3
dmf          35088  ai  cdc  ph
```



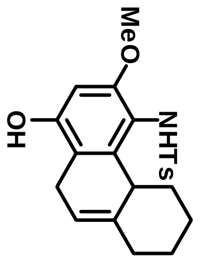
Compound 12



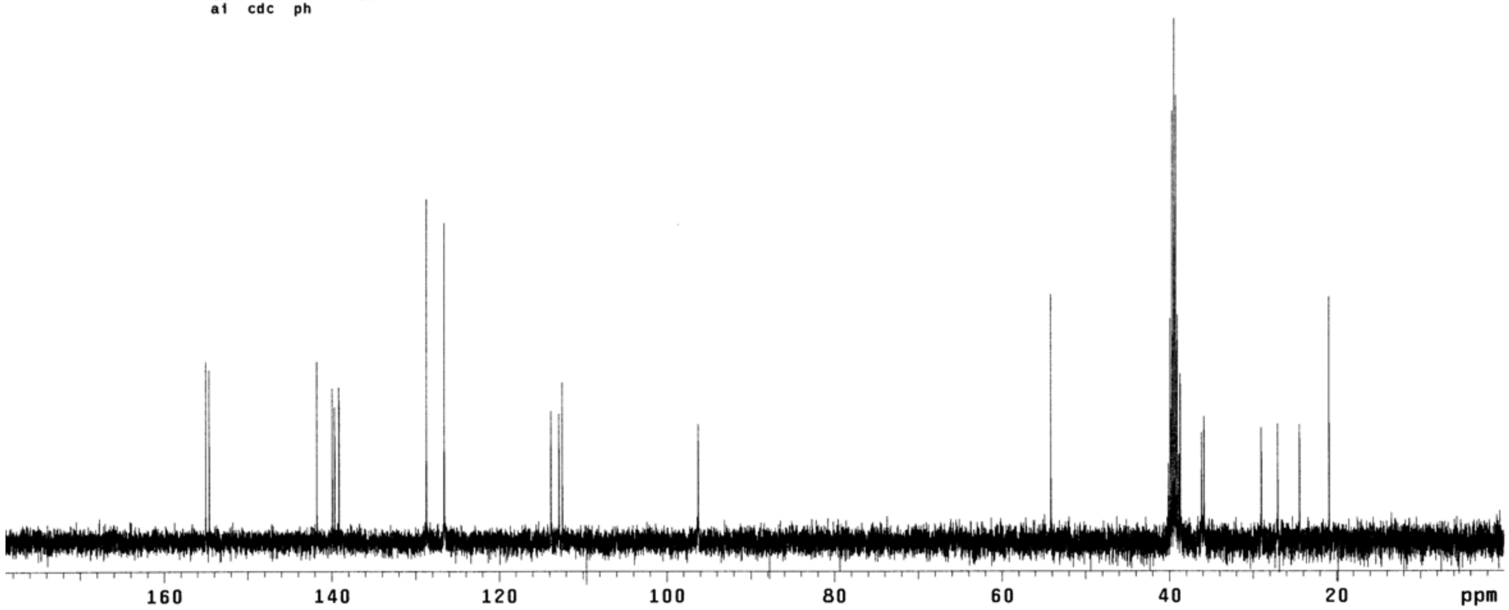
```
STANDARD CARBON PARAMETERS

exp1  CARBON

      SAMPLE              PRESATURATION
date   Feb 17 2007   satmode             n
solvent        dmso   wet                 n
file /home/kerr/vn~         SPECIAL
mrsys/data/TPL-I-0~   temp            -60.0
61acarbon_20070217~   gain         not used
_01/I_061carbona_0~   spin               20
                  1   hst             0.008
   ACQUISITION        pw90           11.800
sw          25133.5   alfa           20.000
at            1.304          FLAGS
np            65536   il                  n
fb            14000   in                  n
bs               64   dp                  y
d1            1.000   hs                 nn
nt              750        PROCESSING
ct              750   lb               0.50
   TRANSMITTER        lsfid              -9
tn              C13   fn           not used
sfrq        100.531         DISPLAY
tof          1530.6   sp                2.0
tpwr             52   wp            18093.1
pw            5.900   rfl            5523.3
    DECOUPLER         rfp            3970.5
dn               H1   rp             -116.3
dof               0   lp             -110.2
dm              yyy          PLOT
decwave           w   wc                250
dpwr             39   sc                  0
dmf            9000   vs                751
                      th                 18
                      ai   cdc   ph
```



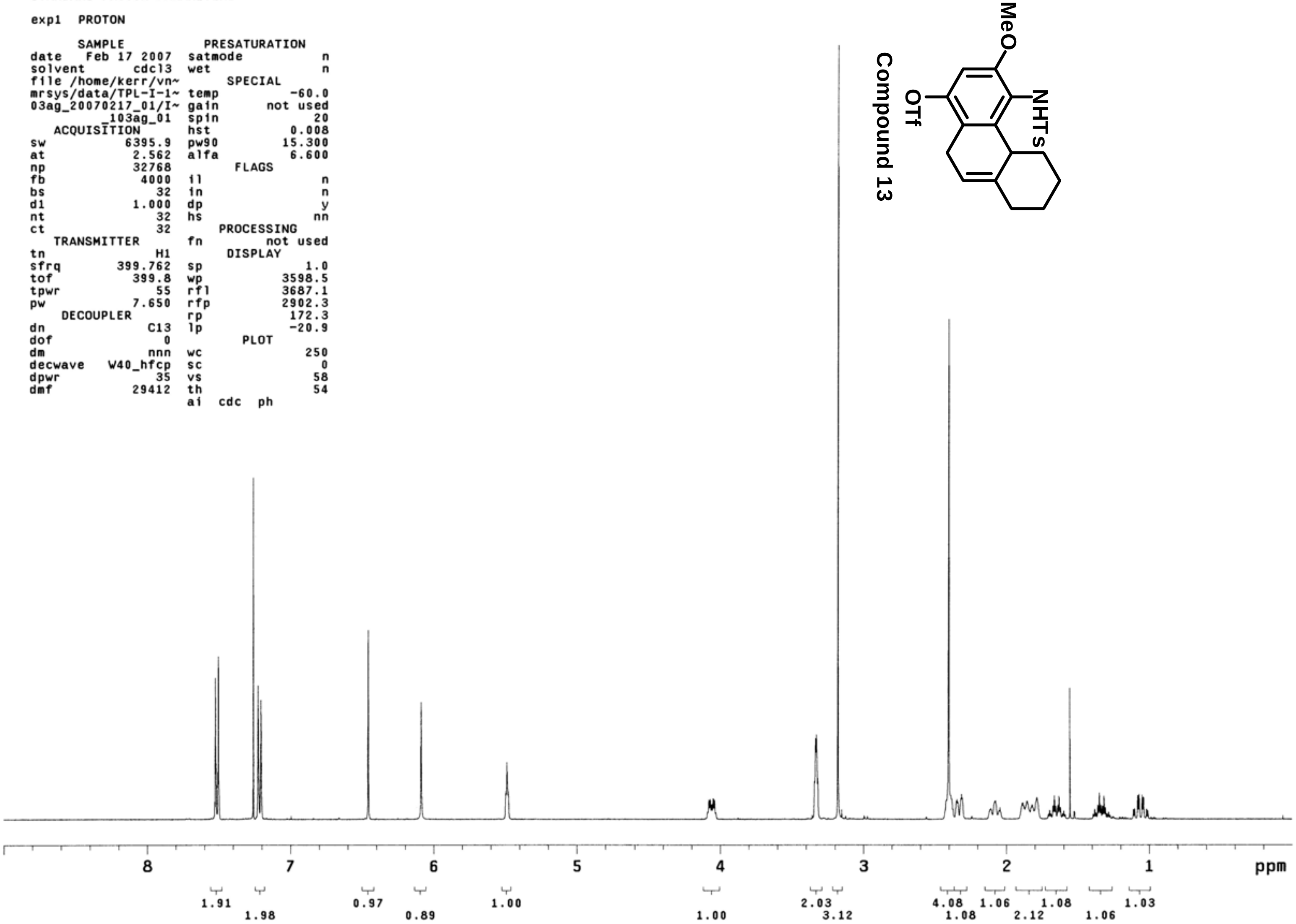
Compound 12



```
STANDARD PROTON PARAMETERS

exp1  PROTON

      SAMPLE              PRESATURATION
date   Feb 17 2007   satmode              n
solvent       cdcl3   wet                  n
file /home/kerr/vn~        SPECIAL
mrsys/data/TPL-I-1~  temp             -60.0
03ag_20070217_01/I~  gain          not used
         _103ag_01   spin                20
   ACQUISITION        hst              0.008
sw           6395.9   pw90            15.300
at            2.562   alfa             6.600
np            32768            FLAGS
fb             4000   il                   n
bs               32   in                   n
d1            1.000   dp                   y
nt               32   hs                  nn
ct               32        PROCESSING
   TRANSMITTER        fn            not used
tn               H1          DISPLAY
sfrq        399.762   sp                 1.0
tof           399.8   wp              3598.5
tpwr             55   rfl             3687.1
pw            7.650   rfp             2902.3
    DECOUPLER         rp               172.3
dn              C13   lp               -20.9
dof               0            PLOT
dm              nnn   wc                 250
decwave   W40_hfcp   sc                    0
dpwr             35   vs                  58
dmf           29412   th                  54
                      ai   cdc   ph
```

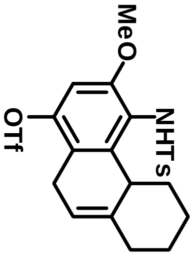


Compound 13

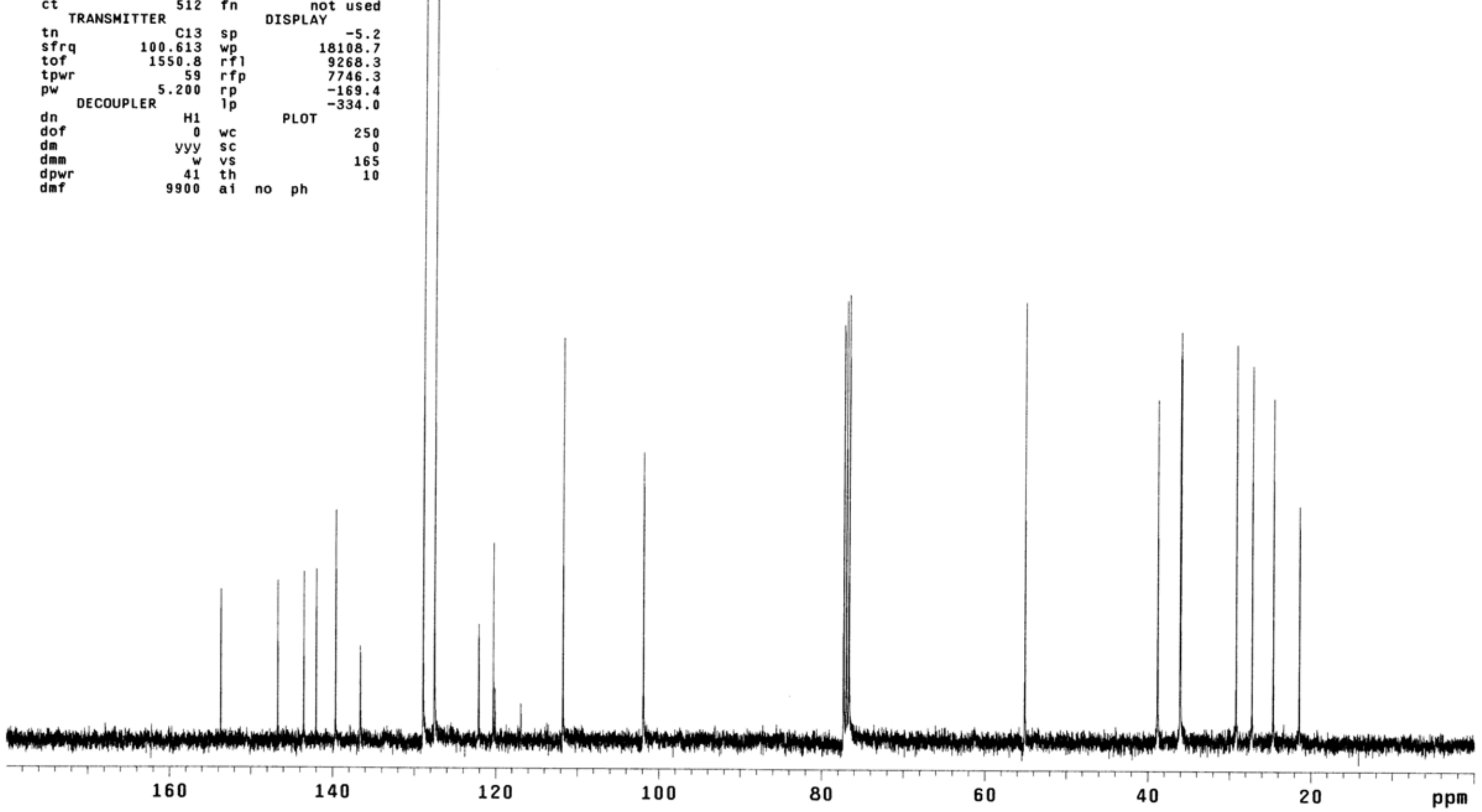
```
TPL-I-103carb
STANDARD 1H OBSERVE

exp1  s2pul

      SAMPLE              SPECIAL
date   Feb 17 2007  temp        not used
solvent       cdcl3  gain        not used
file /export/home/~ spin        not used
vnmr1/walkup/auto_~ hst            0.008
    17.02.07/0206   pw90          10.400
   ACQUISITION      alfa          20.000
sw          25125.6         FLAGS
at            1.199  il                n
np            60270  in                n
fb            13800  dp                y
bs               64  hs               nn
d1            1.000        PROCESSING
nt              512  lb             1.00
ct              512  fn         not used
   TRANSMITTER              DISPLAY
tn              C13  sp             -5.2
sfrq        100.613  wp          18108.7
tof          1550.8  rfl          9268.3
tpwr             59  rfp          7746.3
pw            5.200  rp           -169.4
    DECOUPLER        lp           -334.0
dn               H1          PLOT
dof               0  wc              250
dm              yyy  sc                0
dmm               w  vs              165
dpwr             41  th               10
dmf            9900  ai  no   ph
```



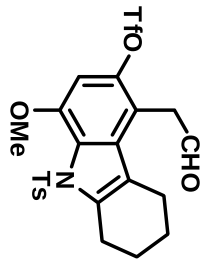
Compound 13



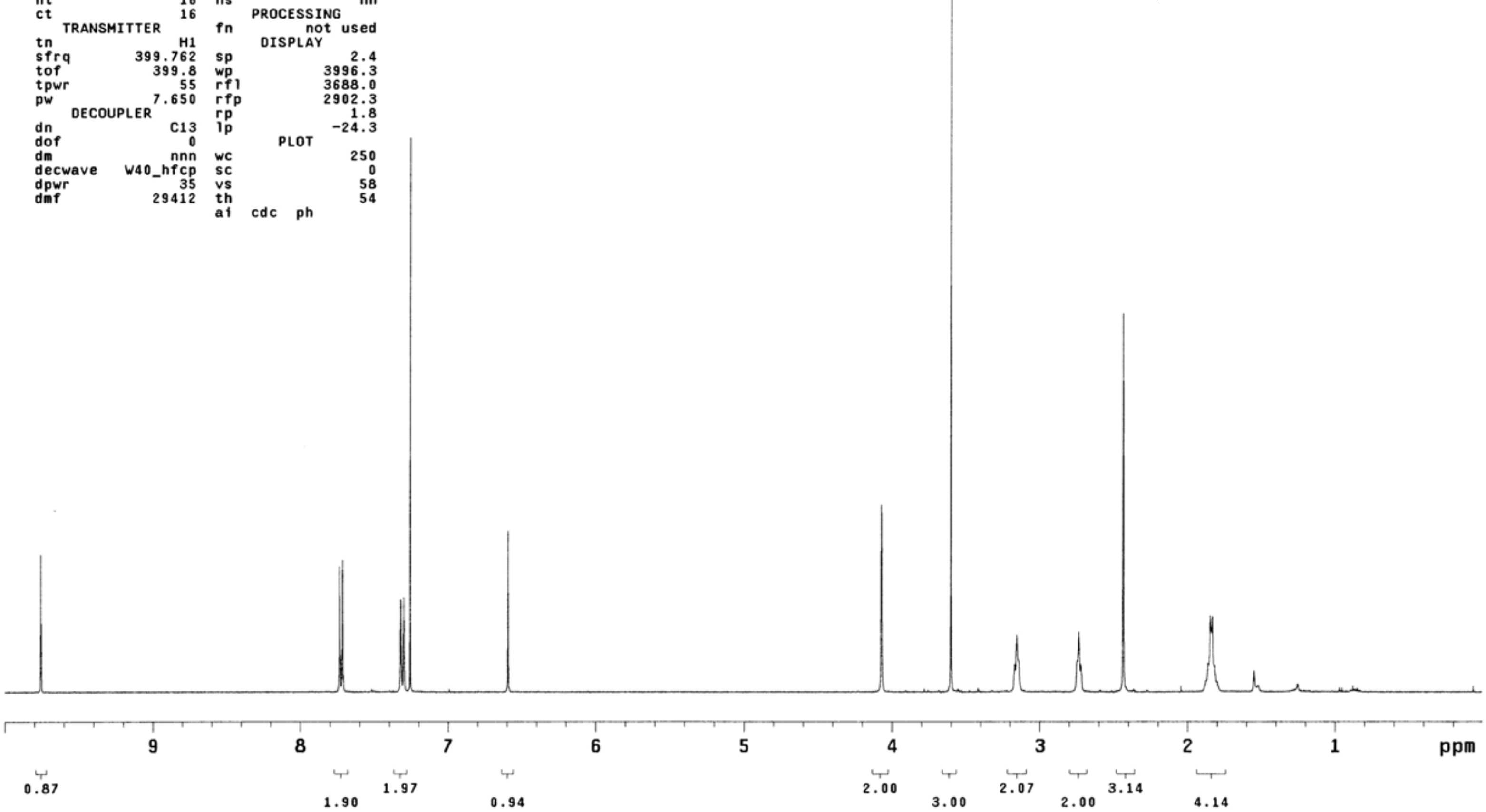
```
STANDARD PROTON PARAMETERS

exp1  PROTON

      SAMPLE            PRESATURATION
date   Jan 31 2007   satmode             n
solvent      cdcl3   wet                 n
file /home/kerr/vn~       SPECIAL
mrsys/data/TPL-I-0~  temp              8.8
01d_20070131_01/I_~  gain         not used
          001d_01    spin               20
   ACQUISITION       hst             0.008
sw          6395.9   pw90           15.300
at           2.562   alfa            6.600
np           32768         FLAGS
fb            4000   il                  n
bs              32   in                  n
d1           1.000   dp                  y
nt              16   hs                 nn
ct              16       PROCESSING
   TRANSMITTER       fn           not used
tn              H1         DISPLAY
sfrq       399.762   sp                2.4
tof          399.8   wp             3996.3
tpwr            55   rfl            3688.0
pw           7.650   rfp            2902.3
    DECOUPLER        rp                1.8
dn             C13   lp              -24.3
dof              0          PLOT
dm             nnn   wc                250
decwave   W40_hfcp   sc                  0
dpwr            35   vs                 58
dmf          29412   th                 54
                     ai   cdc  ph
```



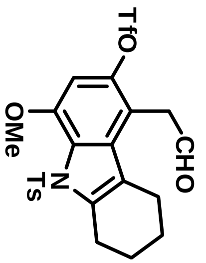
Compound 14



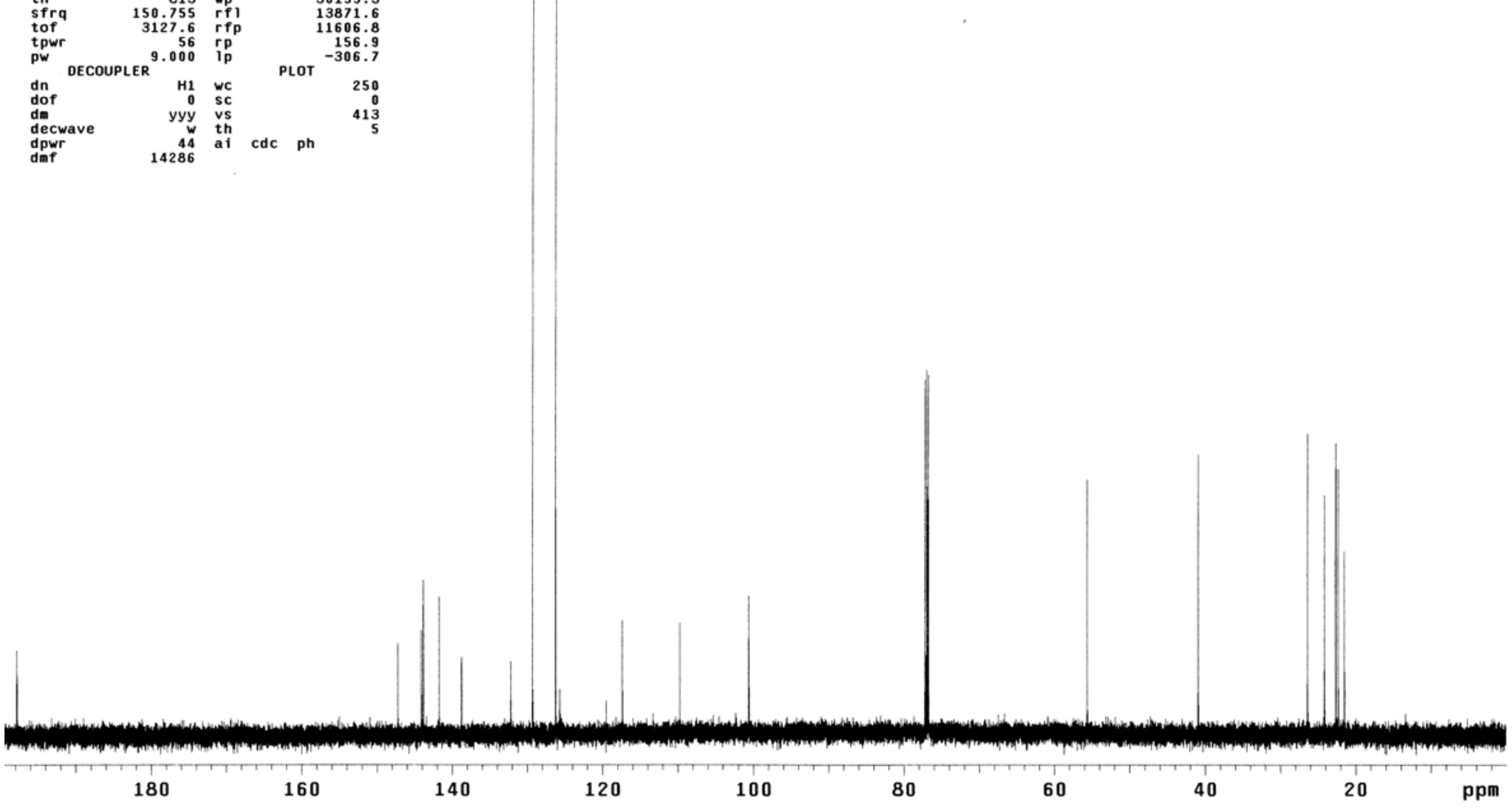
```
TPL-D-061A

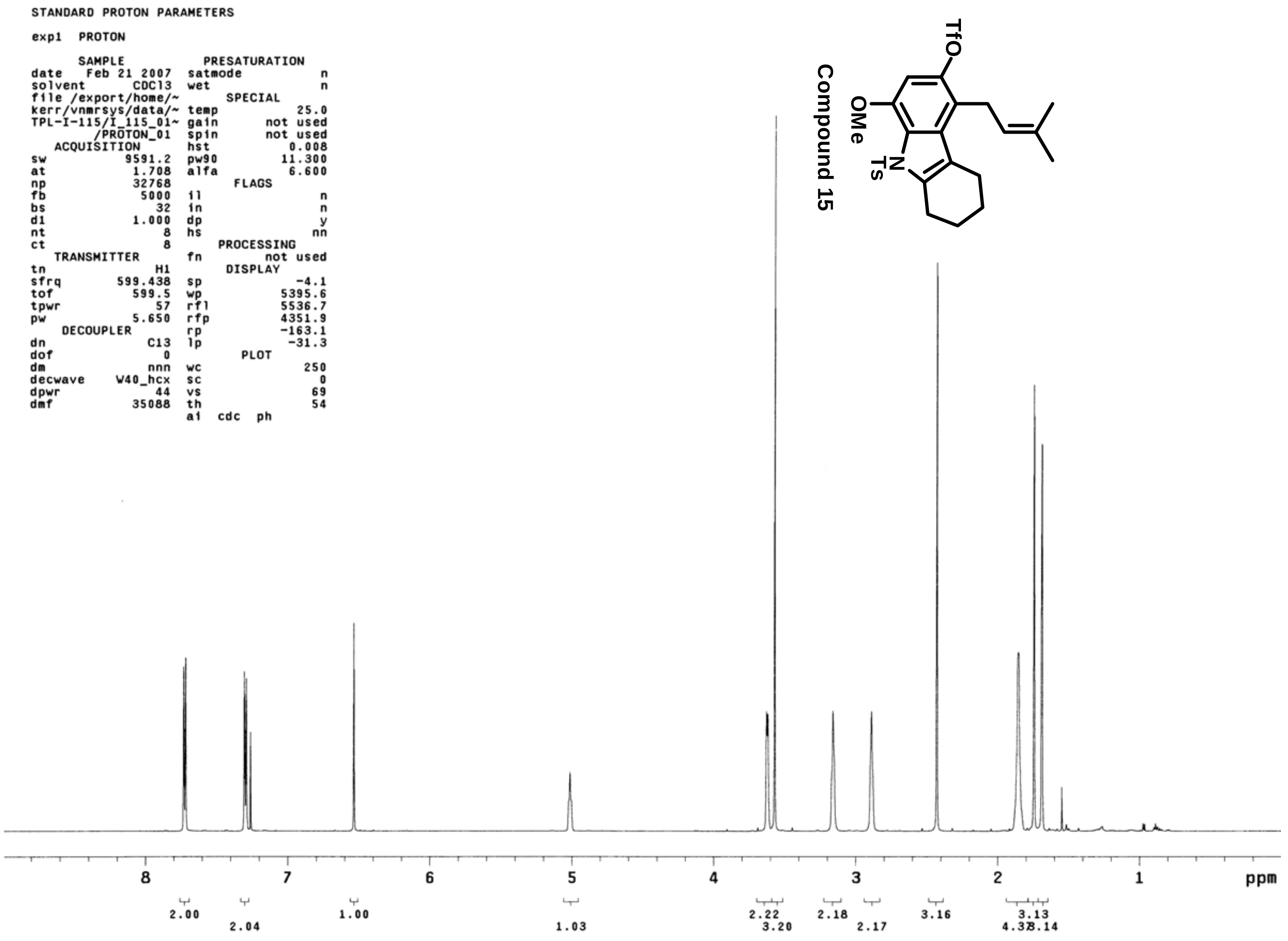
exp1  CARBON

      SAMPLE                 SPECIAL
date    Dec 12 2005  temp           25.0
solvent       CDCl3  gain       not used
file /export/home/~  spin             16
kerr/vnmrsys/data/~  hst           0.008
TPL-D-061A_2005-12~  pw90         18.000
 -12/CARBON_01.fid   alfa         10.000
   ACQUISITION                FLAGS
sw          37682.5  il                n
at            1.300  in                n
np            98010  dp                y
fb            21000  hs               nn
bs               64      PROCESSING
d1            1.000  lb             0.50
nt              256  fn         not used
ct              256         DISPLAY
   TRANSMITTER       sp             13.3
tn              C13  wp          30155.3
sfrq        150.755  rfl         13871.6
tof          3127.6  rfp         11606.8
tpwr             56  rp            156.9
pw            9.000  lp           -306.7
    DECOUPLER                 PLOT
dn               H1  wc              250
dof               0  sc                0
dm              yyy  vs              413
decwave           w  th                5
dpwr             44  ai  cdc  ph
dmf           14286
```



Compound 14





```
STANDARD PROTON PARAMETERS

exp1  PROTON

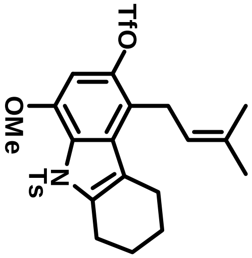
     SAMPLE             PRESATURATION
date   Feb 21 2007  satmode            n
solvent      CDCl3  wet                n
file /export/home/~       SPECIAL
kerr/vnmrsys/data/~ temp            25.0
TPL-I-115/I_115_01~ gain        not used
        /PROTON_01  spin        not used
   ACQUISITION      hst            0.008
sw          9591.2  pw90          11.300
at           1.708  alfa           6.600
np           32768         FLAGS
fb            5000  il                 n
bs              32  in                 n
d1           1.000  dp                 y
nt               8  hs                nn
ct               8       PROCESSING
   TRANSMITTER      fn          not used
tn              H1        DISPLAY
sfrq       599.438  sp              -4.1
tof          599.5  wp            5395.6
tpwr            57  rfl           5536.7
pw           5.650  rfp           4351.9
    DECOUPLER       rp            -163.1
dn             C13  lp             -31.3
dof              0           PLOT
dm             nnn  wc               250
decwave   W40_hcx   sc                 0
dpwr            44  vs                69
dmf          35088  th                54
                    ai   cdc   ph
```

Compound 15

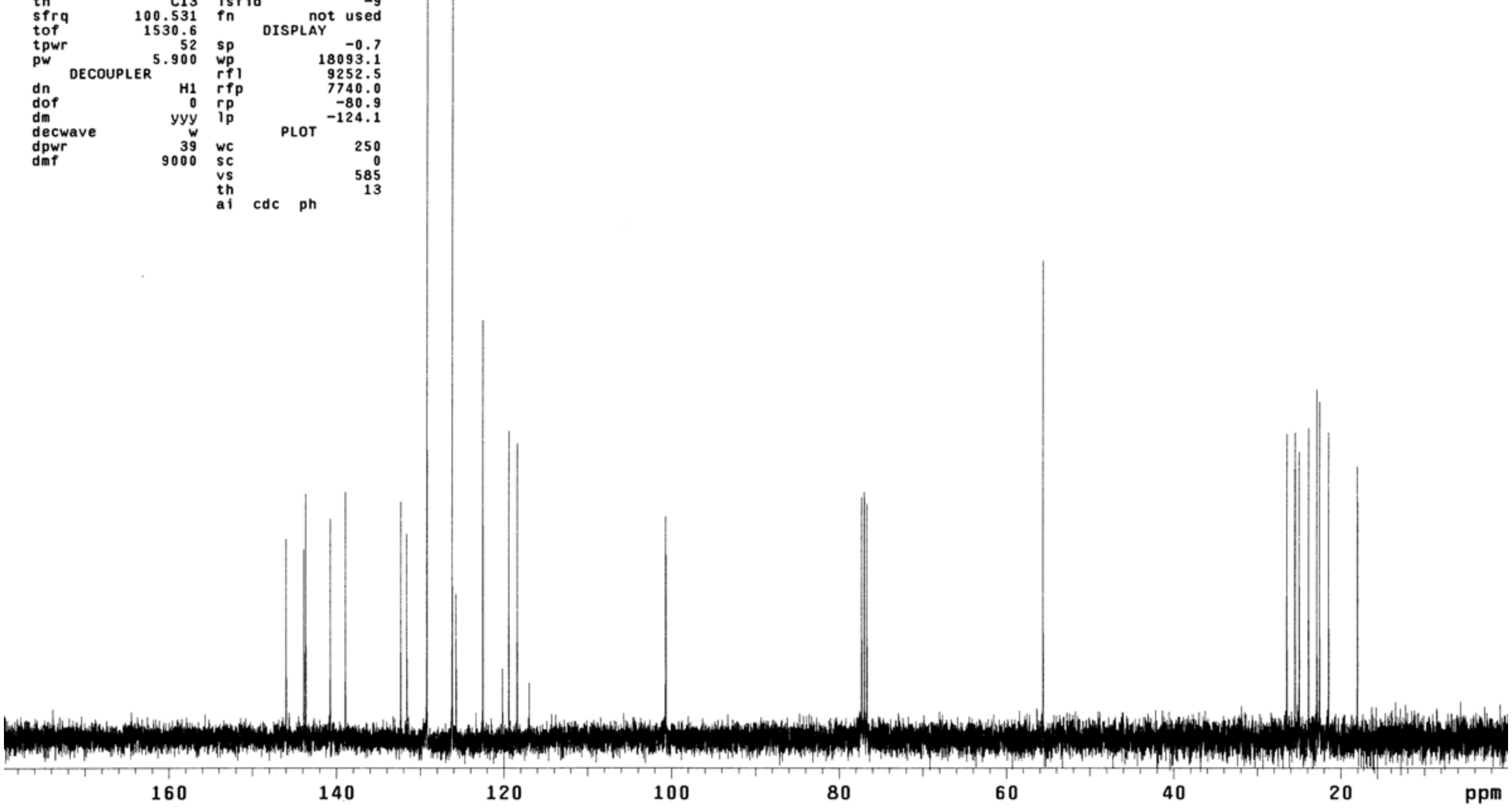
```
STANDARD CARBON PARAMETERS

exp1  CARBON

      SAMPLE              PRESATURATION
date   Feb 21 2007  satmode             n
solvent      cdcl3  wet                 n
file /home/kerr/vn~        SPECIAL
mrsys/data/TPL-I-1~ temp             20.0
15carb_20070221_01~ gain         not used
     /I_115carb_01  spin               20
   ACQUISITION      hst             0.008
sw         25133.5  pw90           11.800
at           1.304  alfa           20.000
np           65536          FLAGS
fb           14000  il                  n
bs              64  in                  n
d1           1.000  dp                  y
nt            1000  hs                 nn
ct            1000       PROCESSING
   TRANSMITTER      lb               0.50
tn             C13  lsfid              -9
sfrq       100.531  fn           not used
tof         1530.6         DISPLAY
tpwr            52  sp               -0.7
pw           5.900  wp            18093.1
    DECOUPLER       rfl            9252.5
dn              H1  rfp            7740.0
dof              0  rp              -80.9
dm             yyy  lp             -124.1
decwave          w           PLOT
dpwr            39  wc                250
dmf           9000  sc                  0
                    vs                585
                    th                 13
                    ai   cdc   ph
```



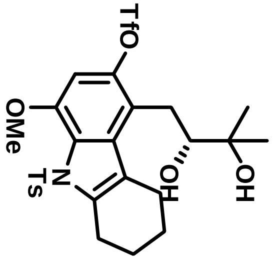
Compound 15



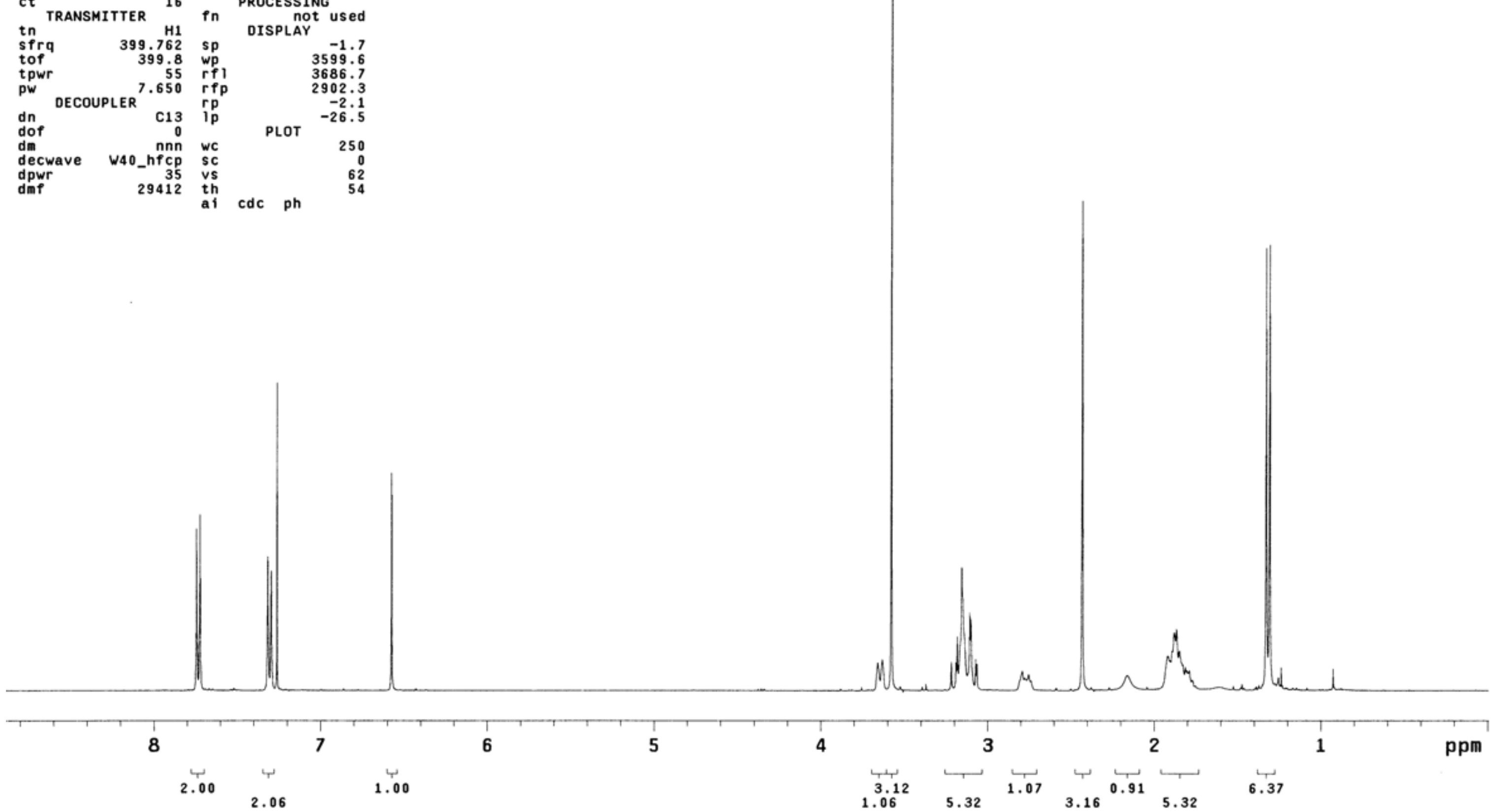
```
STANDARD PROTON PARAMETERS

exp1  PROTON

      SAMPLE              PRESATURATION
date    Mar  4 2007   satmode            n
solvent       cdcl3   wet                n
file /home/kerr/vn~         SPECIAL
mrsys/data/TPL-I-1~   temp            20.0
29agg_20070304_01/~   gain        not used
      I_129agg_01     spin              20
   ACQUISITION        hst            0.008
sw           6395.9   pw90          15.300
at            2.562   alfa           6.600
np            32768          FLAGS
fb             4000   il                 n
bs               32   in                 n
d1            1.000   dp                 y
nt               16   hs                nn
ct               16        PROCESSING
   TRANSMITTER        fn          not used
tn               H1         DISPLAY
sfrq        399.762   sp              -1.7
tof           399.8   wp            3599.6
tpwr             55   rfl           3686.7
pw            7.650   rfp           2902.3
    DECOUPLER         rp              -2.1
dn              C13   lp             -26.5
dof               0          PLOT
dm              nnn   wc               250
decwave   W40_hfcp    sc                 0
dpwr             35   vs                62
dmf           29412   th                54
                      ai   cdc   ph
```



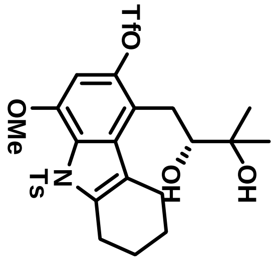
Intermediate B



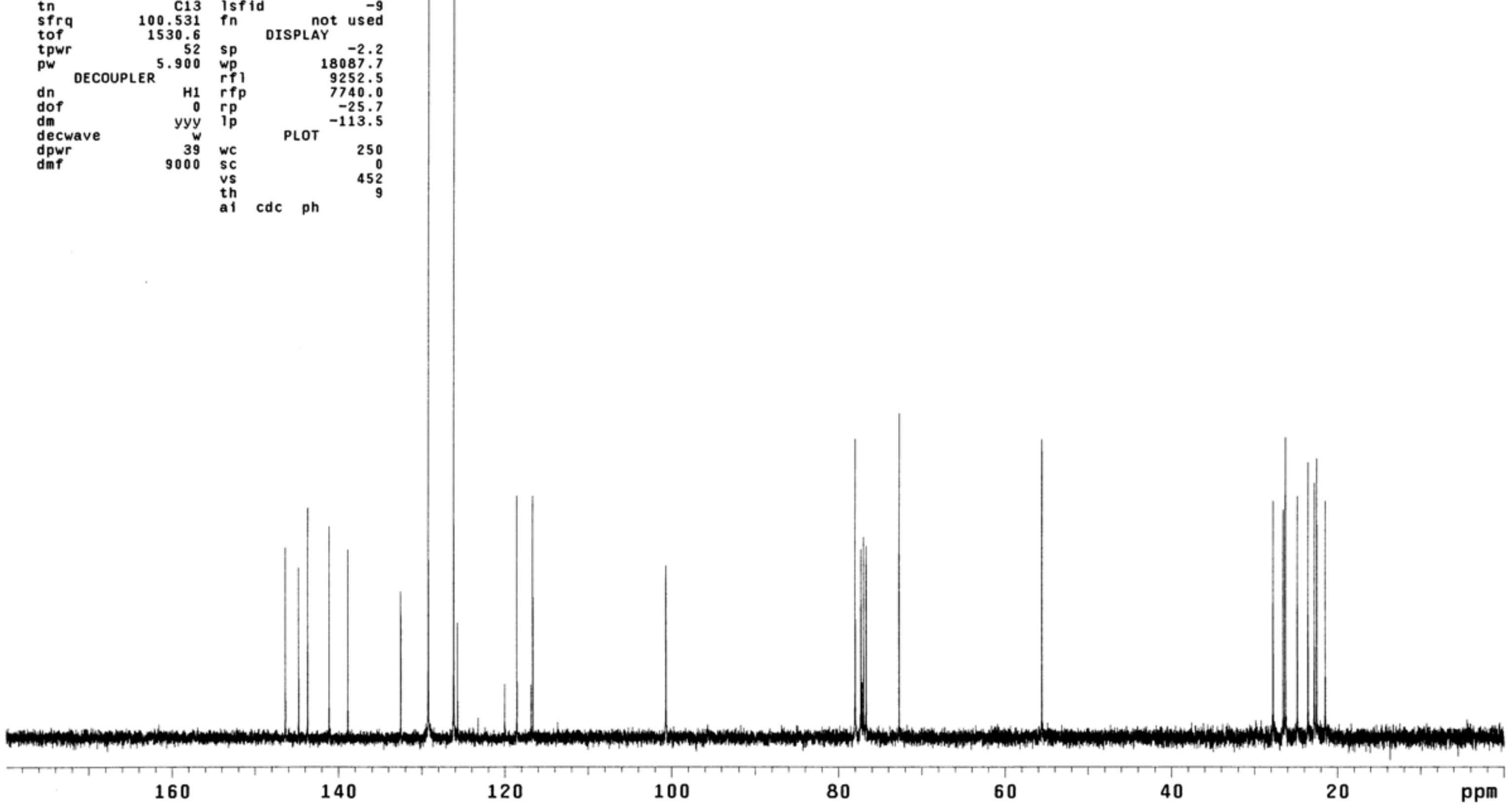
```
STANDARD CARBON PARAMETERS

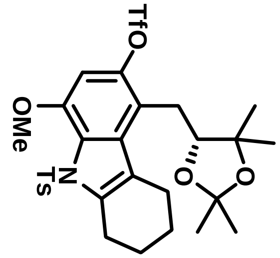
exp1  CARBON

      SAMPLE              PRESATURATION
date   Mar  4 2007   satmode             n
solvent      cdcl3   wet                 n
file /home/kerr/vn~         SPECIAL
mrsys/data/TPL-I-1~ temp              20.0
29carbon_20070304_~ gain          not used
 01/I_129carbon_01   spin                20
   ACQUISITION       hst              0.008
sw         25133.5   pw90            11.800
at           1.304   alfa            20.000
np           65536          FLAGS
fb           14000   il                  n
bs              64   in                  n
d1           1.000   dp                  y
nt            1000   hs                 nn
ct            1000        PROCESSING
   TRANSMITTER       lb                0.50
tn             C13   lsfid               -9
sfrq       100.531   fn           not used
tof         1530.6          DISPLAY
tpwr            52   sp                -2.2
pw           5.900   wp             18087.7
    DECOUPLER        rfl             9252.5
dn              H1   rfp             7740.0
dof              0   rp               -25.7
dm             yyy   lp              -113.5
decwave          w           PLOT
dpwr            39   wc                 250
dmf           9000   sc                   0
                     vs                 452
                     th                   9
                     ai   cdc   ph
```



Intermediate B



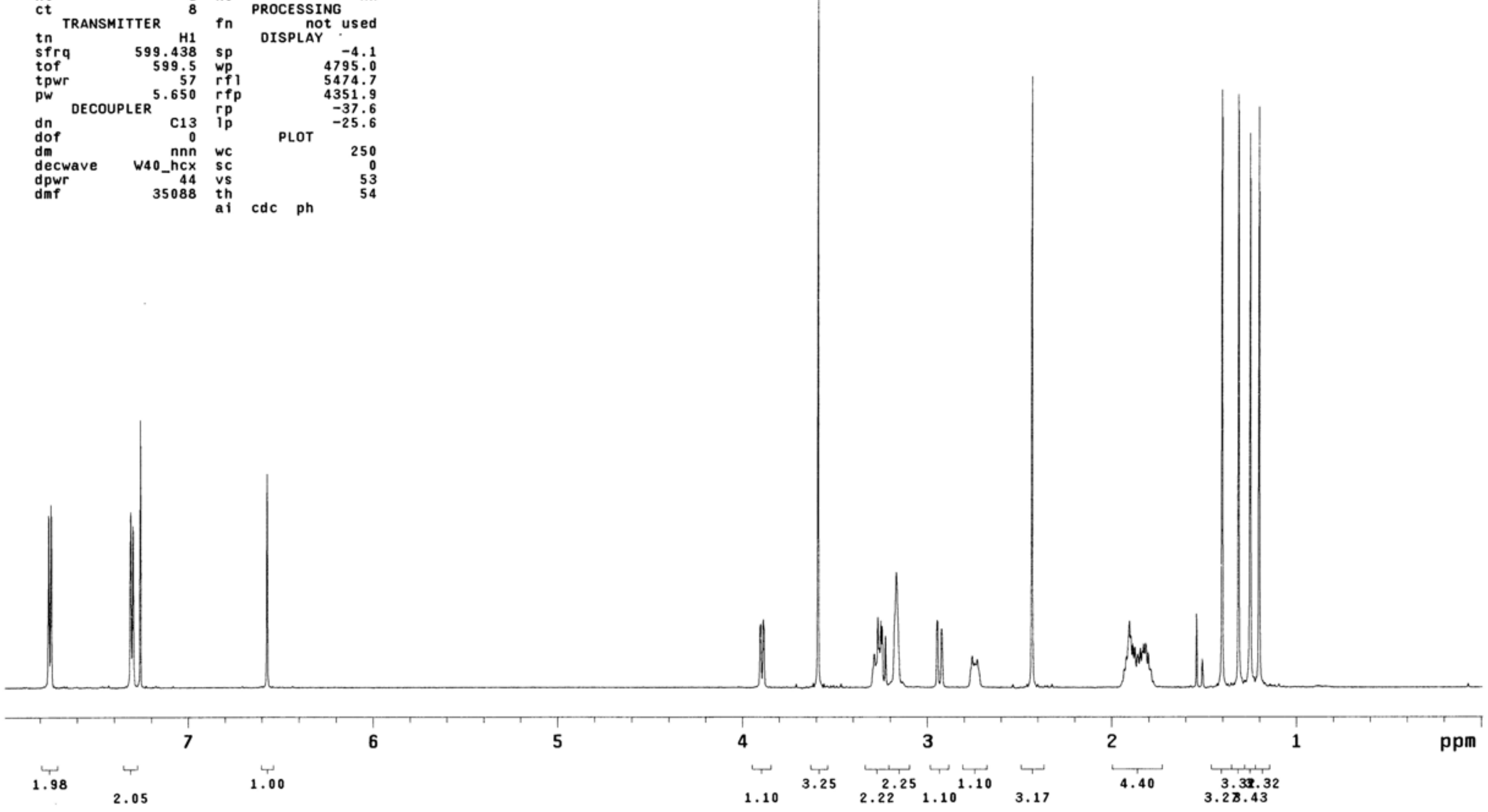


Compound 16

```
STANDARD PROTON PARAMETERS

exp2  PROTON

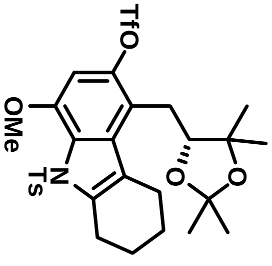
      SAMPLE            PRESATURATION
date   Feb  2 2007  satmode           n
solvent       CDCl3  wet               n
file /export/home/~       SPECIAL
kerr/vnmrsys/data/~ temp           25.0
TPL-I-069/I_069_01~ gain       not used
        /PROTON_01  spin             20
   ACQUISITION      hst           0.008
sw           9591.2  pw90         11.300
at            1.708  alfa          6.600
np            32768         FLAGS
fb             5000  il                n
bs               32  in                n
d1            1.000  dp                y
nt                8  hs               nn
ct                8      PROCESSING
   TRANSMITTER      fn         not used
tn               H1         DISPLAY
sfrq        599.438  sp            -4.1
tof           599.5  wp          4795.0
tpwr             57  rfl         5474.7
pw            5.650  rfp         4351.9
    DECOUPLER        rp           -37.6
dn              C13  lp           -25.6
dof               0          PLOT
dm              nnn  wc             250
decwave     W40_hcx  sc               0
dpwr             44  vs              53
dmf           35088  th              54
                     ai  cdc  ph
```



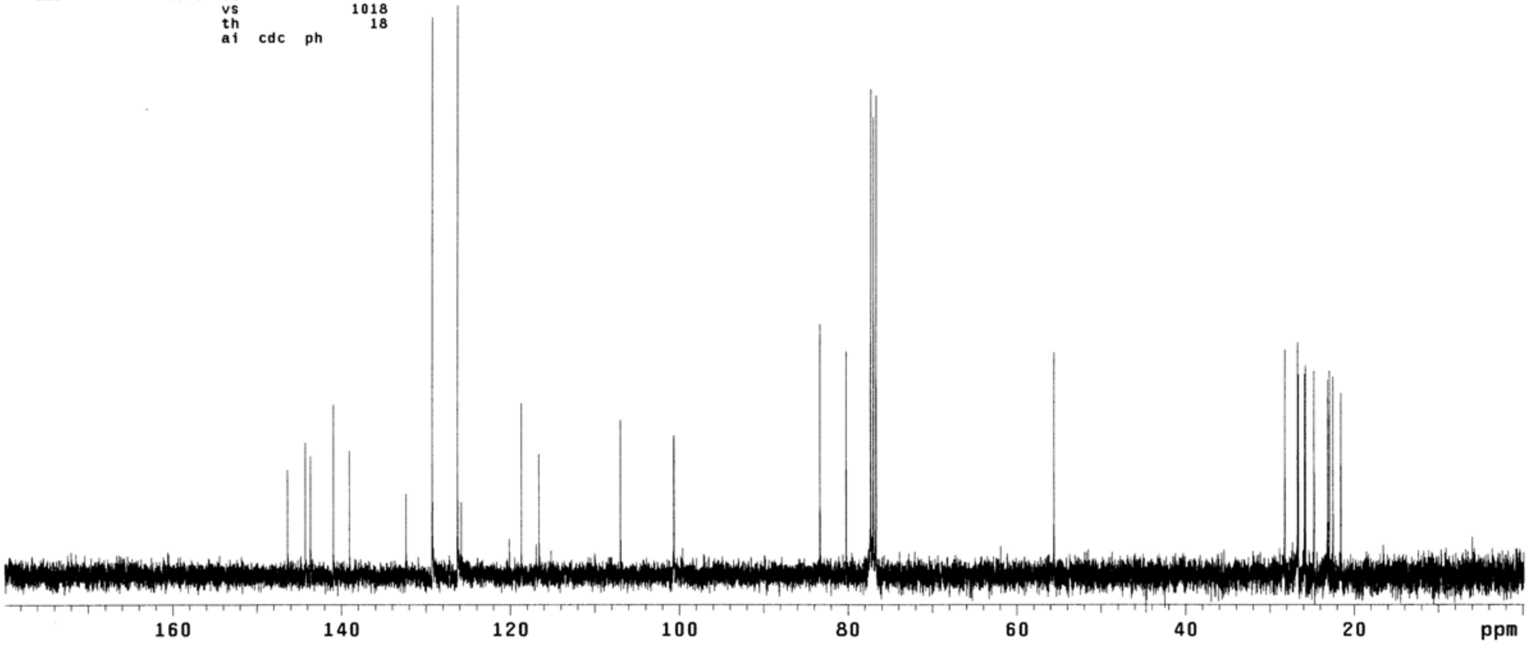
```
STANDARD CARBON PARAMETERS

exp1  CARBON

      SAMPLE             PRESATURATION
date   Feb  2 2007  satmode           n
solvent      cdcl3  wet               n
file /home/kerr/vn~        SPECIAL
mrsys/data/TPL-I-0~ temp            8.8
65carb_20070202_01~ gain       not used
    /I_065carb_01   spin             20
   ACQUISITION      hst           0.008
sw         25133.5  pw90         11.800
at           1.304  alfa         20.000
np           65536          FLAGS
fb           14000  il                n
bs              64  in                n
d1           1.000  dp                y
nt            1000  hs               nn
ct            1000        PROCESSING
   TRANSMITTER      lb             0.50
tn             C13  lsfid            -9
sfrq       100.531  fn         not used
tof         1530.6         DISPLAY
tpwr            52  sp            -17.6
pw           5.900  wp          18096.2
    DECOUPLER       rfl          9249.4
dn              H1  rfp          7740.0
dof              0  rp            103.0
dm             yyy  lp           -212.9
decwave          w          PLOT
dpwr            39  wc              250
dmf           9000  sc                0
                    vs             1018
                    th               18
                    ai   cdc   ph
```



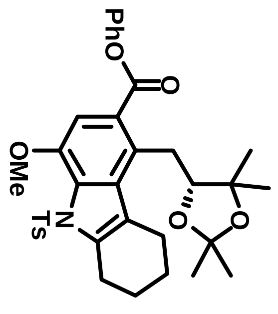
Compound 16



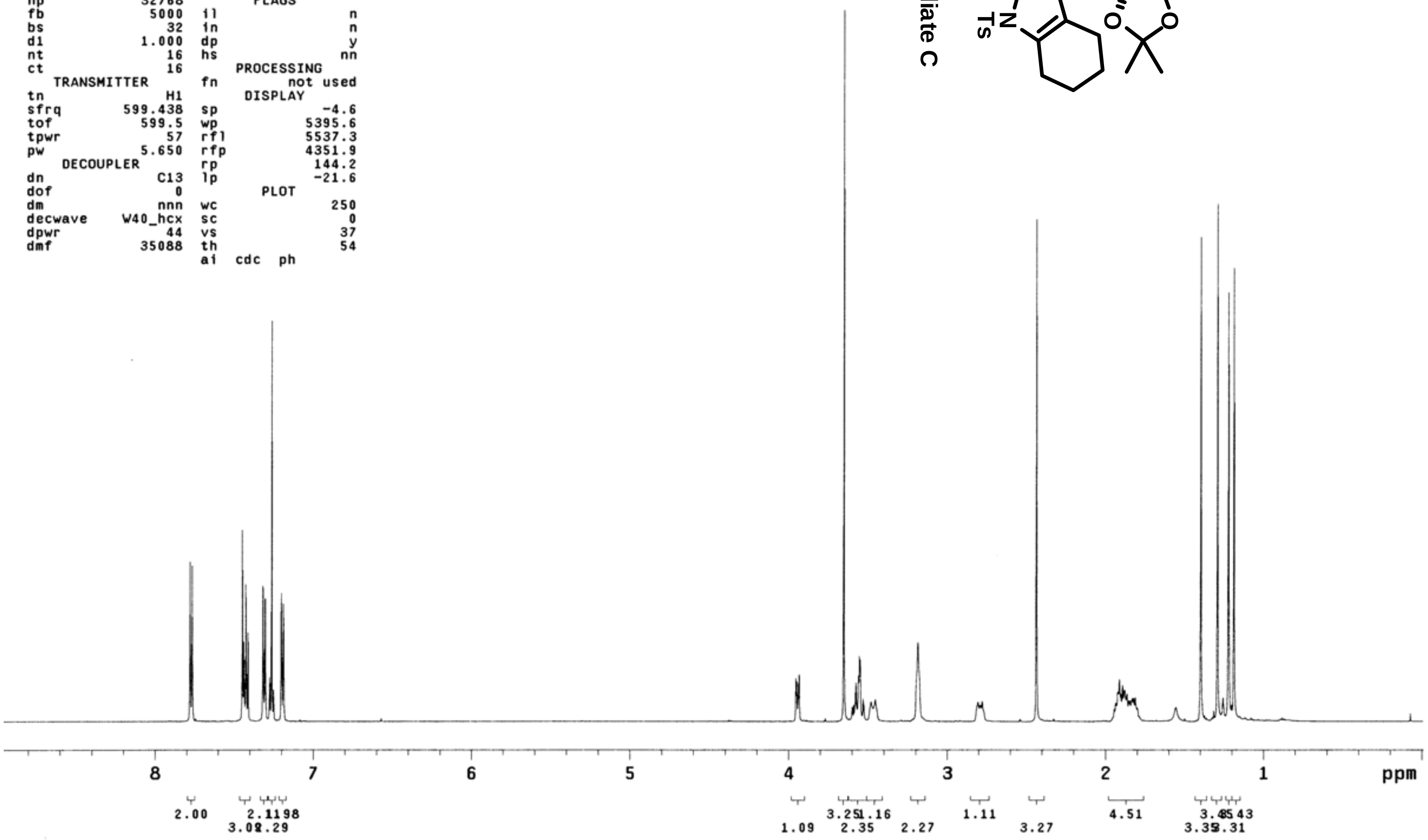
```
TPL-J-051

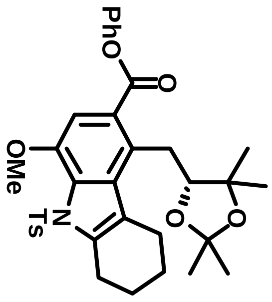
exp1  PROTON

      SAMPLE              PRESATURATION
date   Apr  1 2007  satmode            n
solvent      CDCl3  wet                n
file /export/home/~       SPECIAL
kerr/vnmrsys/data/~ temp            23.0
TPL-J-051/J_051_01~ gain        not used
        /PROTON_01  spin              20
   ACQUISITION      hst            0.008
sw          9591.2  pw90          11.300
at           1.708  alfa           6.600
np           32768         FLAGS
fb            5000  il                 n
bs              32  in                 n
d1           1.000  dp                 y
nt              16  hs                nn
ct              16      PROCESSING
   TRANSMITTER      fn          not used
tn              H1        DISPLAY
sfrq       599.438  sp              -4.6
tof          599.5  wp            5395.6
tpwr            57  rfl           5537.3
pw           5.650  rfp           4351.9
    DECOUPLER       rp             144.2
dn             C13  lp             -21.6
dof              0           PLOT
dm             nnn  wc               250
decwave    W40_hcx  sc                 0
dpwr            44  vs                37
dmf          35088  th                54
                    ai  cdc  ph
```



Intermediate C



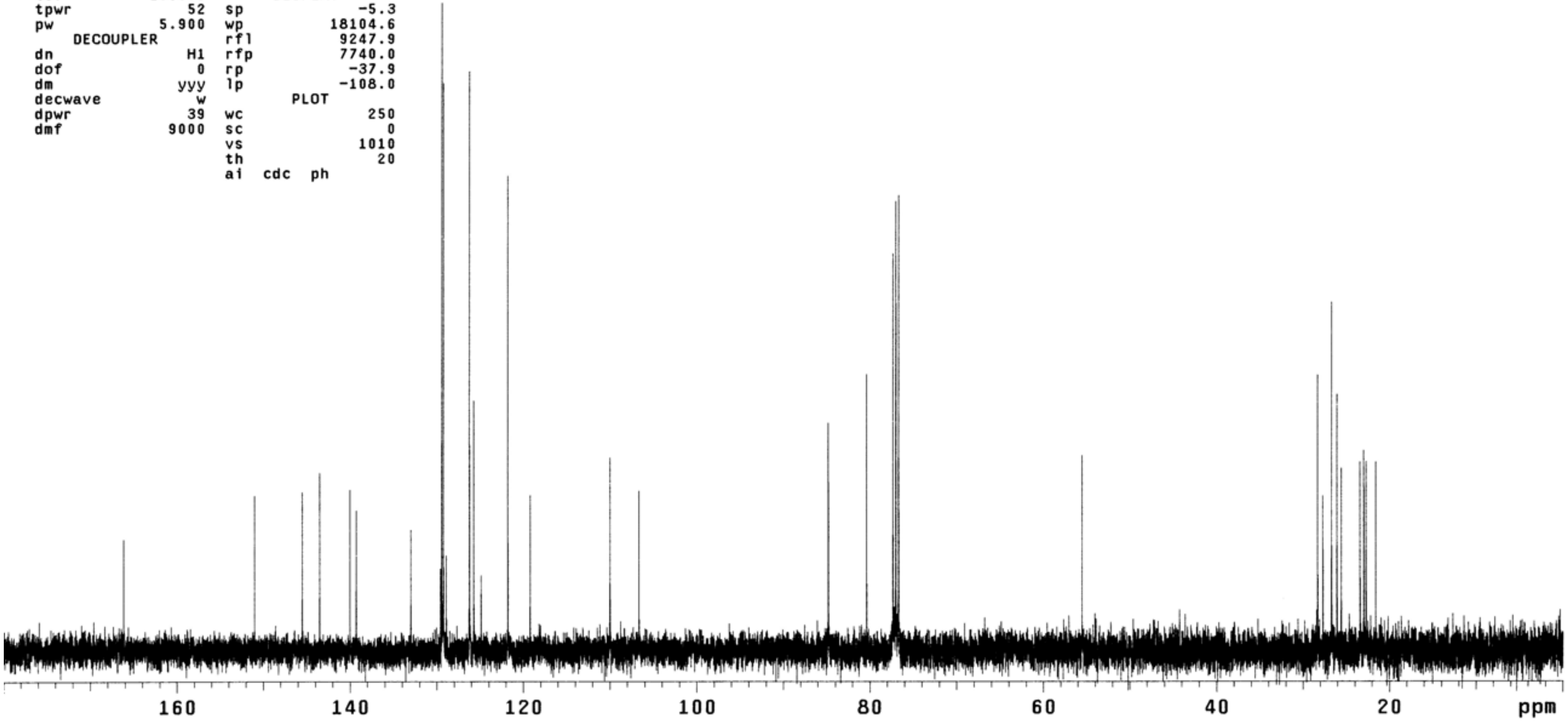


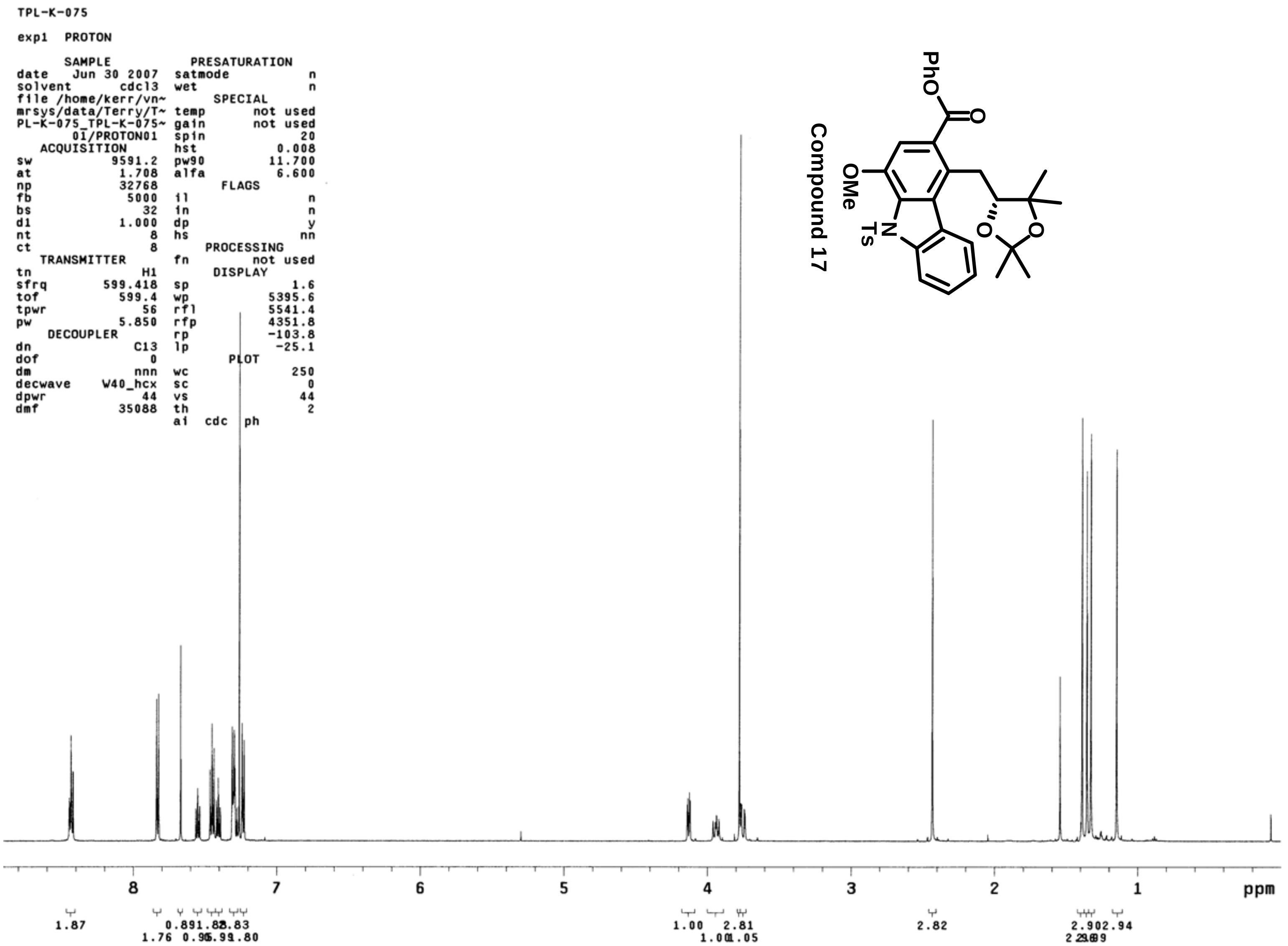
Intermediate C

```
TPL-J-051carbon

exp1  CARBON

      SAMPLE              PRESATURATION
date   Apr  1 2007   satmode            n
solvent      cdcl3   wet                n
file /home/kerr/vn~       SPECIAL
mrsys/data/TPL-J-0~  temp            26.0
51carb_20070401_01~  gain        not used
   /J_051carbon_01   spin              20
    ACQUISITION      hst            0.008
sw         25133.5   pw90          11.800
at           1.304   alfa          20.000
np           65536          FLAGS
fb           14000   il                 n
bs              64   in                 n
d1           1.000   dp                 y
nt            1000   hs                nn
ct            1000        PROCESSING
    TRANSMITTER      lb              0.50
tn             C13   lsfid             -9
sfrq       100.531   fn          not used
tof         1530.6         DISPLAY
tpwr            52   sp              -5.3
pw           5.900   wp           18104.6
     DECOUPLER       rfl           9247.9
dn              H1   rfp           7740.0
dof              0   rp             -37.9
dm             yyy   lp            -108.0
decwave          w          PLOT
dpwr            39   wc               250
dmf           9000   sc                 0
                     vs              1010
                     th                20
                     ai   cdc   ph
```





Compound 17

```
TPL-K-075

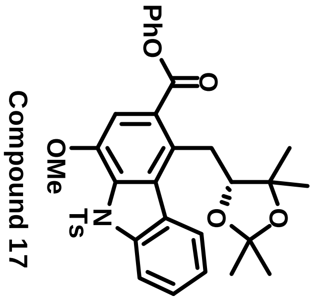
exp1  PROTON

      SAMPLE            PRESATURATION
date   Jun 30 2007   satmode           n
solvent      cdcl3   wet               n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~  temp       not used
PL-K-075_TPL-K-075~  gain       not used
      01/PROTON01    spin             20
   ACQUISITION       hst           0.008
sw          9591.2   pw90         11.700
at           1.708   alfa          6.600
np           32768           FLAGS
fb            5000   il                n
bs              32   in                n
d1           1.000   dp                y
nt               8   hs               nn
ct               8        PROCESSING
   TRANSMITTER       fn         not used
tn              H1          DISPLAY
sfrq       599.418   sp              1.6
tof          599.4   wp           5395.6
tpwr            56   rfl          5541.4
pw           5.850   rfp          4351.8
    DECOUPLER        rp           -103.8
dn             C13   lp            -25.1
dof              0           PLOT
dm             nnn   wc              250
decwave    W40_hcx   sc                0
dpwr            44   vs               44
dmf          35088   th                2
                     ai   cdc   ph
```

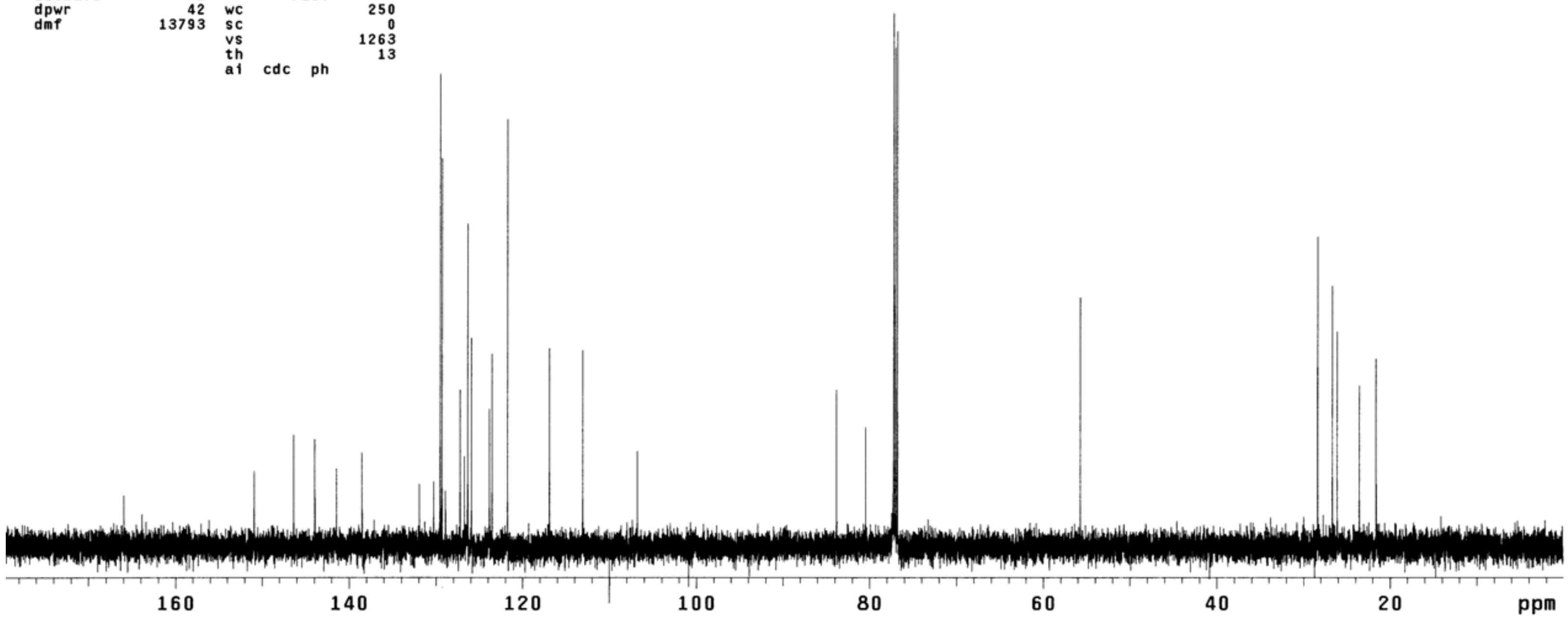
```
TP1-K-075carbon

exp1  CARBON

      SAMPLE              PRESATURATION
date    Jun 30 2007   satmode            n
solvent       cdcl3   wet                n
file /home/kerr/vn~         SPECIAL
mrsys/data/Terry/T~   temp        not used
PL-K-075_carbon01/~   gain        not used
           CARBON01   spin              20
    ACQUISITION       hst            0.008
sw          37682.5   pw90          21.700
at            0.870   alfa          10.000
np            65536            FLAGS
fb            21000   il                 n
bs               64   in                 n
d1            1.000   dp                 y
nt             1000   hs                nn
ct             1000         PROCESSING
    TRANSMITTER       lb              0.50
tn              C13   lsfid             -1
sfrq        150.740   fn          not used
tof          2295.0          DISPLAY
tpwr             56   sp              15.0
pw           10.850   wp           27101.6
     DECOUPLER        rfl          13867.6
dn               H1   rfp          11605.7
dof               0   rp            -173.1
dm              yyy   lp              -0.0
decwave           w            PLOT
dpwr             42   wc               250
dmf           13793   sc                 0
                      vs              1263
                      th                13
                      ai   cdc   ph
```



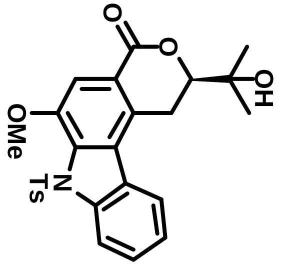
Compound 17



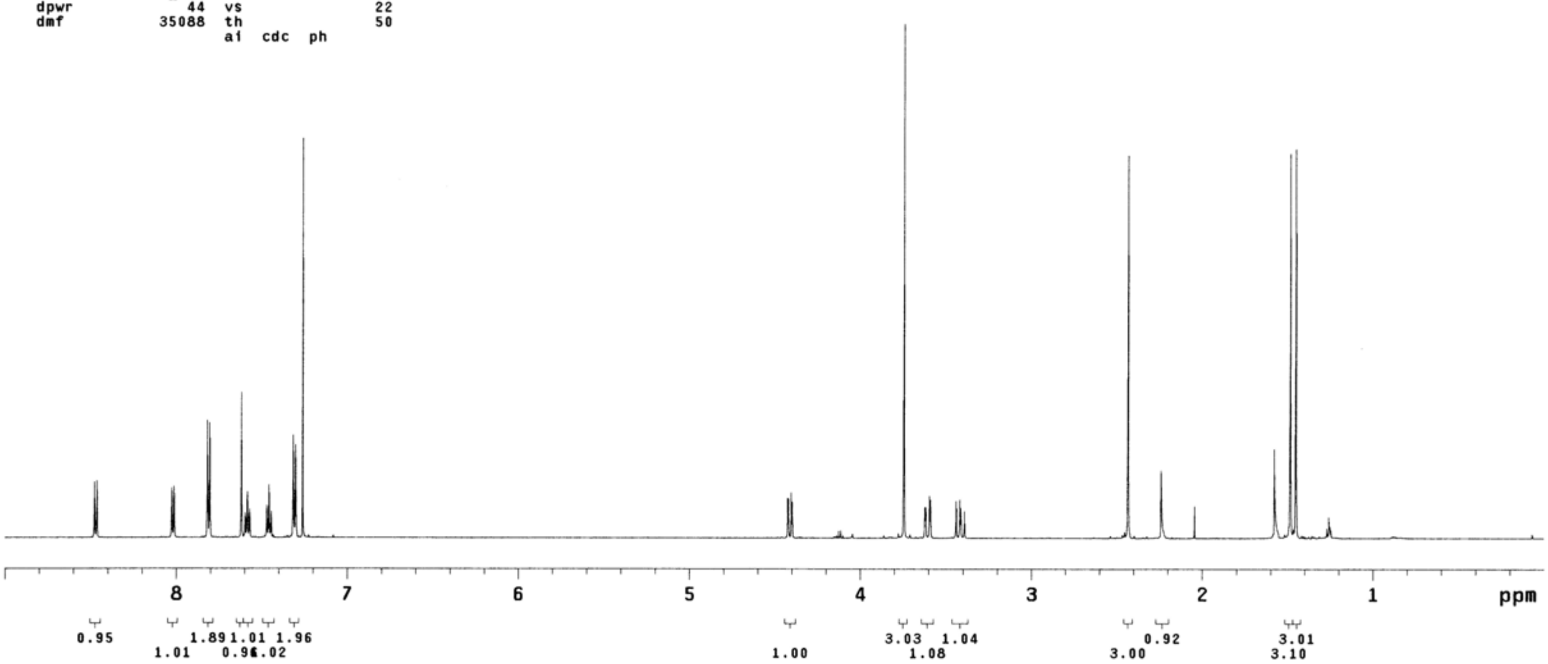
```
TPL-K-183AA

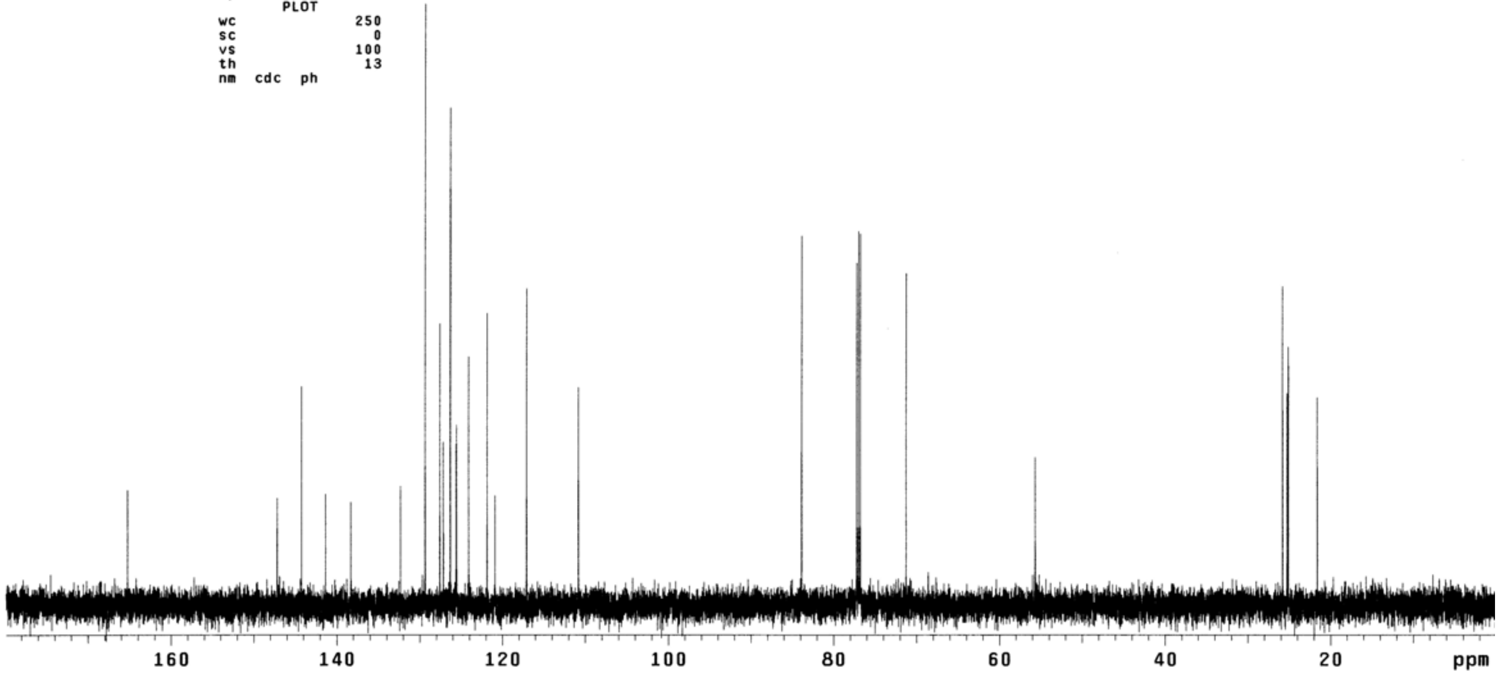
exp1  PROTON

      SAMPLE              PRESATURATION
date   Jul  4 2007  satmode            n
solvent       cdcl3  wet                n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~  temp      not used
PL-K-183B_TPL-K-18~  gain      not used
     3B01/PROTON03  spin              20
   ACQUISITION       hst           0.008
sw           9591.2  pw90         11.700
at            1.708  alfa          6.600
np            32768          FLAGS
fb             5000  il                n
bs               32  in                n
d1            1.000  dp                y
nt                8  hs               nn
ct                8       PROCESSING
   TRANSMITTER       fn        not used
tn               H1         DISPLAY
sfrq        599.418  sp              1.7
tof           599.4  wp           5395.6
tpwr             56  rfl          5541.4
pw            5.850  rfp          4351.8
    DECOUPLER        rp            -69.2
dn              C13  lp            -31.4
dof               0            PLOT
dm              nnn  wc              250
decwave     W40_hcx  sc                0
dpwr             44  vs               22
dmf           35088  th               50
                     ai   cdc   ph
```



Compound 18

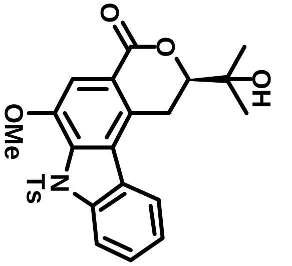




```
TPL-K-083A

exp1  CARBON

      SAMPLE              PRESATURATION
date   Jul  4 2007    satmode             n
solvent       cdcl3   wet                 n
file            exp         SPECIAL
   ACQUISITION        temp         not used
sw          37682.5   gain         not used
at            0.870   spin               20
np            65536   hst             0.008
fb            21000   pw90           21.700
bs               64   alfa           10.000
d1            1.000          FLAGS
nt             1000   il                  n
ct              256   in                  n
   TRANSMITTER        dp                  y
tn              C13   hs                 nn
sfrq        150.740        PROCESSING
tof          2295.0   lb               0.50
tpwr             56   lsfid              -1
pw           10.850   fn           not used
    DECOUPLER              DISPLAY
dn               H1   sp                9.3
dof               0   wp            27101.6
dm              yyy   rfl           13873.4
decwave           w   rfp           11605.7
dpwr             42   rp             -153.6
dmf           13793   lp              -44.5
                              PLOT
                      wc                250
                      sc                  0
                      vs                100
                      th                 13
                      nm  cdc  ph
```



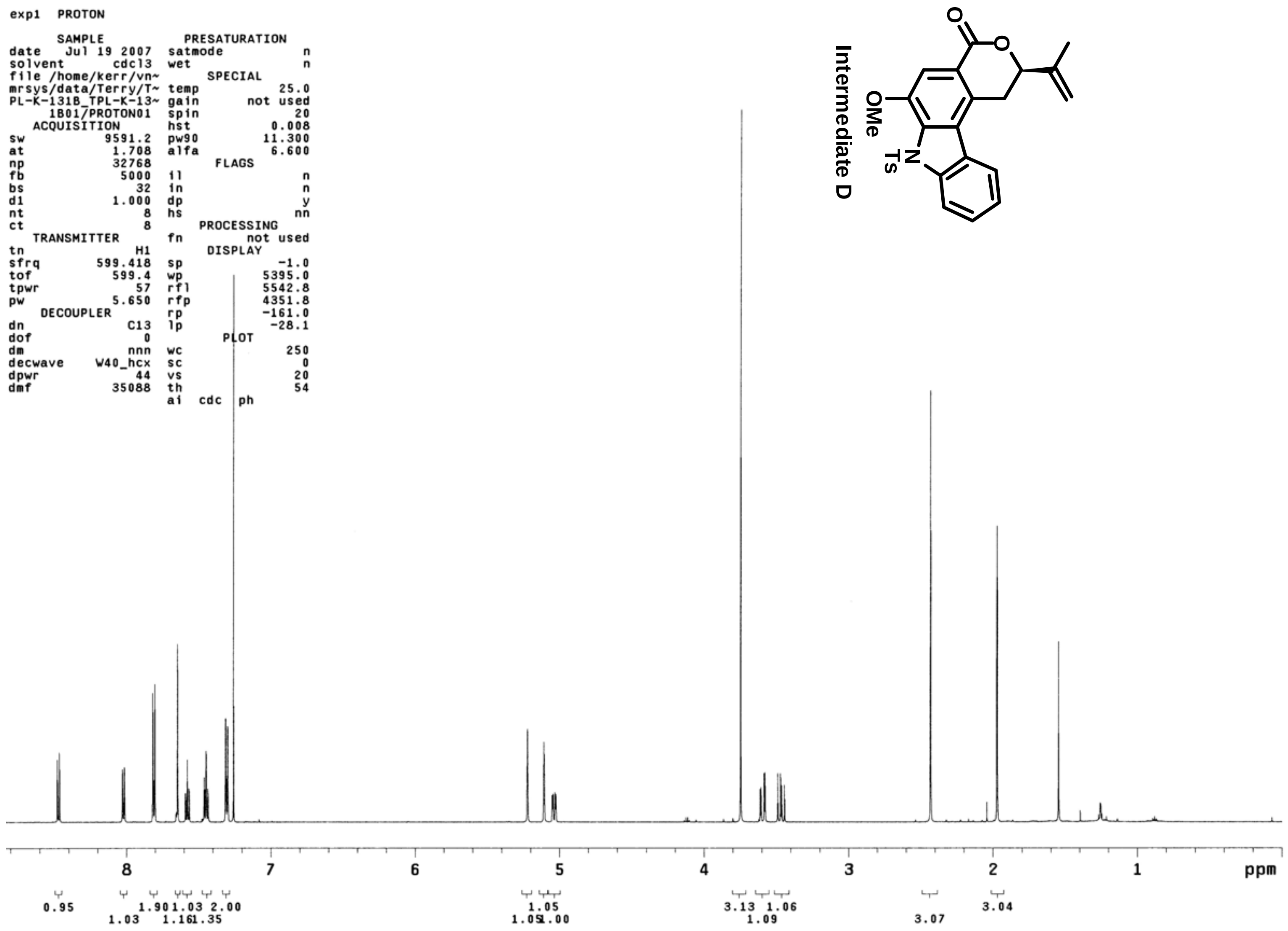
Compound 18

Intermediate D

```
TPL-K-131B

exp1  PROTON

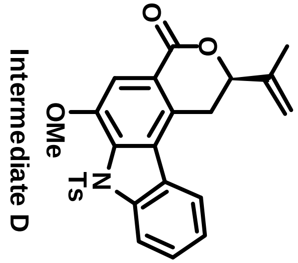
       SAMPLE            PRESATURATION
date   Jul 19 2007   satmode            n
solvent       cdcl3  wet                n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~  temp            25.0
PL-K-131B_TPL-K-13~  gain        not used
    1B01/PROTON01    spin              20
   ACQUISITION       hst            0.008
sw           9591.2  pw90          11.300
at            1.708  alfa           6.600
np            32768           FLAGS
fb             5000  il                 n
bs               32  in                 n
d1            1.000  dp                 y
nt                8  hs                nn
ct                8        PROCESSING
   TRANSMITTER       fn          not used
tn               H1          DISPLAY
sfrq        599.418  sp              -1.0
tof           599.4  wp            5395.0
tpwr             57  rfl           5542.8
pw            5.650  rfp           4351.8
    DECOUPLER        rp            -161.0
dn              C13  lp             -28.1
dof               0           PLOT
dm              nnn  wc               250
decwave    W40_hcx   sc                 0
dpwr             44  vs                20
dmf           35088  th                54
                     ai   cdc   ph
```



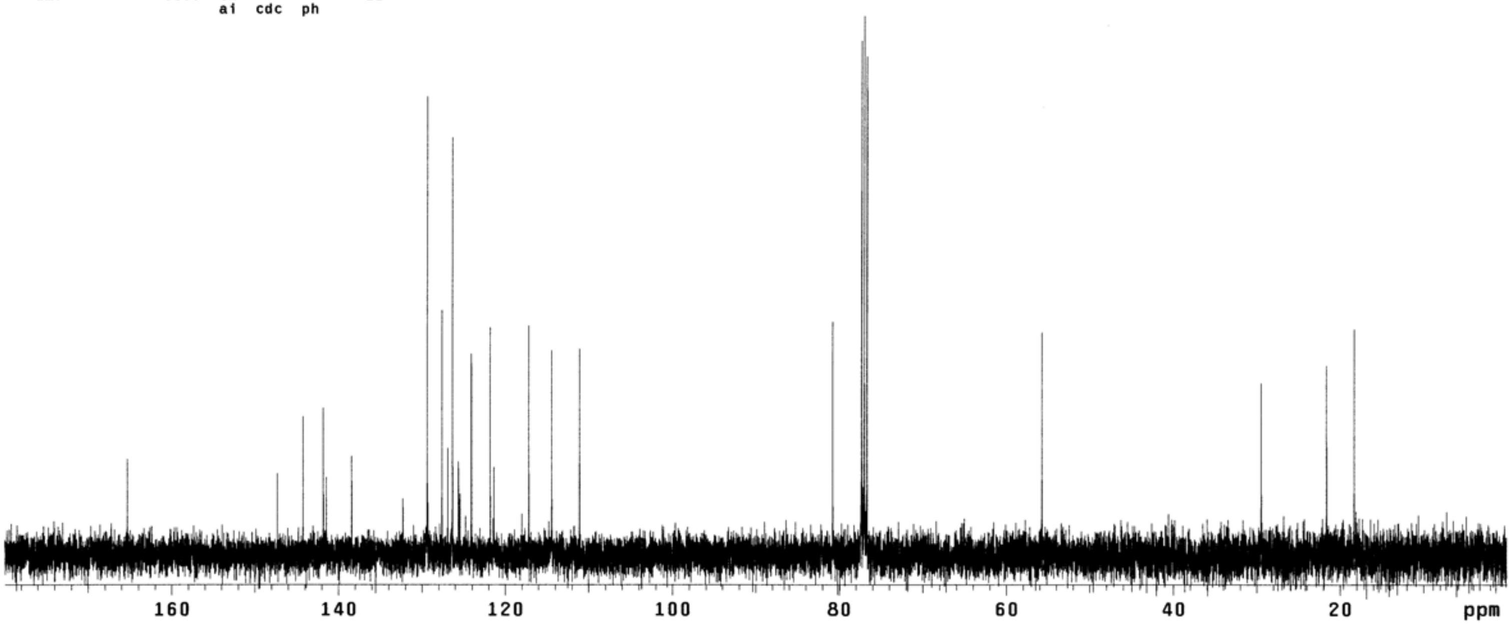
```
TPL-K-131Bcarb

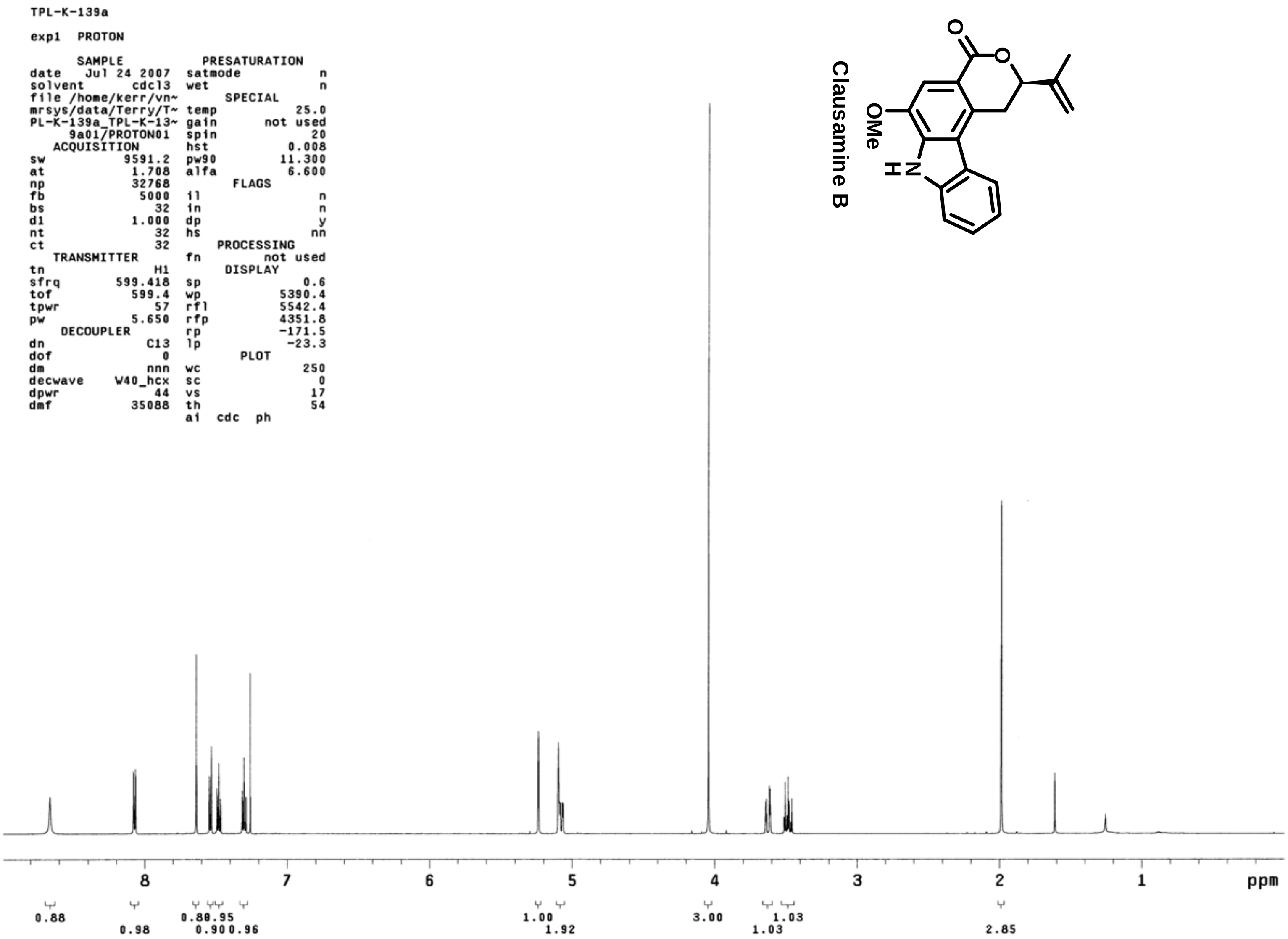
exp1  CARBON

      SAMPLE              PRESATURATION
date   Jul 19 2007  satmode            n
solvent       cdcl3  wet                n
file /home/kerr/vn~       SPECIAL
mrsys/data/Terry/T~  temp             26.0
PL-K-131Bcarb_TPL-~  gain         not used
K-131Bcarb_01/CARB~  spin               20
               ON01  hst             0.008
    ACQUISITION      pw90           10.200
sw          25133.5  alfa           20.000
at            1.304         FLAGS
np            65536  il                 n
fb            14000  in                 n
bs               64  dp                 y
d1            1.000  hs                nn
nt              500       PROCESSING
ct              500  lb               0.50
    TRANSMITTER      fn           not used
tn              C13       DISPLAY
sfrq        100.531  sp                4.7
tof          1530.6  wp            18086.2
tpwr             53  rfl            9247.1
pw            5.100  rfp            7740.0
     DECOUPLER       rp              -29.0
dn               H1  lp             -271.4
dof               0         PLOT
dm              yyy  wc                250
decwave           w  sc                  0
dpwr             39  vs               1287
dmf            9300  th                 12
                     ai  cdc  ph
```



Intermediate D





```
TPL-K-139a

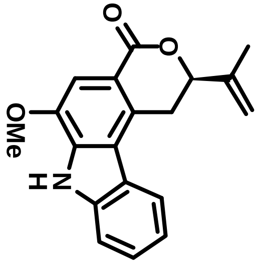
exp1  PROTON

      SAMPLE              PRESATURATION
date   Jul 24 2007  satmode             n
solvent      cdcl3  wet                 n
file /home/kerr/vn~       SPECIAL
mrsys/data/Terry/T~ temp             25.0
PL-K-139a_TPL-K-13~ gain         not used
    9a01/PROTON01   spin               20
    ACQUISITION     hst             0.008
sw          9591.2  pw90           11.300
at           1.708  alfa            6.600
np           32768          FLAGS
fb            5000  il                  n
bs              32  in                  n
d1           1.000  dp                  y
nt              32  hs                 nn
ct              32       PROCESSING
    TRANSMITTER     fn           not used
tn              H1         DISPLAY
sfrq       599.418  sp                0.6
tof          599.4  wp             5390.4
tpwr            57  rfl            5542.4
pw           5.650  rfp            4351.8
     DECOUPLER      rp             -171.5
dn             C13  lp              -23.3
dof              0           PLOT
dm             nnn  wc                250
decwave    W40_hcx  sc                  0
dpwr            44  vs                 17
dmf          35088  th                 54
                    ai  cdc  ph
```

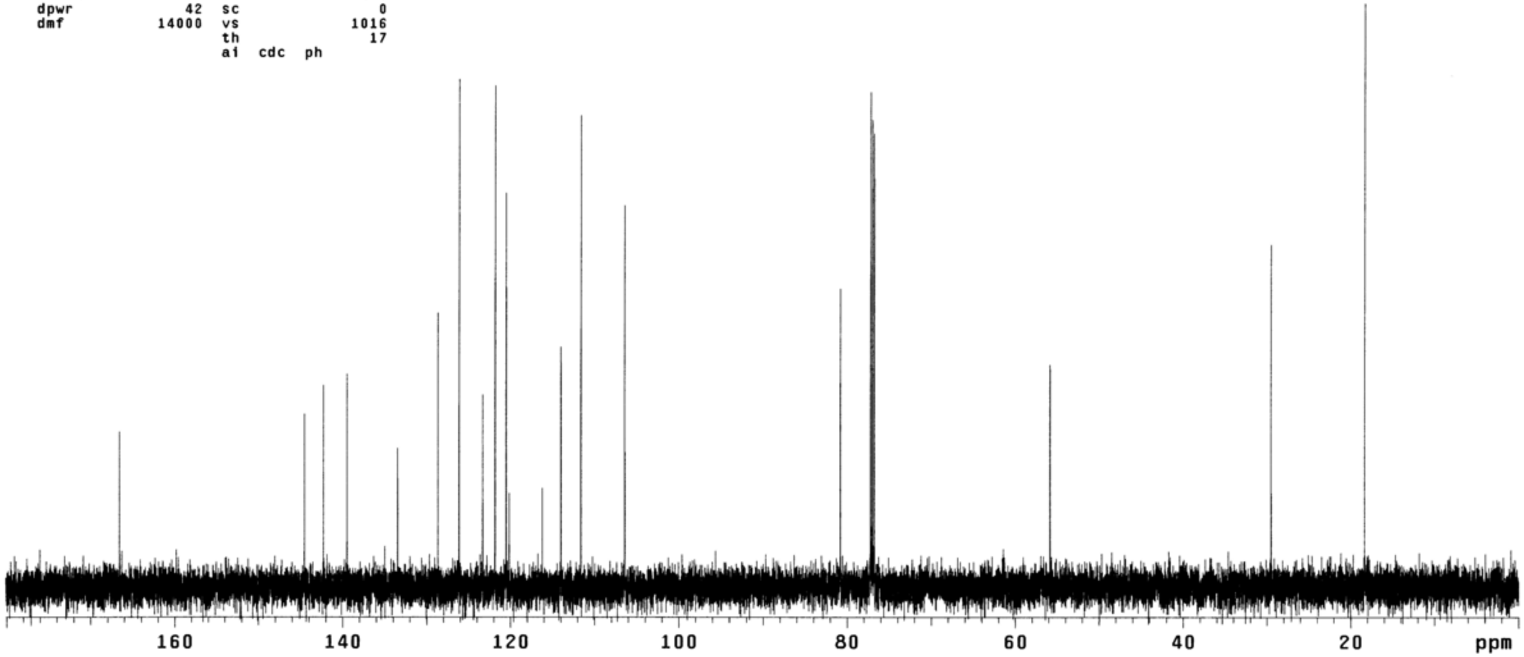
```
TPL-K-139carb

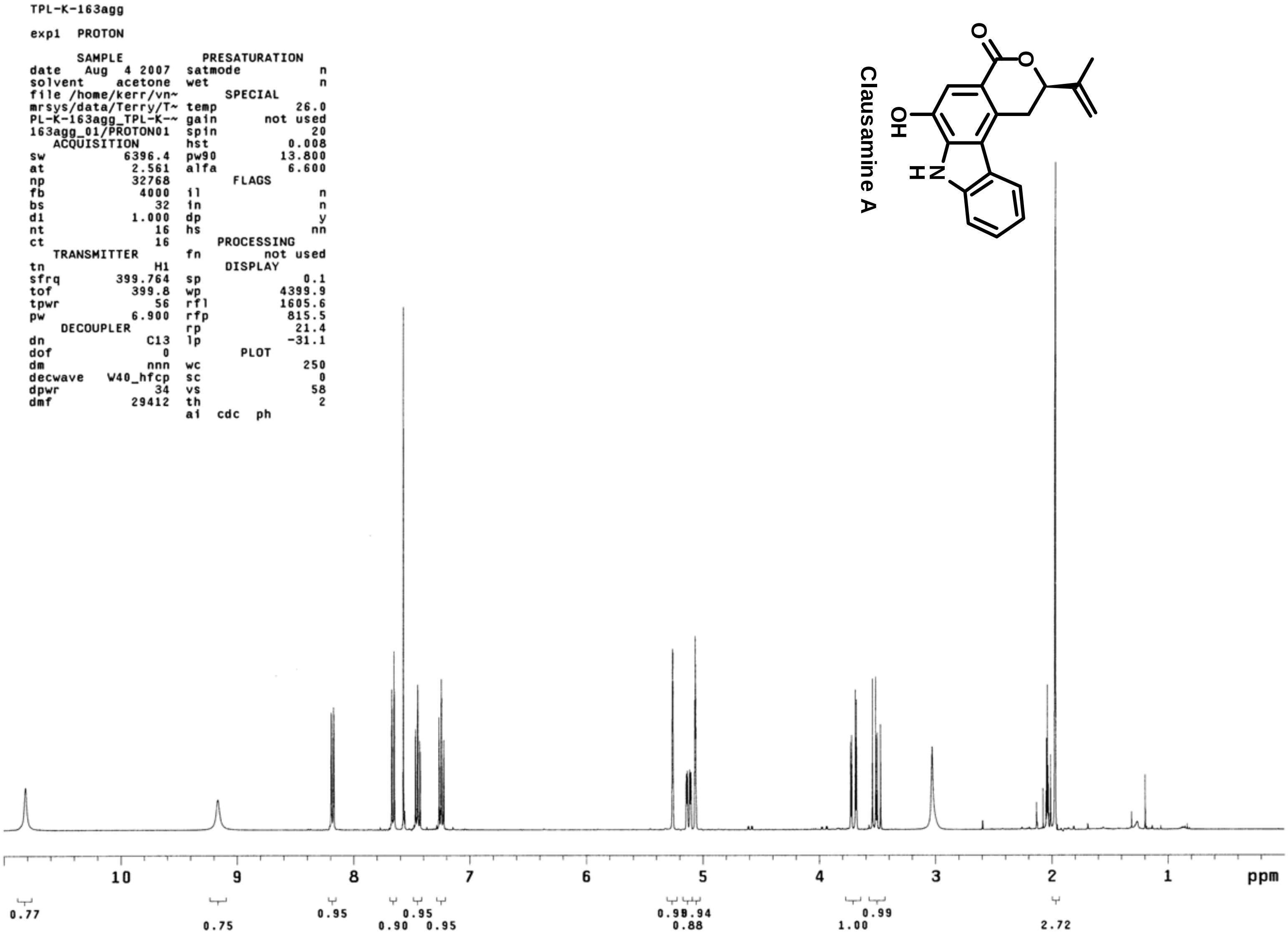
exp1  CARBON

      SAMPLE            PRESATURATION
date   Jul 24 2007   satmode           n
solvent      cdcl3   wet               n
file /home/kerr/vn~         SPECIAL
mrsys/data/Terry/T~  temp           25.0
PL-K-139carb_TPL-K~  gain       not used
-139carb01/CARBON0~  spin             20
                  1  hst           0.008
    ACQUISITION      pw90         21.700
sw          37682.5  alfa         10.000
at            0.870         FLAGS
np            65536  il                n
fb            21000  in                n
bs               32  dp                y
d1            1.000  hs               nn
nt             1000       PROCESSING
ct              320  lb             0.50
    TRANSMITTER      lsfid            -1
tn              C13  fn         not used
sfrq        150.740         DISPLAY
tof          2295.0  sp             -4.5
tpwr             56  wp          27151.0
pw           10.850  rfl         13869.9
    DECOUPLER        rfp         11605.7
dn               H1  rp             98.4
dof               0  lp              0.3
dm              yyy           PLOT
decwave           w  wc              250
dpwr             42  sc                0
dmf           14000  vs             1016
                     th               17
                     ai   cdc   ph
```



Clausamine B



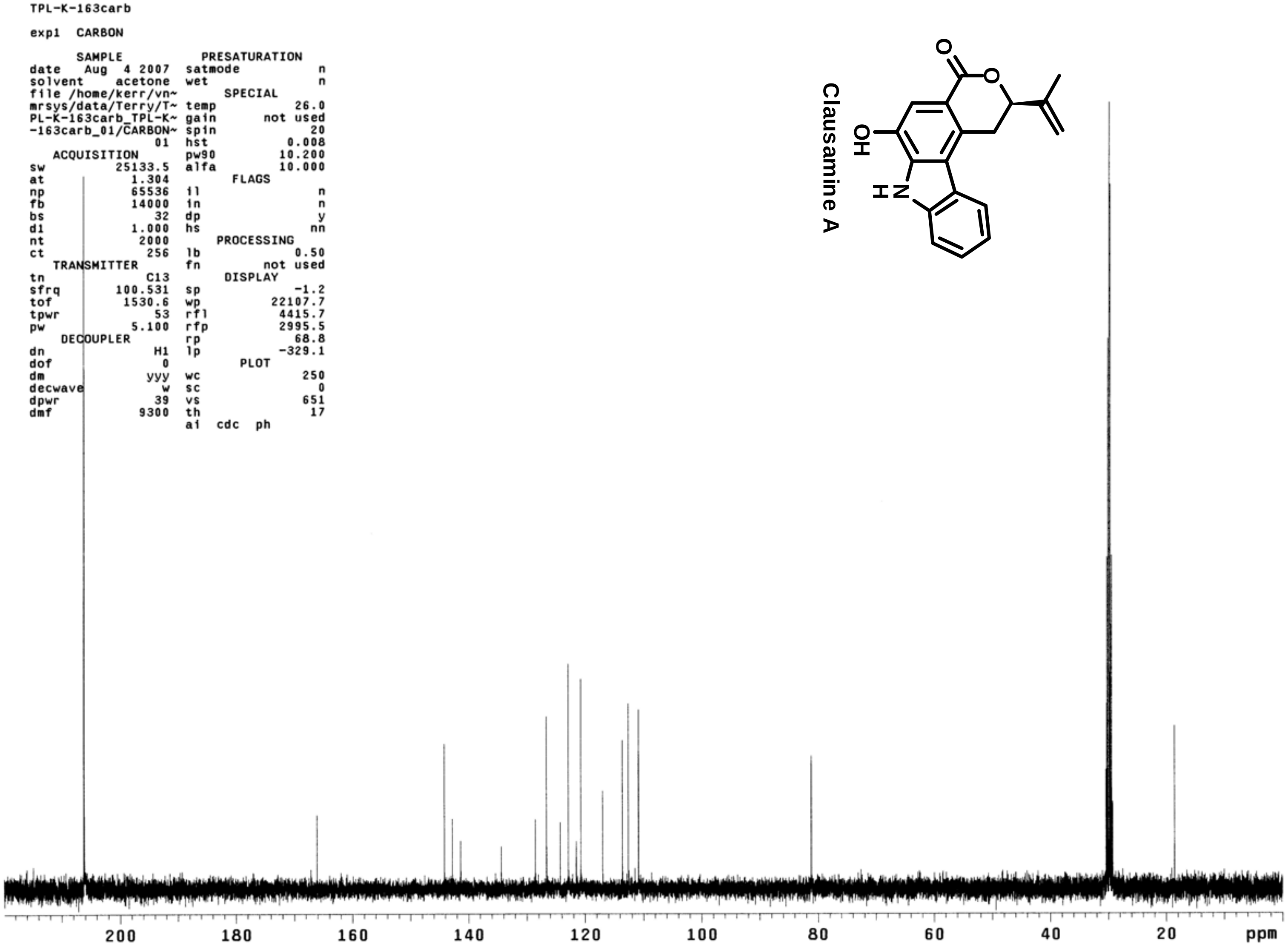


Clausamine A

```
TPL-K-163agg

exp1  PROTON

       SAMPLE            PRESATURATION
date   Aug  4 2007   satmode          n
solvent     acetone  wet              n
file /home/kerr/vn~       SPECIAL
mrsys/data/Terry/T~  temp          26.0
PL-K-163agg_TPL-K-~  gain      not used
163agg_01/PROTON01   spin            20
   ACQUISITION       hst          0.008
sw           6396.4  pw90        13.800
at            2.561  alfa         6.600
np            32768         FLAGS
fb             4000  il               n
bs               32  in               n
d1            1.000  dp               y
nt               16  hs              nn
ct               16      PROCESSING
    TRANSMITTER      fn        not used
tn               H1        DISPLAY
sfrq        399.764  sp             0.1
tof           399.8  wp          4399.9
tpwr             56  rfl         1605.6
pw            6.900  rfp          815.5
     DECOUPLER       rp            21.4
dn              C13  lp           -31.1
dof               0          PLOT
dm              nnn  wc             250
decwave    W40_hfcp  sc               0
dpwr             34  vs              58
dmf           29412  th               2
                     ai   cdc  ph
```



Clausamine A

```
TPL-K-163carb

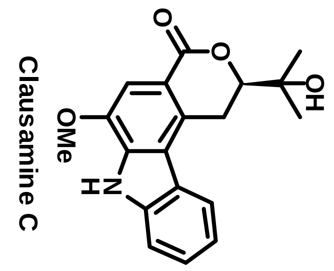
exp1  CARBON

      SAMPLE              PRESATURATION
date   Aug  4 2007  satmode            n
solvent     acetone  wet                n
file /home/kerr/vn~         SPECIAL
mrsys/data/Terry/T~ temp            26.0
PL-K-163carb_TPL-K~ gain        not used
-163carb_01/CARBON~ spin              20
                 01 hst            0.008
   ACQUISITION      pw90          10.200
sw          25133.5 alfa          10.000
at            1.304          FLAGS
np            65536 il                 n
fb            14000 in                 n
bs               32 dp                 y
d1            1.000 hs                nn
nt             2000       PROCESSING
ct              256 lb              0.50
   TRANSMITTER      fn          not used
tn              C13         DISPLAY
sfrq        100.531 sp              -1.2
tof          1530.6 wp           22107.7
tpwr             53 rfl           4415.7
pw            5.100 rfp           2995.5
    DECOUPLER       rp              68.8
dn               H1 lp            -329.1
dof               0            PLOT
dm              yyy wc               250
decwave           w sc                 0
dpwr             39 vs               651
dmf            9300 th                17
                    ai   cdc   ph
```

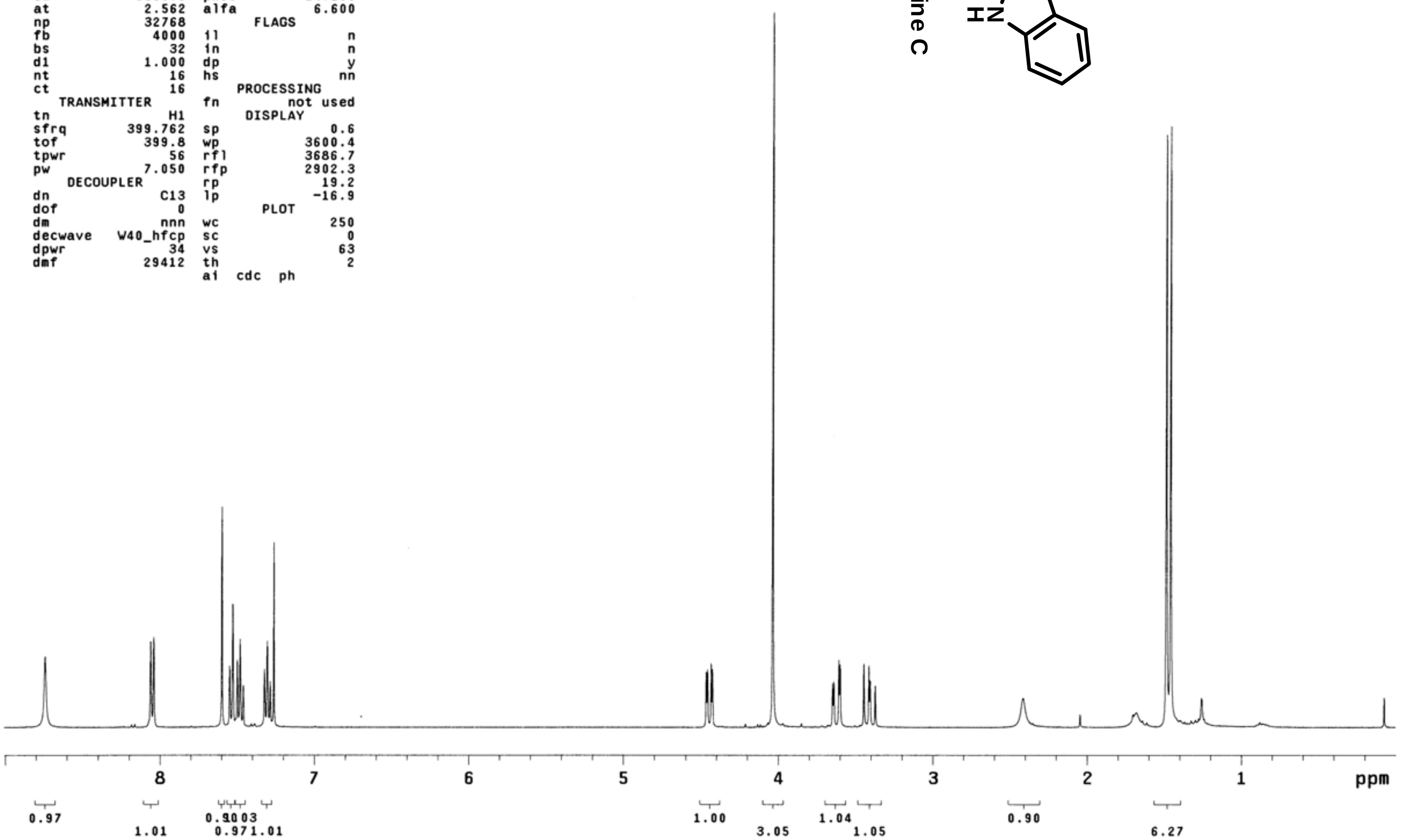
```
TPL-J-021agg

exp1  PROTON

      SAMPLE              PRESATURATION
date   Mar 24 2007   satmode             n
solvent      cdcl3   wet                 n
file /home/kerr/vn~        SPECIAL
mrsys/data/TPL-J-0~  temp             26.0
21agg_20070324_01/~  gain         not used
      J_021agg_01    spin               20
   ACQUISITION       hst             0.008
sw          6395.9   pw90           14.100
at           2.562   alfa            6.600
np           32768          FLAGS
fb            4000   il                  n
bs              32   in                  n
d1           1.000   dp                  y
nt              16   hs                 nn
ct              16        PROCESSING
   TRANSMITTER       fn           not used
tn              H1          DISPLAY
sfrq       399.762   sp                0.6
tof          399.8   wp             3600.4
tpwr            56   rfl            3686.7
pw           7.050   rfp            2902.3
    DECOUPLER        rp               19.2
dn             C13   lp              -16.9
dof              0            PLOT
dm             nnn   wc                250
decwave  W40_hfcp    sc                  0
dpwr            34   vs                 63
dmf          29412   th                  2
                     ai   cdc   ph
```



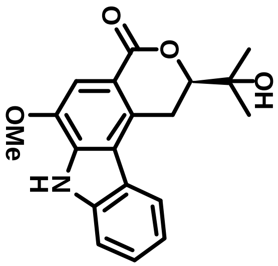
Clausamine C



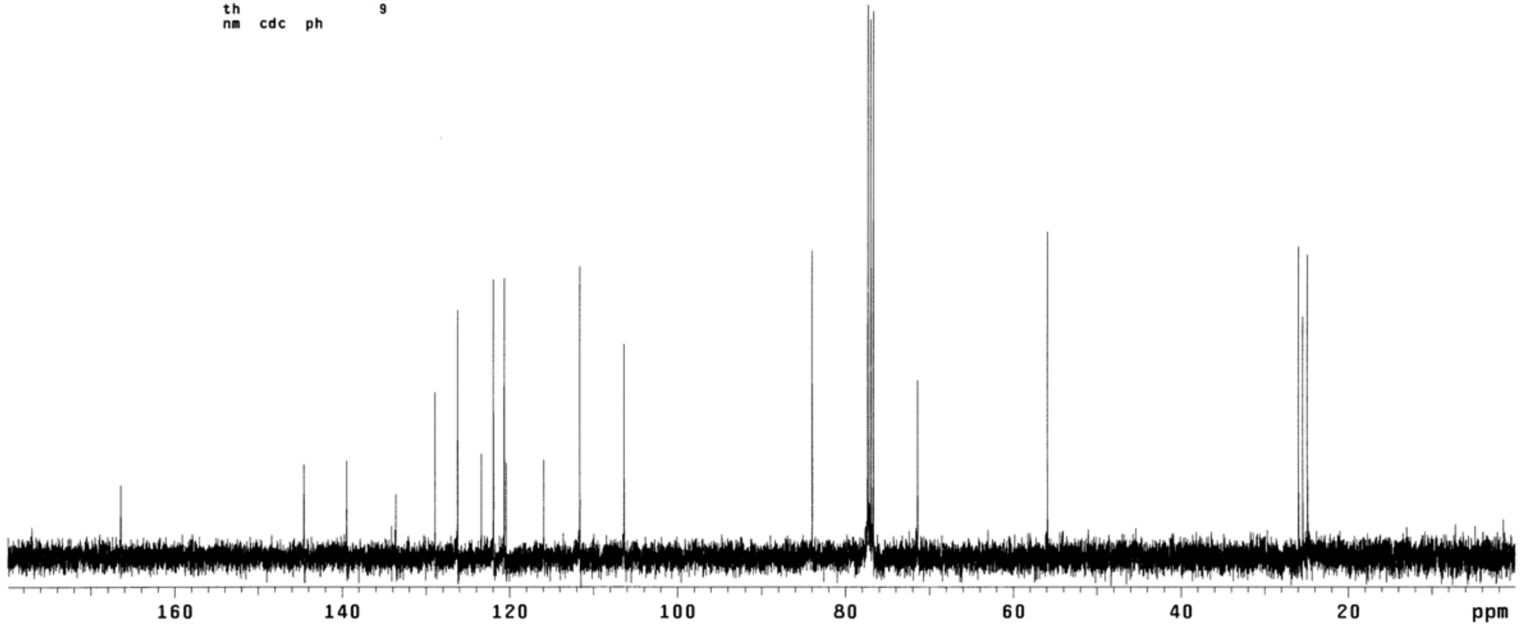
```
TPL-J-021carb

exp1  CARBON

      SAMPLE              PRESATURATION
date   Mar 24 2007     satmode            n
solvent       cdcl3    wet                n
file            exp           SPECIAL
   ACQUISITION         temp            26.0
sw          25133.5    gain        not used
at            1.304    spin              20
np            65536    hst            0.008
fb            14000    pw90          11.800
bs               64    alfa          20.000
d1            1.000           FLAGS
nt             2000    il                 n
ct              512    in                 n
   TRANSMITTER         dp                 y
tn              C13    hs                nn
sfrq        100.531         PROCESSING
tof          1530.6    lb              0.50
tpwr             52    lsfid             -9
pw            5.900    fn          not used
   DECOUPLER                 DISPLAY
dn               H1    sp               8.5
dof               0    wp           18071.6
dm              yyy    rfl           9247.1
decwave           w    rfp           7740.0
dpwr             39    rp             -74.0
dmf            9000    lp              -0.5
                              PLOT
                       wc               250
                       sc                 0
                       vs                91
                       th                 9
                       nm  cdc  ph
```



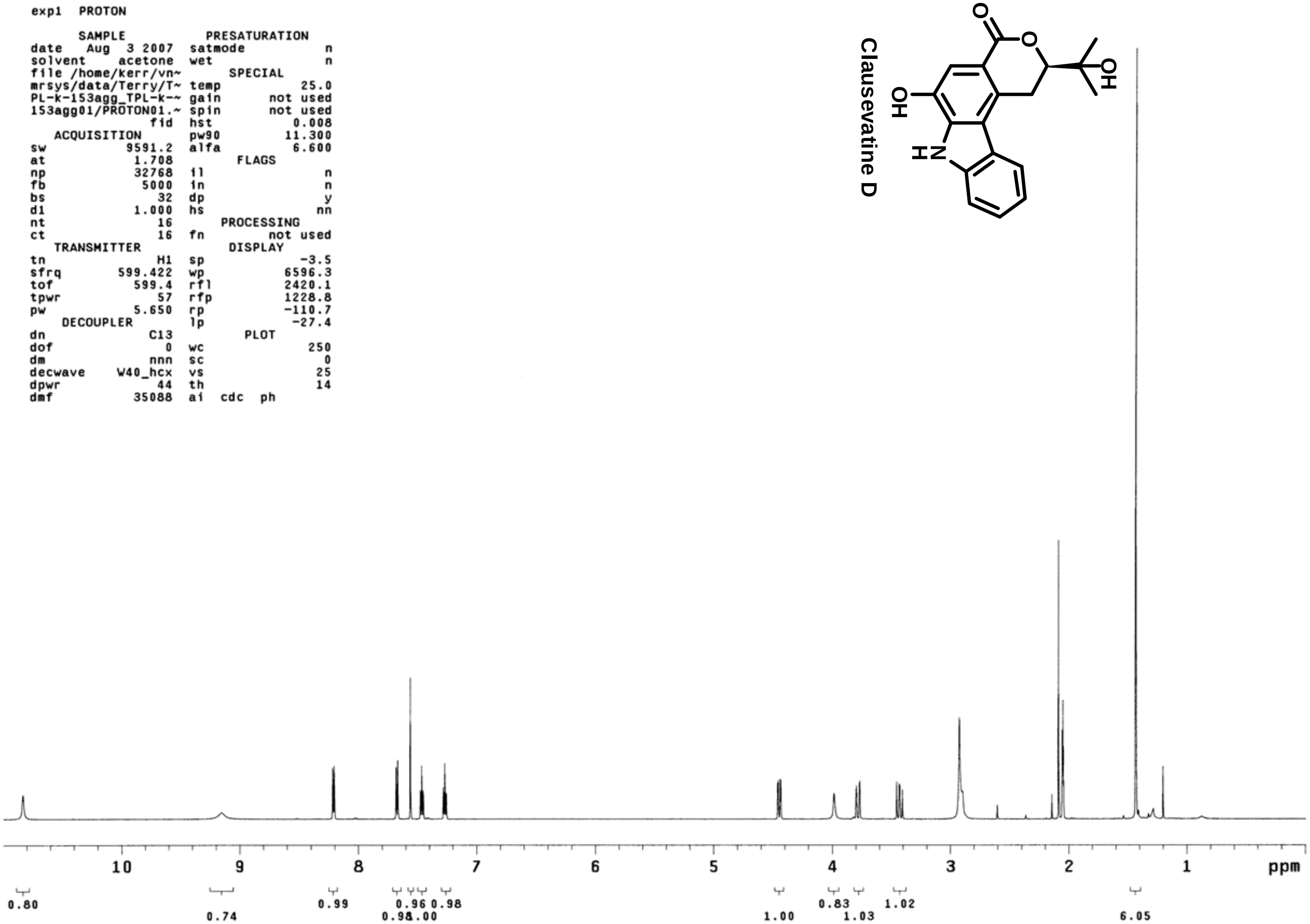
Clausamine C



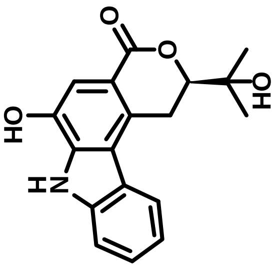
```
TPL-k-153agg

exp1  PROTON

      SAMPLE              PRESATURATION
date   Aug  3 2007  satmode             n
solvent    acetone  wet                 n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~ temp             25.0
PL-k-153agg_TPL-k-~ gain         not used
153agg01/PROTON01.~ spin         not used
                fid hst             0.008
   ACQUISITION      pw90           11.300
sw           9591.2 alfa            6.600
at            1.708          FLAGS
np            32768 il                  n
fb             5000 in                  n
bs               32 dp                  y
d1            1.000 hs                 nn
nt               16      PROCESSING
ct               16 fn           not used
   TRANSMITTER             DISPLAY
tn               H1 sp               -3.5
sfrq        599.422 wp             6596.3
tof           599.4 rfl            2420.1
tpwr             57 rfp            1228.8
pw            5.650 rp             -110.7
    DECOUPLER       lp              -27.4
dn              C13           PLOT
dof               0 wc                250
dm              nnn sc                  0
decwave    W40_hcx  vs                 25
dpwr             44 th                 14
dmf           35088 ai   cdc   ph
```



Clausevatine D



Clausevatine D

```
TPL-K-165carb

exp1  CARBON

      SAMPLE              PRESATURATION
date   Aug  4 2007  satmode              n
solvent    acetone  wet                  n
file /home/kerr/vn~        SPECIAL
mrsys/data/Terry/T~ temp              26.0
PL-K-165carb_TPL-K~ gain          not used
-165carb_01/CARBON~ spin                20
                 01 hst              0.008
    ACQUISITION     pw90            10.200
sw          25133.5 alfa            10.000
at            1.304           FLAGS
np            65536 il                   n
fb            14000 in                   n
bs               32 dp                   y
d1            1.000 hs                  nn
nt             2000         PROCESSING
ct              256 lb                0.50
    TRANSMITTER     fn            not used
tn              C13        DISPLAY
sfrq        100.531 sp                -0.5
tof          1530.6 wp             22107.7
tpwr             53 rfl             4414.9
pw            5.100 rfp             2995.5
     DECOUPLER      rp                58.7
dn               H1 lp              -313.9
dof               0           PLOT
dm              yyy wc                 250
decwave           w sc                   0
dpwr             39 vs                 605
dmf            9300 th                   7
                    ai   cdc   ph
```