Supplemental materials for:

Progress Toward the Total Synthesis of Saudin: The Development of a Tandem Stille-Oxa-Electrocyclization Reaction

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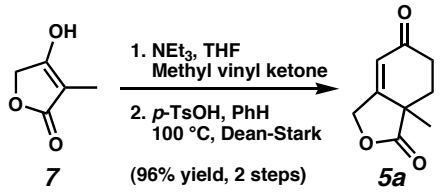
Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen atmosphere using dry, deoxygenated solvents. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining. ICN silica gel (particle size 0.032 - 0.063 mm) was used for flash chromatography. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or a Varian Inova 500 (at 500 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as

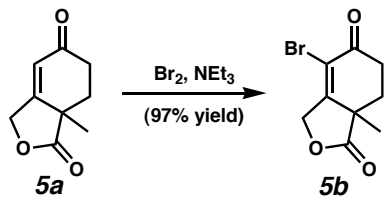
follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 75 MHz), or a Varian Inova 500 (at 125 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility.

Synthesis of Vinyl Stannane 5c

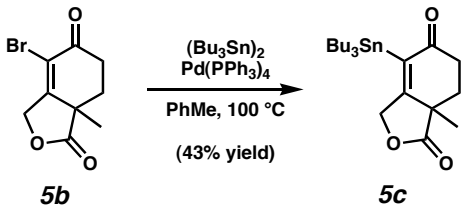


Enone 5a. To a cooled (0 °C) solution of methyl tetronic acid **7**[1] (150 g, 1.31 mol) in THF (1.3 L) was slowly added Et_3N (366 mL, 2.63 mol). Methyl vinyl ketone **8** (131 mL, 1.58 mol) was then added. After stirring for 30 minutes, the reaction mixture was washed with 1N HCl. The organic layer was separated and dried over Na_2SO_4 and evaporated to provide the conjugate addition product (242.2 g, 1.31 mol) as a yellow oil, which was used without further purification: ^1H NMR (300 MHz, $CDCl_3$) δ 4.73 (d, J = 16.8 Hz, 1H), 4.63 (d, J = 16.8 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H), 2.12 (s, 3H), 2.00 (m, 2H), 1.31 (s, 3H).

To a solution of this conjugate addition product (242.2 g, 1.31 mol) in benzene (650 mL) was added *p*-TsOH (24.9 g, 131 mol). The mixture was refluxed with azeotropic removal of H_2O. After stirring for 40 hours, the reaction mixture was cooled to room temperature and concentrated. The resulting oil was dissolved in CH_2Cl_2 (300 mL) and washed with water (200 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 40 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided enone **5a** (211 g, 96% yield over 2 steps) as a clear oil: R_F 0.40 (1:3 hexanes/EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.01 (dd, J = 14.6, 2.1 Hz, 1H), 4.83 (d, J = 14.6 Hz, 1H), 2.60-2.36 (m, 2H), 2.22-1.92 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 177.5, 161.6, 122.2, 68.2, 41.3, 32.6, 29.5, 20.7; IR (film) 2940, 1780, 1676 cm^{-1}; HRMS (EI^+) calc'd for $[C_9H_{10}O_3]^+$: *m/z* 166.0630, found 166.0629.

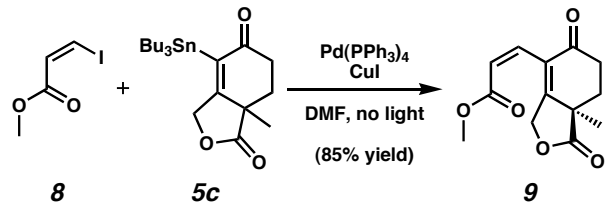


Bromoenone 5b. To a cooled solution (0 °C) of enone **5a** (5.0 g, 30 mmol) in CH_2Cl_2 (60 mL) was added a solution of Br_2 (1.7 ml, 33 mmol) in CH_2Cl_2 (30 mL) in a dropwise fashion. Following addition, Et_3N (4.6 mL, 33 mmol) was added. After stirring for 5 minutes, the reaction mixture was washed with water (3 x 50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided bromoenone **5b** (7.16 g, 97% yield) as a clear oil: R_F 0.30 (2:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (s, 2H), 2.83-2.77 (m, 2H), 2.33-2.14 (m, 2H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 176.7, 160.2, 117.8, 69.4, 45.2, 33.3, 29.5, 21.7; IR (film) 2935, 1782, 1689, 1655 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_9H_9O_3Br]^+$: *m/z* 243.9735, found 243.9732.



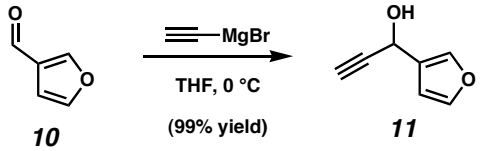
Vinyl stannane 5c. A solution of bromoenone **5b** (5.0 g, 20.4 mmol), $(Bu_3Sn)_2$ (20.6 mL, 40.8 mmol), $Pd(PPh_3)_4$ (306 mg, 0.265 mmol), and $NaHCO_3$ (8.57g, 102 mol) in toluene (200 mL) was stirred at -78 °C under reduced pressure for 30 minutes. The mixture was then stirred at reflux under N_2. After 24 hours, the reaction mixture was cooled to room temperature and filtered through a celite plug with pentane washing. The filtrate was concentrated to an oil, which was purified by flash chromatography (9:1 hexanes/EtOAc eluent) to give vinyl stannane **5c** as a clear oil (4.0 g, 43% yield): R_F 0.45 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (d, *J* = 14.65 Hz, 1H), 4.79 (d, *J* = 14.65 Hz, 1H), 2.67-2.47 (m, 2H), 2.23 (ddd, *J* = 13.3, 5.3, 2.1 Hz, 1H), 2.04 (td, *J* = 13.3, 6.6 Hz, 1H), 1.66-1.58 (m, 3H), 1.48 (s, 3H), 1.47-1.24 (m, 13H), 1.03-0.86 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 169.6, 139.5, 69.9, 42.2, 32.1, 29.2, 28.3, 27.2, 26.8, 21.6, 17.3, 13.7, 11.0; IR (film) 1784, 1654 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $[C_{21}H_{35}O_3Sn]^+$: 455.1608, found 455.1603.

Synthesis of Model Stille Product 9



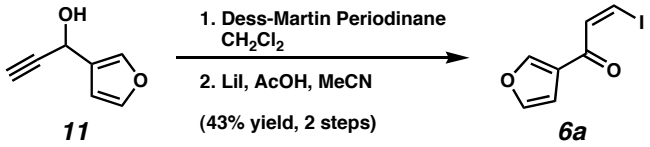
Enone 9. To a flask containing $Pd(PPh_3)_4$(14 mg, 0.012 mmol), vinyl stannane **5c** (50 mg, 0.12 mmol), and vinyl iodide **8**[2] (30 mg, 0.12 mmol) was added DMF (2.5 mL). CuI (17.5 mg, 0.09 mmol) was added, and the flask was covered in Aluminum foil. After stirring for 9 hours, the mixture was diluted with water (10 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (1:1 hexanes/EtOAc eluent) provided enone **9** (25.5 mg, 85% yield): R_F 0.25 (1:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (ddd, *J* = 12.2, 1.9, 0.8 Hz, 1H), 6.15 (d, *J* = 12.2 Hz, 1H), 5.02 (dd, *J* = 15.0, 2.0 Hz, 1H), 4.72 (dd, *J* = 15.0, 0.7 Hz, 1H), 3.69 (s, 3H), 2.77-2.53 (m, 2H), 2.32-2.11 (m, 2H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 177.9, 165.5, 158.7, 136.0, 128.7, 125.6, 77.7, 68.6, 51.9, 42.0, 33.0, 29.9, 21.0; IR (film) 2952, 1781, 1722, 1675, 1197, 1179 cm^{-1}; HRMS (EI^+) calc'd for $[C_{13}H_{14}O_5]^+$: *m/z* 250.0841, found 250.0844.

Synthesis of Vinyl Iodides 6a, 14, 15, and 16



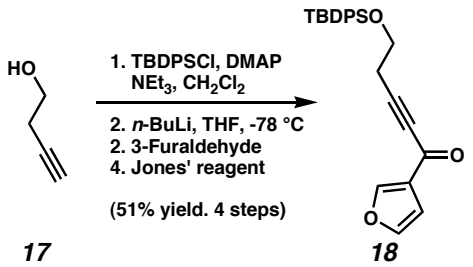
Alcohol 11. A 3-neck flask was connected to an addition funnel. The flask was charged with 3-furaldehyde **10** (17.3 mL, 200 mmol) and THF (170 mL), and the solution was cooled (0 °C). A 0.5M solution of ethynyl magnesium bromide (500 mL, 250 mmol) was slowly added from the addition funnel over 2 hours. Following addition the cold bath was allowed to warm to room temperature, and the mixture was stirred for 5 hours. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (500 mL). The mixture was extracted with Et_2O (2 x 400 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided alcohol **11** (25.41 g, 99% yield) as a clear oil: R_F 0.25 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 0.8 Hz, 1H), 7.37 (t, *J* = 1.7 Hz, 1H), 6.48 (d, *J* = 0.8 Hz, 1H), 5.35 (d, *J* = 1.3 Hz, 1H),

3.14 (s, 1H), 2.58 (d, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.4, 126.0, 109.2, 83.2, 73.5, 57.0; IR (film) 3293, 1505, 1158, 1021 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_7H_6O_2]^+$: *m/z* 122.0368, found 122.0367.



Vinyl Iodide 6a. To a cooled (0 °C) solution of Dess-Martin Periodinane (1.91 g, 4.50 mmol) in CH_2Cl_2 (18 mL) was added alcohol **11** (500 mg, 4.09 mmol) in CH_2Cl_2 (3 mL). After 1 hour the reaction was quenched by addition of a 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (20 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under a slight reduction of pressure (produced by a water aspirator) while submerged in a cold bath (0 °C). The resulting oil was purified by flash chromatography on silica gel (3:1 petroleum ether/ether eluent) to provide the volatile ynone product (442 mg, 3.68 mmol) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (m, 1H), 7.46 (m, 1H), 6.83 (m, 1H), 3.26 (d, J = 1.2 Hz, 1H).

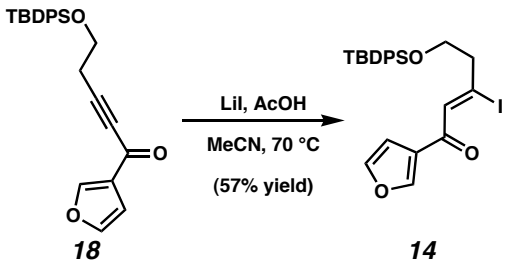
To a solution of the volatile ynone (5 g, 41.6 mmol) and LiI (6.13 g, 45.8 mmol) in MeCN (42 mL) was added concentrated AcOH (2.63 mL, 45.8 mmol). Following addition, the mixture was stirred for 2 hours and then poured onto ice water (75 mL). Solid K_2CO_3 was added until bubbling ceased, and the mixture was extracted with Et_2O (2 x 75 mL). The combined organic layers were dried over $MgSO_4$. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (10:1 pentane/ether eluent) provided vinyl iodide **6a** (5.46 g, 43% yield over 2 steps) as a yellow solid: R_F 0.29 (5:1 pentane/ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 1.4, 0.8 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.47 (dd, J = 1.9, 1.4 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 6.85 (dd, J = 1.9, 0.8 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 183.0, 147.7, 144.8, 133.9, 129.0, 109.3, 91.6; IR (film) 3130, 1655, 1295 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_7H_5O_2I]^+$: *m/z* 247.9335, found 247.9346.



Ynone 18. To a solution of alcohol **17** (1.73 mL, 22.9 mmol), *t*-butyldiphenylsilyl chloride (5.72 g, 22 mmol), and DMAP (98 mg, 0.8 mmol) in CH_2Cl_2 (20 mL) was added a Et_3N (3.1 mL, 022 mmol). After stirring for 1 hour, the reaction was washed with H_2O (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was dissolved in benzene and concentrated to azeotropically remove water, and the resulting protected alcohol was taken on to the next step without further purification.

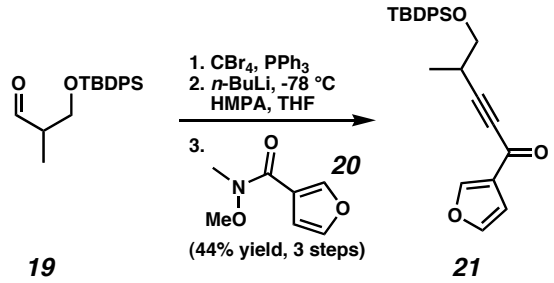
The product from the previous step was dissolved in THF (40 mL) and cooled to -78 °C. A 2.5 M solution of *n*-butyllithium in hexanes (8.8 mL, 22 mmol) was slowly added. After 20 minutes, 3-furaldehyde (1.9 mL, 22 mmol) was slowly added. Following addition, the mixture was warmed to room temperature and stirred for 10 minutes. The reaction was quenched with 1N Hcl (40 mL). The mixture was concentrated to remove THF, and the resulting solution was extracted with ether (2 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated, and the resulting coupled alcohol was taken onto the next step without further purification.

The product from the previous step was dissolved in acetone (40 mL) and cooled to 0 °C. To this solution was added a 2.67 M solution of Jones' reagent (15 mL, 40 mmol). After stirring for 10 minutes, *i*-PrOH (5 mL) was added to quench the remaining oxidant. The reaction was diluted with ether (100 mL) and extracted with a 1:1 mixture of brine and saturated aqueous $NaHCO_3$ (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. Purification by flash chromatography (30:1 hexanes/EtOAc eluent) provided ynone **18** (4.47 g, 51% yield): R_F 0.56 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, J = 1.3, 0.8 Hz, 1H), 7.75-7.66 (m, 5H), 7.48-7.35 (m, 6H), 6.81 (dd, J = 1.9, 0.8 Hz, 1H), 3.88 (t, J = 6.6 Hz, 2H), 2.68 (t, J = 6.5 Hz, 2H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 150.6, 144.6, 135.7, 135.0, 133.4, 130.1, 129.8, 129.4, 128.0, 127.9, 108.6, 90.6, 80.8, 61.7, 27.0, 26.8, 23.4, 19.4; IR (film) 2931, 2858, 2217, 1642, 1428, 1308, 1164, 1112 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{25}H_{26}O_3Si]^+$: *m/z* 402.1651, found 402.1664.



18 ***14***

Vinyl Iodide 14. To a solution of ynone **18** (402 mg, 1.0 mmol) and LiI (147 g, 1.1 mmol) in MeCN (1.0 mL) was added concentrated AcOH (63 μL, 1.1 mmol). Following addition, the mixture was refluxed for 20 hours. The mixture was concentrated and purified by flash chromatography (50:1 to 4:1 hexanes/EtOAc eluent) to provide vinyl iodide **14** (302 mg, 57% yield): R_F 0.45 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.75-7.68 (m, 4H), 7.45 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.25-7.19 (m, 6H), 6.77 (t, *J* = 1.7 Hz, 1H), 6.72 (t, *J* = 1.1 Hz, 1H), 6.68 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.61 (dt, *J* = 5.9, 0.9 Hz, 2H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 182.5, 147.4, 144.7, 136.4, 136.3, 135.6, 134.1, 132.0, 130.5, 130.2, 129.2, 128.5, 128.2, 113.6, 109.6, 62.7, 51.2, 27.4, 27.3, 27.1, 19.8, 19.6; IR (film) 2930, 2857, 1662, 1591, 1428, 1157, 1112 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{25}H_{28}O_3SiI]^+$: *m/z* 531.0853, found 531.0856.

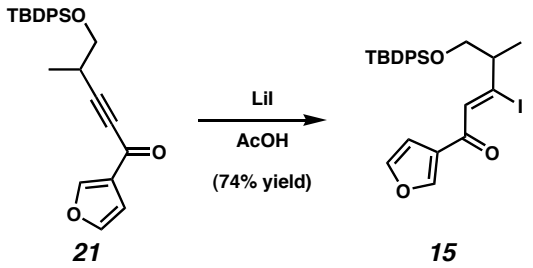


19 ***21***

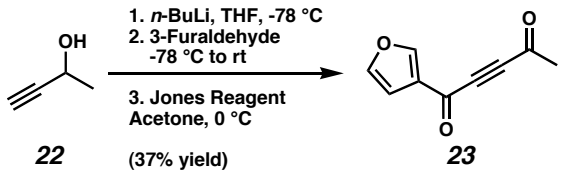
Ynone 21. To a cooled (0 °C) solution of PPh_3 (8.53 g, 32.5 mmol) in CH_2Cl_2 (10 mL) was added a solution of CBr_4 (5.4 g, 16.3 mmol) in CH_2Cl_2 (4 mL). After 10 minutes aldehyde **19**[3] (2.66 g, 8.13 mmol) in CH_2Cl_2 (6 mL) was slowly added. Following addition, the reaction was stirred for 4 hours at 0 °C. A spatula full of celite was added to the reaction mixture, which was then slowly poured onto a stirring solution of celite in petroleum ether (500 mL). The mixture was filtered, and the filtrate was concentrated and purified by flash chromatography on silica gel (20:1 petroleum ether/EtOAc eluent) to provide the vinyl dibromide (3.46 g, 91% yield) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.41 (m, 6H), 6.27 (d, *J* = 8.7 Hz, 1H), 3.55 (m, 2H), 2.69 (m, 1H), 1.06 (s, 9H), 1.04 (d, *J* = 6.9 Hz, 3H).

To a cooled (-78 °C) solution of the resulting vinyl dibromide (2.29 mg, 4.91 mmol) in THF (25 mL) was slowly added a 2.5 M solution of *n*-butyllithium in hexanes (4.3 mL, 10.8 mmol). After 15 minutes the mixture was warmed to 0 °C. Following addition, the reaction was stirred for 30 minutes at this temperature and then

cooled back to -78 °C. HMPA (2.5 μL) was added, and the mixture was stirred for 20 minutes. The reaction was then warmed to -40 °C, and a solution of Weinreb amide **20**[4] (1.73 g, 11.1 mmol) in THF (12.5 mL) was slowly added. The cold bath was allowed to warm to room temperature, and after 2.5 hours the reaction was quenched with saturated aqueous NH_4Cl (50 mL). The mixture was extracted with ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided ynone **21** (989.2 mg, 48% yield, 44% yield over 2 steps) as a clear oil: R_F 0.54 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.70-7.65 (m, 4H), 7.47-7.34 (m, 7H), 6.80 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.78 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.67 (dd, *J* = 9.7, 6.5 Hz, 1H), 2.95-2.82 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 150.6, 144.6, 135.8, 133.4, 133.4, 130.1, 129.4, 128.0, 108.6, 95.1, 80.6, 77.4, 67.0, 29.7, 27.0, 19.5, 16.7; IR (film) 2932, 2858, 2215, 1643, 1113 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{26}H_{27}O_3Si]^+$: *m/z* 415.1730, found 415.1727.

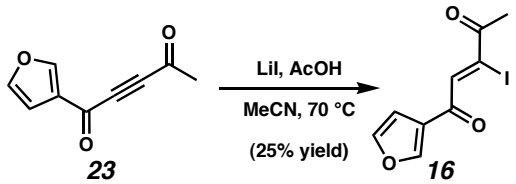


Vinyl Iodide 15. To a solution of ynone **21** (387 mg, 0.929 mmol) in concentrated AcOH (10 mL) was added LiI (250 mg, 1.86 mmol). Following addition, the mixture was stirred for 10 hours and then poured onto ice water (50 mL). Solid K_2CO_3 was added until bubbling ceased, and the mixture was extracted with Et_2O (4 x 50 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided vinyl iodide **15** (373.5 mg, 74% yield) as a yellow oil: R_F 0.50 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.78-7.71 (m, 4H), 7.54 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.27-7.20 (m, 6H), 6.83 (d, *J* = 0.8 Hz, 1H), 6.79 (t, *J* = 1.7 Hz, 1H), 6.70 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.68 (dd, *J* = 10.2, 7.6 Hz, 1H), 3.51 (dd, *J* = 10.1, 5.1 Hz, 1H), 2.31-2.19 (m, 1H), 1.12 (s, 9H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 183.4, 147.7, 144.7, 136.5, 136.3, 136.3, 134.3, 134.1, 131.1, 130.5, 130.5, 130.5, 129.0, 128.5, 123.4, 109.6, 67.9, 51.2, 27.4, 27.4, 19.9, 17.9; IR (film) 2931, 2858, 1664, 1590, 1156, 1112 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{26}H_{30}O_3SiI]^+$: *m/z* 545.1009, found 545.0997.



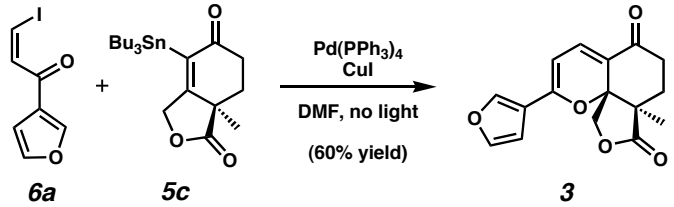
Ynone 23. Alcohol **22** (3.14 mL, 40 mmol) was dissolved in THF (80 mL) and cooled to -78 °C. A 2.5 M solution of *n*-butyllithium in hexanes (32 mL, 80 mmol) was slowly added. After 20 minutes, 3-furaldehyde (3.63 mL, 42 mmol) was slowly added. Following addition, the mixture was warmed to room temperature and stirred for 10 minutes. The reaction was quenched with 1N HCl (100). The mixture was concentrated to remove THF, and the resulting solution was extracted with ether (2 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting coupled alcohol was taken onto the next step without further purification.

The product from the previous step was dissolved in acetone (100 mL) and cooled to 0 °C. To this solution was added a 2.67 M solution of Jones' reagent (35 mL, 93 mmol). After stirring for 10 minutes, *i*-PrOH (5 mL) was added to quench the remaining oxidant. The reaction was diluted with ether (150 mL) and extracted with a 1:1 mixture of brine and saturated aqueous $NaHCO_3$ (150 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. Purification by flash chromatography (9:1 hexanes/EtOAc eluent) provided ynone **23** (2.37 g, 37% yield): R_F 0.37 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, J = 1.6, 0.8 Hz, 1H), 7.49 (t, J = 1.7 Hz, 1H), 6.83 (dd, J = 1.9, 0.8 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 169.4, 151.4, 145.4, 128.6, 108.3, 83.6, 83.0, 32.8; IR (film) 3133, 1681, 1641, 1556, 1510, 1305, 1200, 1156 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_9H_6O_3]^+$: *m/z* 162.0317, found 162.0321.

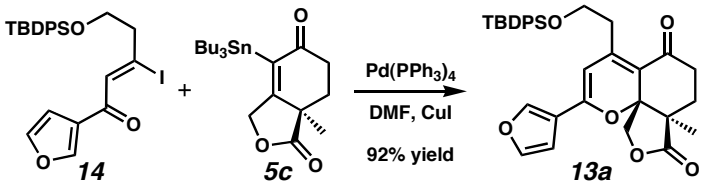


Vinyl Iodide 16. To a solution of ynone **23** (2.37 g, 14.6 mmol) and LiI (2.15 g, 16.1 mmol) in MeCN (160 mL) was added concentrated AcOH (922 µL, 1.1 mmol). Following addition, the mixture was refluxed for 20 hours. The mixture was concentrated and purified by flash chromatography (6:1 hexanes/EtOAc eluent) to provide vinyl iodide **16** (1.0 g, 25% yield): R_F 0.27 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 6.86 (dd, J = 1.3, 0.8 Hz, 1H), 6.65 (dd, J = 2.0, 1.5 Hz, 1H), 6.50 (s, 1H), 6.41 (dd, J = 2.1, 0.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 198.8, 180.7, 148.5, 144.8, 135.4, 127.4, 118.1, 109.2, 25.6; IR (film) 3134, 1706, 1654, 1576, 1512, 1156 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_9H_7O_3I]^+$: *m/z* 289.9440, found 289.9432.

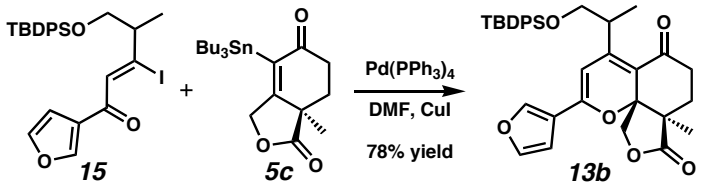
Synthesis of Tandem Stille-Oxa-Electrocyclization Products 3 and 13a-c



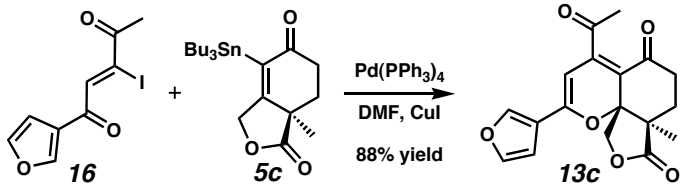
Polycycle 3. To a mixture containing $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol), vinyl stannane **5c** (9.0 g, 20.0 mmol), and vinyl iodide **6a** (6.13 g, 24.7 mmol) was added DMF (100 mL). Freshly recrystalized CuI (3.81 g, 20.0 mmol) was added, and the flask was cooled to -78 °C under vacuum. The reaction mixture was kept in the dark. After 30 minutes of degassing, the mixture was allowed to warm to room temperature under N_2. After stirring for 12 hours, the mixture was diluted with water (200 mL) and extracted with Et_2O (2 x 200 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (3:2 hexanes/EtOAc eluent) provided polycycle **3** (3.37g, 60% yield) as an orange solid: R_F 0.31 (1:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.45 (m, 1H), 7.35 (d, *J* = 6.6 Hz, 1H), 6.54 (m, 1H), 5.89 (d, *J* = 6.6 Hz, 1H), 4.80 (d, *J* = 11.1 Hz, 1H), 4.08 (d, *J* = 11.1 Hz, 1H), 2.51 (m, 2H), 2.06 (m, 2H), 1.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 178.8, 153.6, 144.4, 143.1, 134.5, 120.8, 118.0, 107.2, 99.2, 85.6, 71.6, 44.5, 32.9, 27.7, 14.3; 3131, 2947, 1782, 1673, 1561, 1526, 1160, 1015 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{16}H_{14}O_5]^+$: *m/z* 286.0841, found 286.0838.



Polycycle 13a. Vinyl stannane **5c** (1.78 g, 3.90 mmol) and vinyl iodide **14** (2.07 g, 3.90 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described above for the synthesis of polycycle **3**. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided polycycle **13a** (2.05g, 3.59 mmol) as an orange solid: R_F 0.26 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.66-7.61 (m, 4H), 7.45-7.32 (m, 7H), 6.46 (d, *J* = 2.1 Hz, 1H), 5.82 (s, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 3.97-3.88 (m, 3H), 3.10 (dt, *J* = 2.4, 6 Hz, 2H), 2.68-2.37 (m, 2H), 2.04-2.00 (m, 2H), 1.54 (s, 3H), 1.07 (s, 9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 179.2, 151.5, 144.3, 143.1, 135.6, 133.7, 133.6, 129.7, 172.7, 120.7, 113.9, 107.3, 105.5, 86.5, 71.53, 63.3, 44.9, 36.6, 35.0, 27.8, 26.9, 19.3, 14.9; IR (film) 2932, 2858, 1785, 1659, 1112 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $[C_{34}H_{37}O_6Si]^+$: 569.2359, found 569.2346.



Polycycle 13b (2 diastereomers). Vinyl stannane **5c** (611 mg, 1.34 mmol) and vinyl iodide **29** (665 mg, 1.22 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described above for the synthesis of polycycle **3**. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided a 1:1 diastereomeric mixture of polycycle **23** (554 mg, 78% yield) as an orange oil. *Diastereomer 1:* R_F 0.27 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.71-7.63 (m, 4H), 7.28 (d, *J* = 0.8 Hz, 1H); 7.21-7.18 (m, 6H), 6.85 (t, *J* = 1.7 Hz, 1H), 6.15 (s, 1H), 6.06 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.74 (s, 1H), 4.80-4.66 (m, 1H), 4.28 (d, *J* = 11.0 Hz, 1H), 3.69-3.55 (m, 2H), 3.30 (d, *J* = 11.0 Hz, 1H), 2.31-2.04 (m, 2H), 1.54-1.43 (m, 2H), 1.40 (s, 3H), 1.18-1.10 (m, 2H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 195.2, 178.8, 153.7, 152.3, 144.5, 143.4, 136.3, 136.2, 134.3, 134.2, 130.4, 130.3, 128.7, 128.5, 128.4, 128.3, 121.7, 116.5, 107.9, 99.8, 87.3, 71.0, 67.6, 45.5, 36.2, 36.0, 28.4, 27.3, 19.8, 15.6, 15.4; IR (film) 2930, 1784, 1654, 1522, 1110 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{35}H_{39}O_6Si]^+$: *m/z* 583.2516, found 583.2534. *Diastereomer 2:* R_F 0.23 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) d 7.84-7.75 (m, 4H), 7.28-7.20 (m, 6H), 6.83 (t, *J* = 1.8 Hz, 1H), 6.14 (s, 1H), 6.07 (t, *J* = 1.1 Hz, 1H), 5.93 (s, 1H), 4.72-4.62 (m, 1H), 4.47 (d, *J* = 11.0 Hz, 1H), 3.91 (d, *J* = 5.8 Hz, 2H), 3.48 (d, *J* = 11.0 Hz, 1H), 2.15-1.99 (m, 2H), 1.44-1.36 (m, 2H), 1.30 (s, 3H), 1.16 (s, 9H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) d 194.7, 178.7, 155.2, 152.3, 144.6, 143.5, 136.5, 136.4, 134.3, 134.3, 130.5, 121.7, 115.2, 107.7, 101.0, 87.5, 74.9, 71.1, 68.6, 45.3, 36.2, 35.8, 33.4, 28.0, 27.6, 27.5, 20.0, 15.9, 15.2; IR (film) 2931, 1784, 1657, 1515, 1112 cm^{-1}; HRMS (FAB$^+$) calc'd for $[C_{35}H_{39}O_6Si]^+$: *m/z* 583.2516, found 583.2533.

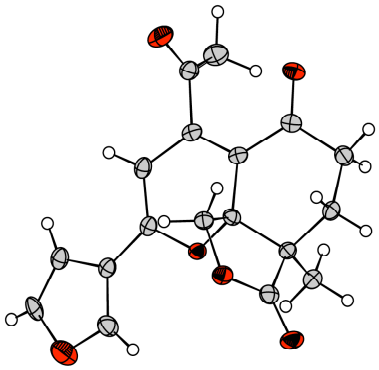


Polycycle 13c. Vinyl stannane **5c** (1.57 g, 3.45 mmol) and vinyl iodide **16** (1.0 g, 3.45 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described above for the synthesis of polycycle **3**. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided polycycle **13c** (1.0g, 88% yield) as an orange solid: R_F 0.26 (3:1 hexanes/EtOAc); R_F 0.24 (1:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 6.78 (t, *J* = 1.7 Hz, 1H), 6.18 (s, 1H), 5.90 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.36 (s, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 3.20 (d,

J = 11.2 Hz, 1H), 2.17 (s, 3H), 1.95-1.88 (m, 2H), 1.40-1.22 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 201.9, 192.8, 178.1, 154.9, 149.9, 145.1, 144.8, 144.2, 107.7, 98.3, 86.3, 70.5, 44.8, 33.4, 29.1, 27.7, 26.6, 14.4; IR (film) 3135, 2918, 1782, 1705, 1668, 1560, 1519, 1499, 1161 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_{18}H_{16}O_6]^+$: *m/z* 328.0947, found 328.0946.

Molecular Structure and Crystallographic Data for 13c

Figure S01. Pyran **13c** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 201414.



13C

Table 1. Crystal data and structure refinement for **13C** (CCDC 201414).

Empirical formula	$C_{18}H_{16}O_6$
Formula weight	328.31
Crystallization Solvent	Hexanes/ethylacetate
Crystal Habit	Fragment
Crystal size	0.28 x 0.22 x 0.15 mm^3
Crystal color	Yellow

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 7975 reflections used in lattice determination	2.26 to 28.15°
Unit cell dimensions	a = 12.3799(11) Å b = 7.2521(7) Å β= 101.892(2)° c = 17.2138(15) Å
Volume	1512.3(2) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.442 Mg/m^3
F(000)	688
Data collection program	Bruker SMART v5.054
θ range for data collection	1.86 to 28.22°
Completeness to θ = 28.22°	94.4 %
Index ranges	$-15 \le h \le 16$, $-9 \le k \le 9$, $-22 \le l \le 21$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	21320
Independent reflections	3525 [R_{int}= 0.0530]
Absorption coefficient	0.109 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9838 and 0.9701

Table 1 (cont.)

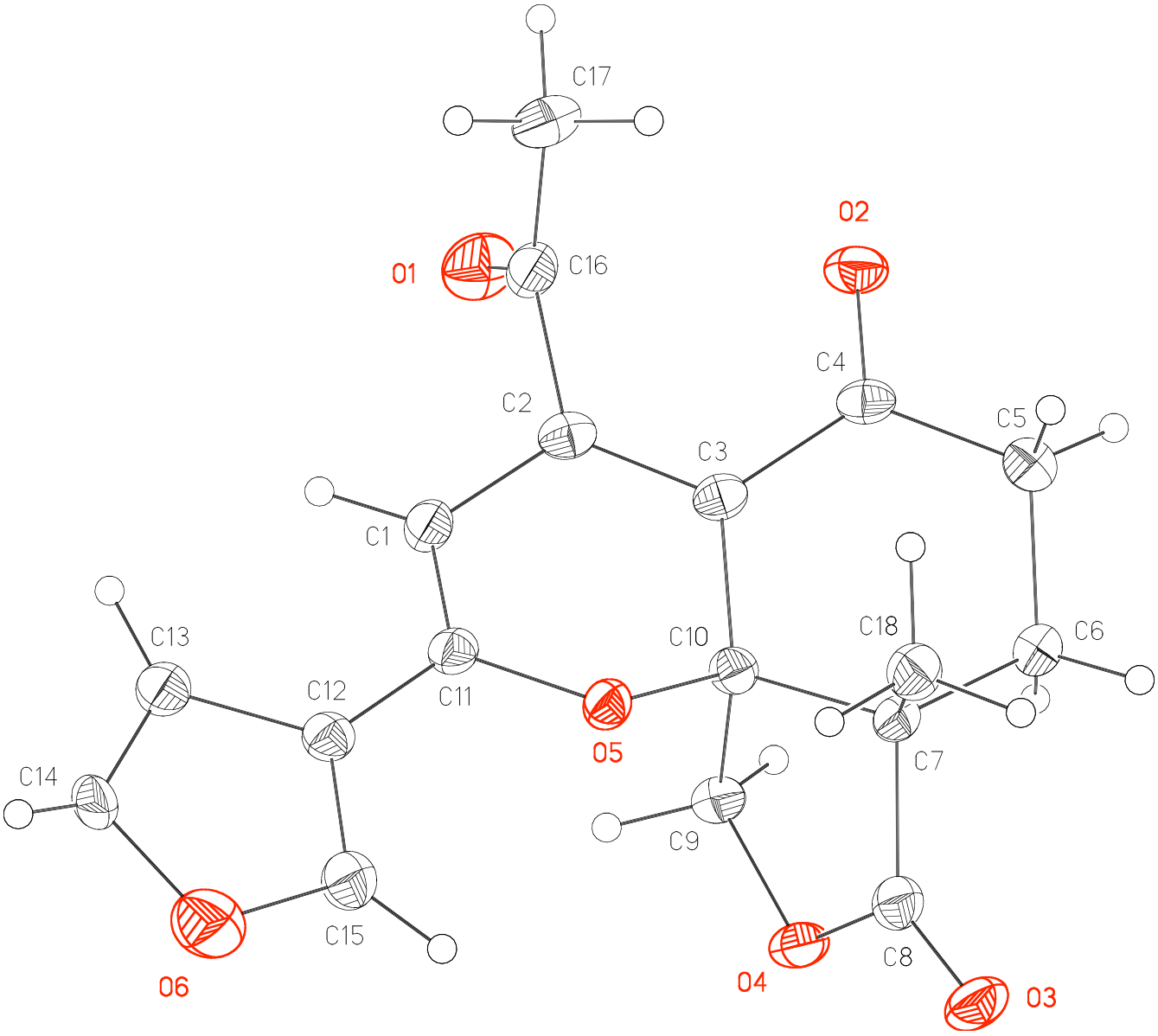
Structure solution and Refinement

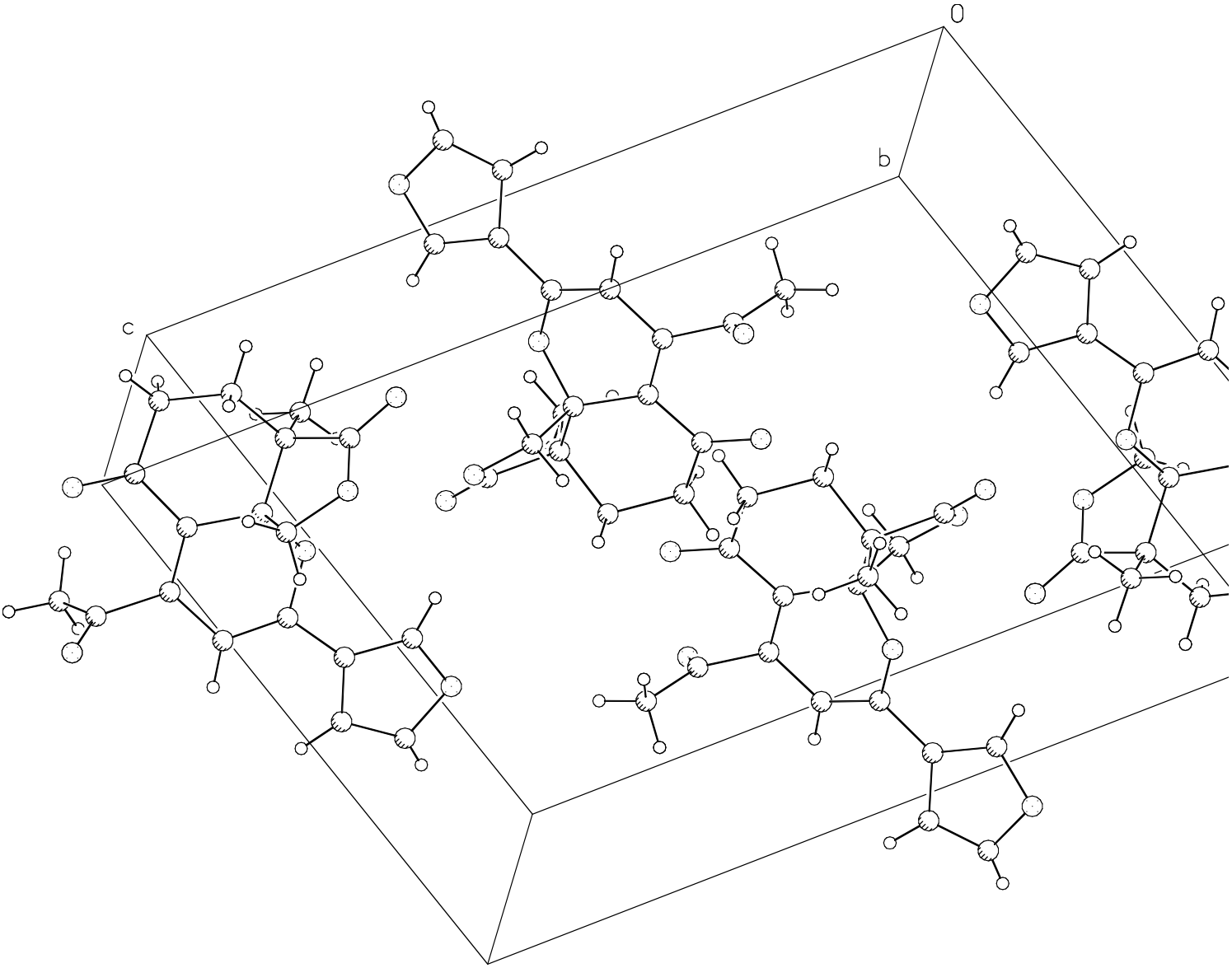
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3525 / 0 / 281
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.948
Final R indices [I>2σ(I), 2658 reflections]	R1 = 0.0425, *w*R2 = 0.0689
R indices (all data)	R1 = 0.0606, *w*R2 = 0.0710
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.376 and -0.393 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C17
O1
C16
O2
C4
C2
C5
C3
C1
C13
C18
C10
C6
C12
C11
O5
C7
C14
C9
C15
C8
O6
O4
O3


0
b
c

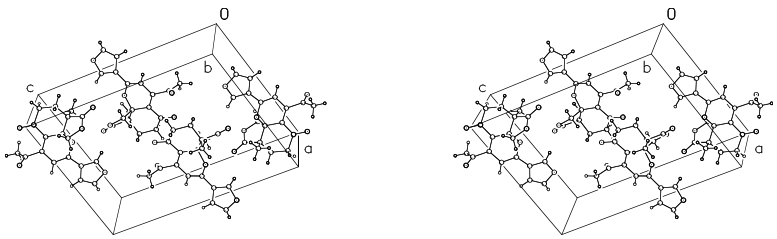

0
c
b
a
0
c
b
a

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 13C (CCDC 201414). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	7557(1)	-202(1)	-1544(1)	32(1)
O(2)	9763(1)	1794(1)	-583(1)	23(1)
O(3)	9007(1)	2746(1)	3057(1)	27(1)
O(4)	8289(1)	483(1)	2230(1)	22(1)
O(5)	7079(1)	2940(1)	971(1)	18(1)
O(6)	3873(1)	3651(2)	1211(1)	39(1)
C(1)	6423(1)	1692(2)	-309(1)	20(1)
C(2)	7531(1)	1661(2)	-435(1)	18(1)
C(3)	8392(1)	1951(2)	179(1)	17(1)
C(4)	9524(1)	2132(2)	62(1)	18(1)
C(5)	10385(1)	2853(2)	743(1)	22(1)
C(6)	10145(1)	2438(2)	1559(1)	21(1)
C(7)	8975(1)	3043(2)	1635(1)	17(1)
C(8)	8765(1)	2161(2)	2391(1)	21(1)
C(9)	8083(1)	134(2)	1380(1)	20(1)
C(10)	8135(1)	2030(2)	997(1)	17(1)
C(11)	6232(1)	2420(2)	372(1)	18(1)
C(12)	5164(1)	2845(2)	541(1)	18(1)
C(13)	4133(1)	2958(2)	1(1)	22(1)
C(14)	3386(1)	3403(2)	410(1)	23(1)
C(15)	4958(1)	3270(2)	1271(1)	25(1)
C(16)	7661(1)	1354(2)	-1282(1)	22(1)
C(17)	7785(2)	2990(2)	-1776(1)	29(1)
C(18)	8853(1)	5134(2)	1645(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for 13C (CCDC 201414).

O(1)-C(16)	1.2118(16)
O(2)-C(4)	1.2302(15)
O(3)-C(8)	1.2008(15)
O(4)-C(8)	1.3562(17)
O(4)-C(9)	1.4550(16)
O(5)-C(11)	1.3639(15)
O(5)-C(10)	1.4564(16)
O(6)-C(15)	1.3551(18)
O(6)-C(14)	1.3979(19)
C(1)-C(11)	1.3495(19)
C(1)-C(2)	1.433(2)
C(1)-H(1)	0.947(14)
C(2)-C(3)	1.3548(18)
C(2)-C(16)	1.5151(19)
C(3)-C(4)	1.4630(19)
C(3)-C(10)	1.5061(18)
C(4)-C(5)	1.507(2)
C(5)-C(6)	1.5238(19)
C(5)-H(5A)	1.013(14)
C(5)-H(5B)	0.982(15)
C(6)-C(7)	1.5453(19)
C(6)-H(6A)	0.963(14)
C(6)-H(6B)	1.007(14)
C(7)-C(8)	1.5191(19)
C(7)-C(10)	1.5352(18)
C(7)-C(18)	1.524(2)
C(9)-C(10)	1.5325(19)
C(9)-H(9A)	0.956(15)
C(9)-H(9B)	1.028(14)
C(11)-C(12)	1.4439(19)
C(12)-C(15)	1.367(2)
C(12)-C(13)	1.4186(19)
C(13)-C(14)	1.313(2)
C(13)-H(13)	0.963(14)
C(14)-H(14)	0.706(15)
C(15)-H(15)	0.951(15)
C(16)-C(17)	1.487(2)
C(17)-H(17A)	0.951(18)
C(17)-H(17B)	1.000(17)
C(17)-H(17C)	0.990(17)
C(18)-H(18A)	1.024(15)
C(18)-H(18B)	0.972(15)
C(18)-H(18C)	0.986(15)
C(8)-O(4)-C(9)	109.86(10)
C(11)-O(5)-C(10)	116.28(10)
C(15)-O(6)-C(14)	105.53(12)
C(11)-C(1)-C(2)	118.85(14)
C(11)-C(1)-H(1)	118.0(8)
C(2)-C(1)-H(1)	122.5(8)
C(3)-C(2)-C(1)	120.16(13)

C(3)-C(2)-C(16)	123.44(13)
C(1)-C(2)-C(16)	116.37(12)
C(2)-C(3)-C(4)	121.86(12)
C(2)-C(3)-C(10)	116.87(12)
C(4)-C(3)-C(10)	121.25(12)
O(2)-C(4)-C(3)	121.49(13)
O(2)-C(4)-C(5)	120.57(13)
C(3)-C(4)-C(5)	117.86(12)
C(4)-C(5)-C(6)	114.14(12)
C(4)-C(5)-H(5A)	105.8(8)
C(6)-C(5)-H(5A)	110.0(8)
C(4)-C(5)-H(5B)	108.1(8)
C(6)-C(5)-H(5B)	109.9(8)
H(5A)-C(5)-H(5B)	108.6(11)
C(5)-C(6)-C(7)	112.68(12)
C(5)-C(6)-H(6A)	109.4(8)
C(7)-C(6)-H(6A)	108.0(8)
C(5)-C(6)-H(6B)	107.4(8)
C(7)-C(6)-H(6B)	110.9(8)
H(6A)-C(6)-H(6B)	108.5(11)
C(8)-C(7)-C(10)	101.65(11)
C(8)-C(7)-C(18)	111.96(12)
C(10)-C(7)-C(18)	115.50(12)
C(8)-C(7)-C(6)	106.35(11)
C(10)-C(7)-C(6)	108.23(11)
C(18)-C(7)-C(6)	112.29(12)
O(3)-C(8)-O(4)	121.56(13)
O(3)-C(8)-C(7)	128.07(13)
O(4)-C(8)-C(7)	110.30(11)
O(4)-C(9)-C(10)	105.25(11)
O(4)-C(9)-H(9A)	107.7(9)
C(10)-C(9)-H(9A)	111.4(9)
O(4)-C(9)-H(9B)	111.4(8)
C(10)-C(9)-H(9B)	110.5(8)
H(9A)-C(9)-H(9B)	110.5(11)
O(5)-C(10)-C(3)	110.50(10)
O(5)-C(10)-C(7)	106.03(10)
C(3)-C(10)-C(7)	116.40(11)
O(5)-C(10)-C(9)	107.60(11)
C(3)-C(10)-C(9)	113.81(11)
C(7)-C(10)-C(9)	101.72(11)
C(1)-C(11)-O(5)	121.35(13)
C(1)-C(11)-C(12)	126.13(13)
O(5)-C(11)-C(12)	112.43(11)
C(15)-C(12)-C(13)	106.02(13)
C(15)-C(12)-C(11)	125.81(13)
C(13)-C(12)-C(11)	128.15(13)
C(14)-C(13)-C(12)	107.52(14)
C(14)-C(13)-H(13)	124.6(9)
C(12)-C(13)-H(13)	127.9(9)
C(13)-C(14)-O(6)	110.62(15)
C(13)-C(14)-H(14)	136.8(13)
O(6)-C(14)-H(14)	112.3(13)
O(6)-C(15)-C(12)	110.27(14)

O(6)-C(15)-H(15)	117.5(9)
C(12)-C(15)-H(15)	132.2(9)
O(1)-C(16)-C(2)	118.03(13)
O(1)-C(16)-C(17)	123.07(14)
C(2)-C(16)-C(17)	118.53(13)
C(16)-C(17)-H(17A)	108.8(10)
C(16)-C(17)-H(17B)	111.6(9)
H(17A)-C(17)-H(17B)	108.0(14)
C(16)-C(17)-H(17C)	112.2(9)
H(17A)-C(17)-H(17C)	107.1(13)
H(17B)-C(17)-H(17C)	108.9(13)
C(7)-C(18)-H(18A)	109.3(8)
C(7)-C(18)-H(18B)	111.6(8)
H(18A)-C(18)-H(18B)	110.3(12)
C(7)-C(18)-H(18C)	108.4(8)
H(18A)-C(18)-H(18C)	109.7(12)
H(18B)-C(18)-H(18C)	107.5(12)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 13C (CCDC 201414). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	418(7)	297(6)	249(6)	-92(5)	72(5)	-20(5)
O(2)	260(6)	276(6)	180(6)	23(4)	93(5)	30(5)
O(3)	301(6)	360(6)	136(6)	-24(5)	30(5)	22(5)
O(4)	269(6)	256(6)	146(5)	28(4)	46(4)	-23(5)
O(5)	162(5)	229(5)	155(5)	-18(4)	26(4)	11(4)
O(6)	329(7)	498(8)	371(7)	25(6)	133(6)	42(6)
C(1)	194(8)	211(8)	173(8)	14(6)	1(7)	-24(6)
C(2)	248(8)	126(7)	164(8)	9(6)	48(6)	5(6)
C(3)	213(8)	148(7)	151(7)	7(6)	39(6)	16(6)
C(4)	236(8)	154(7)	168(8)	44(6)	59(6)	28(6)
C(5)	194(9)	256(9)	220(8)	8(7)	61(7)	-4(7)
C(6)	186(8)	250(9)	167(8)	1(6)	13(7)	-14(7)
C(7)	167(8)	212(8)	135(7)	-3(6)	22(6)	0(6)
C(8)	167(8)	257(8)	195(8)	10(6)	34(6)	40(6)
C(9)	216(9)	234(8)	152(8)	7(6)	42(7)	-15(7)
C(10)	154(7)	188(7)	165(7)	7(6)	45(6)	26(6)
C(11)	197(8)	162(7)	161(7)	31(6)	19(6)	-21(6)
C(12)	206(8)	160(7)	184(8)	13(6)	40(6)	-20(6)
C(13)	241(9)	205(8)	216(9)	33(6)	25(7)	-47(7)
C(14)	113(9)	313(9)	256(9)	79(7)	35(7)	21(7)
C(15)	195(9)	326(9)	236(9)	5(7)	47(7)	30(7)
C(16)	189(8)	270(9)	177(8)	-14(6)	15(6)	19(7)
C(17)	360(11)	336(10)	175(9)	44(7)	42(8)	8(9)
C(18)	228(9)	234(8)	207(9)	-31(7)	36(7)	-18(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 13C (CCDC 201414).

	x	y	z	U_{iso}
H(1)	5805(11)	1389(18)	-713(8)	19(4)
H(5A)	10412(11)	4230(20)	661(8)	28(4)
H(5B)	11101(12)	2324(19)	701(8)	25(4)
H(6A)	10670(12)	3082(19)	1959(8)	23(4)
H(6B)	10250(11)	1070(20)	1653(8)	19(4)
H(9A)	7364(13)	-399(19)	1229(8)	28(4)
H(9B)	8668(12)	-733(19)	1235(8)	22(4)
H(13)	3987(12)	2801(19)	-567(9)	28(4)
H(14)	2817(13)	3610(20)	328(9)	27(5)
H(15)	5430(12)	3399(19)	1778(9)	27(4)
H(17A)	7096(15)	3620(20)	-1906(10)	47(5)
H(17B)	8001(13)	2630(20)	-2283(10)	44(5)
H(17C)	8333(13)	3880(20)	-1492(9)	38(5)
H(18A)	8984(11)	5666(19)	1121(9)	26(4)
H(18B)	8131(13)	5499(19)	1731(8)	25(4)
H(18C)	9410(12)	5627(19)	2091(9)	27(4)

References

[1] For the synthesis of **7**, see: Knight, D. W.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 635-640.
[2] For the synthesis of **8**, see: Piers, E.; Wong, T.; Coish, P.; Rogers, C. *Can. J. Chem.* **1994**, *72*, 1816-1819.
[3] For the synthesis of **19**, see: Kiyooka, S; Shahid, K. A.; Goto, F.; Okazaki, M.; Shuto, Y. *J. Org. Chem.* **2003**, *68*, 7967-7978.
[4] For the synthesis of **20**, see: Kinoshita, T.; Ichinari, D.; Sinya, J. *J. Heterocycl. Chem.* **1996**, *33*, 1313-1317.

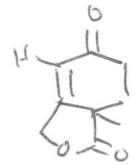
uktXV-127C

Automation directory:
/export/home/alluser/auto/auto_21.07.04
File : 4802

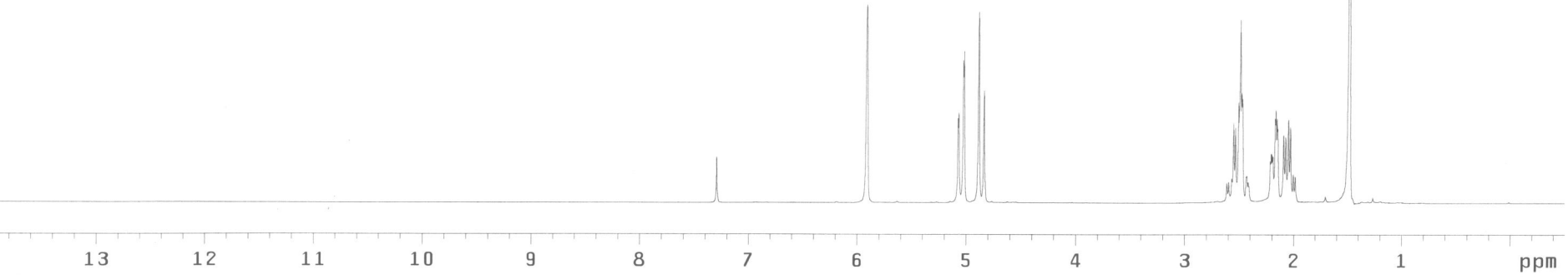
Pulse Sequence: s2pul
Solvent: cdcl3

Temp. 25.9 C / 299.1 K
Sample #48

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
32 repetitions
OBSERVE H1, 300.0865730 MHz
DATA PROCESSING
FT size 32768
Total time 3 min



5a

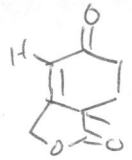


uktXV-127C

Automation directory:
/export/home/alluser/auto/auto_21.07.04
File : 4803

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Sample #48

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
64 repetitions
OBSERVE C13, 75.4568288 MHz
DECOUPLE H1, 300.0881168 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



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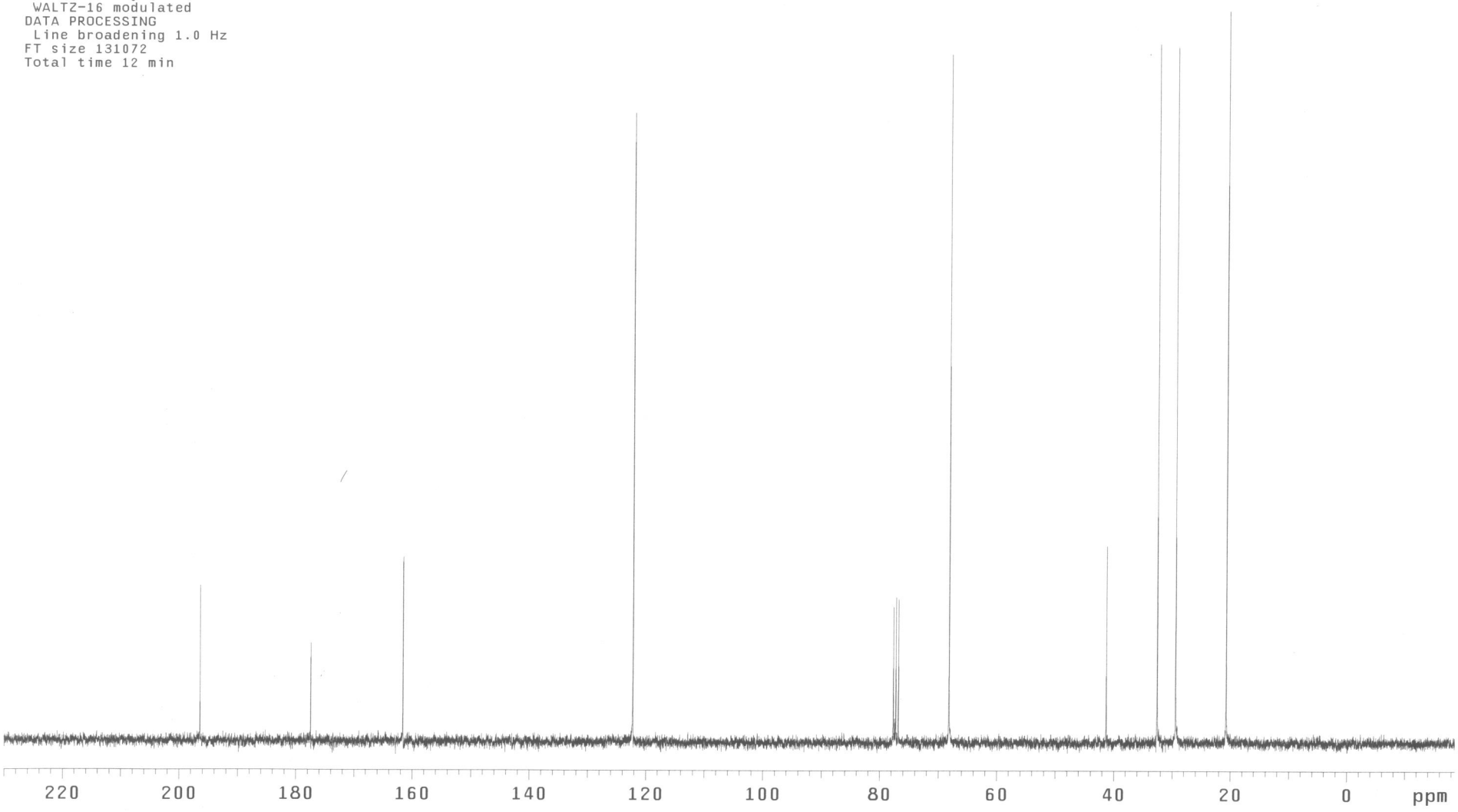


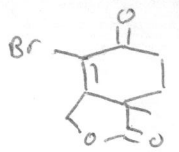
uktVII-57B2

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-14
File: uktVII-57B2_proton

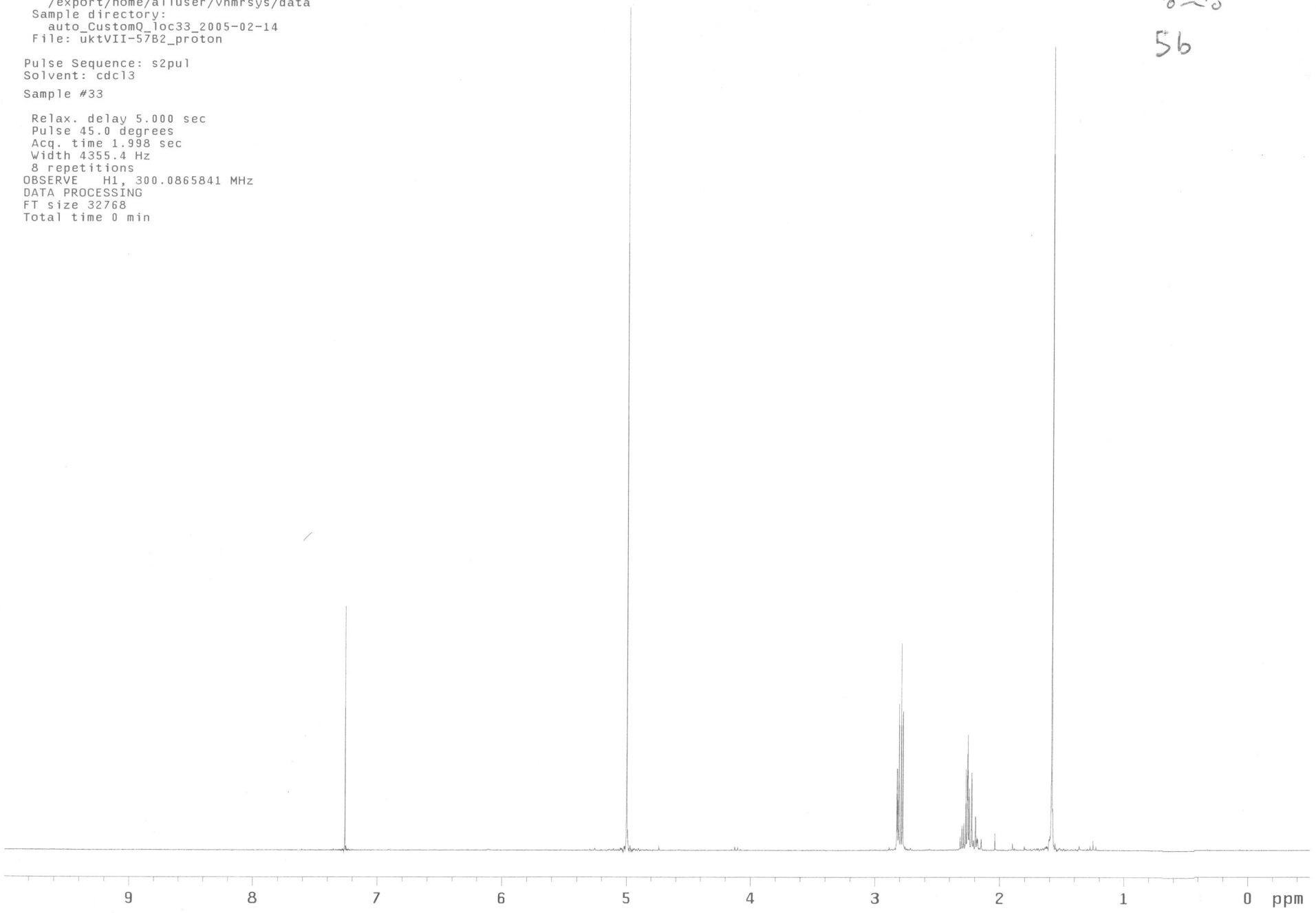
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
8 repetitions
OBSERVE H1, 300.0865841 MHz
DATA PROCESSING
FT size 32768
Total time 0 min



5b



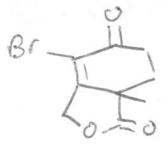
uktVII-57B2

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-14
File: uktVII-57B2_carbon

Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4568154 MHz
DECOUPLE H1, 300.0881168 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



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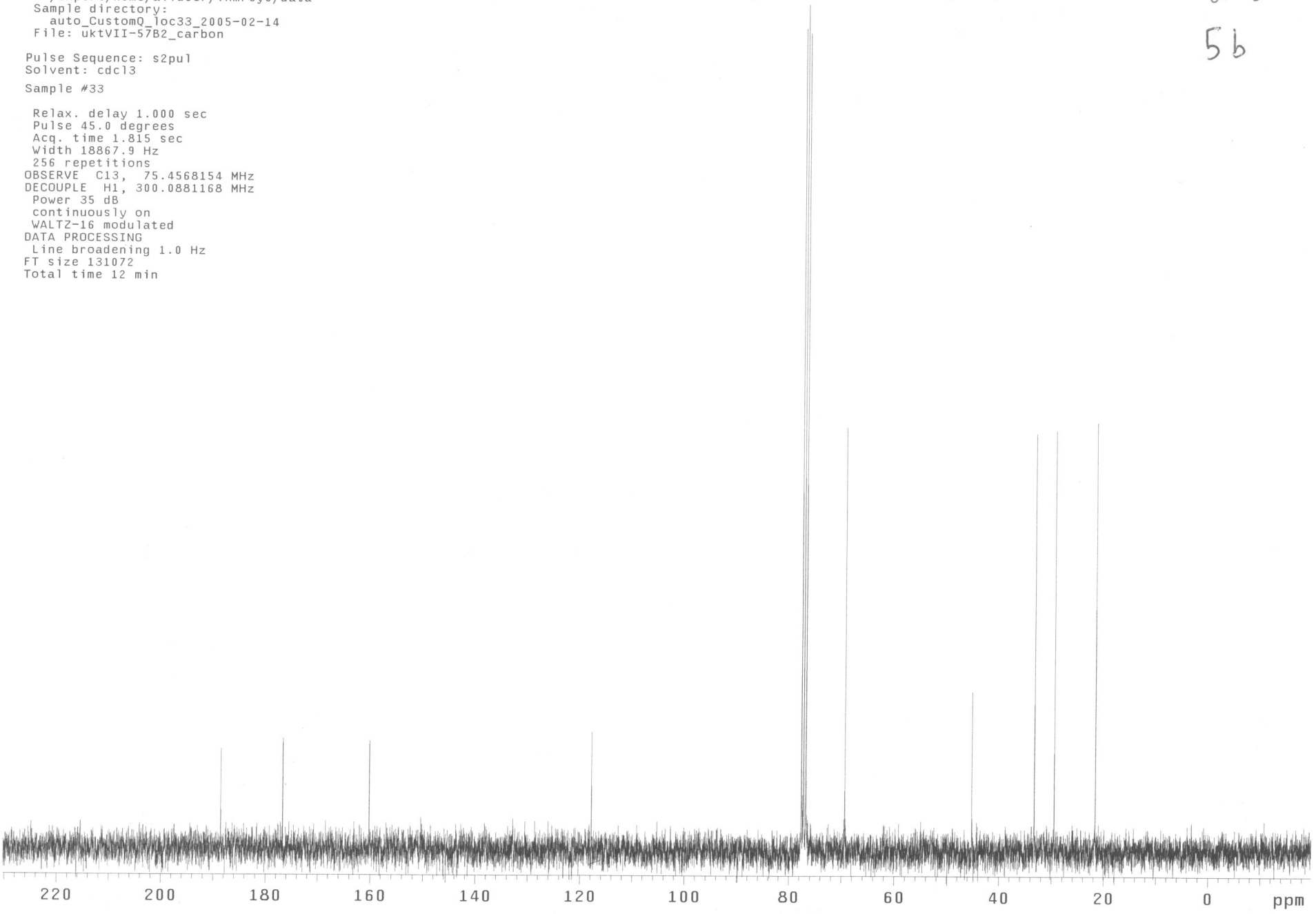
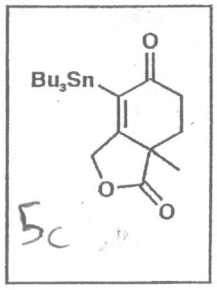
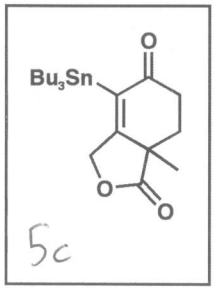




^{1}H NMR Spectrum of Bicyclic Stannane 5c (300 MHz, CDCl3).



^{13}C NMR Spectrum of Bicyclic Stannane 5c (75 MHz, $CDCl_3$).

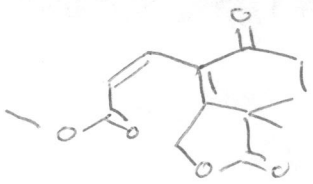
uktXX-59C1

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc34_2005-03-06
File: uktXX-59C1_proton

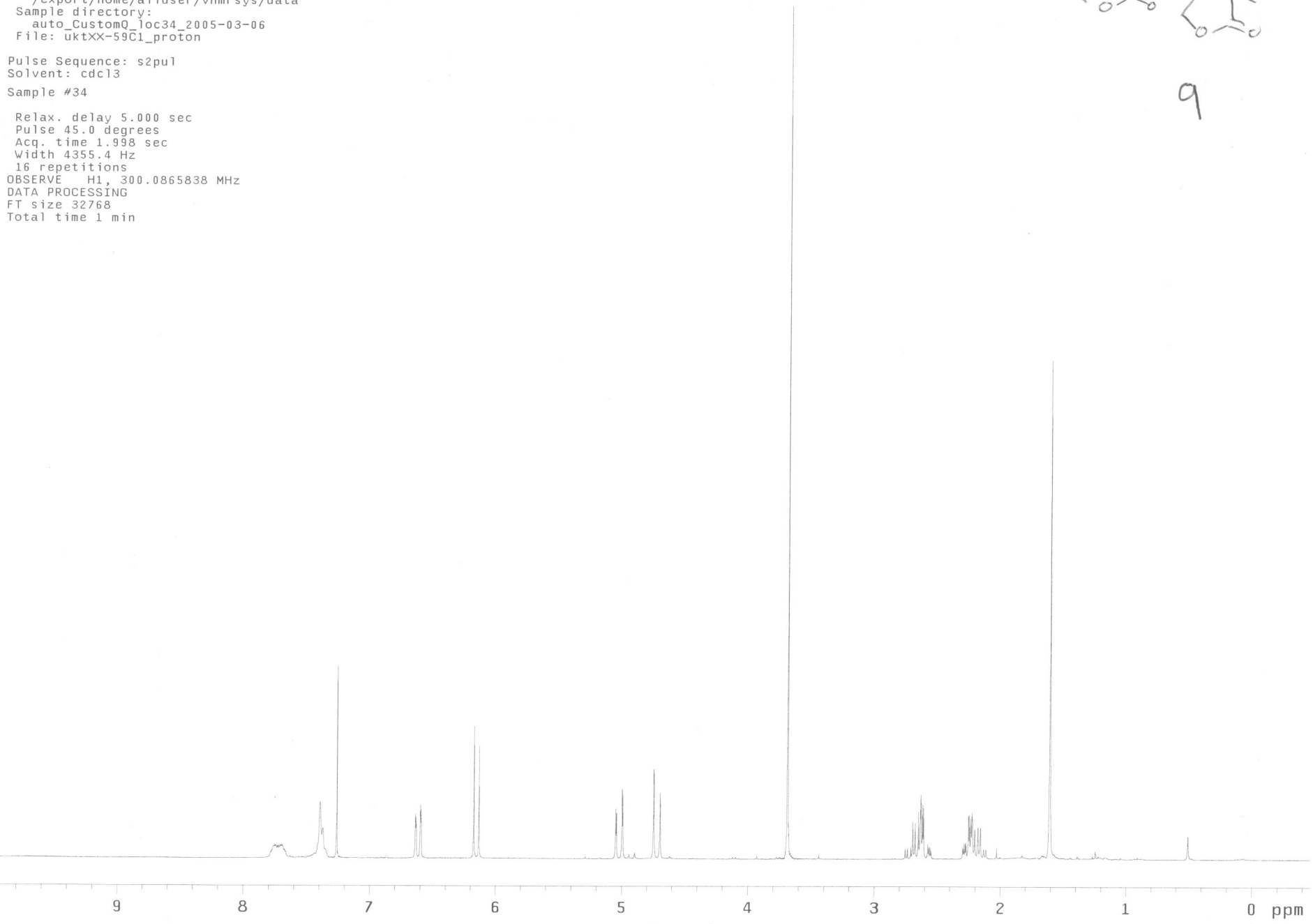
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #34

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865838 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



9



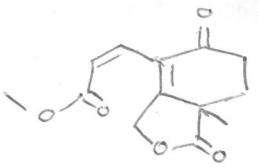
uktXX-59C1

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc34_2005-03-06
File: uktXX-59C1_carbon

Pulse Sequence: s2pul
Solvent: cdcl3

Sample #34

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
512 repetitions
OBSERVE C13, 75.4568174 MHz
DECOUPLE H1, 300.0881168 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 24 min



9

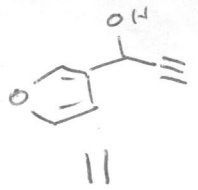
uktIII-287Bii

Automation directory:
/export/home/alluser/auto/auto_22.07.04
File : 3303

Pulse Sequence: s2pul
Solvent: cdcl3

Temp. 26.1 C / 299.2 K
Sample #33

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
32 repetitions
OBSERVE H1, 300.0865730 MHz
DATA PROCESSING
FT size 32768
Total time 3 min



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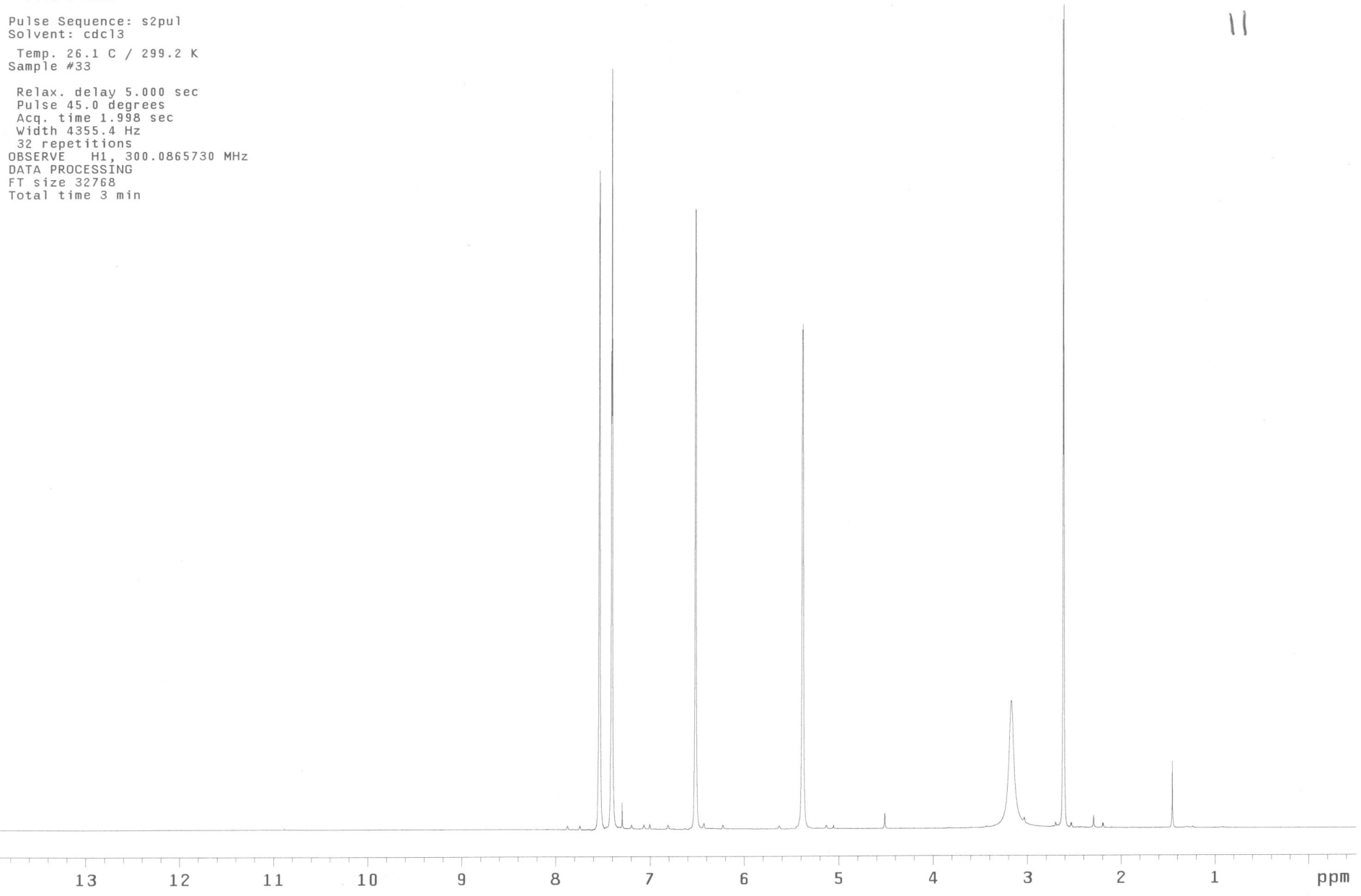


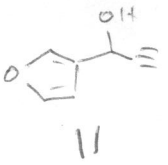
uktIII-287Bii

Automation directory:
/export/home/alluser/auto/auto_22.07.04
File : 3304

Pulse Sequence: s2pul
Solvent: cdcl3

Temp. 26.1 C / 299.2 K
Sample #33

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
64 repetitions
OBSERVE C13, 75.4568288 MHz
DECOUPLE H1, 300.0881168 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



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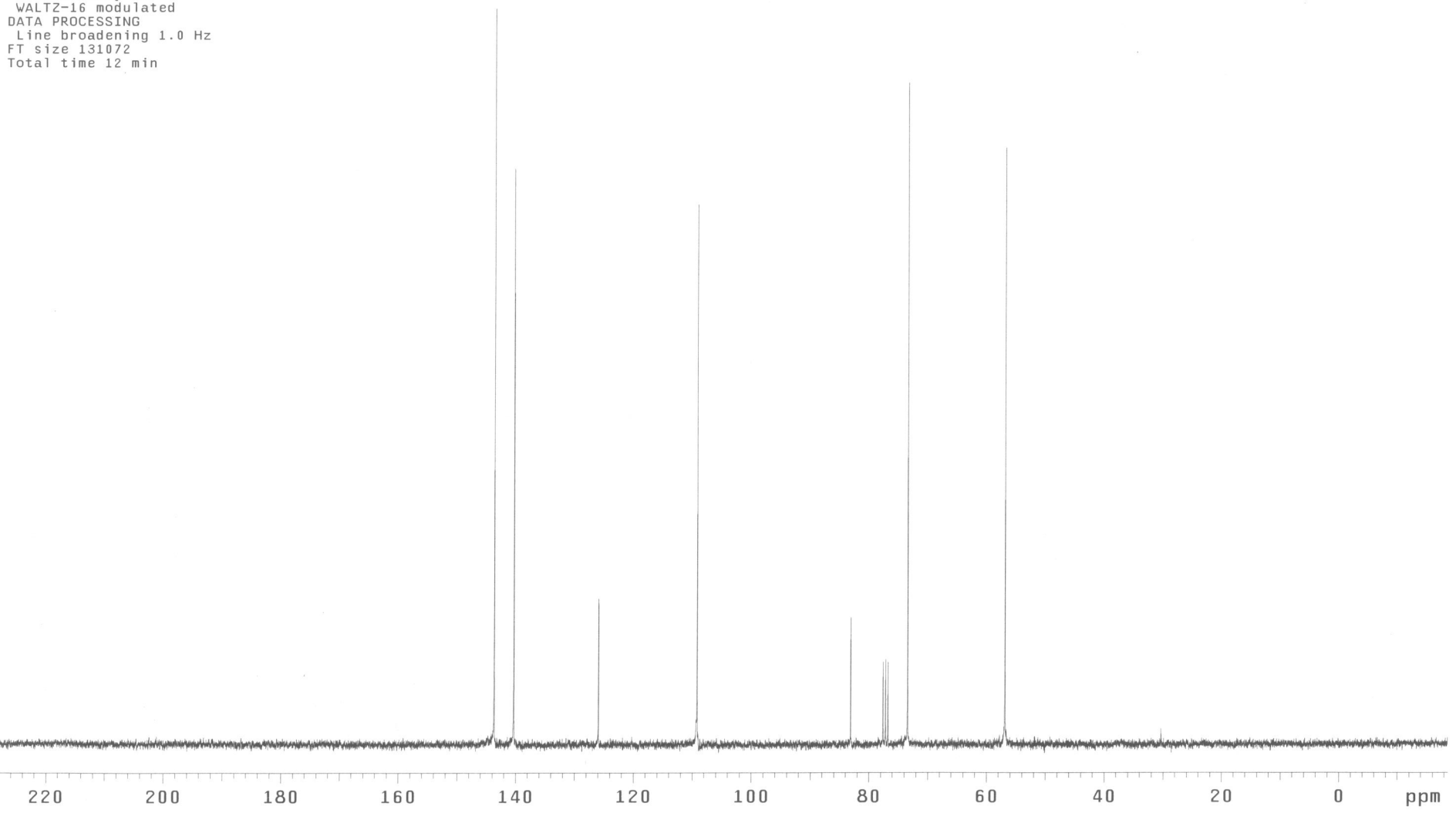
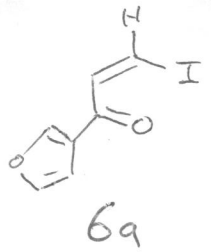


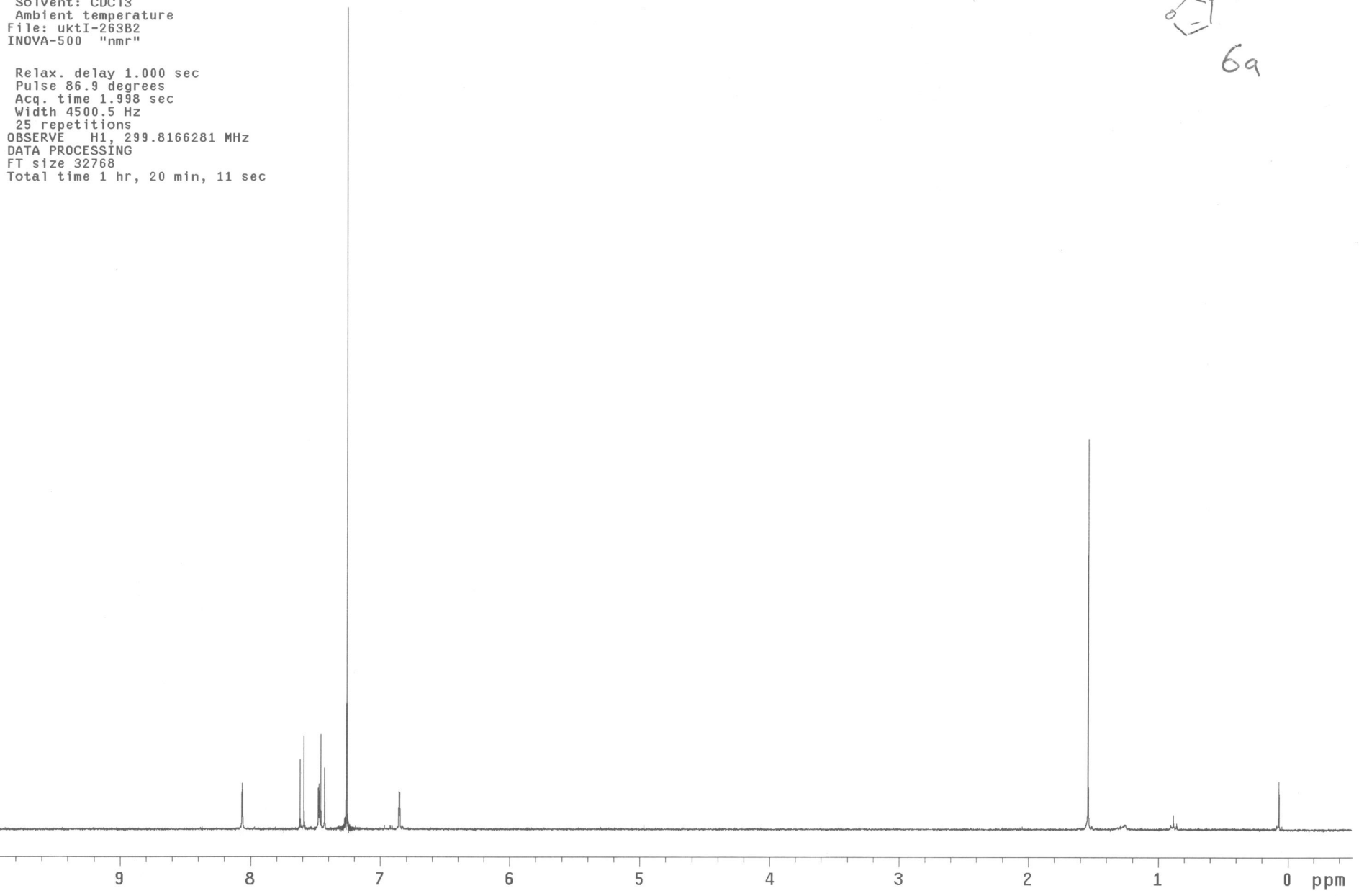
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: uktI-263B2
INOVA-500 "nmr"

Relax. delay 1.000 sec
Pulse 86.9 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
25 repetitions
OBSERVE H1, 299.8166281 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 20 min, 11 sec



6a



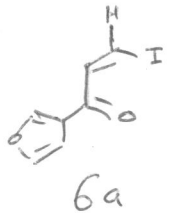
uktIV-75B1

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc28_2005-02-28
File: uktIV-75B1_carbon

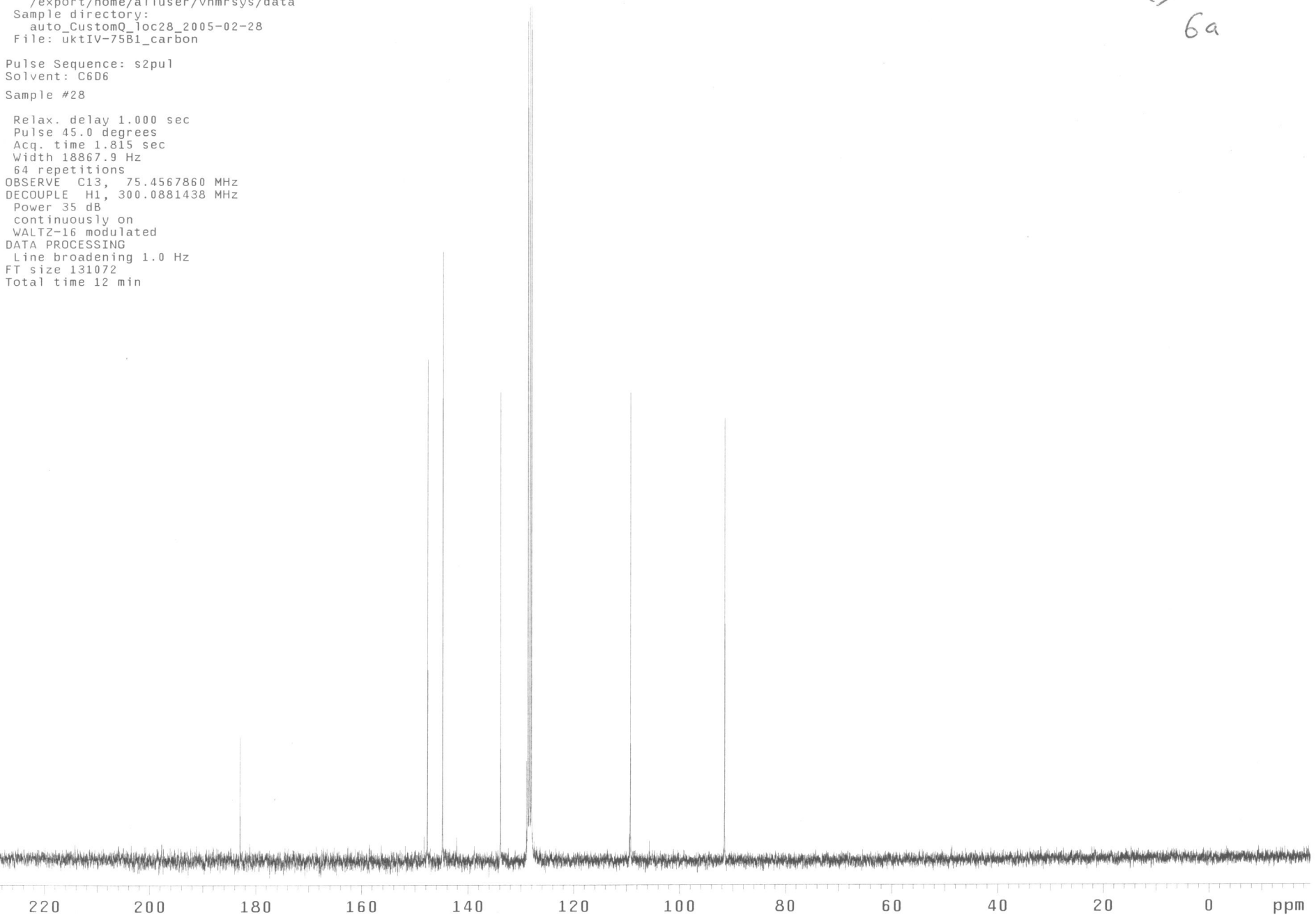
Pulse Sequence: s2pul
Solvent: C6D6

Sample #28

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
64 repetitions
OBSERVE C13, 75.4567860 MHz
DECOUPLE H1, 300.0881438 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



6a



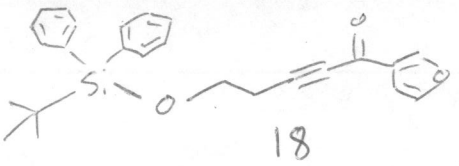
uktVII-205B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-15
File: uktVII-205B_proton

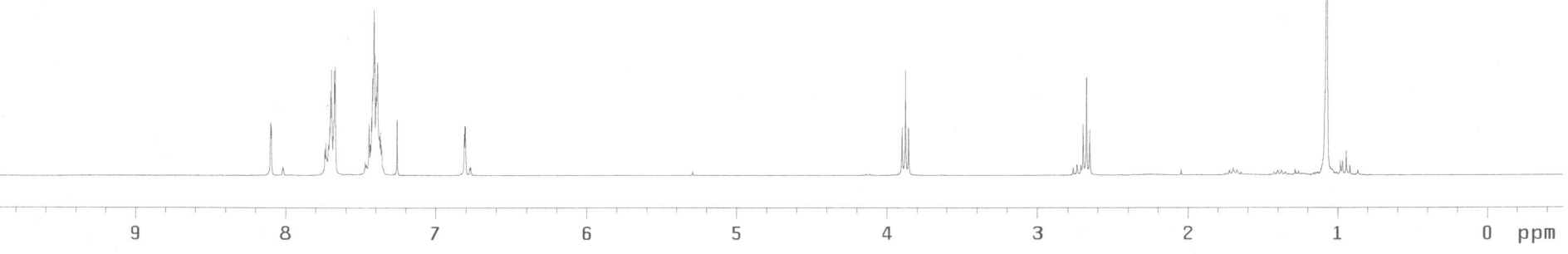
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865844 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



18



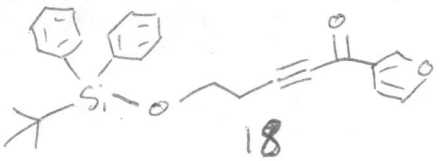
uktVII-205B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-15
File: uktVII-205B_carbon

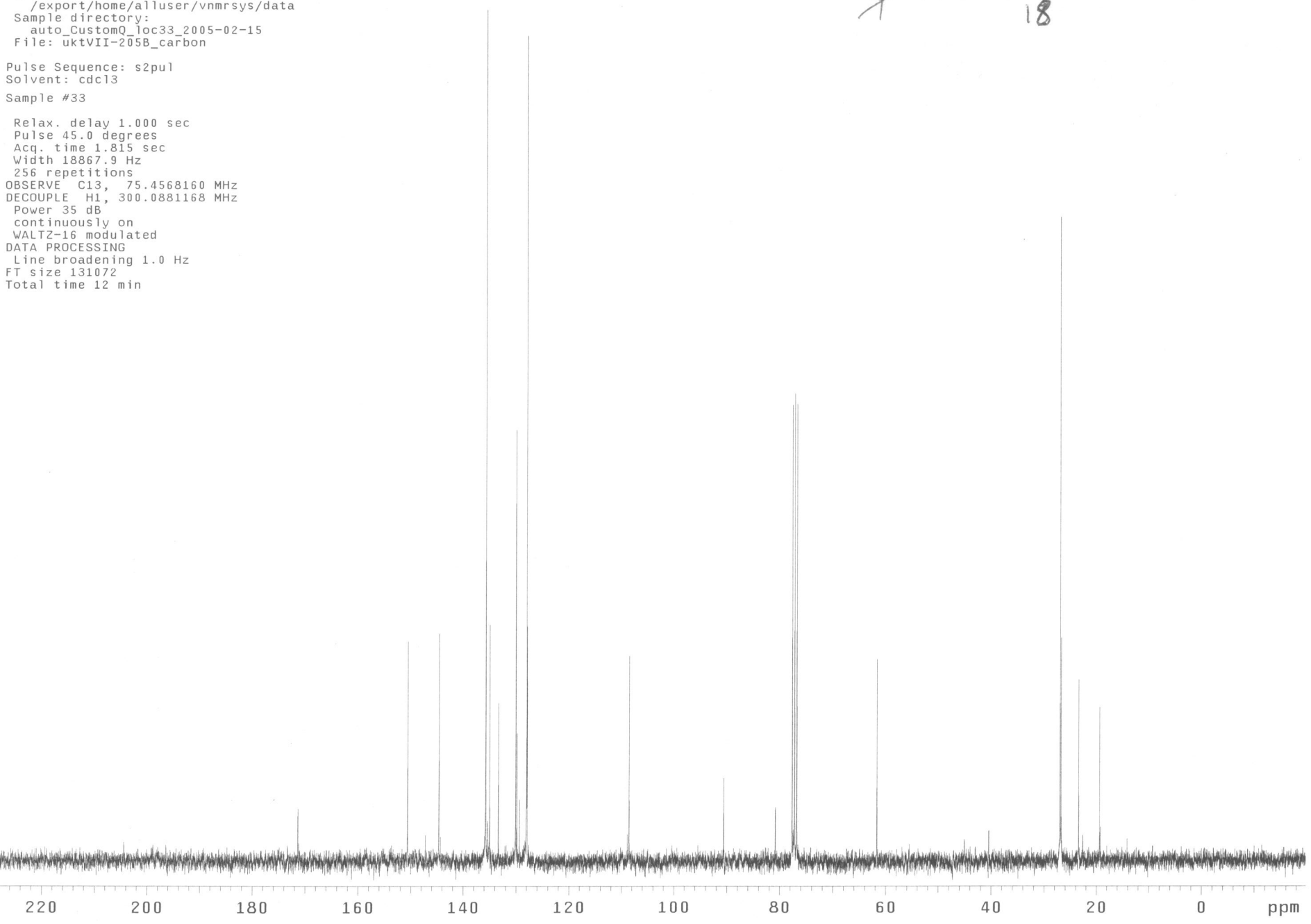
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4568160 MHz
DECOUPLE H1, 300.0881168 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



18



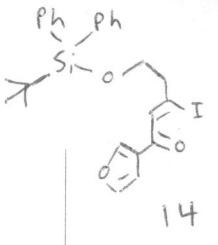
uktXX-51B1ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc7_2005-02-17
File: uktXX-51B1ii_proton

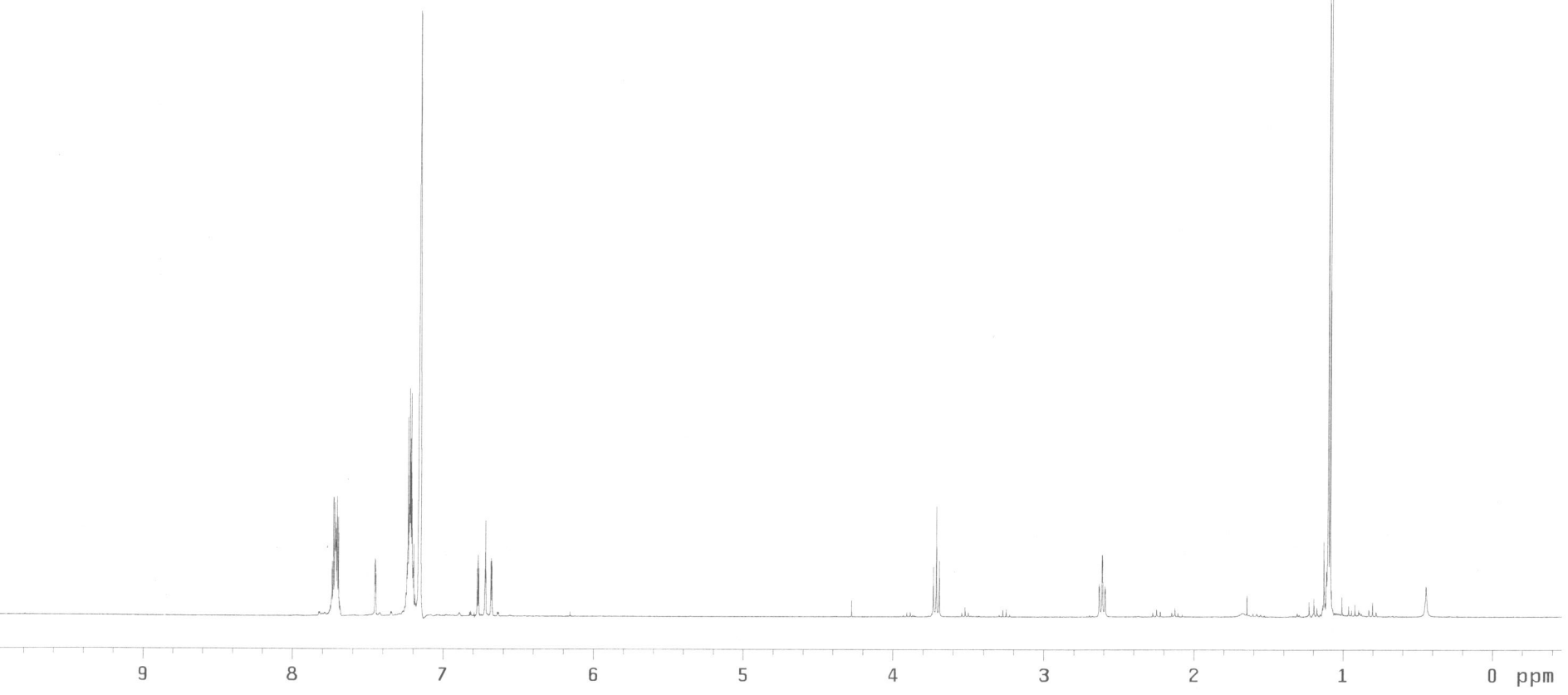
Pulse Sequence: s2pul
Solvent: C6D6

Sample #7

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865986 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



14



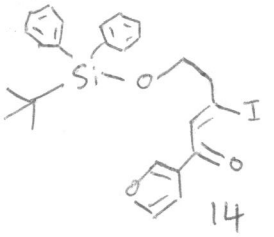
uktXX-51B1ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc7_2005-02-17
File: uktXX-51B1ii_carbon

Pulse Sequence: s2pul
Solvent: C6D6

Sample #7

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
5000 repetitions
OBSERVE C13, 75.4567831 MHz
DECOUPLE H1, 300.0881438 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 hr, 2 min



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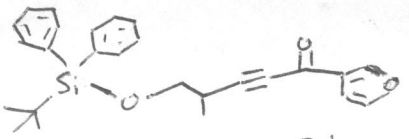
uktX-137B1ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-15
File: uktX-137B1ii_proton

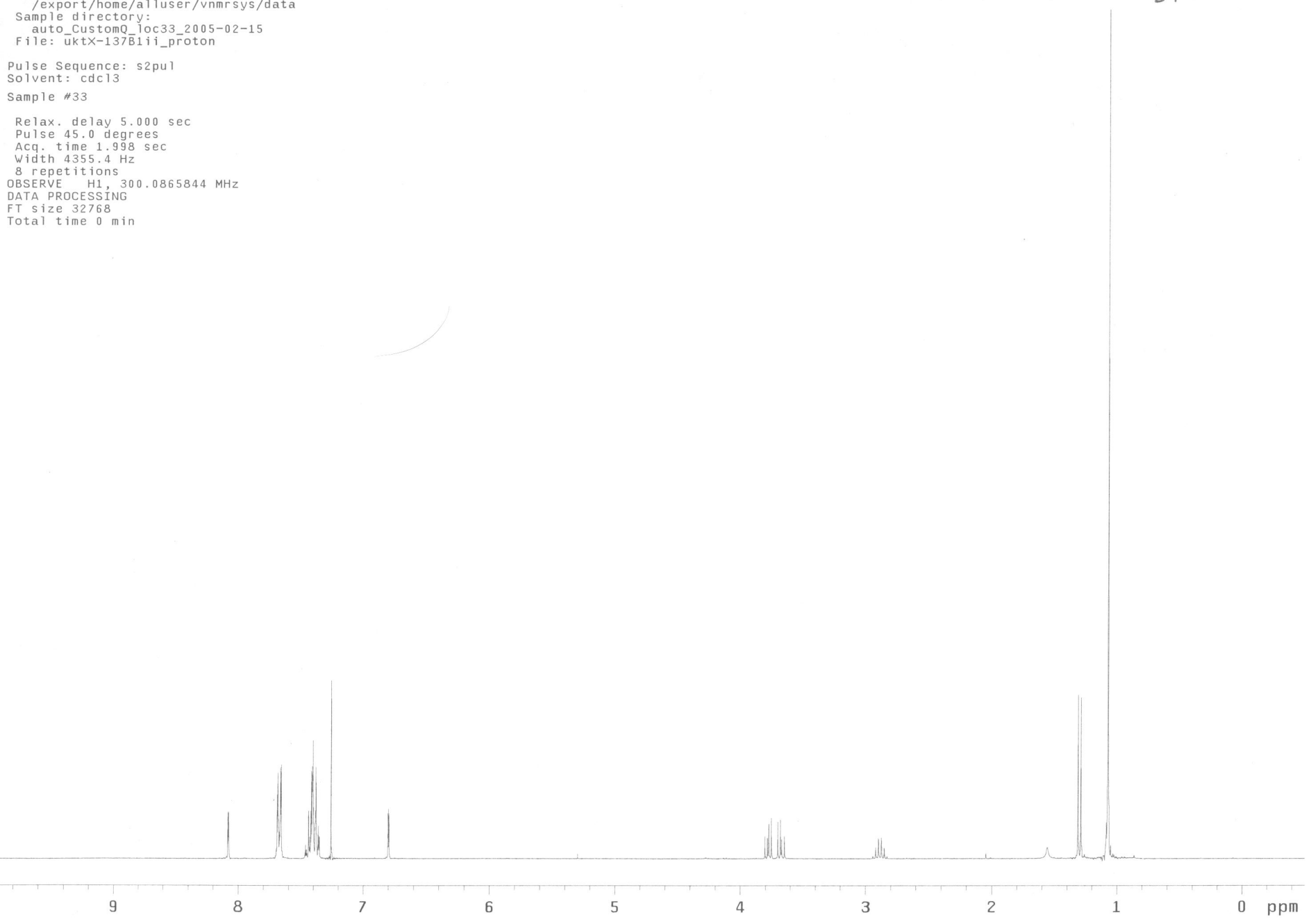
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
8 repetitions
OBSERVE H1, 300.0865844 MHz
DATA PROCESSING
FT size 32768
Total time 0 min



21



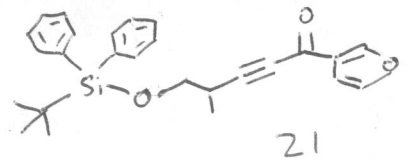
uktX-137B1ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc33_2005-02-15
File: uktX-137B1ii_carbon

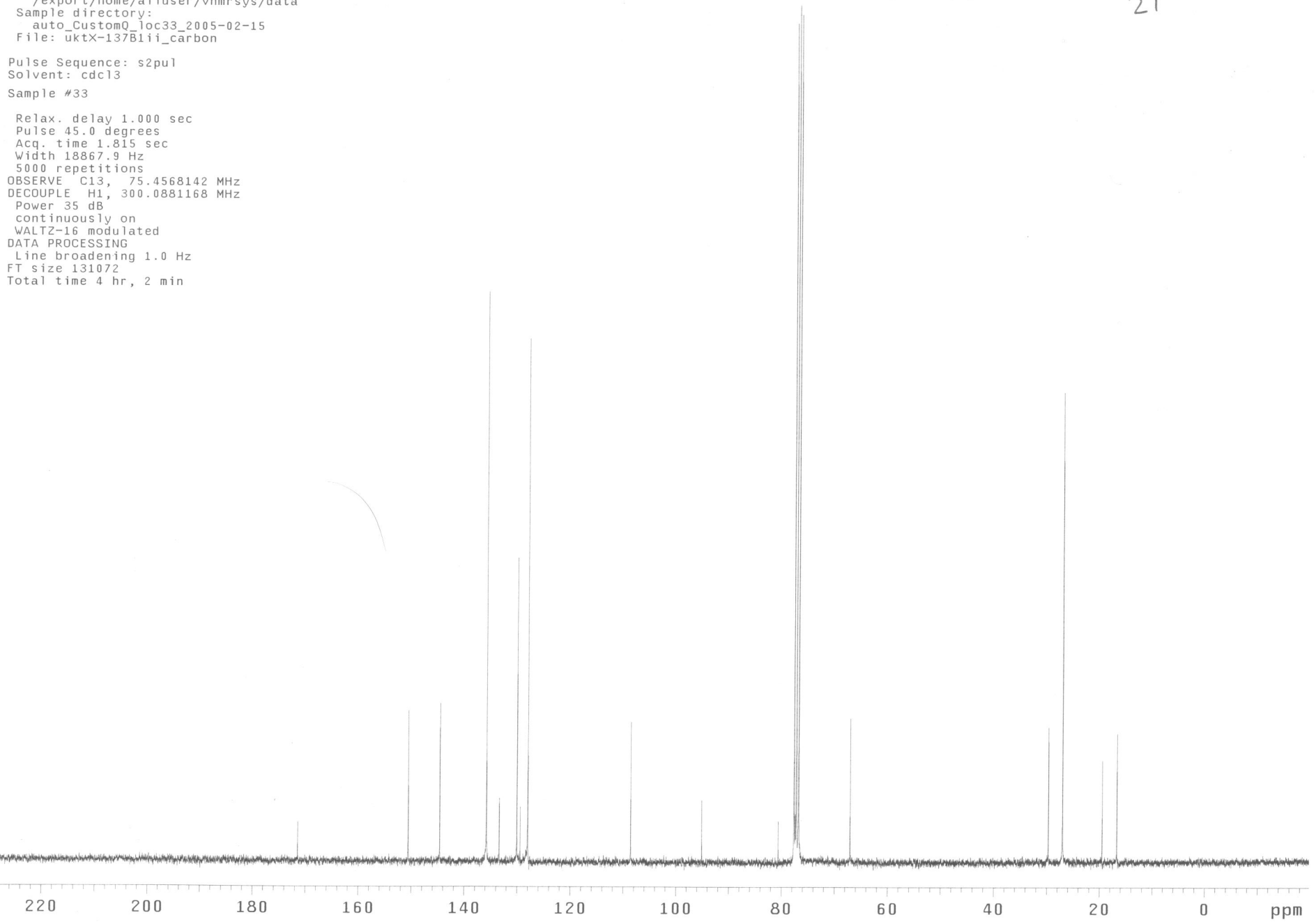
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #33

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
5000 repetitions
OBSERVE C13, 75.4568142 MHz
DECOUPLE H1, 300.0881168 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 hr, 2 min



21



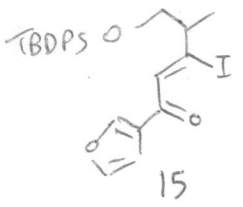
uktXX-47B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc40_2005-02-16
File: uktXX-47B_proton

Pulse Sequence: s2pul
Solvent: C6D6

Sample #40

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865986 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



15

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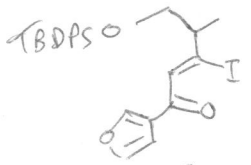
uktXX-47B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc40_2005-02-16
File: uktXX-47B_carbon

Pulse Sequence: s2pul
Solvent: C6D6

Sample #40

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4567837 MHz
DECOUPLE H1, 300.0881438 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



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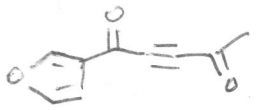
uktXX-55C1

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc34_2005-03-01
File: uktXX-55C1_proton

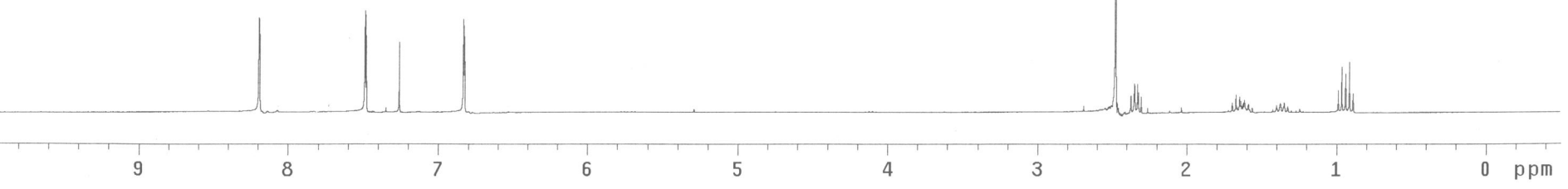
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #34

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865841 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



23



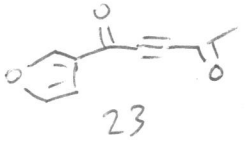
uktXX-55C1

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc34_2005-03-01
File: uktXX-55C1_carbon

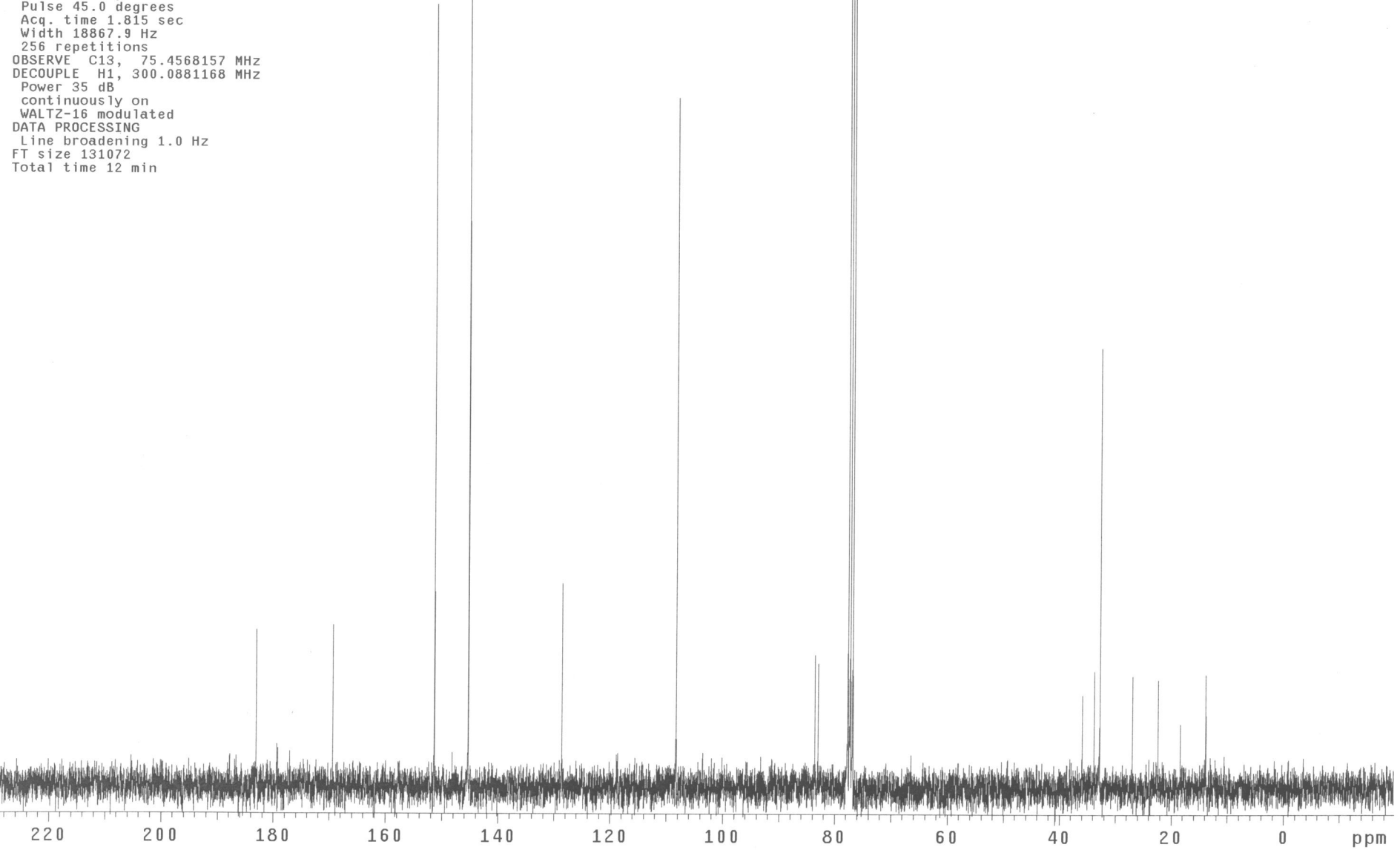
Pulse Sequence: s2pul
Solvent: cdcl3

Sample #34

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4568157 MHz
DECOUPLE H1, 300.0881168 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min



23



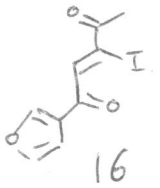
uktXX-57B2ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc4_2005-03-02
File: uktXX-57B2ii_proton

Pulse Sequence: s2pul
Solvent: C6D6

Sample #4

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865983 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



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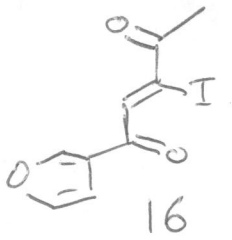
uktXX-57B2ii

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc4_2005-03-02
File: uktXX-57B2ii_carbon

Pulse Sequence: s2pul
Solvent: C6D6

Sample #4

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
5000 repetitions
OBSERVE C13, 75.4567834 MHz
DECOUPLE H1, 300.0881438 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 hr, 2 min



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STANDARD PROTON PARAMETERS

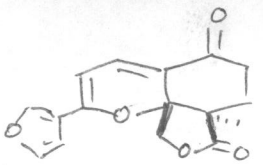
Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: tkI-tricycle-H1

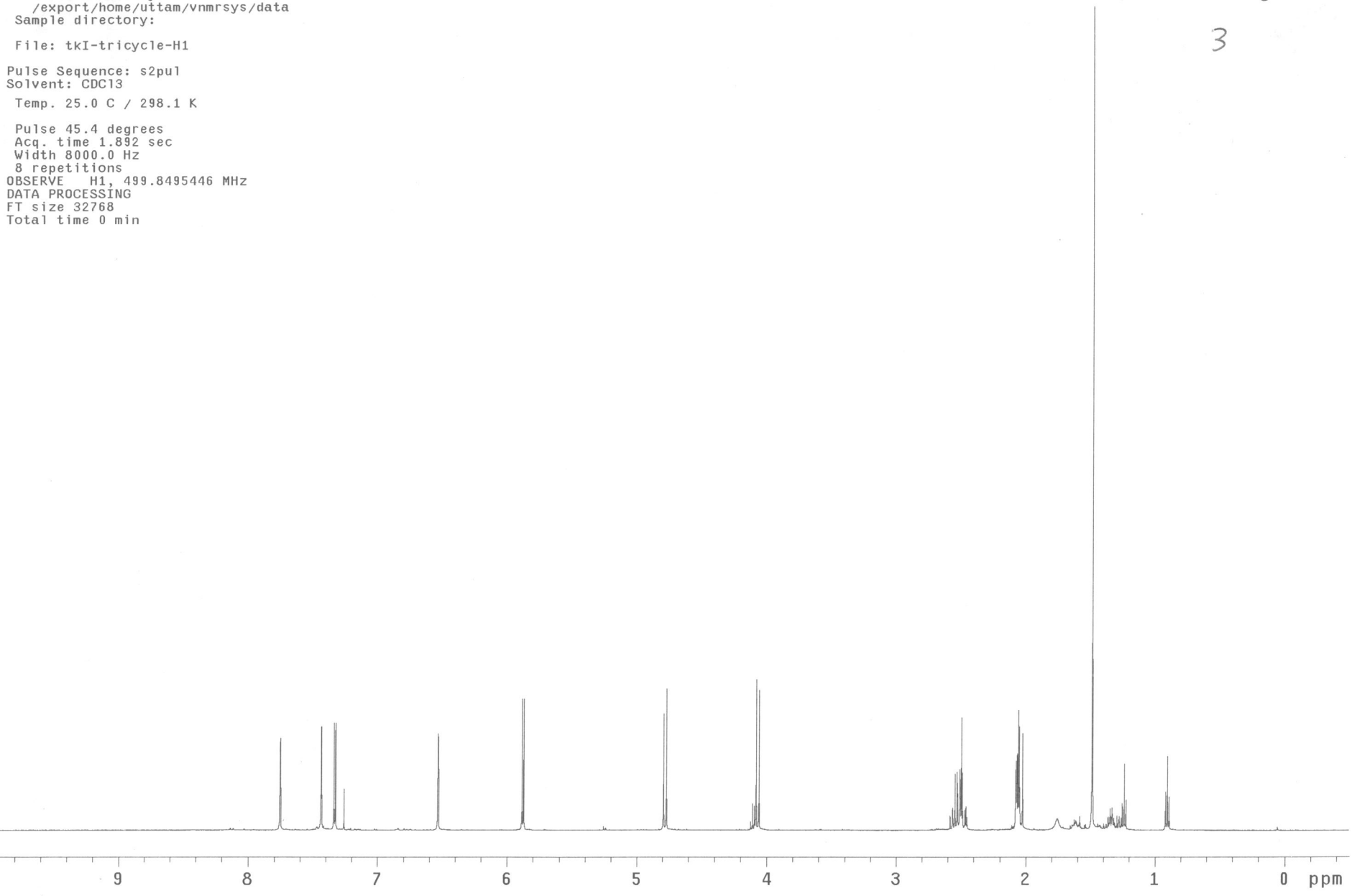
Pulse Sequence: s2pul
Solvent: CDCl3

Temp. 25.0 C / 298.1 K

Pulse 45.4 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.8495446 MHz
DATA PROCESSING
FT size 32768
Total time 0 min



3



STANDARD CARBON PARAMETERS

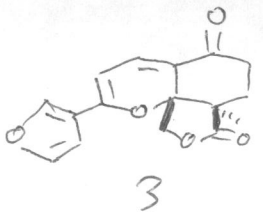
Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: tkI-tricycle-C13

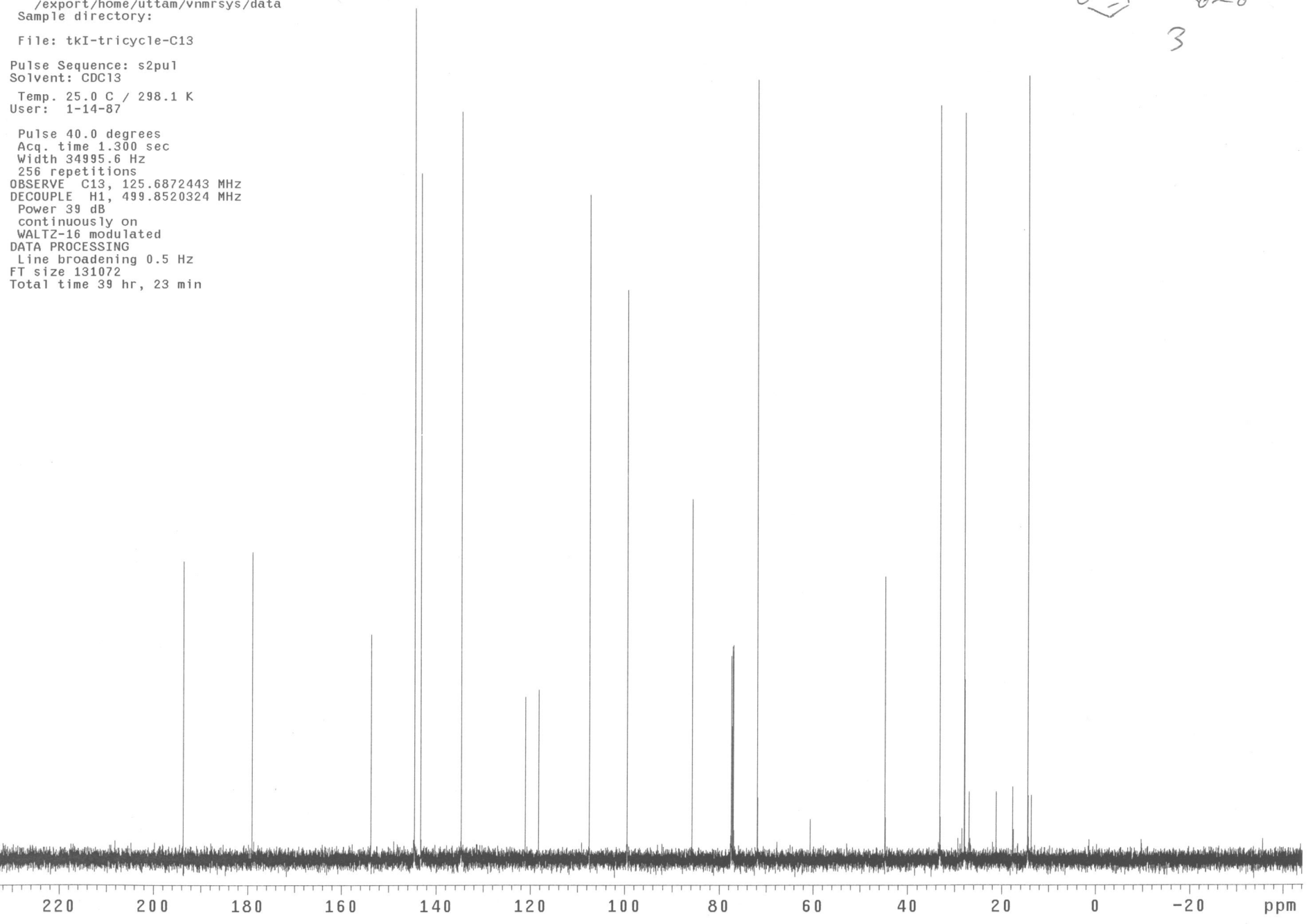
Pulse Sequence: s2pul
Solvent: CDCl3

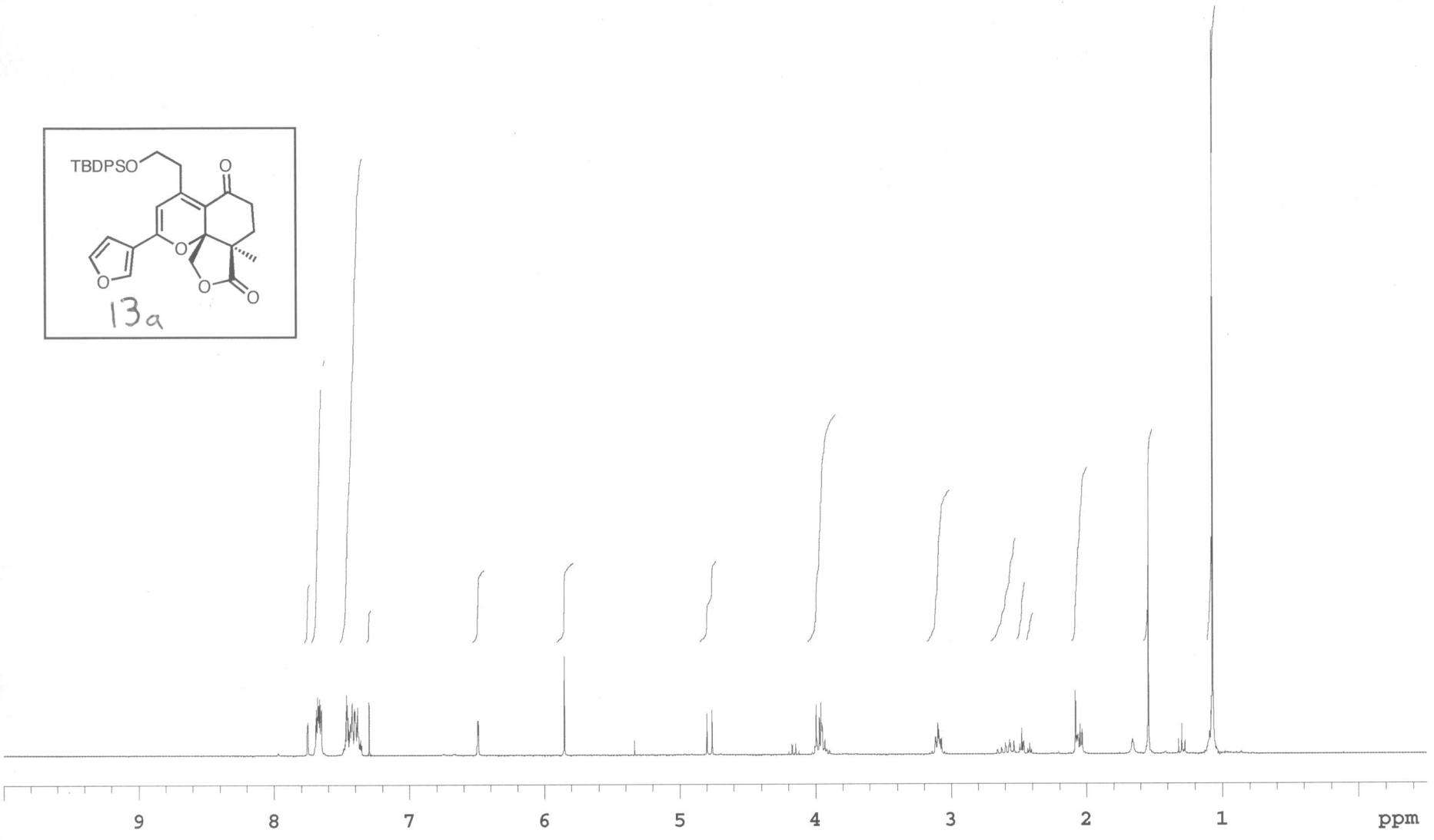
Temp. 25.0 C / 298.1 K
User: 1-14-87

Pulse 40.0 degrees
Acq. time 1.300 sec
Width 34995.6 Hz
256 repetitions
OBSERVE C13, 125.6872443 MHz
DECOUPLE H1, 499.8520324 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 39 hr, 23 min

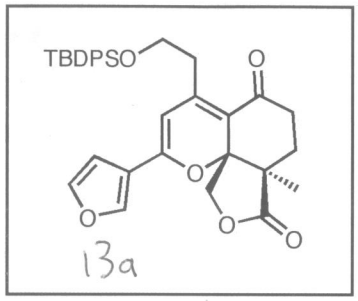


3



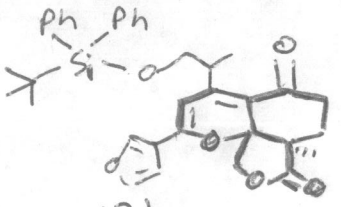


^{1}H NMR Spectrum of Furan Appended Tricycle 13a (300 MHz, $CDCl_3$).



^{13}C NMR Spectrum of Furan Appended Tricycle 13a (75 MHz, $CDCl_3$).

S-FAT



13b

(Diastereomer 1)

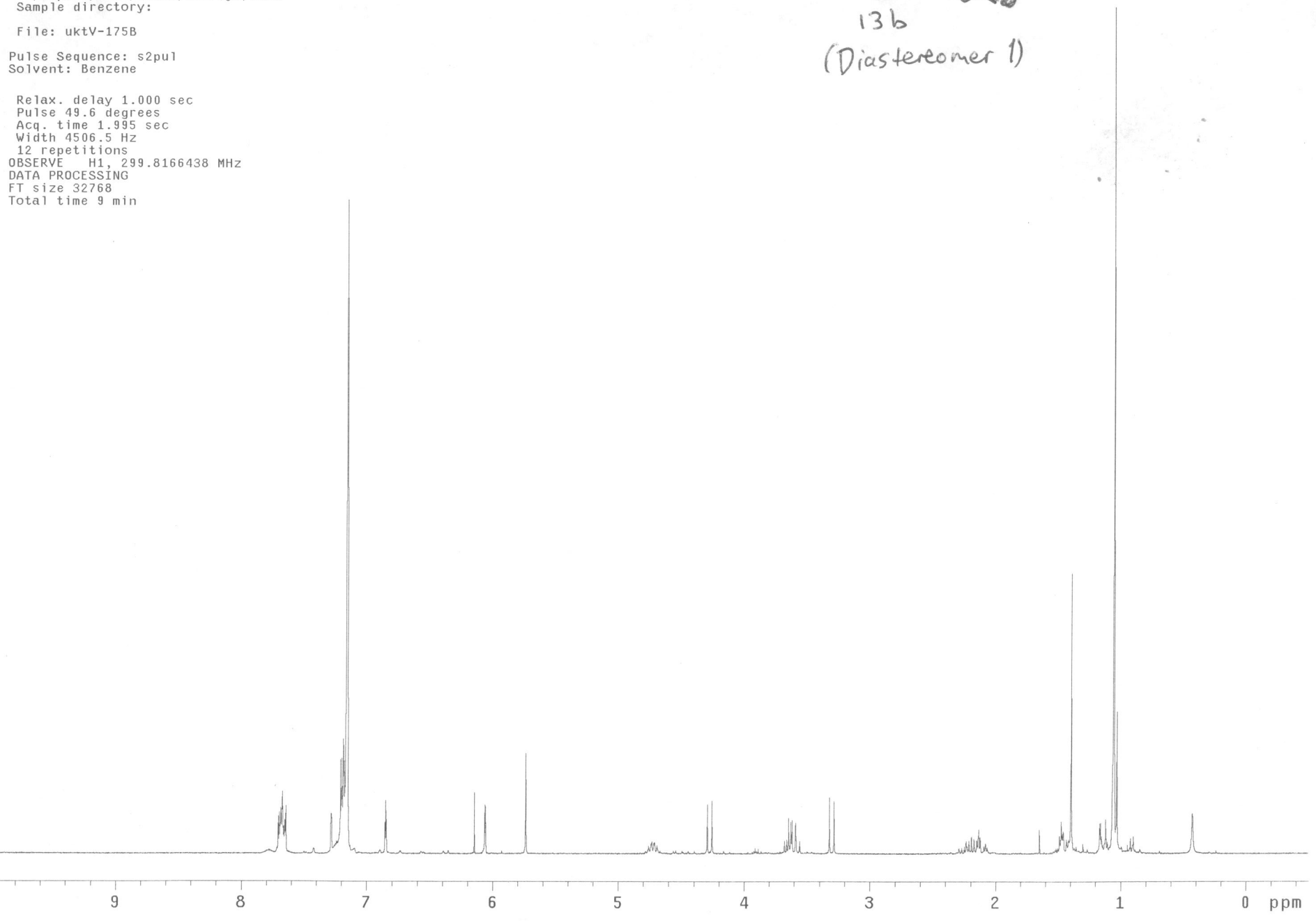
uktV-175B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: uktV-175B

Pulse Sequence: s2pul
Solvent: Benzene

Relax. delay 1.000 sec
Pulse 49.6 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
12 repetitions
OBSERVE H1, 299.8166438 MHz
DATA PROCESSING
FT size 32768
Total time 9 min



uktV-175B_carbon

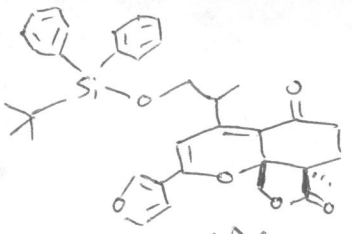
Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: uktV-175B_carbon

Pulse Sequence: s2pul
Solvent: Benzene

User: 1-14-87

Relax. delay 1.000 sec
Pulse 77.6 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
6137 repetitions
OBSERVE C13, 125.6870223 MHz
DECOUPLE H1, 499.8514260 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 997613 hr



13b

(Diastereomer 1)

S-FAT

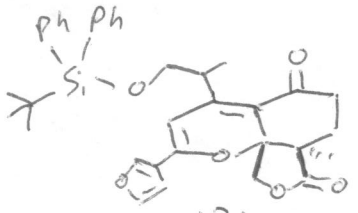
uktV-177B

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: uktV-177B

Pulse Sequence: s2pul
Solvent: Benzene

Relax. delay 1.000 sec
Pulse 49.6 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
13 repetitions
OBSERVE H1, 299.8166438 MHz
DATA PROCESSING
FT size 32768
Total time 9 min



13b (Diastereomer Z)

S-FAT

uktV-177B_carbon

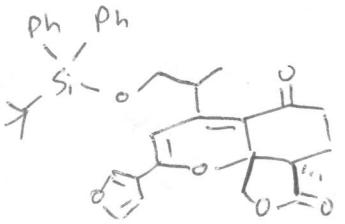
Data Collected on:
hg3-mercury300
Archive directory:
/export/home/uttam/vnmrsys/data
Sample directory:

File: uktV-177B_carbon

Pulse Sequence: s2pul
Solvent: Benzene

User: 1-14-87

Relax. delay 1.000 sec
Pulse 77.6 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
6073 repetitions
OBSERVE C13, 125.6870223 MHz
DECOUPLE H1, 499.8514260 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 159618 hr, 4 min



13b (Diastereomer 2)

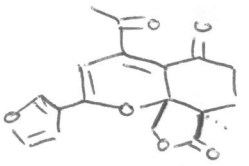
tkII-282D

Data Collected on:
hg3-mercury300
Archive directory:
/export/home/alluser/vnmrsys/data
Sample directory:
auto_CustomQ_loc34_2005-03-07
File: tkII-282D_proton

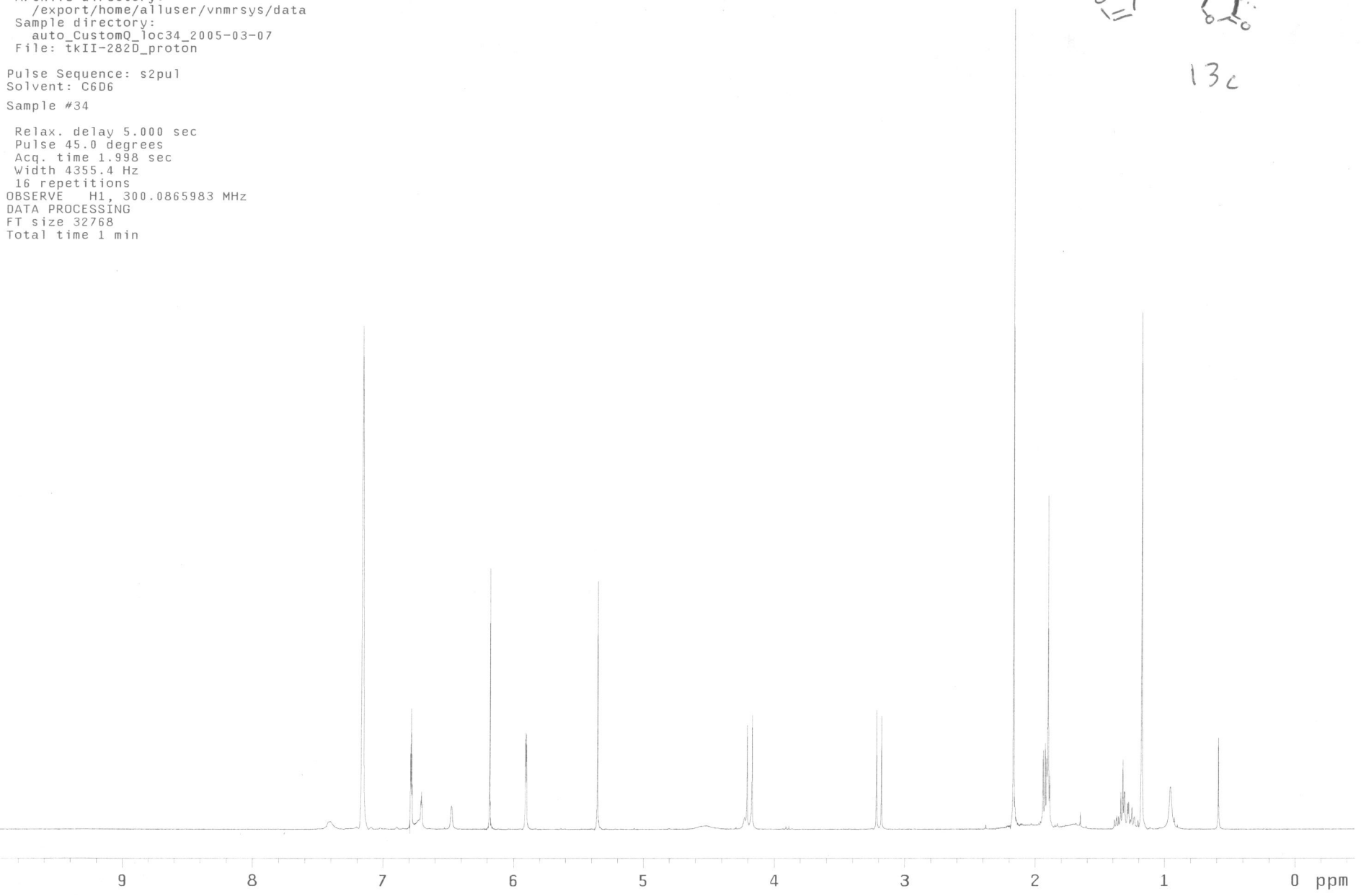
Pulse Sequence: s2pul
Solvent: C6D6

Sample #34

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4355.4 Hz
16 repetitions
OBSERVE H1, 300.0865983 MHz
DATA PROCESSING
FT size 32768
Total time 1 min



13c

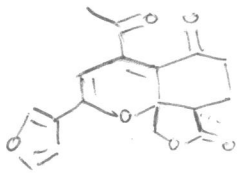


tkII-282D_carbon

Pulse Sequence: s2pul

Solvent: Benzene
Ambient temperature
Mercury-300BB "hg1"

Pulse 49.4 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
16465 repetitions
OBSERVE C13, 75.4013362 MHz
DECOUPLE H1, 299.8675964 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12937 hr, 12 min, 56 sec



13C