Supplementary information for

Studies Towards the Total Synthesis of Oroidin Dimers

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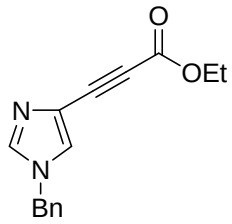
Contents

All NMR spectra were recorded in $CDCl_3$ unless otherwise indicated and at 500 MHz for proton and 125 MHz for carbon spectra, unless indicated otherwise.

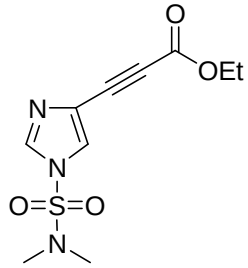
(1-Benzyl-1H-imidazol-4-yl)-propynoic acid ethyl ester (16a): DMF (50 mL) was



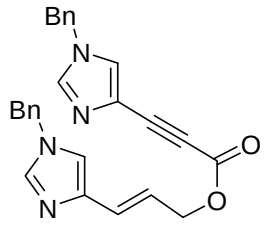
purged with N_2 then the Bn-protected 4-iodoimidazole **14a** (5.0 g, 0.02 mole) was added followed by $Pd(PPh_3)_2Cl_2$ (0.37 g, 0.53 mmol), copper iodide (200 mg, 1.06 mmol), orthoester **15**[1] (4.54 mL, 26 mmol) and finally triethylamine (6.1 mL, 40 mmol) under an N_2 atmosphere. The reaction mixture was heated at 50 ºC for 8 h. *p*-TsOH (400 mg) was added to the above reaction mixture and then stirred at rt overnight. The organic solvent was washed with water (200 mL), the organic layer was dried with anhydrous Na_2SO_4 concentrated and the residue was purified by chromatography on silica gel (hexane/EtOAc, 3:2) providing **16a** as a thick yellow liquid was obtained (2.68 g, 60%). ^{1}H NMR (300 MHz): δ = 7.38 (s, 1H), 7.38-7.36 (m, 4H), 7.18-7.17 (m, 2H), 5.11 (s, 2H), 4.26 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz): δ = 154.2, 138.4, 134.9, 129.4, 128.9, 127.6, 127.5, 121.9, 81.7, 80.8, 61.9, 51.5, 14.27; FT-IR (neat, cm^{-1}): 2360, 2340, 2223, 1749, 173, 1716, 1699, 1497, 1489, 1473, 1457, 1436, 1419, 1396, 1374, 1362, 1339, 1318, 1094; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{15}H_{14}N_2O_2$ is 255.1128, found 255.1120.

(1-Dimethylsulfamoyl-1*H*-imidazol-4-yl)-propynoic acid ethyl ester (16b): DMF (55 mL) was purged by bubbling N_2 through it for 10 min then DMAS-protected 4-iodoimidazole **14b** (5.5 g, 18 mmol) was added followed by $Pd(PPh_3)_2Cl_2$ (0.38 g, 0.54

mmol), copper iodide (0.21 g, 1.09 mmol), ortho ester **15**[1] (4.7 mL, 27 mmol) and triethylamine (6.3 mL, 45 mmol) under an N_2 atmosphere. The reaction mixture was heated at 45-50 ºC for 8 h. *p*-TsOH (500 mg) was added to the above reaction mixture followed by stirring at rt overnight. The organic solvent was washed with water (250 mL), the organic layer was dried with anhydrous Na_2SO_4 concentrated and the residue was purified by chromatography on silica gel (hexane/EtOAc, 3:2) to provide **16b** a yellow solid (3.30 g, 67%). M.p. 72-74 ºC. ^{1}H NMR: δ = 7.85 (s, 1H), 7.59 (s, 1H), 4.25 (q, *J* = 6.9 Hz, 2H), 2.87 (s, 6H), 1.31 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR: δ = 153.6, 137.1, 124.6, 123.4, 82.5, 78.2, 62.3, 38.3, 14.10; FT-IR (neat, cm^{-1}): 3131, 2984, 2223, 1706, 1474, 1421, 1396, 1332, 1288, 1218, 1176, 1080, 1024, 1010, 965, 856, 728; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{10}H_{13}N_3O_4S$ 272.0699, found 272.0700.

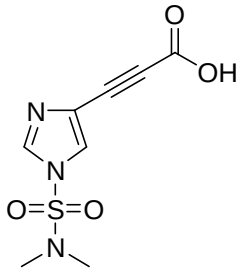


(1-Benzyl-1H-imidazol-4-yl)-propynoic acid 3-(1-benzyl-1H-imidazol-4-yl)-allyl ester (19a): Ester **16a** (1.7 g, 6.6 mmol) was dissolved in a mixture of THF (17 mL) and LiOH (1N in water, 19.6 mL) and stirred at rt for 3 h. The pH of the solution was adjusted to pH = 4 through the addition of 1N HCl, then the resulting solution was extracted with EtOAc. The organic solvent was evaporated and a yellow solid (1.46 g) was obtained which consists of the corresponding acid and a trace of ester. The acid was not purified any further and was used directly in the preparation of the propriolate derivative. In a round bottom flask the crude acid **17a** (0.90 g, 3.97



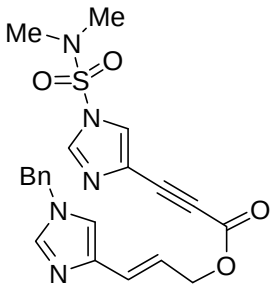
mmol), alcohol **18** (1.02 g, 4.77 mmol), DMAP (0.04 g, 0.39 mmol) and camphorsulfonic acid (500 mg, 0.21 mmol) were dissolved in dry CH_2Cl_2 (30 mL).[2] The mixture was cooled to (-78 ºC) and DCC (1.23 g, 5.96 mmol) in dry CH_2Cl_2 (8 mL) was added dropwise. The reaction mixture was allowed to warm up to rt and stirred for 2 h. The resulting mixture was filtered through Celite and the filter cake was washed with CH_2Cl_2. Concentration of the filtrate provided the crude product, which was purified by chromatography (hexane/EtOAc, 1:19) to provide **19a** a thick colorless liquid (1.08 g, 60%). ^{1}H NMR: δ = 7.48 (s, 1H), 7.46 (s, 1H), 7.32-7.28 (m, 6H), 7.28 (s, 1H), 7.17-7.12 (m, 4H), 6.84 (s, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.38 (td, *J* = 6.4, 16.0 Hz, 1H), 5.08 (s, 2H), 5.05 (s, 2H), 4.79 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR: δ = 153.9, 139.9, 138.3, 137.9, 135.9, 134.9, 129.3, 129.1, 128.9, 128.4, 127.6, 127.6, 127.4, 126.7, 121.9, 120.6, 117.9, 81.5, 81.2, 66.3, 51.4, 51; FT-IR (neat, cm^{-1}): 2215, 1701, 1540, 1496, 1455, 1377, 1292, 1219, 1148, 1044, 969, 940, 840, 727, 632; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{26}H_{22}N_4O_2$ 423.1816, found 423.1856.

(1-Dimethylsulfamoyl-1H-imidazol-4-yl)-propynoic acid (17b): Ester **16a** (3.10 g, 11 mmol) was dissolved in THF (20 mL) and LiOH (1N in water, 31 mL) and stirred at rt for 2.5 h. The pH of the basic solution was adjusted to pH = 4 by the addition of 1N HCl, and the resulting precipitate was collected by vacuum filtration and washed with small amount of cold water. After drying in vacuo, the corresponding acid **17b** was obtained as a colorless solid (2.00 g, 75%). Mp 138-140 ºC. ^{1}H NMR (DMSO, 300 MHz): δ = 8.32 (s, 1H), 8.31 (s, 1H), 2.85 (s, 6H); ^{13}C NMR



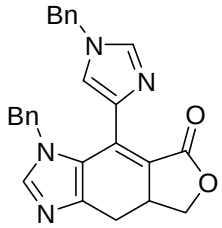
(DMSO, 75 MHz): δ = 154.7, 138.7, 126.7, 122.1, 83.4, 78.6, 39.7; FT-IR (KBr, cm^{-1}): 3393, 3143, 2945, 2773, 2501, 2239, 1891, 1693, 1481, 1458, 1426, 1394, 1336, 1282, 1242, 1205, 1187, 1096, 999, 972, 727, 669, 618.

(1-Dimethylsulfamoyl-1H-imidazol-4-yl)-propynoic acid 3-(1-benzyl-1H-imidazol-4-yl)-allyl ester (19b): In a round bottom flask the acid **17b** (2.00 g, 8.22 mmol), alcohol



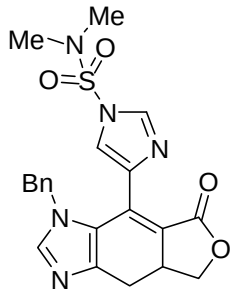
18 (2.11 g, 9.86 mmol), DMAP (100 mg, 0.82 mmol) and camphorsulfonic acid (110 mg, 0.49 mmol) was dissolved in dry CH_2Cl_2 (40 mL) under N_2 atmosphere. The mixture was cooled to (– 78 ºC) and DCC (2.54 g, 12.0 mmol) dissolved in dry CH_2Cl_2 (15 mL) was added dropwise.[2] The reaction mixture was allowed to warm up to rt and stirred for 2 h. The mixture was filtered over Celite and the filter cake was washed with CH_2Cl_2. The filtrate was concentrated and the crude product was purified by chromatography (hexane/EtOAc, 1:19) affording **19b** as a white solid (2.40 g, 68%). Mp 118-120 ºC. ^{1}H NMR (300 MHz): δ = 7.85 (d, *J* = 0.9 Hz, 1H), 7.59 (d, *J* = 0.9 Hz, 1H), 7.50 (s, 1H), 7.37-7.32 (m, 3H), 7.15 (d, *J* = 6.9 Hz, 2H), 6.86 (s, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.42 (td, *J* = 15.8, 6.4 Hz 1H), 5.07 (s, 2H), 4.48 (d, *J* = 6.4 Hz, 2H), 2.88 (s, 6H); ^{13}C NMR (75 MHz): δ = 153.4, 139.7, 137.9, 137.1, 135.9, 129.2, 128.5, 127.4, 126.9, 124.6, 120.4, 117.9, 82.4, 78.9, 66.7, 51.1, 38.3; FT-IR (neat, cm^{-1}): 3125, 2928, 2222, 1705, 1539, 1456, 1421, 1395, 1332, 1286, 1180, 1080, 1008, 967, 842, 728, 617; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{21}H_{21}N_5O_4S$ 440.1387, found 440.1409.

3-Benzyl-4-(1-benzyl-1H-imidazol-4-yl)-3,7,7a,8-tetrahydro-furo[3',4':4,5]benzo[1,2-d]imidazol-5-one (20a): CH_2Cl_2 (75 mL) was placed in a resealable thick-walled tube and was purged with N_2 for 10 minutes, then ester **19a** (0.70 g, 1.65 mmol) was added and again the reaction mixture was purged with N_2 for an additional 5 minutes. After sealing the tube with a Teflon screw cap, the reaction mixture was heated at 130 ºC for 12 h. The reaction mixture was cooled to rt and the CH_2Cl_2 was evaporated under vacuum. The crude product was purified by chromatography (acetone/EtOAc, 7:3) to provide **20a** (490 mg, 70%) as a yellow solid. M.p 202-204 ºC. ^{1}H NMR: δ = 7.59 (s, 1H), 7.55 (s, 1H), 7.50 (s, 2H), 7.36-7.33 (m, 3H), 7.23 (d, *J* = 6.4 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 2H), 6.59 (d, *J* = 7.3 Hz, 2H), 5.15-5.06 (m, 3H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.62 (t, *J* = 9.2 Hz, 1H), 3.56-3.49 (m, 1H), 2.99 (dd, *J* = 15.6, 8.3 Hz, 1H), 2.68 (t, *J* = 16.0 Hz, 1H); ^{13}C NMR: δ = 168.7, 144.6, 140.9, 136.5, 136.3, 135.7, 133.0, 131.5, 129.2, 128.6, 127.9, 127.7, 126.4, 125.4, 116.9, 70.9, 51.3, 51.0, 38.4, 27.7; FT-IR (neat, cm^{-1}): 1732, 1604, 1520, 1497, 1455, 1372, 1252, 1223, 1164, 1097, 1075, 1016, 913, 852, 766, 727; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{26}H_{22}N_4O_2$ 423.1816, found 423.1856.



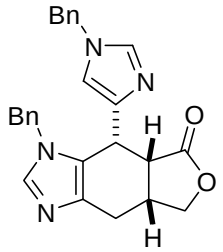
4-(3-Benzyl-5-oxo-5,7,7a,8-tetrahydro-3H-furo[3',4':4,5]benzo[1,2-d]imidazol-4-yl)-imidazole-1-sulfonic acid dimethylamide (20b): CH_2Cl_2 (80 mL) was placed in a thick-walled pressure tube and purged with N_2 for 10 min, then ester **19b** (500 mg, 11.4 mmol) was added and again the reaction mixture was purged with N_2 for 5 min. After sealing the tube with a Teflon screw cap, the reaction mixture was heated to 120 ºC for

12 h. The reaction mixture was cooled to rt., and then the reaction mixture was concentrated. The crude product was purified by chromatography (acetone/EtOAc, 7:3) to provide a yellow solid (410 mg, 82%).



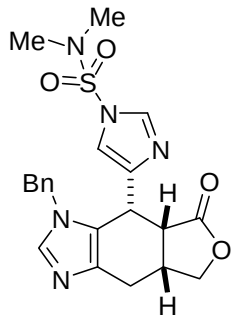
M.p 134-135 ºC. ^{1}H NMR: δ = 7.94 (d, *J* = 1.8 Hz, 1H), 7.52 (s, 1H), 7.34 (d, *J* = 1.4 Hz, 1H), 7.21-7.19 (m, 3H), 6.65 (d, *J* = 6.6 Hz, 2H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 4.66 (t, *J* = 8.7 Hz, 1H), 3.99 (t, *J* = 8.7 Hz, 1H), 3.59-3.55 (quintet, *J* = 8.7 Hz, 1H), 3.03 (dd, *J* = 8.7, 8.3 Hz, 1H), 2.88 (s, 6H), 2.70 (dd, *J* = 16.0, 15.6 Hz, 1H); ^{13}C NMR: δ = 168.4, 144.9, 141.4, 135.9, 135.8, 131.9, 131.2, 128.9, 128.1, 126.9, 126.1, 121.8, 118.6, 71.1, 50.9, 38.4, 38.2, 27.7; FT-IR (neat, cm^{-1}): 3122, 2926, 1736, 1615, 1557, 1521, 1457, 1420, 1392, 1334, 1255, 1176, 1083, 1011, 963, 848, 728, 702, 648; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{21}H_{21}N_5O_4S$ is 440.1387, found 440.1428.

3-Benzyl-4-(1-benzyl-1H-imidazol-4-yl)-3,4,4a,7,7a,8-hexahydro-furo[3',4':4,5]benzo[1,2-d]imidazol-5-one (21a): The Diels-Alder product **20a** (160 mg, 0.37 mmol) was dissolved in dry ethanol (10 ml). To the reaction mixture 10% Pd/C (100 mg) was added. The heterogeneous reaction mixture was stirred at 36 ºC for 8 h under a hydrogen atmosphere. The reaction mixture was filtered over Celite and the filter cake was repeatedly washed with hot ethanol. The filtrate was evaporated under reduced pressure followed by purification of the residue by chromatography on silica gel ($CHCl_3$/MeOH, 49:1) furnished the hydrogenated compound **21a** (110 mg, 71%) as a thick colorless liquid. ^{1}H NMR: δ = 7.45 (s, 1H),



7.37 (s, 1H), 7.34-7.30 (m, 4H), 7.26-7.22 (m, 4H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.53 (s, 1H), 4.98 (q, *J* = 15.1 Hz, 2H), 4.85 (d, *J* = 15.6 Hz, 1H), 4.57 (d, *J* = 16.0 Hz, 1H), 4.31-4.21 (m, 3H), 3.19-3.02 (m, 3H), 2.74 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (75 MHz): δ = 139.8, 137.7, 137.4, 136.2, 136.1, 135.6, 129.1, 128.9, 128.4, 128.1, 127.2, 126.9, 124.5, 118.4, 72.5, 50.9, 48.7, 44.4, 34.9, 30.8, 22.4; FT-IR (neat, cm^{-1}): 2366, 2334, 1773, 1502, 1449, 1207, 1144, 1010, 737, 708. HR-MS (*m/z*): calc for $[M+H]^+$ $C_{26}H_{24}N_4O_2$ 425.1972, found 425.1999.

4-(3-Benzyl-5-oxo-4,4a,5,7,7a,8-hexahydro-3H-furo[3',4':4,5]benzo[1,2-d]imidazol-4-yl)-imidazole-1-sulfonic acid dimethylamide (21b): The Diels-Alder product **20b** (200

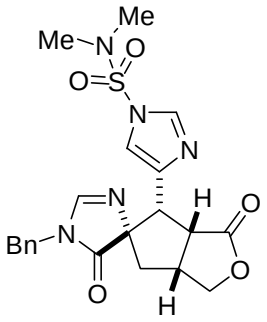


mg, 0.45 mmol) was dissolved in dry ethanol (15 mL), and 10% Pd/C (120 mg) was added. The resulting heterogeneous reaction mixture was stirred at 40 ºC for 12 h under hydrogen atmosphere (60 psi). On completion of the reaction, the reaction mixture was filtered through Celite and the filter cake was washed repeatedly with hot ethanol. The filtrate was evaporated under reduced pressure followed by purification of the residue by chromatography on silica gel ($CHCl_3$/MeOH, 49:1) which furnished reduced compound **21b** (150 mg, 75%) as yellow solid. M.p 158-160 ºC. ^{1}H NMR: δ = 7.68 (s, 1H), 7.54 (s, 1H), 7.27-7.26 (m, 3H), 6.92 (m, 2H), 6.93-6.91 (s, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 15.6 Hz, 1H), 4.28-4.22 (m, 2H), 4.21 (t, *J* = 8.7 Hz, 1H), 3.11-3.06 (m, 3H), 2.80 (d, *J* = 2.8 Hz, 1H), 2.77 (s, 6H); ^{13}C NMR: δ = 176.7, 140.6, 138.2, 136.6, 136.2, 135.6, 129.0, 128.3, 126.8, 123.1,

116.4, 72.3, 49.1, 43.8, 38.3, 34.8, 30.6, 22.7; FT-IR (neat, cm^{-1}): 2360, 1770, 1716, 1652, 1558, 1540, 1497, 1457, 1418, 1390, 1268, 1175, 1078, 1008, 962, 728; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{21}H_{23}N_5O_4S$ 442.1544, found 442.1581.

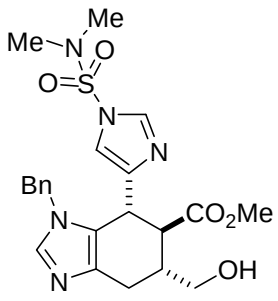
Spiro Imidazolone (22a): The hydrogenated product **21b** (90 mg, 0.21 mmol) was dissolved in chloroform (5 mL) and Davis' oxaziridine (160 mg, 0.53 mmol) was added to the reaction mixture. The reaction mixture was stirred at reflux for 8 h. The organic layer was washed with 2M NaOH solution and the organic layer was dried with anhydrous Na_2SO_4 concentrated and the residue was purified by chromatography on silica gel ($CHCl_3$/MeOH, 49:1) furnished rearranged product **22a** (60 mg, 64%) as a yellow liquid. ^{1}H NMR (300 MHz): δ = 7.43 (s, 1H), 7.22-7.37 (m, 10H), 7.05-6.99 (m, 3H), 6.85 (s, 1H), 4.93 (s, 1H), 4.59 (d, *J* = 15.1 Hz, 1H), 4.53 (d, *J* = 8.6 Hz, 1H), 4.41 (d, *J* = 15.5 Hz, 1H), 4.28 (dd, *J* = 9.3, 3.1 Hz, 1H), 4.07 (d, *J* = 8.3 Hz, 1H), 3.48-3.35 (m, 2H), 2.63 (dd, *J* = 13.4, 8.9 Hz, 1H), 1.84 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (75 MHz): δ = 181.7, 177, 152.6, 136.2, 135.7, 135. 5, 133.8, 128.9, 128.2, 127.7, 127.3, 119.4, 78.9, 72.1, 52, 50.9, 46.3, 44.7, 43.4, 37.4; FT-IR (neat, cm^{-1}): 2363, 2336, 1770, 1733, 1651, 1557, 1542, 1508; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{22}H_{24}N_4O_3$ 441.1808, found 441.1936.

Spiro Imidazolone (22b): The tetrahydrobenzimidazole **21b** (90 mg, 0.20 mmol) was dissolved in chloroform (3.5 mL) and Davis' oxaziridine (150 mg, 0.5 mmol) was added to the reaction mixture. The resulting mixture was stirred at reflux for 8 h. The organic



layer was washed with 2M NaOH solution and the organic layer was dried with anhydrous Na_2SO_4 concentrated and the residue was purified by chromatography on silica gel ($CHCl_3$/MeOH, 49:1) to provide the spiro imidazolone (50 mg, 60%) as a colorless solid. M.p 188 – 190 ºC. ^{1}H NMR: δ = 7.68 (d, *J* = 0.9 Hz, 1H), 7.60 (s, 1H), 7.29-7.25 (m, 3H), 7.09 (d, *J* = 1.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 4.72 (d, *J* = 15.6 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 1H), 4.42 (d, *J* = 15.1 Hz, 1H), 4.26 (dd, *J* = 9.2, 3.8 Hz, 1H), 4.06 (d, *J* = 8.3 Hz, 1H), 3.41-3.39 (m, 2H), 2.78 (s, 6H), 2.60 (dd, *J* = 15.3, 9.2 Hz, 1H), 1.88 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR: δ = 181.2, 176.8, 153.5, 135.1, 134.9, 129.3, 129.2, 128.4, 127.3, 117.2, 79.1, 77.4, 77.1, 76.9, 73.7, 51.1, 46.1, 44.9, 43.7, 38.3, 37.2; FT-IR (neat, cm^{-1}): 2932, 2367, 2328, 1766, 1727, 1598, 1390, 1162, 1079, 954, 726; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{21}H_{23}N_5O_5S$ 458.1471, found 458.1471.

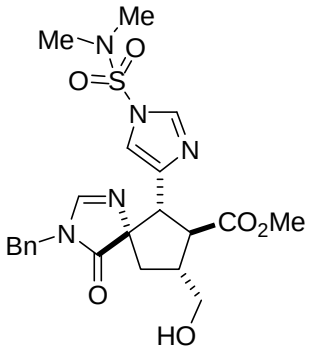
3-Benzyl-4-(1-dimethylsulfamoyl-1H-imidazol-4-yl)-6-hydroxymethyl-4,5,6,7-tetrahydro-3H-benzoimidazole-5-carboxylic acid methyl ester (24): The



tetrahydrobenzimidazole **21b** (200 mg, 0.42 mmol) was dissolved in MeOH (60 mL) under nitrogen atmosphere. To this reaction mixture 0.23 M sodium methoxide was added dropwise.[3] After stirring this reaction at room temperature for 1 h it was heated to 60 ºC for 2 h. Then cooling this reaction mixture to room temperature, saturated ammonium chloride solution (20 mL) was added followed by addition of equal amount of water. Then this aqueous solution

was extracted repeatedly by EtOAc. The organic extracts were dried with anhydrous Na_2SO_4 concentrated and the residue was purified by chromatography on silica gel (CH_2Cl_2/MeOH, 4:1) furnishing the product **24** (120 mg, 52%) as a colorless oil. In addition, unreacted lactone (70 mg, 35%) was recovered. ^{1}H NMR: δ = 7.74 (s, 1H), 7.40 (s, 1H), 7.31-7.25 (m, 4H), 6.85 (d, *J* = 7.3 Hz, 2H), 6.81 (s, 1H), 4.85 (d, *J* = 16.9 Hz, 1H), 4.48 (d, *J* = 18.3 Hz, 1H), 4.20 (d, *J* = 10.5 Hz, 1H), 3.62-3.59 (m, 2H), 3.57 (s, 3H), 3.00 (t, *J* = 9.2 Hz, 1H), 2.90-2.78 (m, 1H), 2.75 (s, 6H), 2.72-2.69 (m, 1H) 2.37 – 2.34 (m, 1H); ^{13}C NMR: δ = 174.5, 142.7, 137.9, 137.2, 136.1, 129.0, 127.9, 126.3, 115.4, 65.1, 51.9, 51.6, 49.2, 40.6, 38.1, 35.8, 26.8; FT-IR (neat, cm^{-1}): 3112, 2935, 1723, 1455, 1394, 1265, 1170, 1074, 953, 733, 603, 598; calc for $[M+H]^+$ $C_{22}H_{27}N_5O_5S$ 474.1806, found 474.1830.

Ring-opened spiro imidazolone (23): The spiroimidazolone **22b** (200 mg, 0.41 mmol) was dissolved in MeOH (60 mL) under nitrogen atmosphere. To this reaction mixture 0.23 M sodium methoxide in MeOH (49 mL) was added dropwise. After stirring this reaction at room temperature for 1 h it was heated to 60 ºC for 18 h.[3] The reaction mixture was cooled to room temperature, then of saturated ammonium chloride solution (20 mL) was added followed by addition of equal amount of water. The resulting aqueous solution was extracted repeatedly with EtOAc. The organic extracts were dried with anhydrous Na_2SO_4 and concentrated and the residue was purified by chromatography on silica gel (CH_2Cl_2/MeOH; 44:6) furnished the



desired product (65 mg, 31%) as a colorless liquid. In addition, unreacted lactone (110 mg, 55%) was recovered. ^{1}H NMR: δ = 7.60 (s, 1H), 7.39 (s, 1H), 7.34-7.28 (m, 4H), 7.15 (d, J = 7.2 Hz, 2H), 7.00 (s, 1H), 4.71 (d, J = 15.1 Hz, 1H), 4.50 (d, J = 15.1 Hz, 1H), 4.02 (d, J = 11.0 Hz, 1H), 3.82-3.78 (m, 2H), 3.70 (s, 3H), 3.66-3.62 (m, 1H), 3.40 (m, 2H), 2.97-2.90 (m, 1H), 2.70-2.61 (m, 1H), 1.74 (d, J = 13.8 Hz, 1H); ^{13}C NMR (75 MHz): δ = 180.9, 174.5, 152.6, 139.8, 135.8, 134.9, 129.1, 128.3, 127.9, 114.5, 77.2, 65.3, 52.2, 51.0, 48.6, 44.9, 43.8, 39.9, 38.2; FT-IR (neat, cm^{-1}): 2944, 2359, 1735, 1397, 1166, 1091, 962, 730; calc for $[M+H]^+$ $C_{22}H_{27}N_5O_6S$ 490.1755, found 490.1758.

X-ray crystallographic data:

A suitable crystal of the compound of interest, covered with a layer of hydrocarbon oil, was selected and mounted with paratone-N oil in a cryo-loop and immediately placed in the low-temperature nitrogen stream for the low temperature work. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å).[4] The data frames were integrated with the Bruker SAINT-Plus software package.[5] Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package.[6] Figures S1 and S2 depicting X-ray crystal structures of compounds **22a** and **22b** were generated using Mercury CSD program (note that compounds **22a** and **22b** are racemates; only one stereoisomer of each is shown in the Figures. There are of course equal numbers of molecules with the

opposite stereochemistries in the crystals).[7] Crystal data and additional experimental details are given in the cif files.

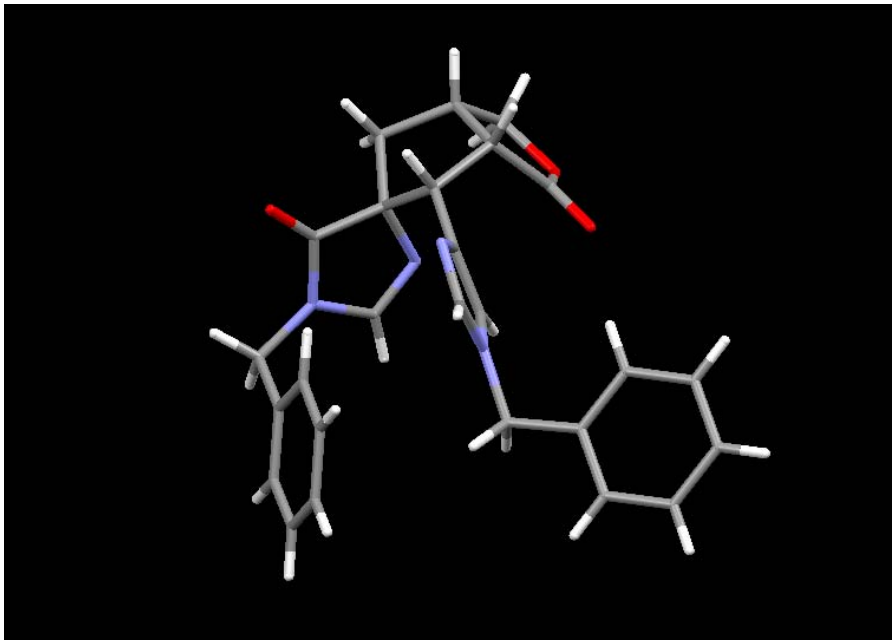


Figure S1: X-ray structure of compound **22a**

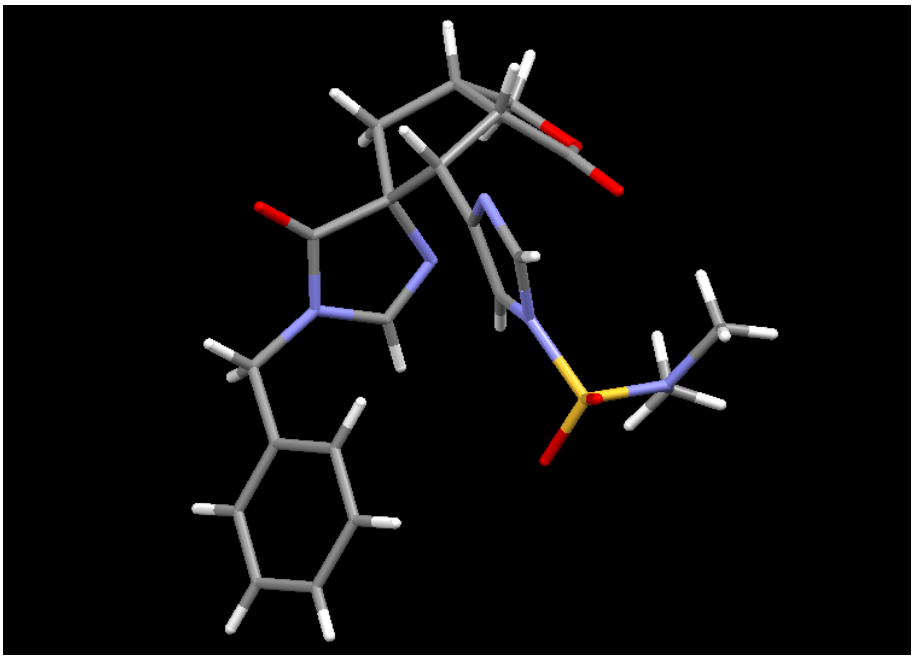


Figure S2: X-ray structure of compound **22b**.

References:

1. Gassman, P. G.; Chavan, S. P. *Tetrahedron Lett.* **1988**, *29*, 3407.
2. Sunazuka, T.; Hirose, T.; Harigaya, Y.; Takamatsu, S.; Hayashi, M.; Komiyama, K.; Mura, S.; Sprengeler, P. A.; Smith, A. B. *J. Am. Chem. Soc.* **1997**, *119*, 10247.
3. Zancanella, M. A.; Romo, D. *Org. Lett.* **2008**, *10*, 3685.
4. SMART, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
5. SAINT-Plus, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
6. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112-122.
7. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.

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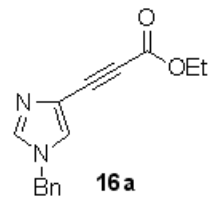

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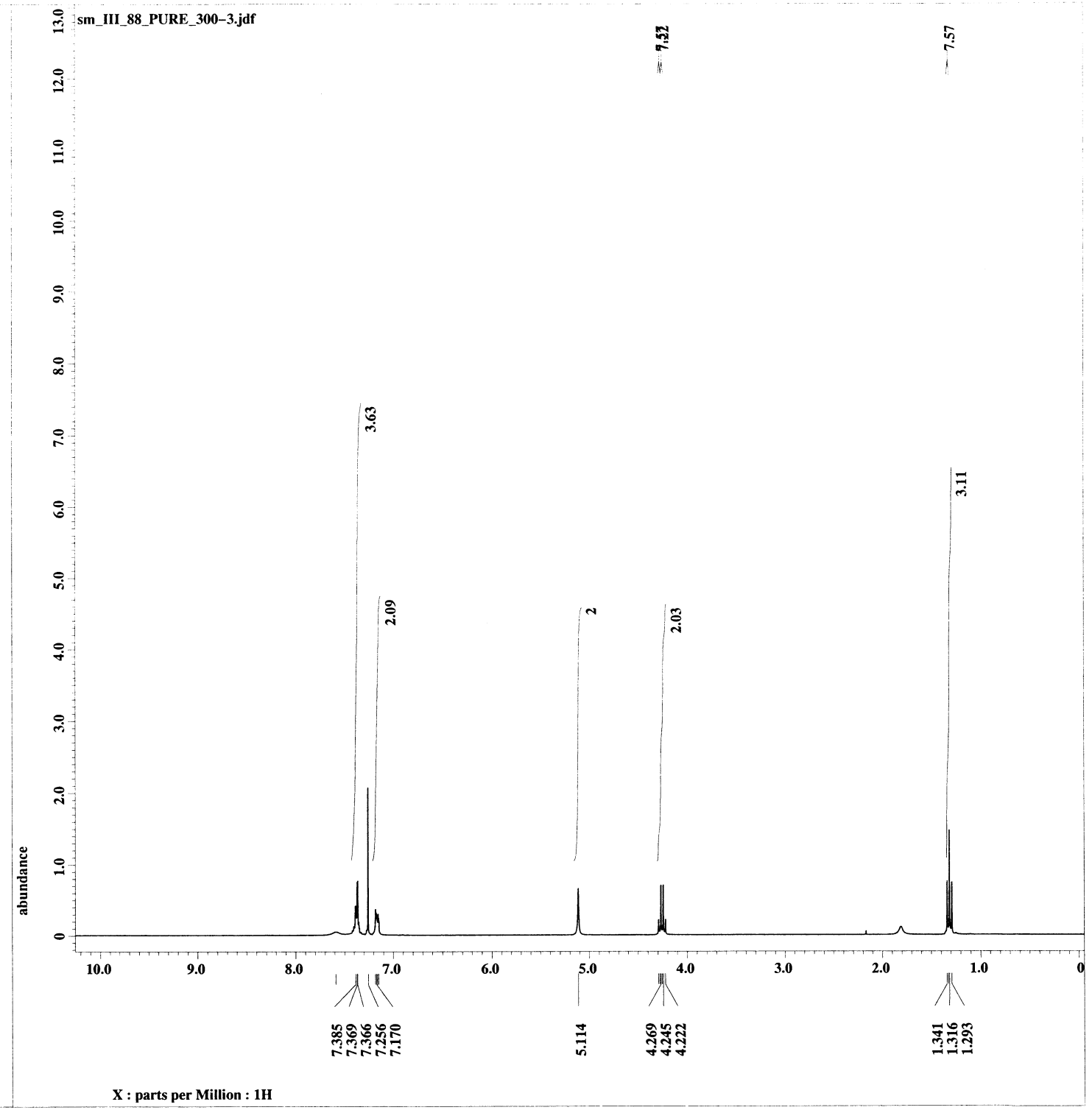

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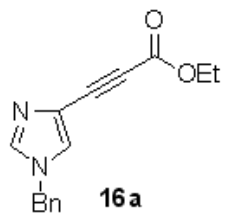

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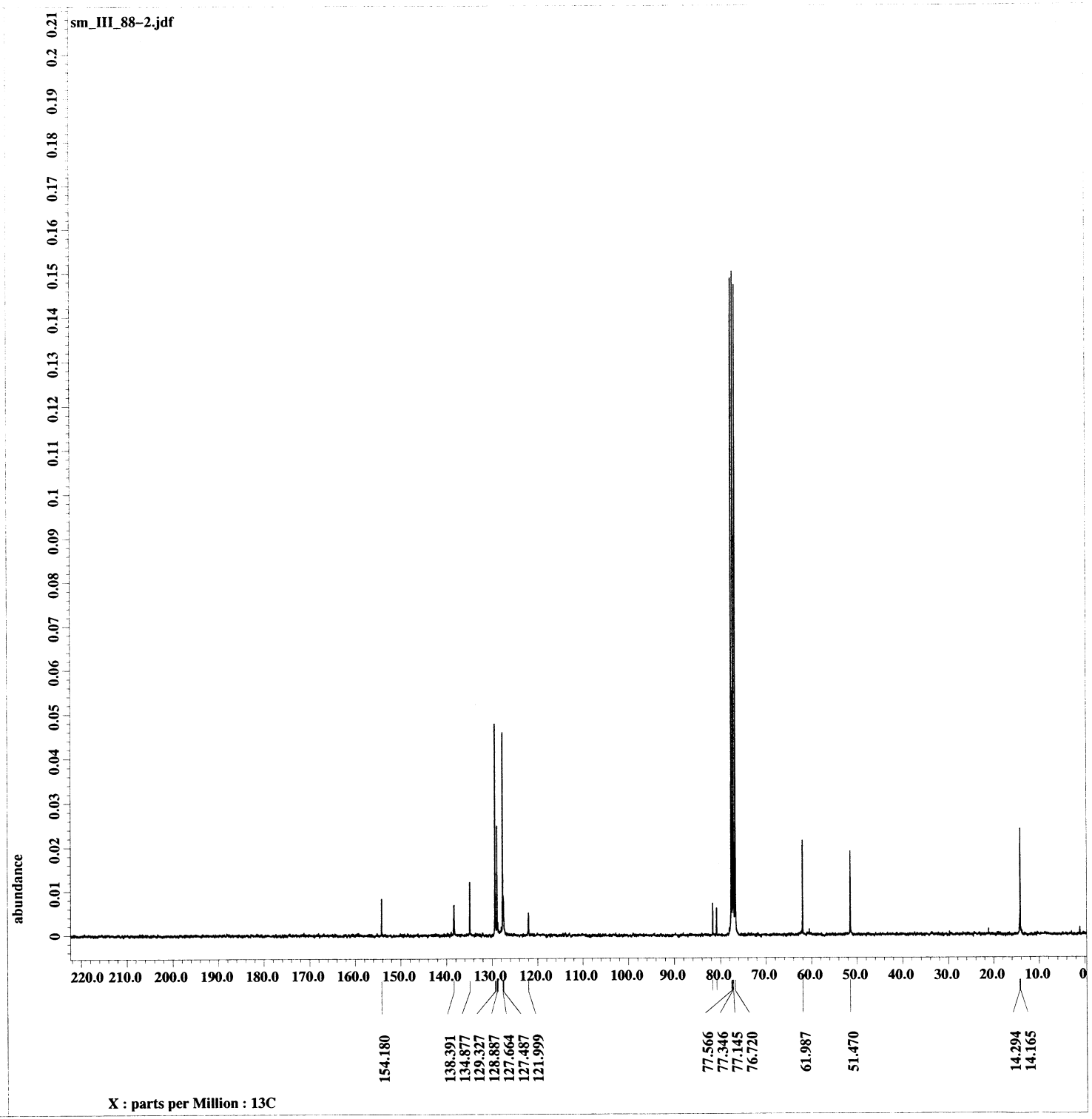

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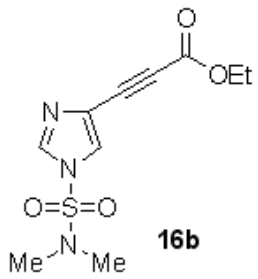

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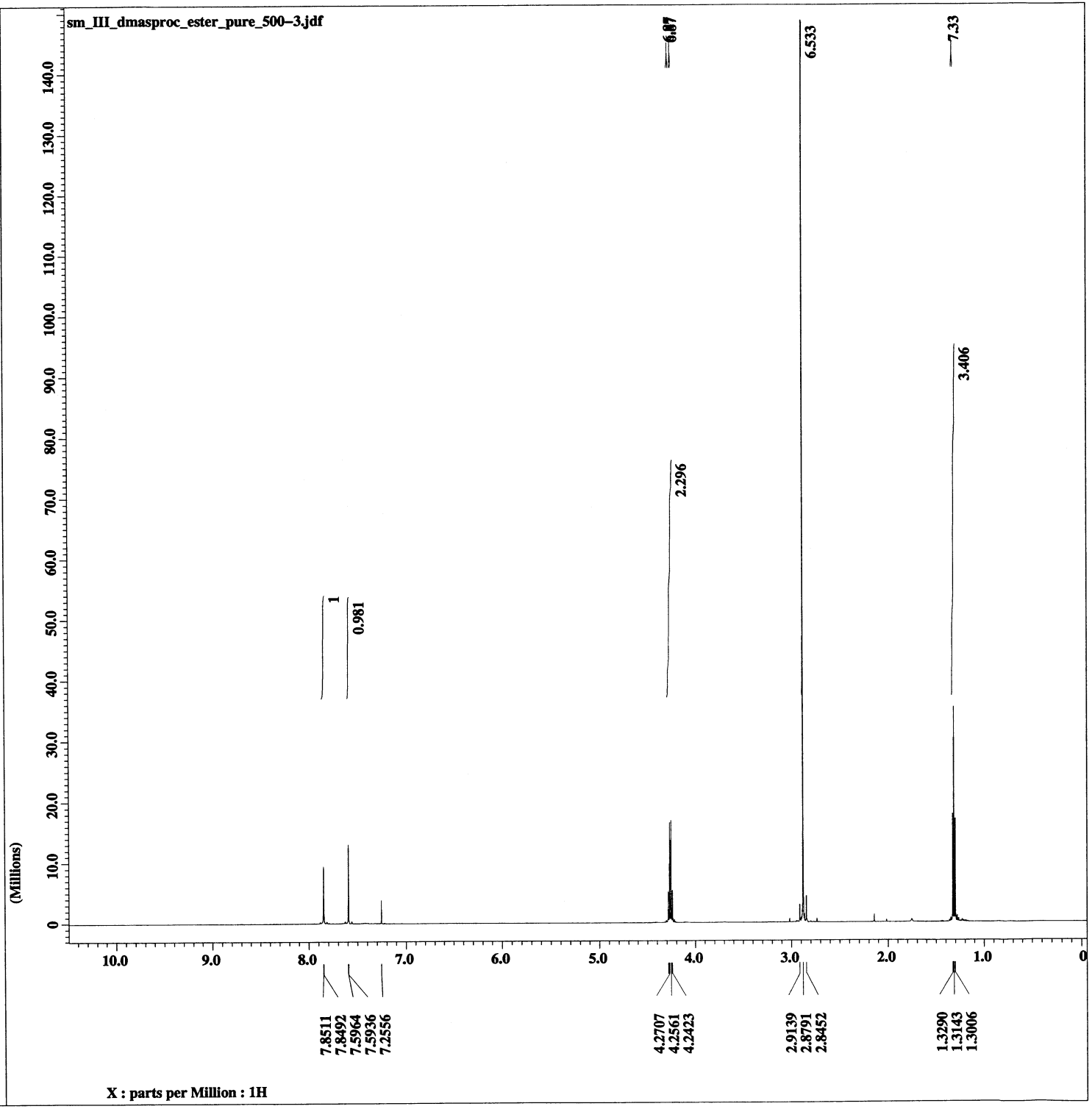

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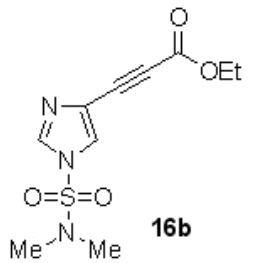

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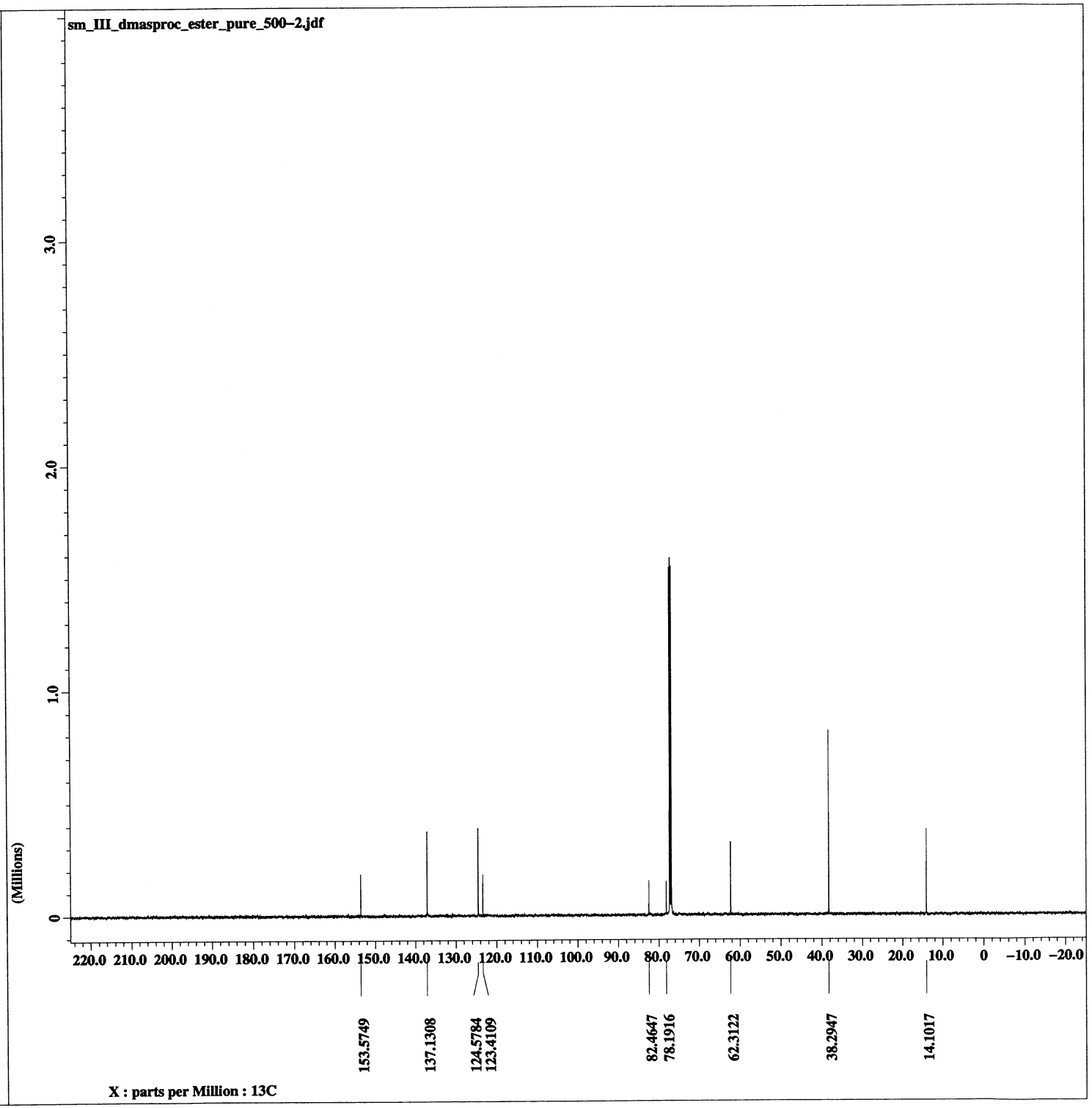

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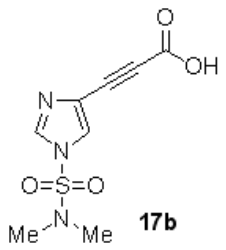

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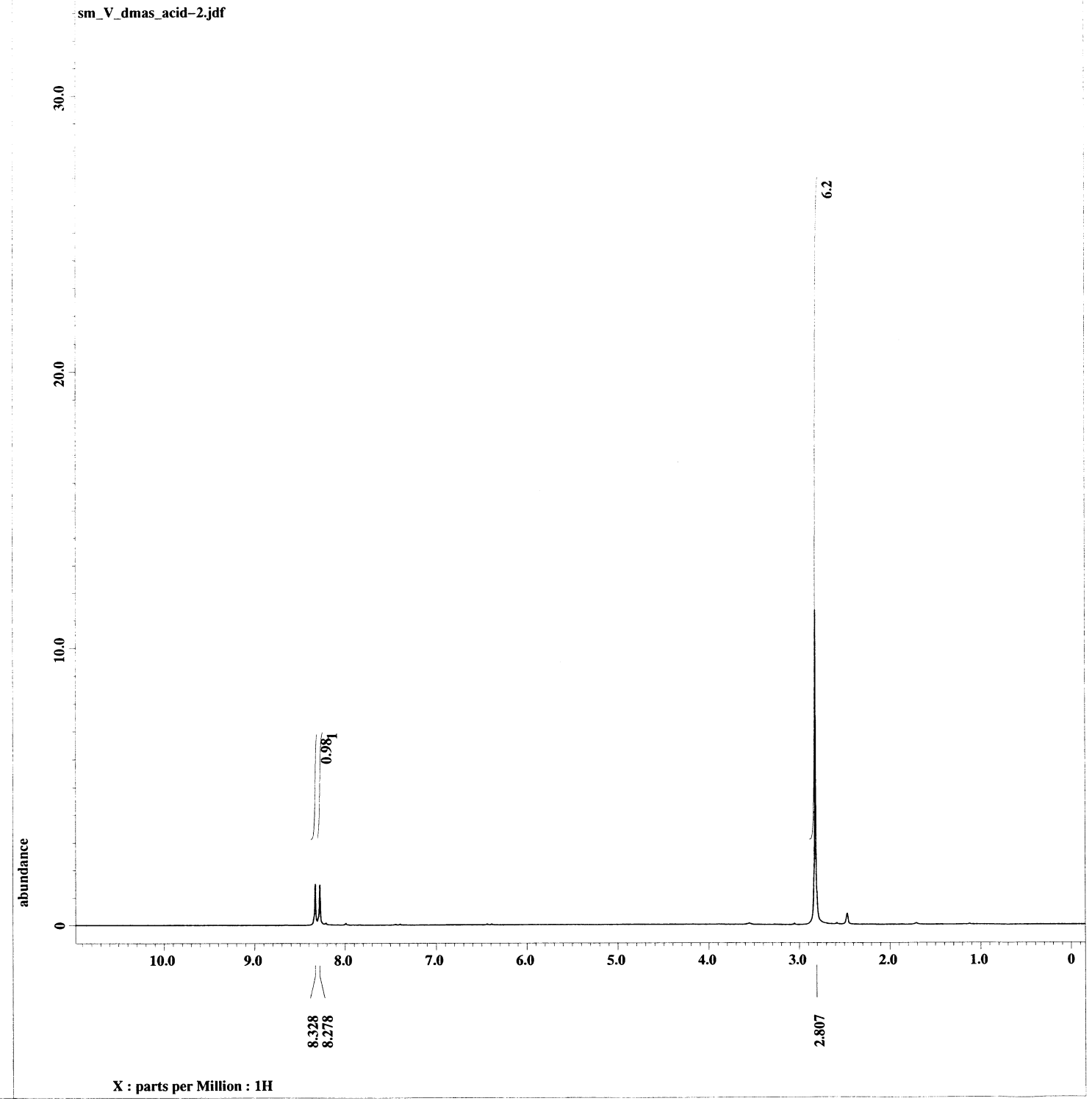

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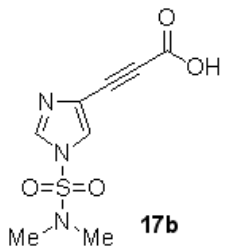

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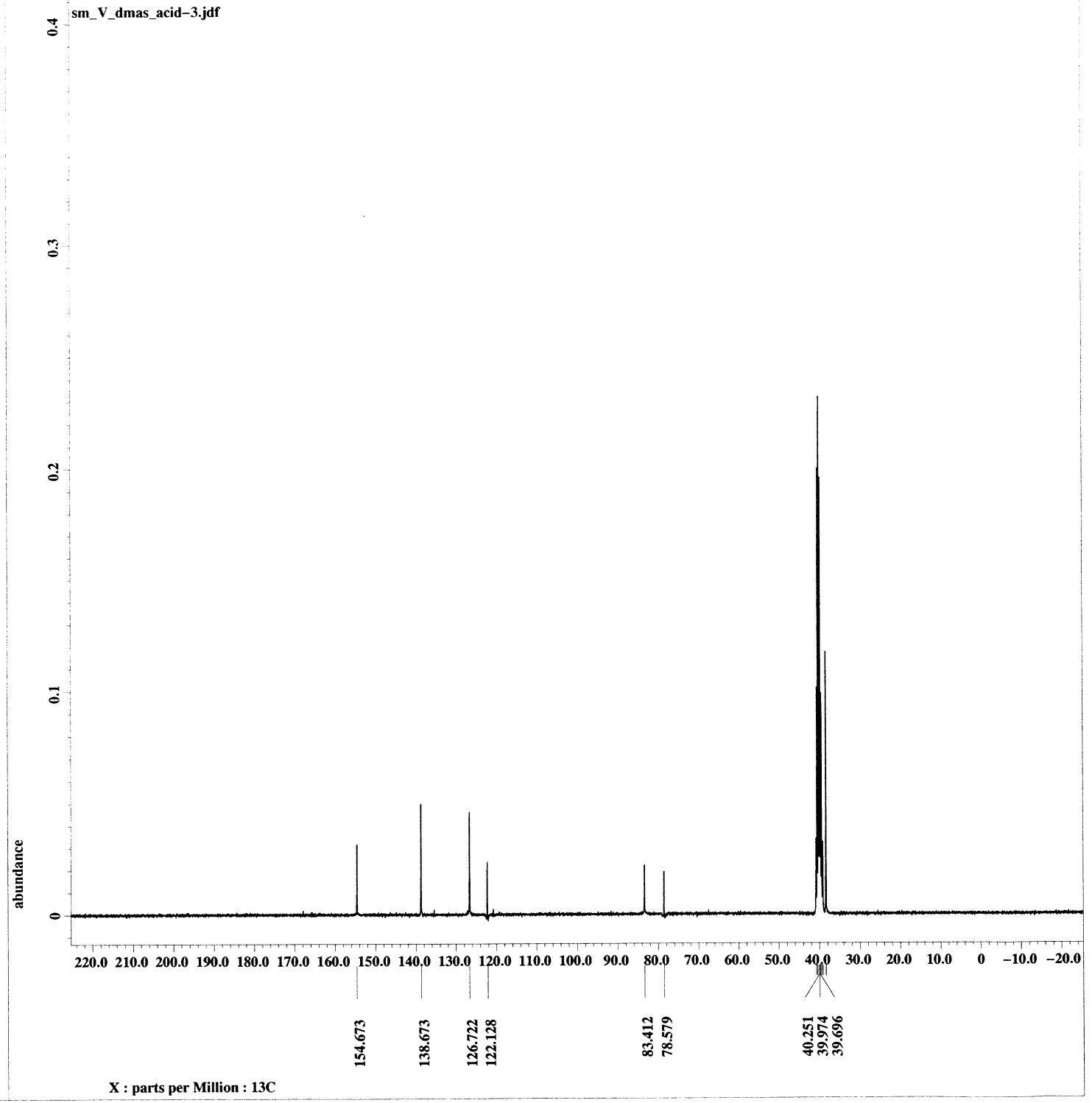

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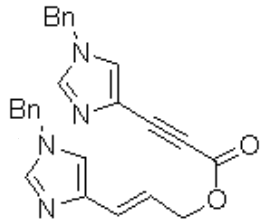

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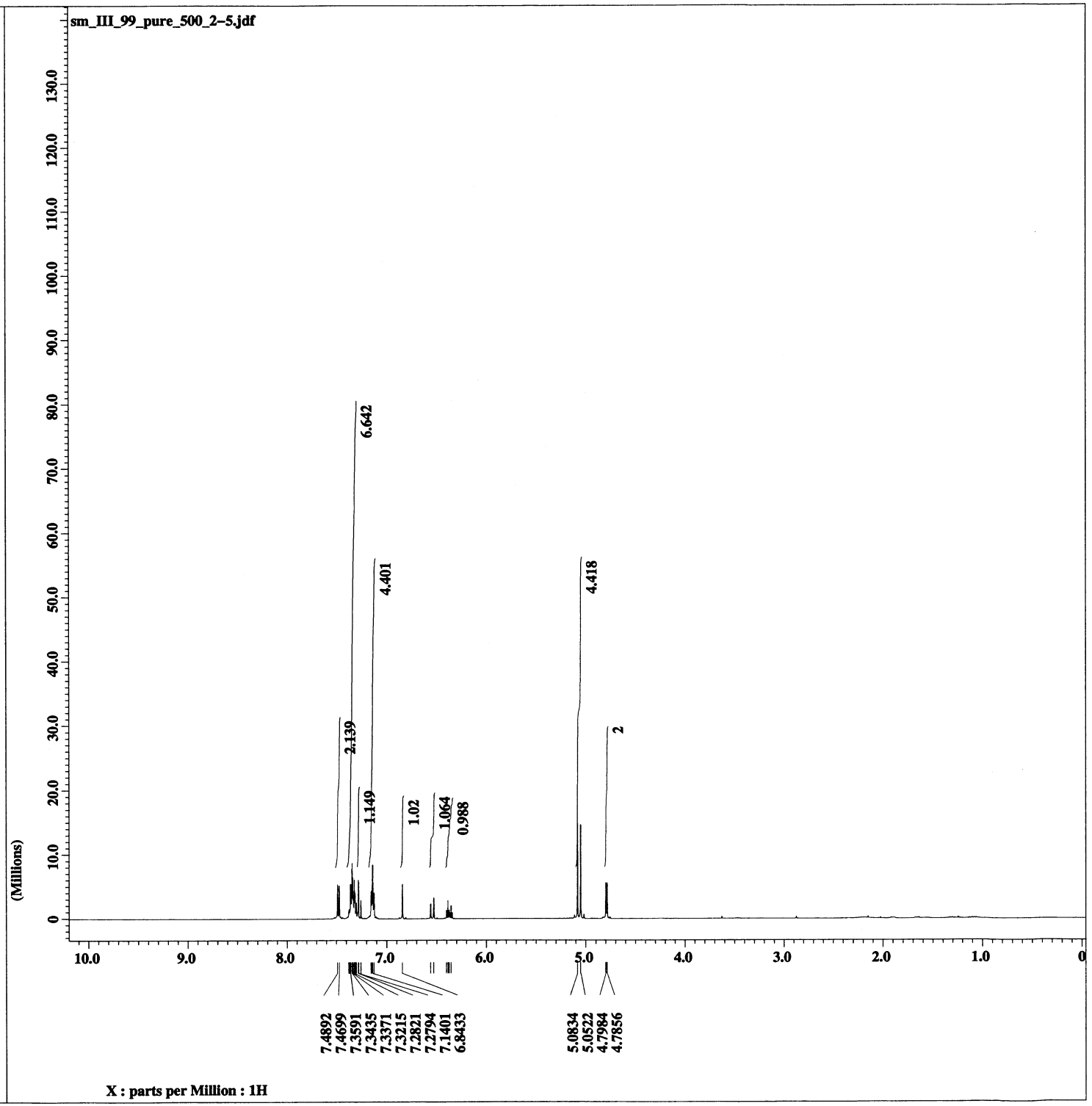

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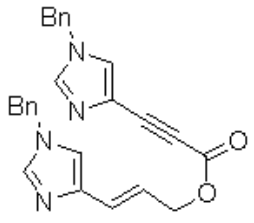
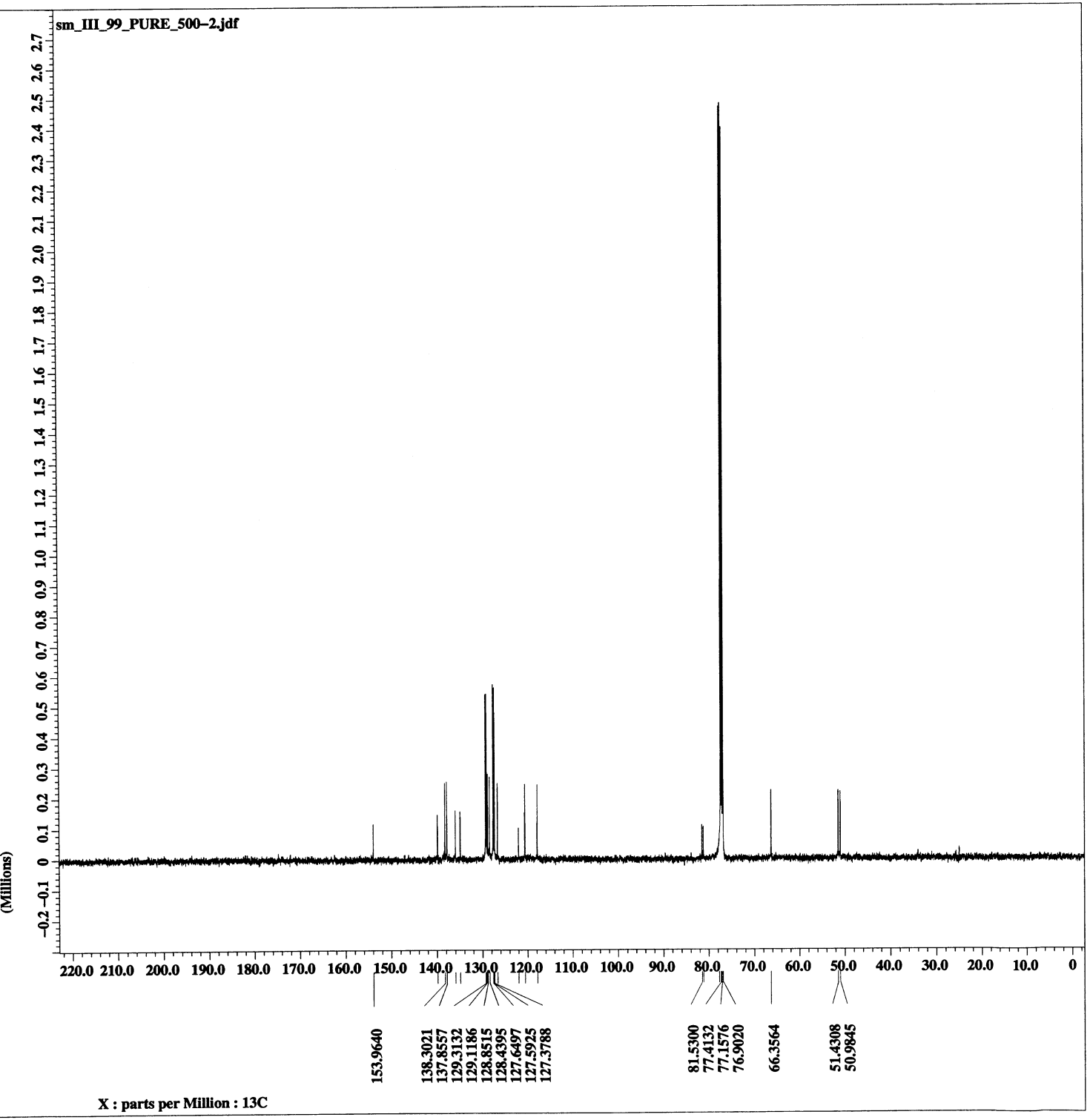
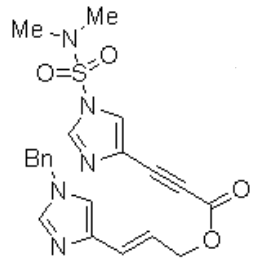
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 10
Scans	= 2000
Total_scans	= 2000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 2[s]
Temp_get	= 27.2[dC]
Unblank_time	= 2[us]



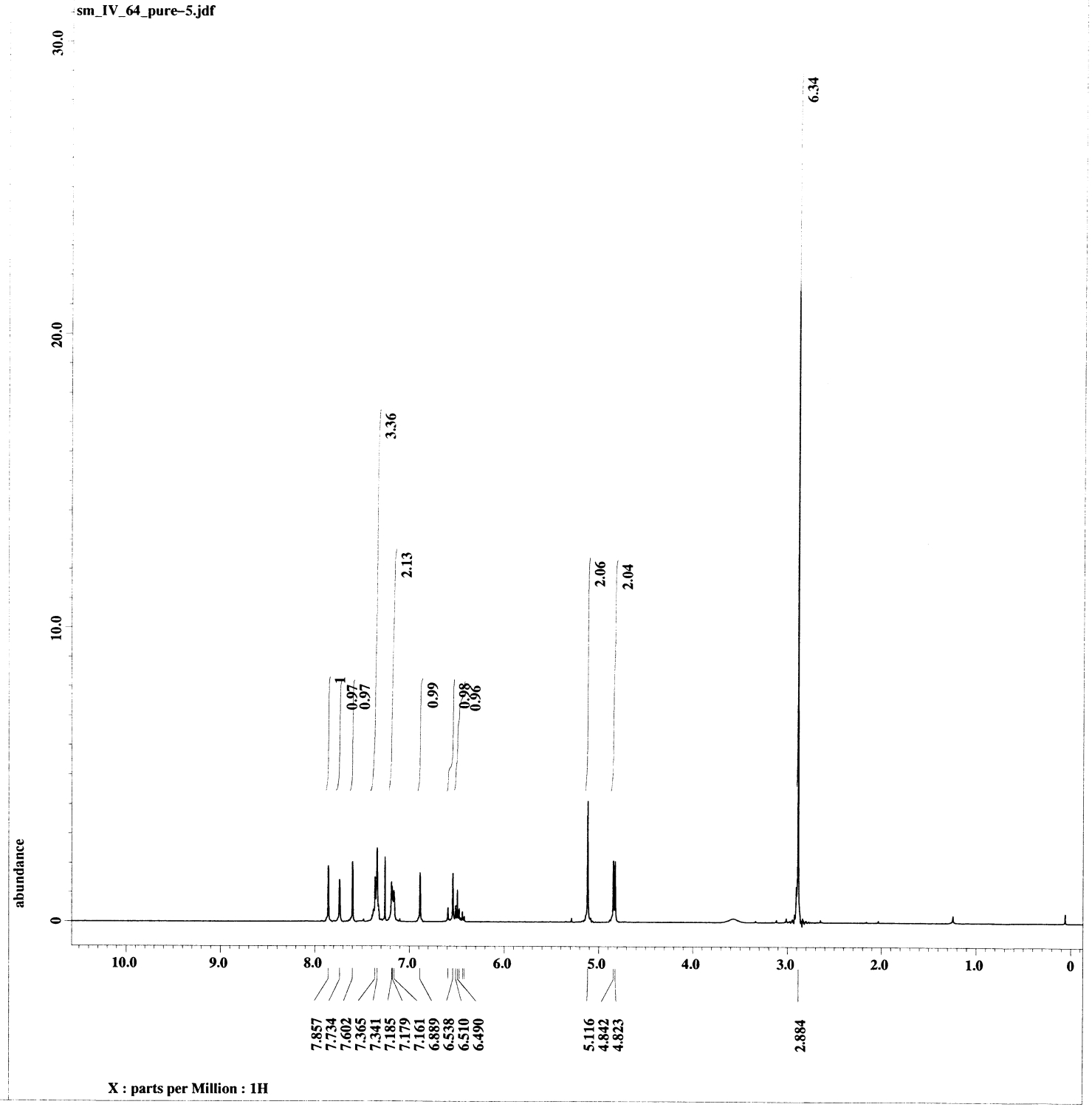
19a



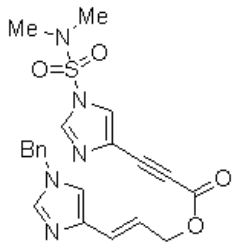
```
Filename          = sm_IV_64_pure-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#8459
Solvent           = CHLOROFORM-D
Creation_time     =  6-MAY-2008 00:27:25
Revision_time     =  6-MAY-2008 00:20:21
Current_time      = 16-APR-2009 12:16:11

Content           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 17
Total_scans       = 17

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.1[dC]
```



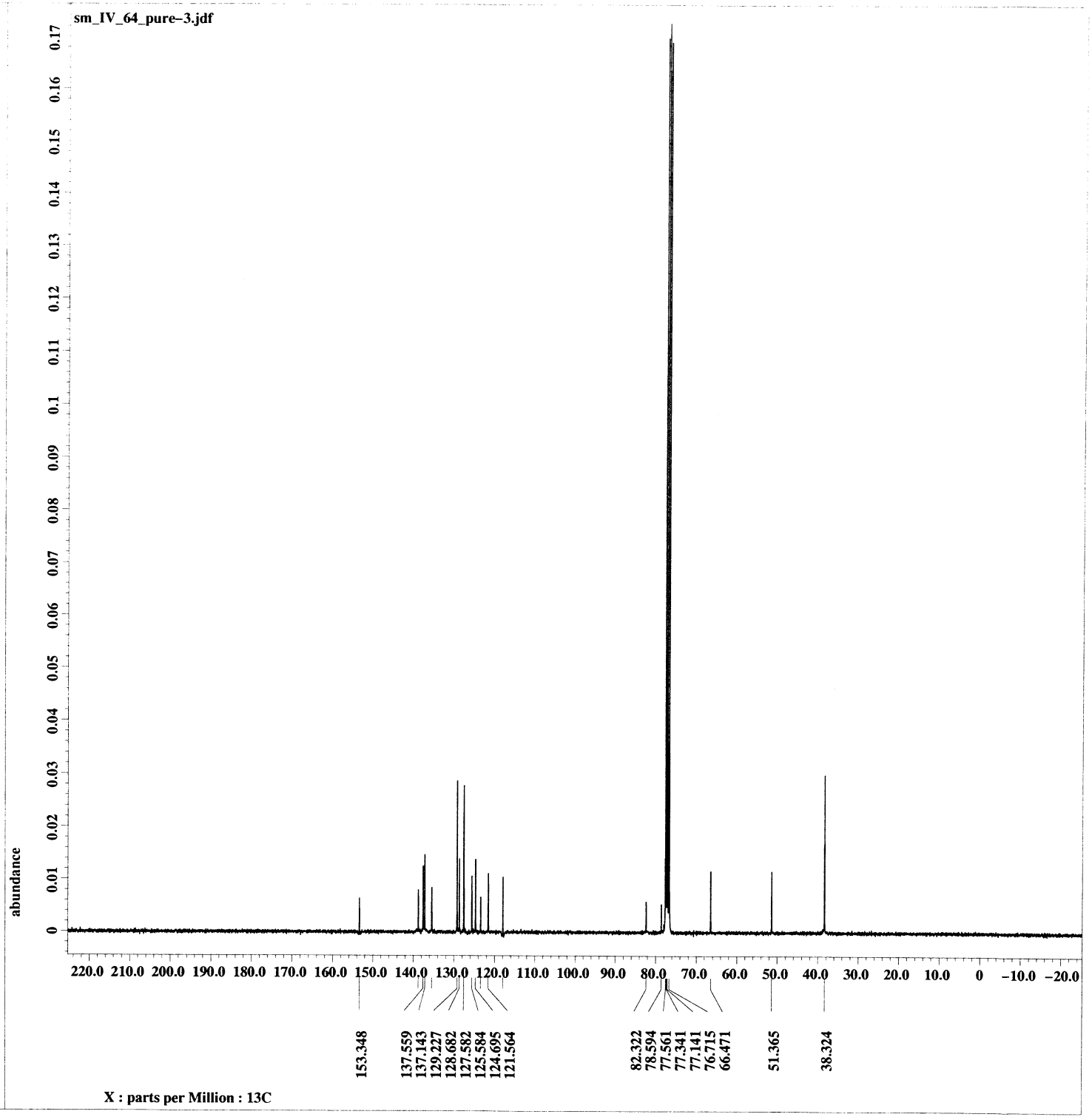
19b



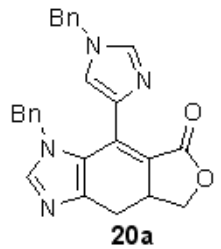
```
Filename          = sm_IV_64_pure-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#10441
Solvent           = CHLOROFORM-D
Creation_time     =  6-MAY-2008 08:29:25
Revision_time     =  6-MAY-2008 11:49:19
Current_time      = 16-APR-2009 12:18:23

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 5000
Total_scans       = 5000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 5.76824064[s]
Temp_get          = 23.3[dC]
```



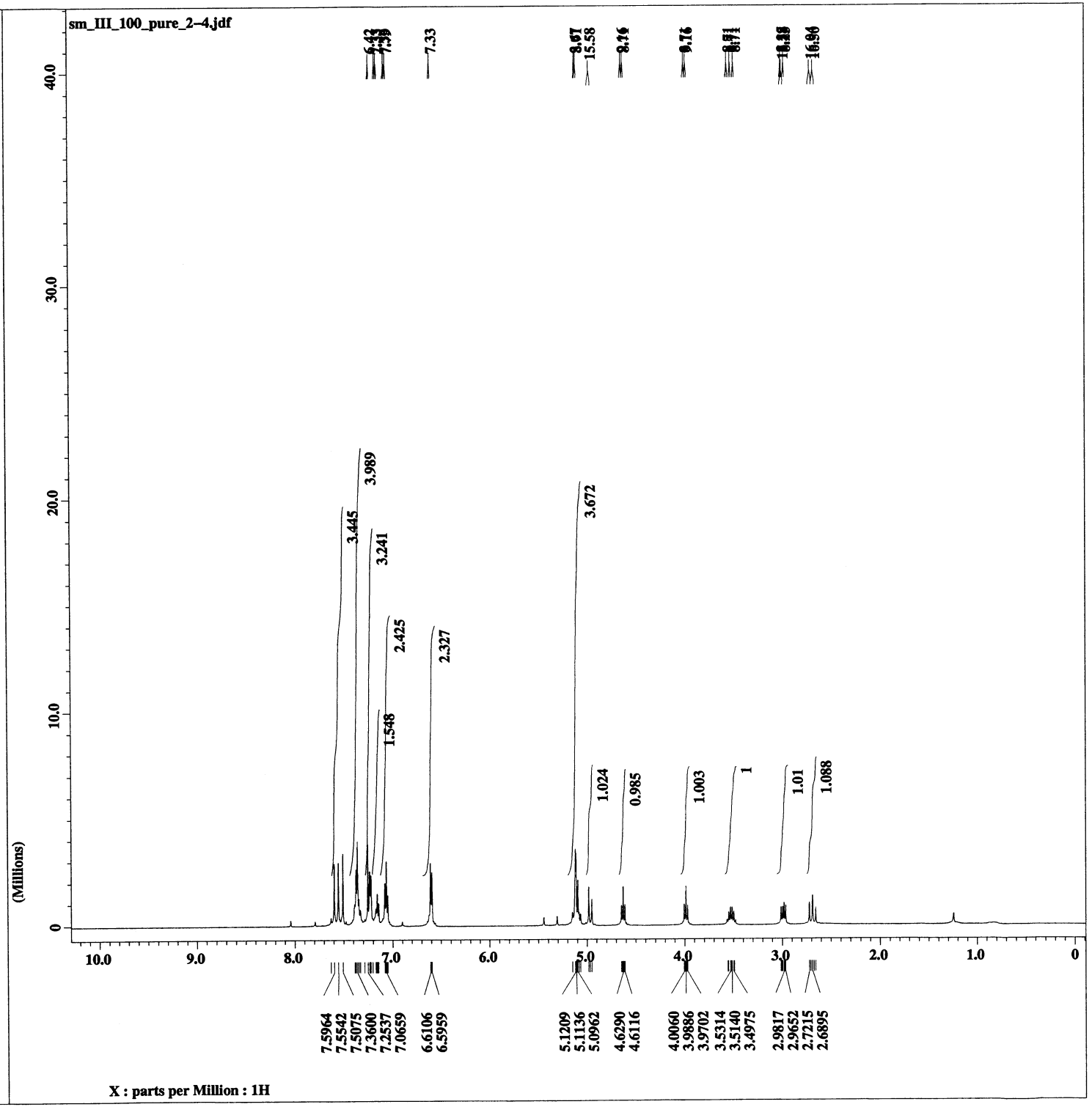
19b



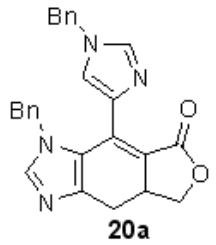
```
Filename          = sm_III_100_pure_2-4.j
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#10791
Solvent           = CHLOROFORM-D
Creation_time     = 20-JAN-2008 05:45:53
Revision_time     = 22-APR-2009 17:08:53
Current_time      = 22-APR-2009 17:09:35

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 7
Total_scans       = 7

X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 4[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



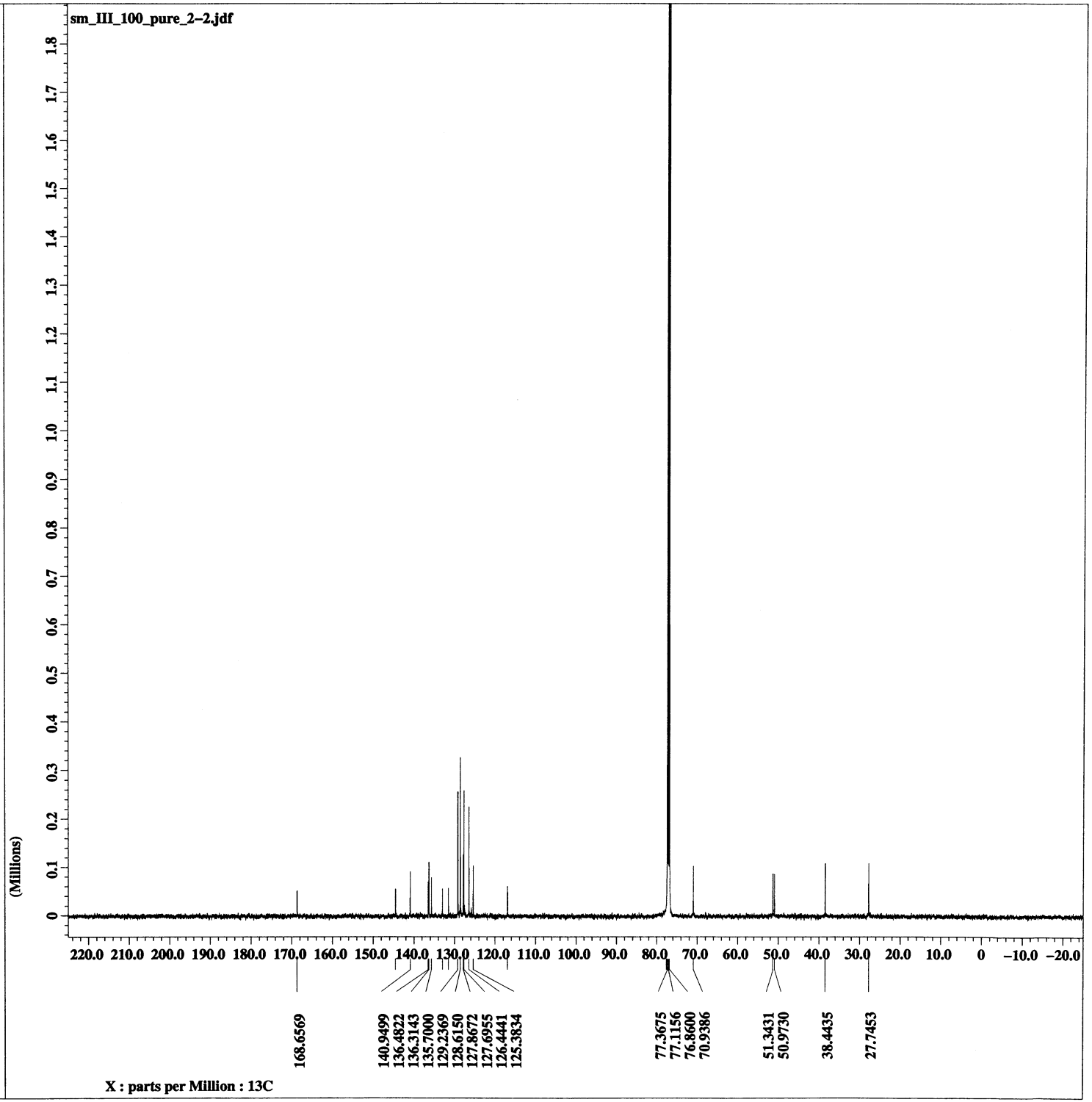
20a



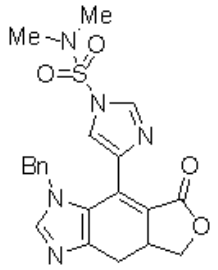
Filename	= sm_III_100_pure_2-2.j
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#12042
Solvent	= CHLOROFORM-D
Creation_time	= 20-JAN-2008 14:17:55
Revision_time	= 20-JAN-2008 13:52:06
Current_time	= 16-APR-2009 10:22:31
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 6000
Total_scans	= 6000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 26.9[dC]
Unblank_time	= 2[us]



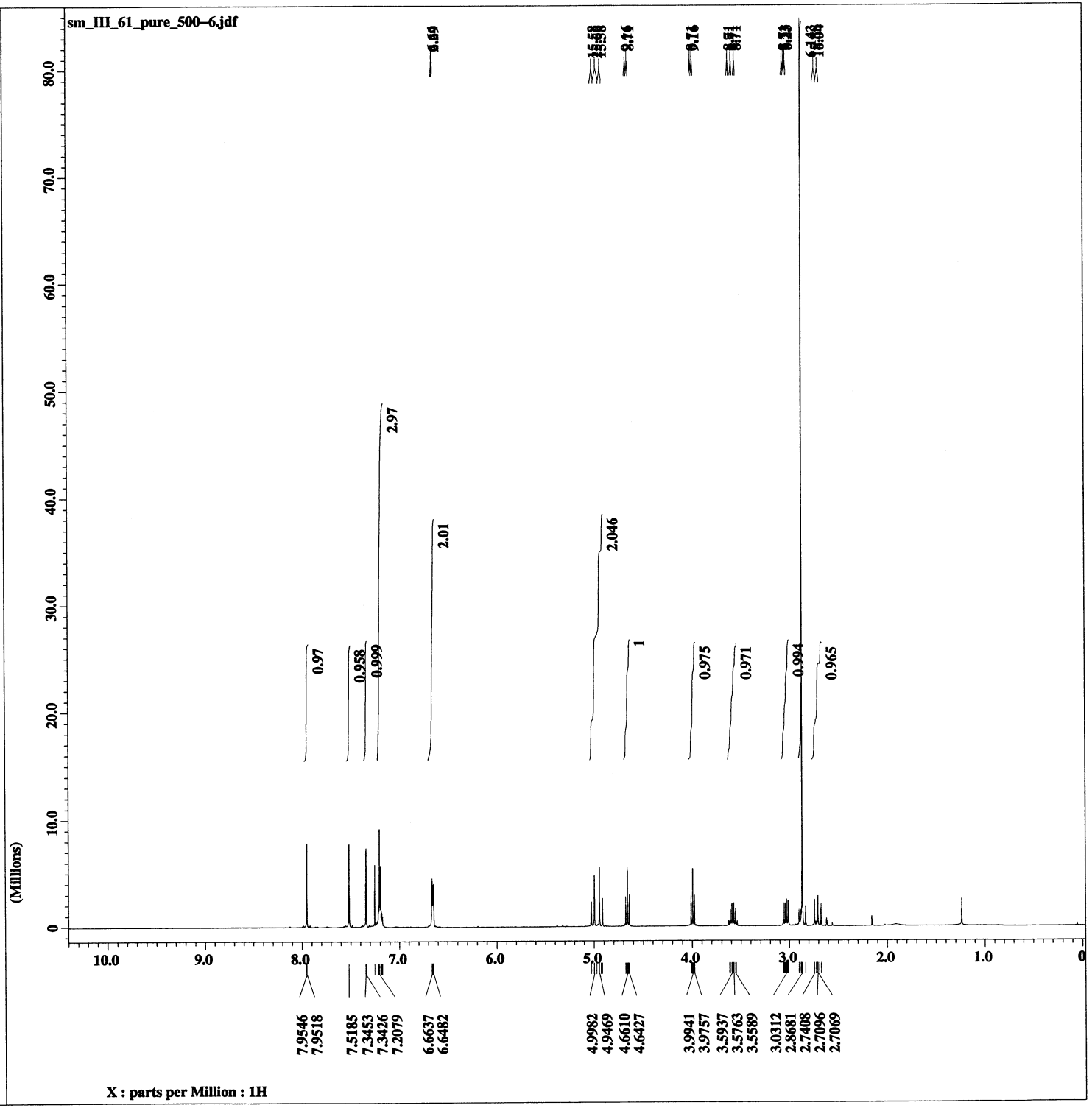
20a



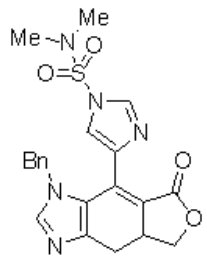
```
Filename          = sm_III_61_pure_500-6.
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#822134
Solvent           = CHLOROFORM-D
Creation_time     =  4-SEP-2007 03:12:00
Revision_time     = 16-APR-2009 10:49:43
Current_time      = 16-APR-2009 10:50:00

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 18
Relaxation_delay  = 4[s]
Temp_get          = 25.1[dC]
Unblank_time      = 2[us]
```



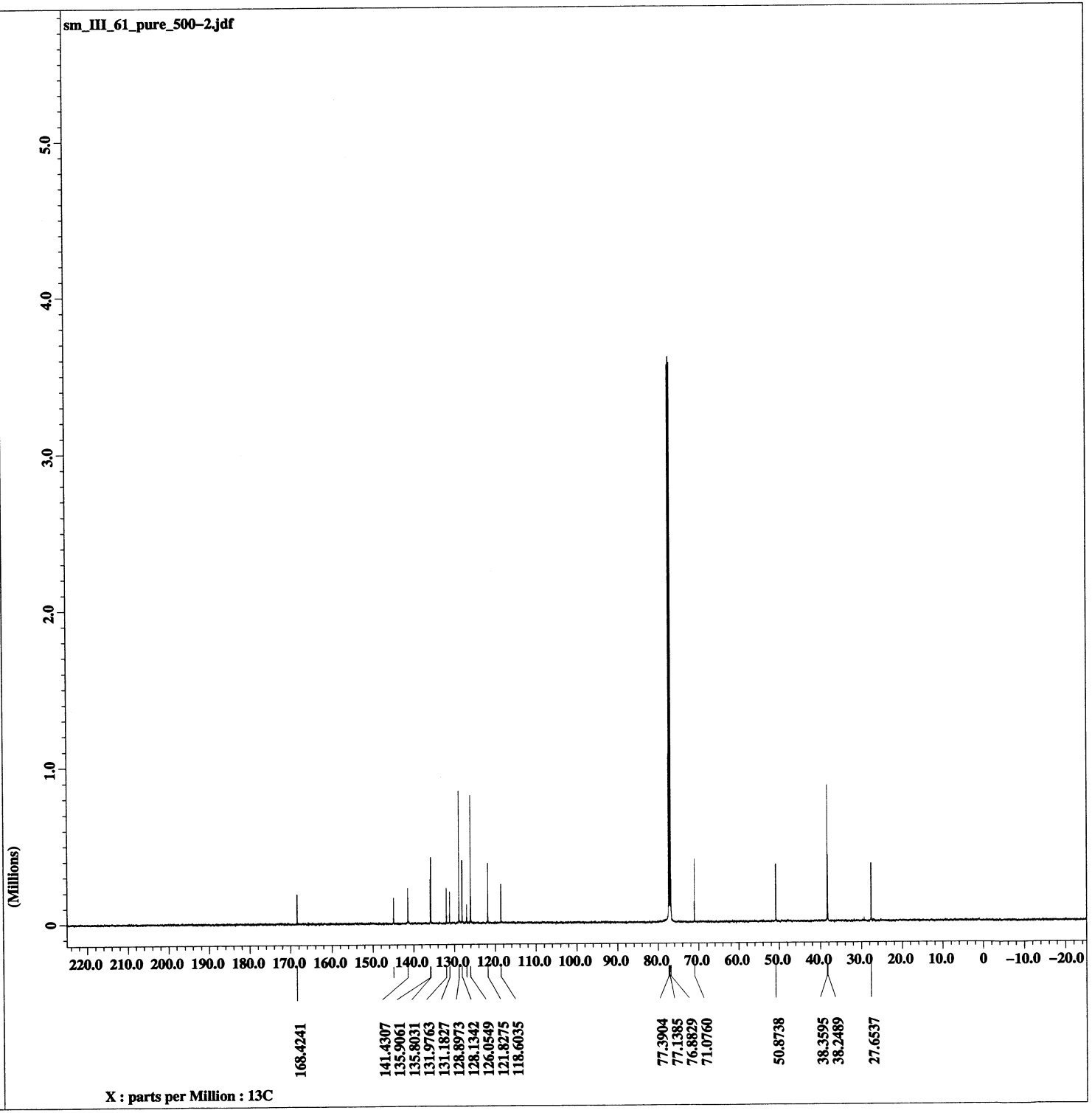
20b



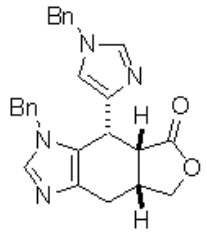
```
Filename          = sm_III_61_pure_500-2.
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#827058
Solvent           = CHLOROFORM-D
Creation_time     =  4-SEP-2007 10:23:45
Revision_time     =  4-SEP-2007 09:55:03
Current_time      = 16-APR-2009 10:53:02

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 5000
Total_scans       = 5000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 25.7[dC]
Unblank_time      = 2[us]
```



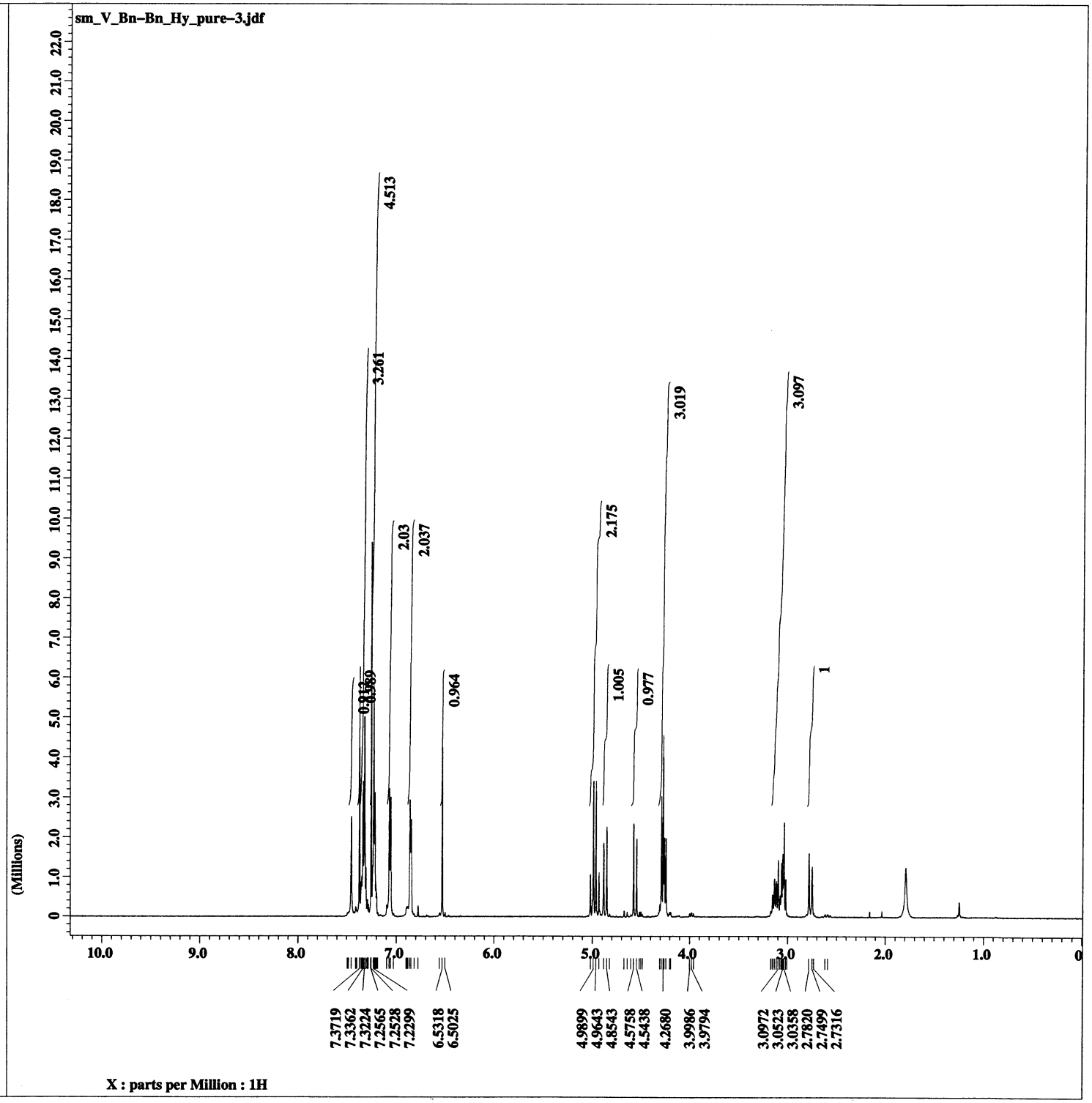
20b



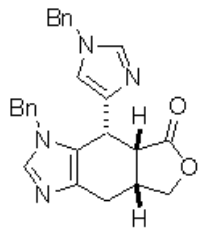
Filename	= sm_V_Bn-Bn_Hy_pure-3.
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#518212
Solvent	= CHLOROFORM-D
Creation_time	= 15-JAN-2009 22:46:52
Revision_time	= 15-JAN-2009 14:29:32
Current_time	= 15-JAN-2009 14:29:53
Content	= Single Pulse Experime
Data_format	= 1D REAL
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 12
Total_scans	= 12
X_90_width	= 18.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 22
Relaxation_delay	= 4[s]
Temp_get	= 26.1[dC]
Unblank_time	= 2[us]



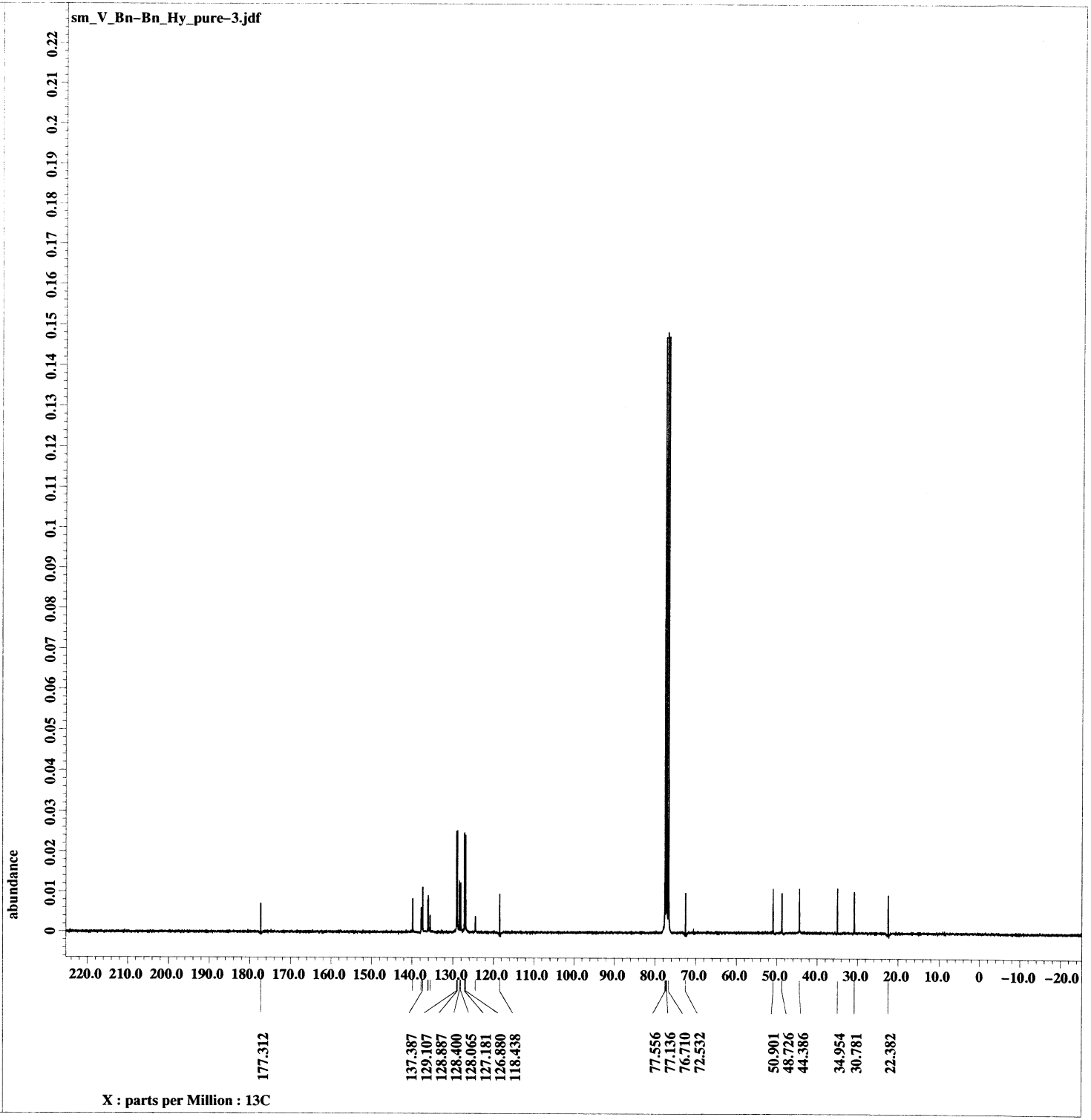
21a



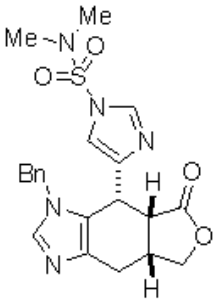
```
Filename          = sm_V_Bn-Bn_Hy_pure-3.
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#835108
Solvent           = CHLOROFORM-D
Creation_time     = 15-JAN-2009 07:31:35
Revision_time     = 15-JAN-2009 11:11:15
Current_time      = 16-APR-2009 11:25:26

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 5000
Total_scans       = 5000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 5.76824064[s]
Temp_get          = 23.3[dC]
```



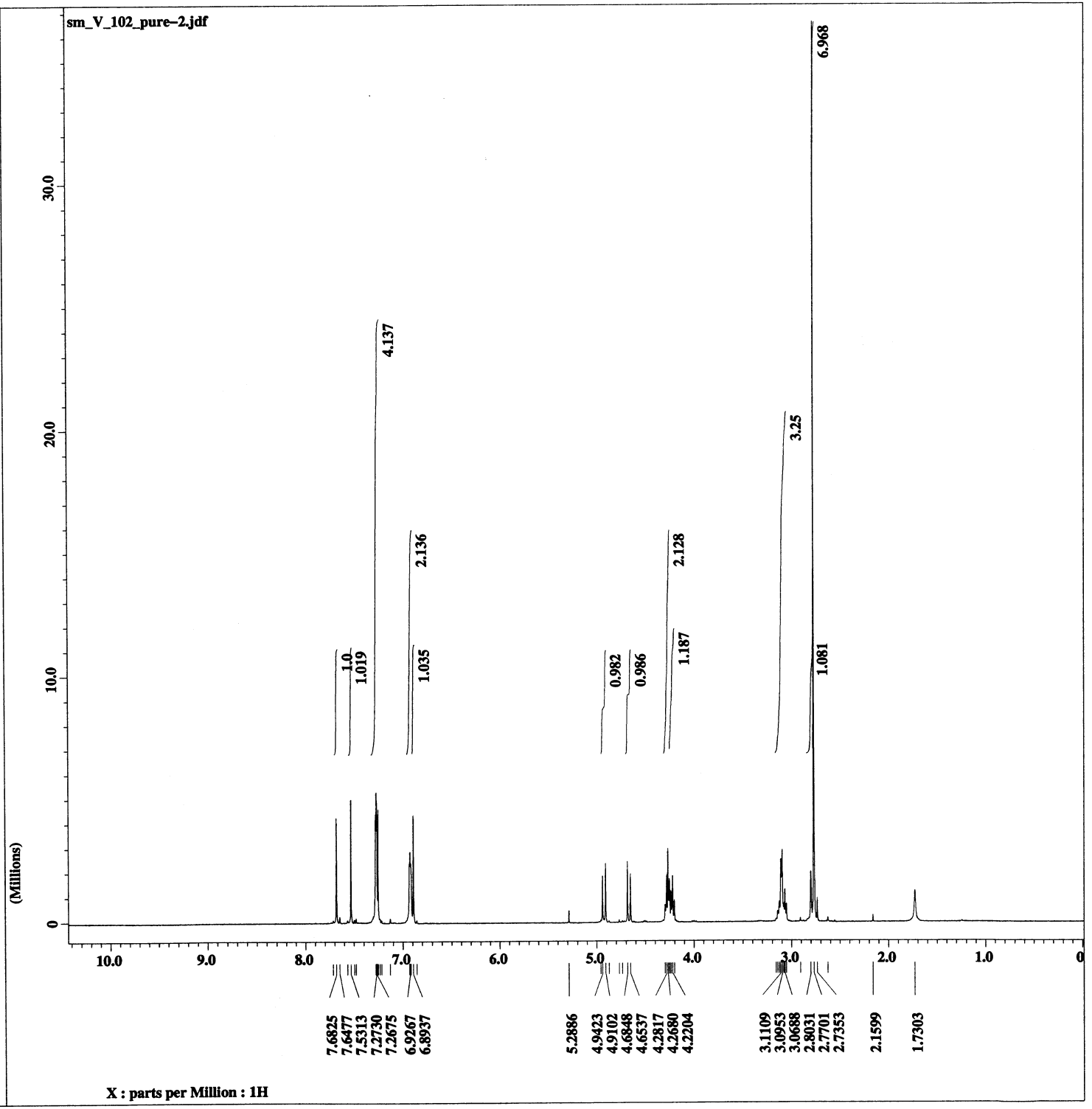
21a



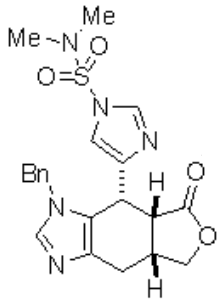
```
Filename          = sm_V_102_pure-2.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#389287
Solvent           = CHLOROFORM-D
Creation_time     = 18-MAR-2009 20:38:58
Revision_time     = 18-MAR-2009 11:19:45
Current_time      = 18-MAR-2009 11:19:55

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 23
Relaxation_delay  = 4[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```



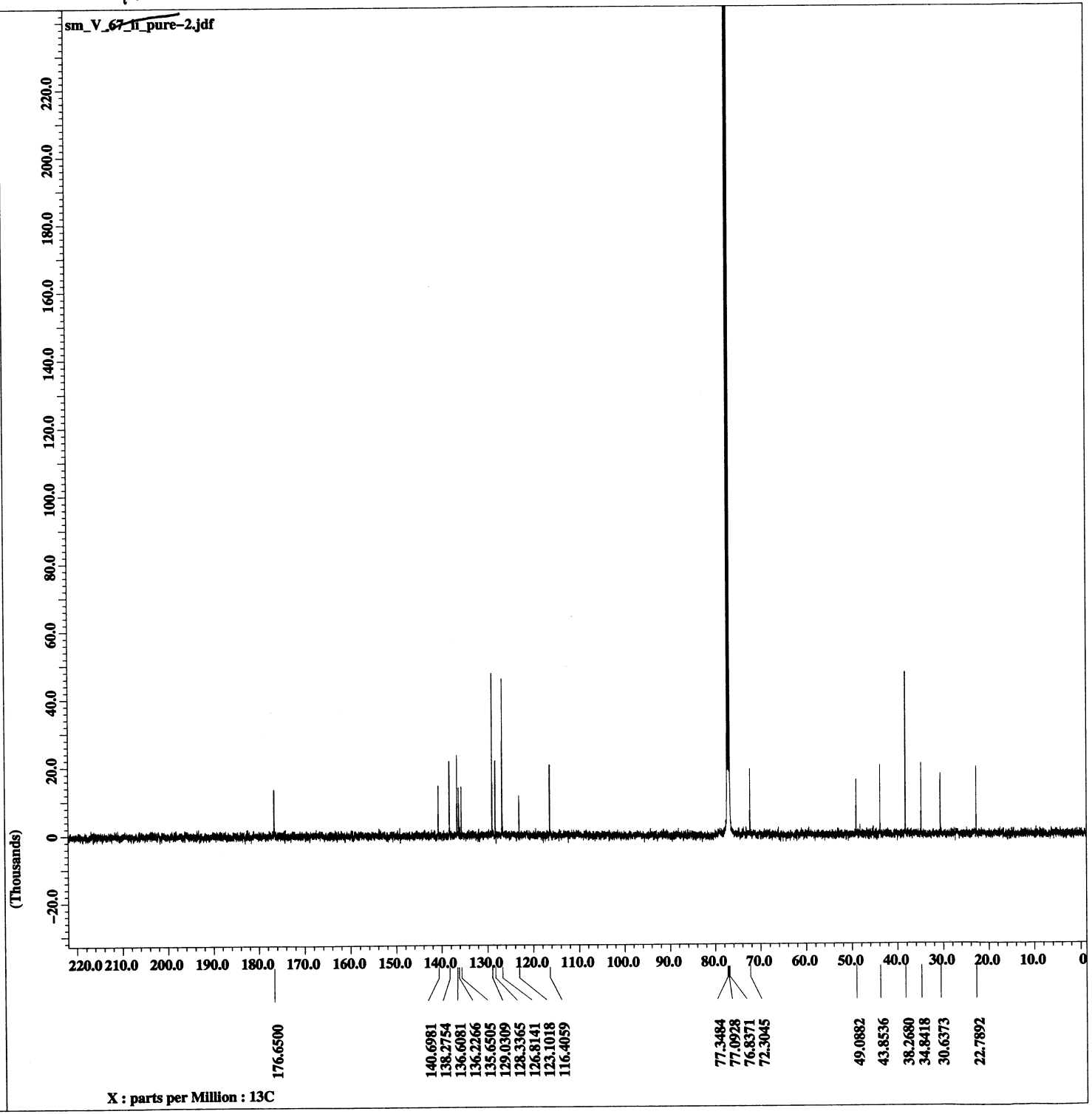
21b



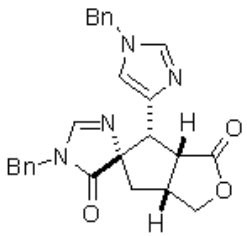
Filename	= sm_V_67_ii_pure-2.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#730303
Solvent	= CHLOROFORM-D
Creation_time	= 19-MAR-2009 14:38:41
Revision_time	= 19-MAR-2009 10:47:05
Current_time	= 19-MAR-2009 10:47:10
Content	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 6000
Total_scans	= 6000
X_90_width	= 14.2[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.73333333[us]
Initial_wait	= 1[s]
Noe_time	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 24
Relaxation_delay	= 2[s]
Temp_get	= 29.3[dC]
Unblank_time	= 2[us]



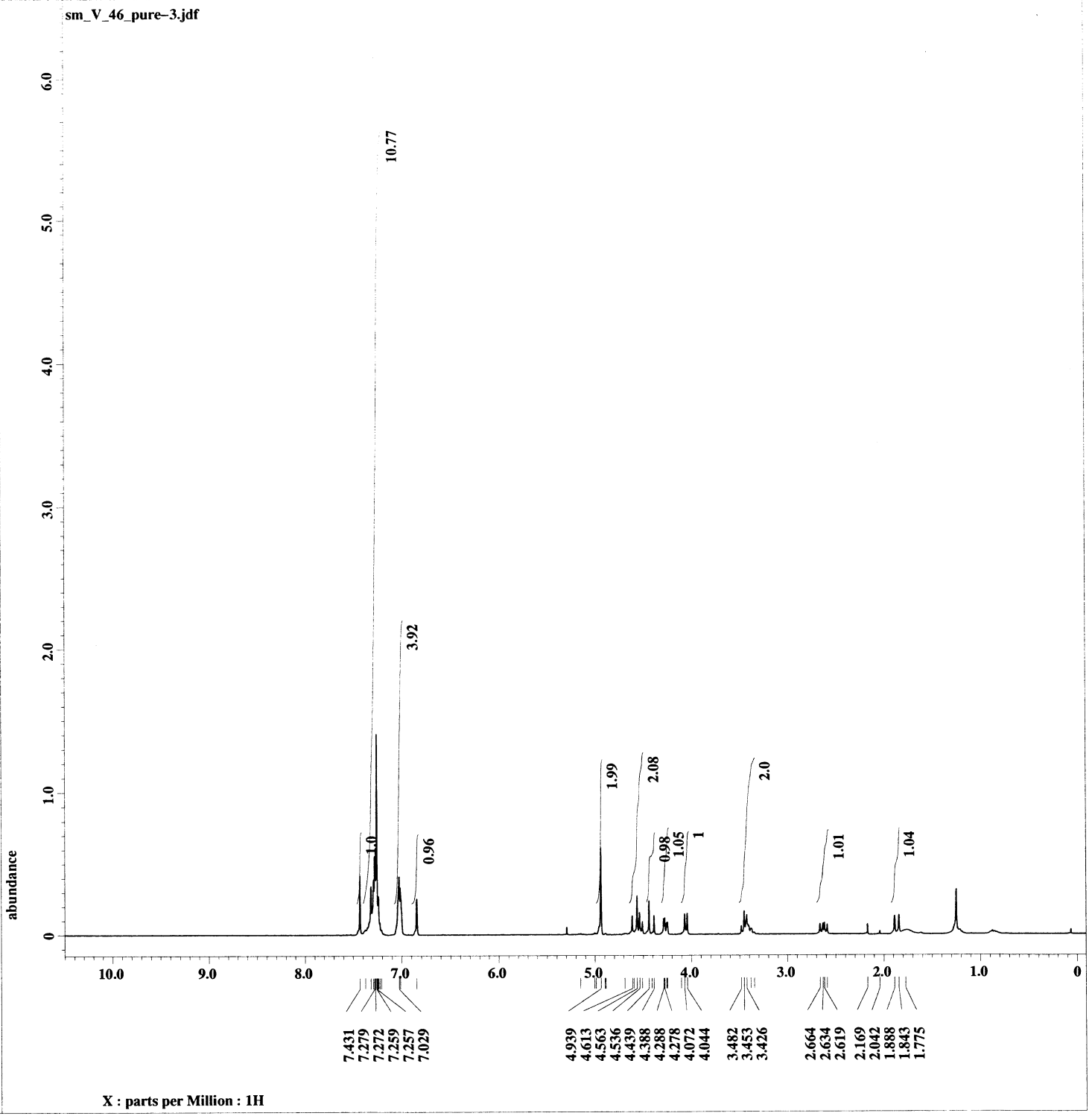
21b



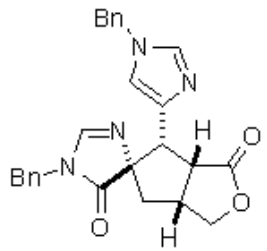
```
Filename          = sm_V_46_pure-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#767039
Solvent           = CHLOROFORM-D
Creation_time     = 16-JAN-2009 21:40:51
Revision_time     = 16-JAN-2009 21:26:17
Current_time      = 16-APR-2009 12:10:45

Content           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 24
Total_scans       = 24

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23[dC]
```



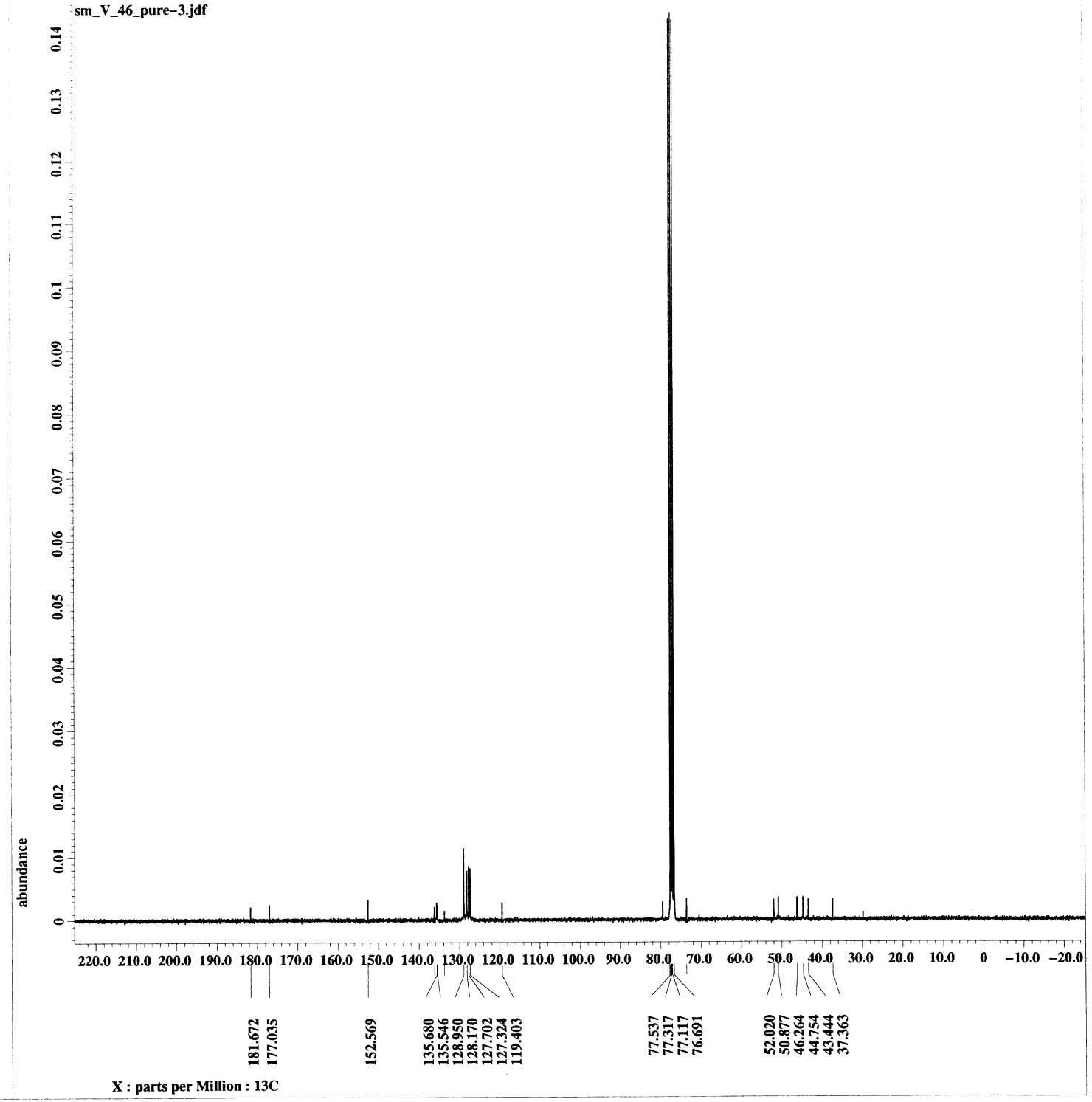
22a



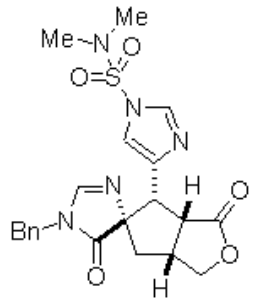
```
Filename          = sm_V_46_pure-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#769604
Solvent           = CHLOROFORM-D
Creation_time     = 17-JAN-2009 07:18:45
Revision_time     = 17-JAN-2009 16:25:45
Current_time      = 16-APR-2009 12:11:50

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 6000
Total_scans       = 6000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 5.76824064[s]
Temp_get          = 23.3[dC]
```



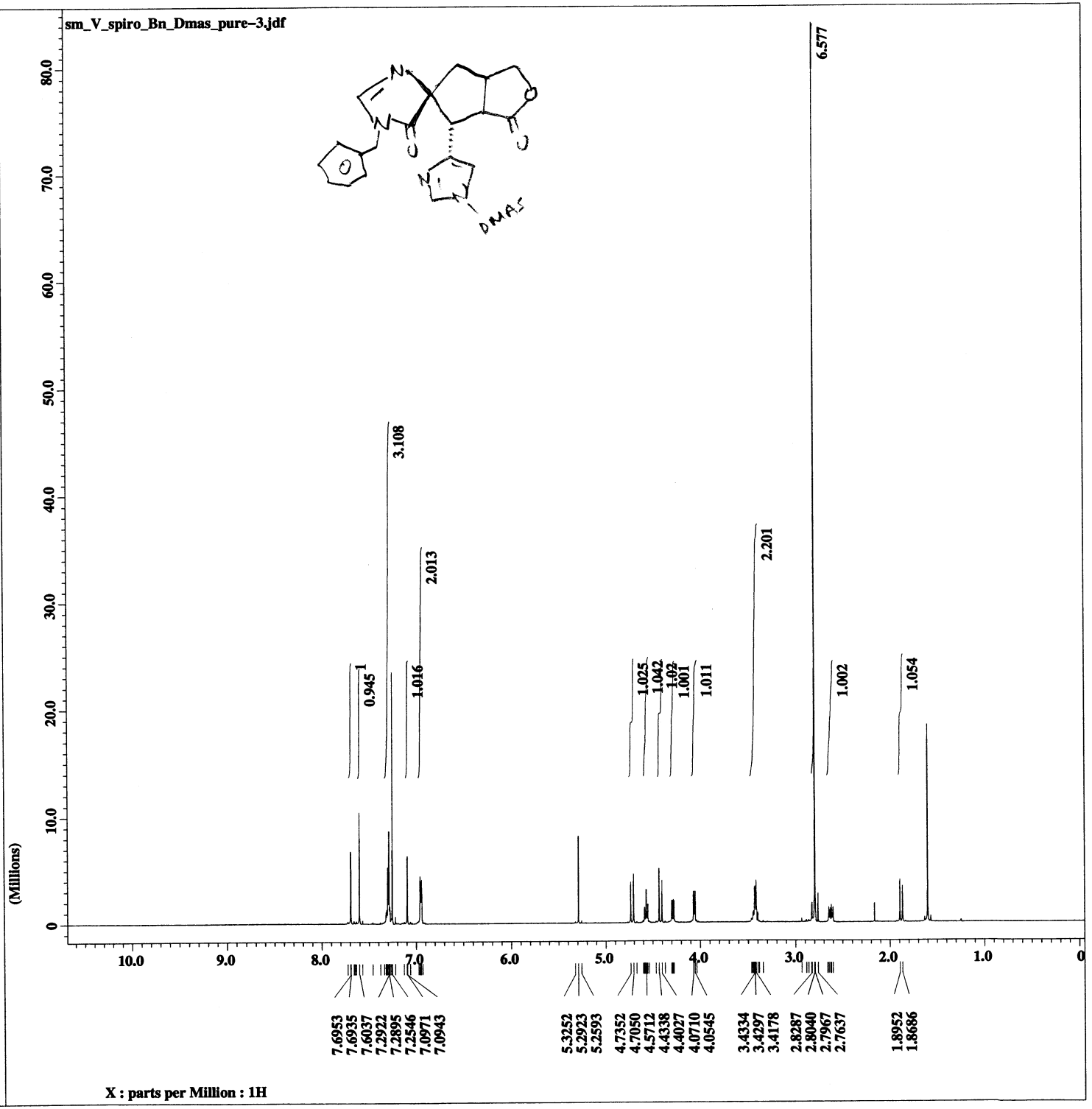
22a



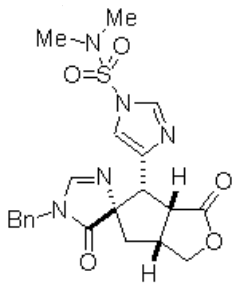
Filename	= sm_V_spiro_Bn_Dmas_pu
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#714680
Solvent	= CHLOROFORM-D
Creation_time	= 22-MAR-2009 05:49:02
Revision_time	= 21-MAR-2009 19:57:34
Current_time	= 21-MAR-2009 19:57:44
Content	= Single Pulse Experime
Data_format	= 1D REAL
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 18
Total_scans	= 18
X_90_width	= 18.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 24
Relaxation_delay	= 4[s]
Temp_get	= 26.1[dC]
Unblank_time	= 2[us]



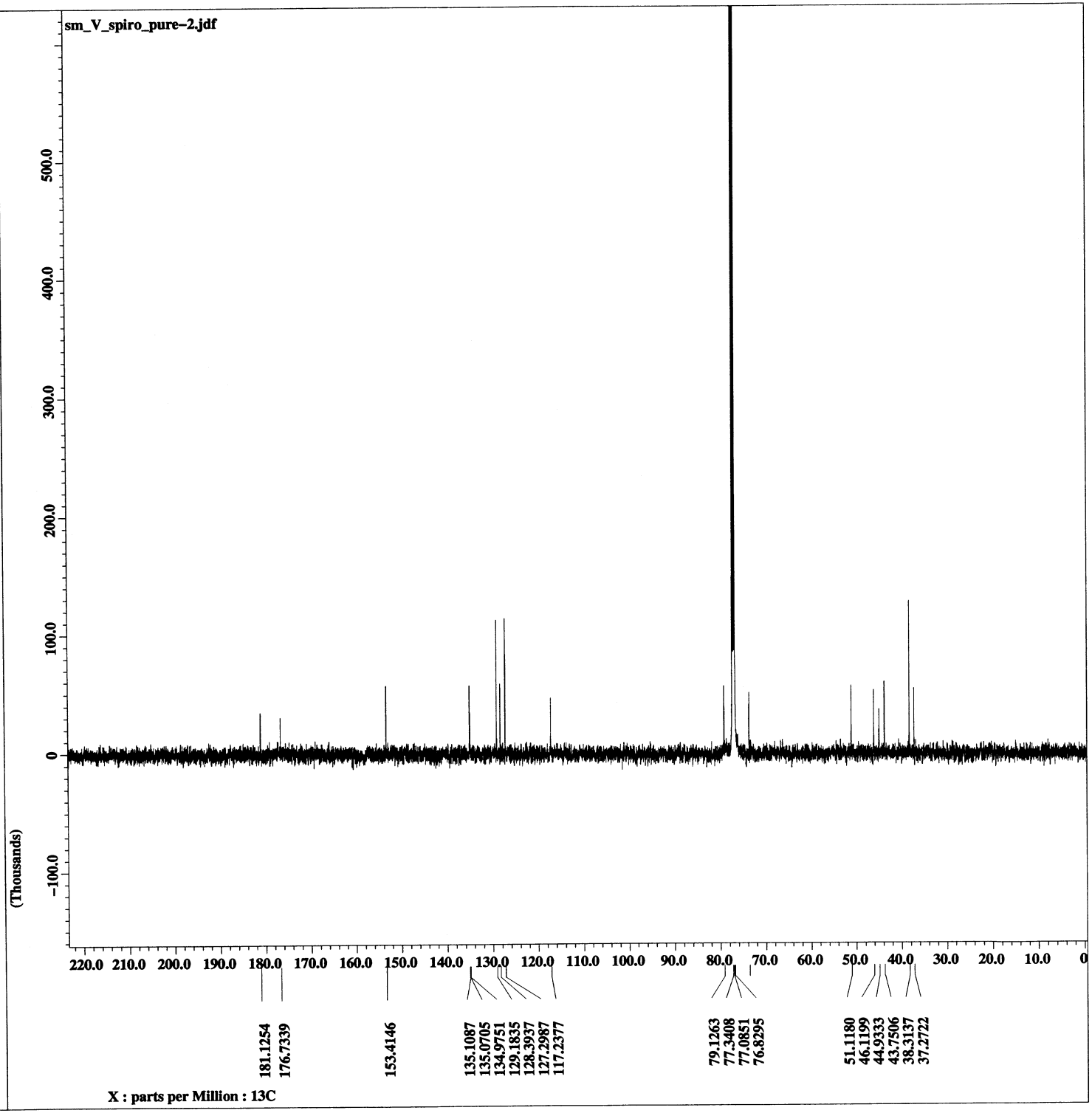
22b



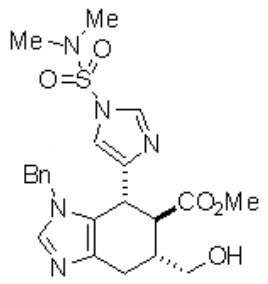
```
Filename          = sm_V_spiro_pure-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#717231
Solvent           = CHLOROFORM-D
Creation_time     = 22-MAR-2009 12:55:48
Revision_time     = 16-APR-2009 10:38:27
Current_time      = 16-APR-2009 10:39:05

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 5000
Total_scans       = 5000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 29.2[dC]
Unblank_time      = 2[us]
```



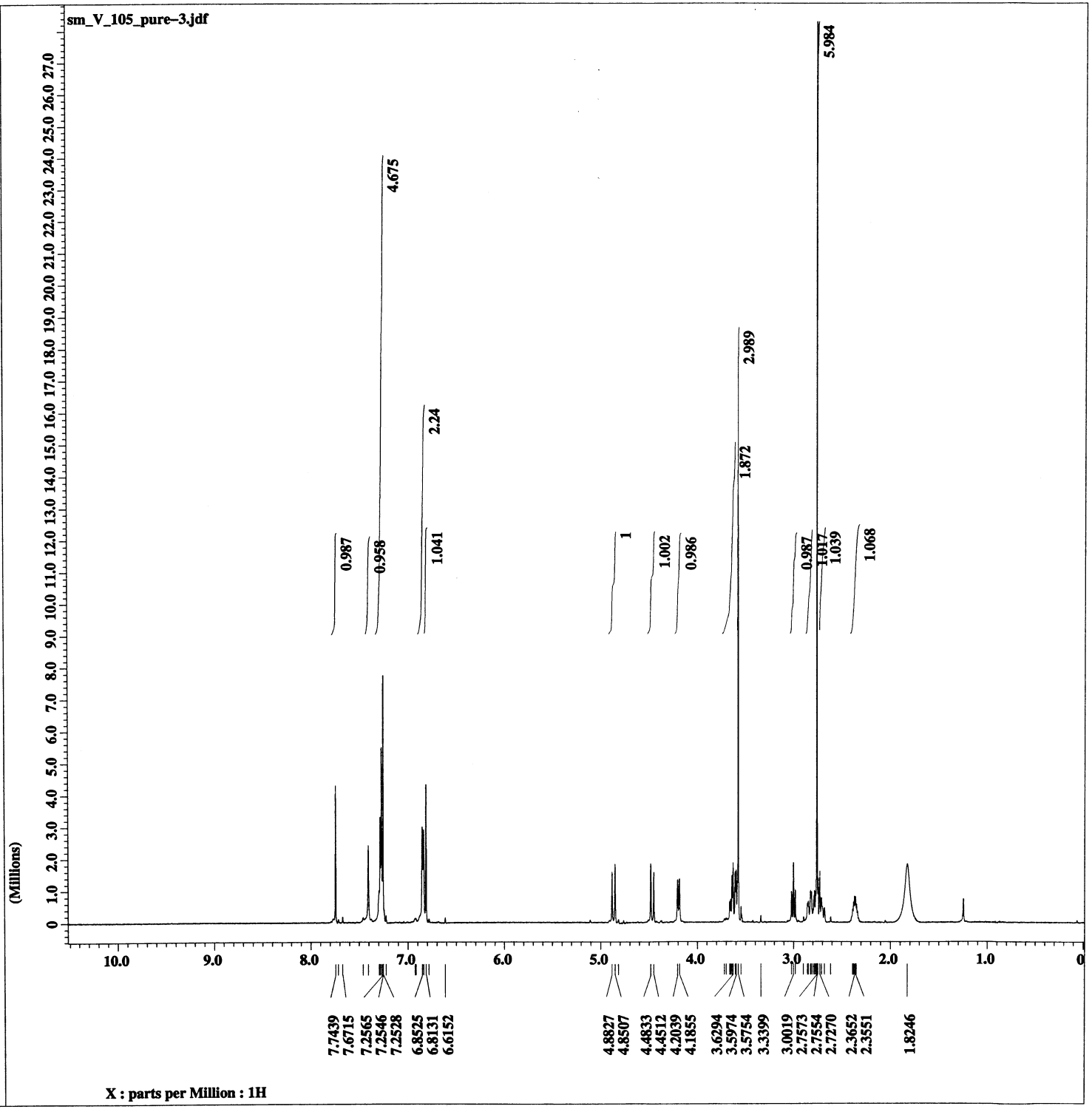
22b



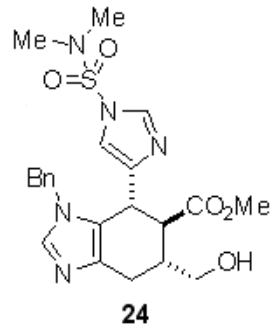
Filename	= sm_V_105_pure-3.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#763077
Solvent	= CHLOROFORM-D
Creation_time	= 23-MAR-2009 07:11:33
Revision_time	= 22-MAR-2009 21:19:04
Current_time	= 22-MAR-2009 21:19:15
Content	= Single Pulse Experime
Data_format	= 1D REAL
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 18.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 24
Relaxation_delay	= 4[s]
Temp_get	= 26[dC]
Unblank_time	= 2[us]



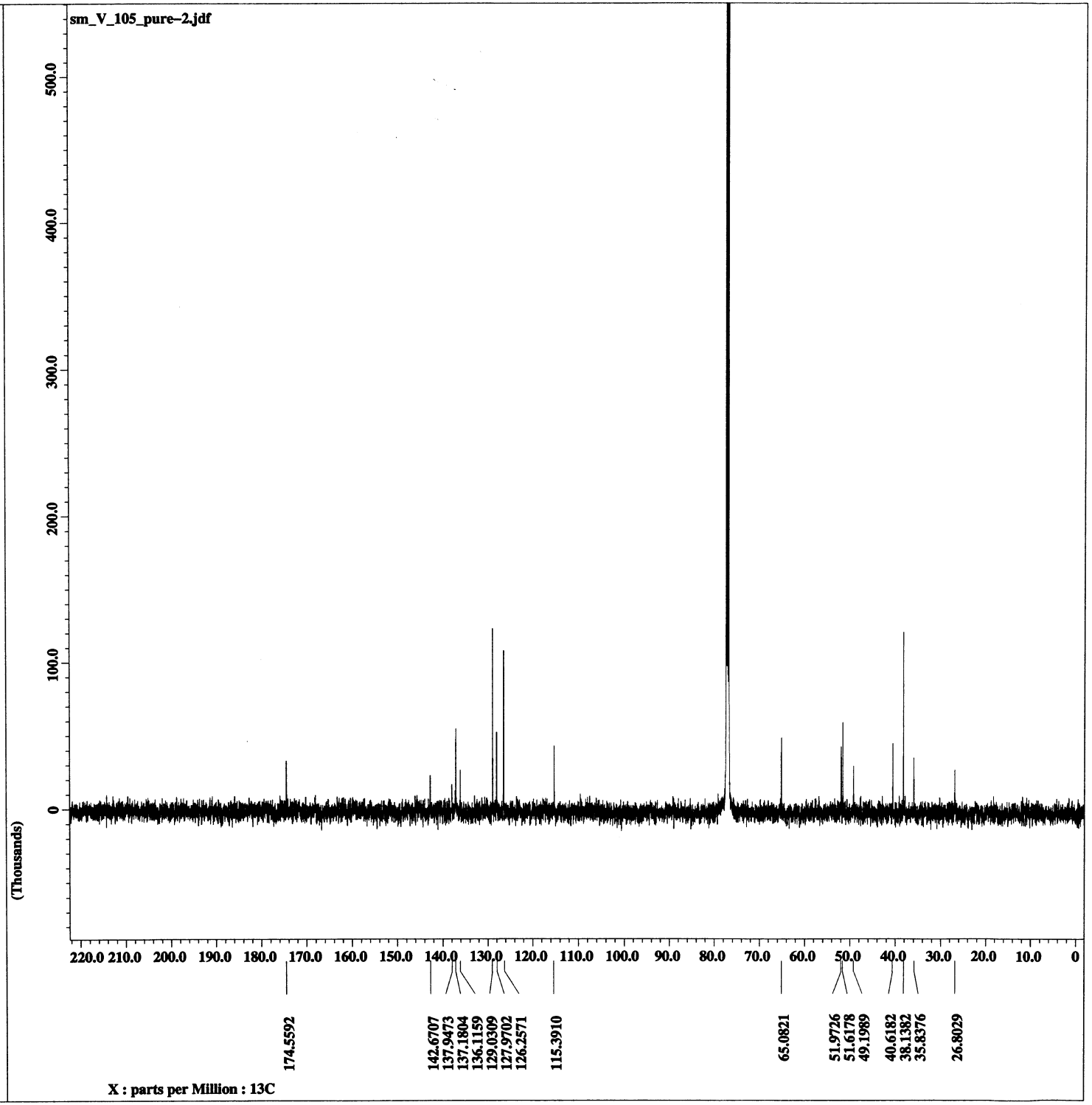
24



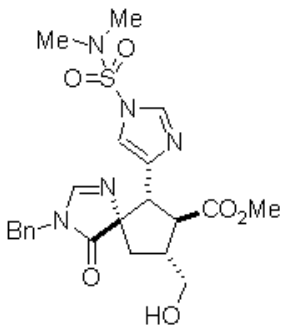
```
Filename          = sm_V_105_pure-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#765343
Solvent           = CHLOROFORM-D
Creation_time     = 23-MAR-2009 14:19:47
Revision_time     = 23-MAR-2009 08:30:23
Current_time      = 23-MAR-2009 08:32:59

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 5000
Total_scans       = 5000

X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 29.3[dC]
Unblank_time      = 2[us]
```



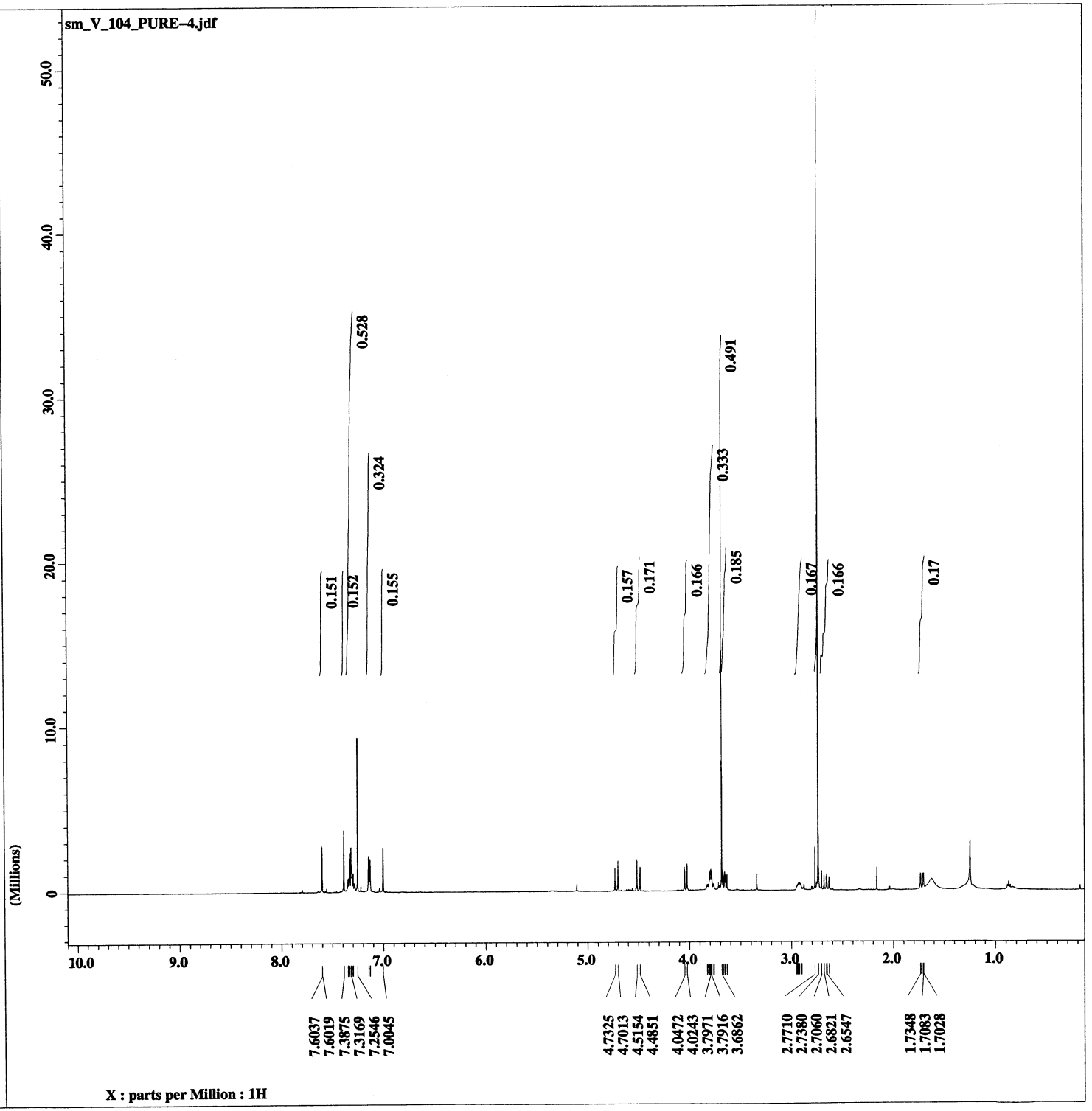
24



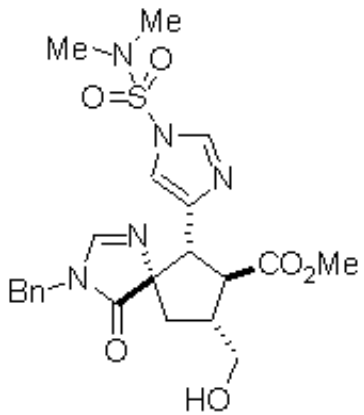
Filename	= sm_V_104_PURE-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#598701
Solvent	= CHLOROFORM-D
Creation_time	= 4-APR-2009 03:00:34
Revision_time	= 16-APR-2009 10:08:27
Current_time	= 16-APR-2009 10:14:19
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 18.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 23
Relaxation_delay	= 4[s]
Temp_get	= 24.9[dC]
Unblank_time	= 2[us]



23



```
Filename          = sm_V_104_pure_ii-2.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#400830
Solvent           = CHLOROFORM-D
Creation_time     = 21-MAR-2009 16:06:14
Revision_time     = 21-MAR-2009 15:45:31
Current_time      = 22-APR-2009 18:23:25

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 2859
Total_scans       = 2859

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 5.76824064[s]
Temp_get          = 23.1[dC]
```



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