Supporting Information for:

Synthesis and DNA-Binding Affinity Studies of Novel Aminosugar-Containing Compounds Designed as Functional Mimics of Anthracycline Antibiotics

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1-Tosyl-3-iodo-2-phenylindole (15)

To a solution of **19** (134 mg, 0.385 mmol) and K_2CO_3 (160 mg, 1.16 mmol) in anhydrous MeCN (3.0 mL) was added I_2 (0.3 g, 1.18 mmol). The reaction mixture was stirred at room temperature for about 12 h, and then the solution was diluted with EtOAc, washed with a satd aqueous solution of $Na_2S_2O_3$ and then brine. The organic solution was dried (Na_2SO_4), filtered, and concentrated to yield the crude product, which was purified by column chromatography (4:1, hexanes–EtOAc) to afford **15** (178 mg, 98%) as a white amorphous solid: R_f 0.48 (4:1, hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.33 (d, 1H, J = 8.0 Hz, Ar), 7.31–7.55 (m, 10H, Ar), 7.10 (d, 2H, J = 8.6 Hz, Ar), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 145.0 (Ar), 141.1 (Ar), 137.0 (Ar), 135.1 (Ar), 132.2 (Ar), 131.7 (2, Ar), 131.6 (Ar), 129.5 (2, Ar), 129.3 (Ar), 127.5 (2, Ar), 126.9 (2, Ar), 126.0 (Ar), 124.6 (Ar), 122.2 (Ar), 116.0 (Ar), 75.7 (Ar-I), 21.6 (CH_3). HRMS (EI) calcd for $C_{21}H_{16}INO_2S$: 472.9947. Found: 472.9961. Anal. calcd for $C_{21}H_{16}INO_2S$: C, 53.29; H, 3.41; N, 2.96; S, 6.77. Found C, 53.38; H, 3.48; N, 3.05; S, 6.93.

3-Iodo-2-phenylindole (16)

To a solution of compound **15** (69 mg, 0.15 mmol) in THF (5.0 mL) was added a solution of tetra-*n*-butylammonium fluoride in THF (1.0 M, 1.0 mL, 1.0 mmol) at room temperature, and the mixture was heated at reflux for 6 h. After cooling to room temperature, a satd aqueous $NaHCO_3$ solution (30 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated to leave a residue, which was purified by column chromatography on silica gel (12:1 hexanes–EtOAc) to give the product **16** (40 mg, 86%) as a brownish oil: R_f 0.55 (4:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.40 (br s, 1H, NH), 7.79 (d, 2H, J = 7.5 Hz, Ar), 7.49–7.58 (m, 3H, Ar), 7.43–7.48 (m, 1H, Ar), 7.34–7.38 (m, 1H, Ar), 7.24–7.32 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 138.0 (Ar), 136.4 (Ar), 132.2 (Ar), 131.9 (Ar), 128.8 (2, Ar), 128.6 (Ar), 128.4 (2, Ar), 123.6 (Ar), 121.7 (Ar), 121.1 (Ar), 111.1 (Ar), 58.3 (Ar-I). HRMS (EI) calcd

for $C_{14}H_{10}IN$: 318.9858. Found: 318.9857. Anal. calcd for $C_{14}H_{10}IN$: C, 52.69; H, 3.16; N, 4.39. Found C, 52.59; H, 3.44; N, 4.38.

_o_-(Phenylethynyl)aniline (18)

To a solution of Et_3N (0.42 mL), $PdCl_2(PPh_3)_2$ (35 mg, 5 mol%), 2-iodoaniline **17** (220 mg, 1.00 mmol), and phenylacetylene (133 mg, 1.30 mmol) in THF (4 mL) was added CuI (10 mg, 5 mol%) under argon. The mixture was stirred at room temperature for 2 h, and then the reaction was quenched by the addition of a satd aqueous solution of NH_4Cl (5 mL). The aqueous solution was then extracted with Et_2O and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated to yield the crude product, which was purified by column chromatography (10:1, hexanes–EtOAc) to obtain pure **18** as a yellow amorphous solid (185 mg, 95%): R_f 0.48 (4:1, hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.51–7.68 (m, 2H, Ar), 7.30–7.40 (m, 4H, Ar), 7.12–7.18 (m, 1H, Ar), 6.70–6.78 (m, 2H, Ar), 4.25 (br s, 2H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 147.7 (Ar), 132.2 (Ar), 131.5 (2, Ar), 129.7 (Ar), 128.4 (2, Ar), 128.2 (Ar), 123.3 (Ar), 118.0 (Ar), 114.4 (Ar), 108.0 (Ar), 94.7 (≡C), 85.9 (≡C). HRMS (EI) calcd for $C_{14}H_{11}N$: 193.0891. Found: 193.0893.

_N_-[2-(Phenylethynyl)phenyl]-_p_-toluenesulfonamide (19)

Compound **18** (78 mg, 0.40 mmol) was dissolved in pyridine–THF (0.22 mL:1 mL), and *p*-toluenesulfonyl chloride (115 mg, 0.62 mmol) was added. The mixture was stirred for 24 h at room temperature. The reaction was then diluted with water, extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. After evaporation, the residue was purified by column chromatography (8:1, hexanes–EtOAc) to obtain pure **19** as a white waxy solid (134 mg, 96%): R_f 0.40 (6:1, hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.69 (d, 2H, J = 8.3 Hz, Ar), 7.64 (d, 1H, J = 8.3 Hz, Ar), 7.46–7.51 (m, 2H, Ar), 7.35–7.42 (m, 4H, Ar), 7.26–7.32 (m, 2H, Ar), 7.16 (d, 2H, J = 8.0 Hz, Ar), 7.04–7.09 (td, 1H, J = 7.6, 1.0 Hz, Ar), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 144.0 (Ar), 137.6 (Ar), 136.1 (Ar), 132.0 (Ar), 131.6 (2, Ar), 129.6 (3, Ar), 129.1 (Ar), 128.6 (2, Ar), 127.3 (2, Ar), 124.7 (Ar), 122.0

(Ar), 120.5 (Ar), 114.7 (Ar), 96.2 (≡C), 83.8 (≡C), 21.5 (CH_3). HRMS (EI) calcd for $C_{21}H_{17}NO_2S$: 347.0980. Found: 347.0980.

2-Phenylbenzo[*b*]furan (20)

n-Butyllithium (1.6 M in hexane, 0.5 mL, 0.80 mmol) was added dropwise to a solution of 3-iodo-2-phenylbenzo[*b*]furan **13** (33 mg, 0.11 mmol) in THF (3.0 mL) at -78 °C. The mixture was stirred at -78 °C for 5 min and a satd aqueous solution of NH_4Cl (2 mL) was then added. After stirring for another 1 min, the reaction mixture was extracted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated to yield the crude product, which was purified by column chromatography (hexanes) to afford **20** (17 mg, 86%) as a white flaky solid: R_f 0.31 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.87–7.92 (m, 2H, Ar), 7.59–7.62 (m, 1H, Ar), 7.53–7.57 (m, 1H, Ar), 7.44–7.50 (m, 2H, Ar), 7.35–7.40 (m, 1H, Ar), 7.28–7.33 (m, 1H, Ar), 7.23–7.28 (m, 1H, Ar), 7.04 (br s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 155.9 (Ar), 154.9 (Ar), 130.5 (Ar), 129.2 (Ar), 128.8 (2, Ar), 128.5 (Ar), 125.0 (2, Ar), 124.3 (Ar), 122.9 (Ar), 120.9 (Ar), 111.2 (Ar), 101.3 (Ar). HRMS (EI) calcd for $C_{14}H_{10}O$: 194.0732. Found: 194.0731. Anal. calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found C, 86.59; H, 5.33.

2-Phenylbenzo[*b*]thiophene (21)

This compound was synthesized as a white flaky solid from **14** in 85% yield by following the same procedure used for the synthesis of **21**: R_f 0.39 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.84–7.87 (m, 1H, Ar), 7.78–7.81 (m, 1H, Ar), 7.72–7.76 (m, 2H, Ar), 7.56 (br s, 1H, Ar), 7.42–7.47 (m, 2H, Ar), 7.31–7.39 (m, 3H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 144.3 (Ar), 140.7 (Ar), 139.5 (Ar), 134.3 (Ar), 129.0 (2, Ar), 128.3 (Ar), 126.5 (2, Ar), 124.5 (Ar), 124.3 (Ar), 123.6 (Ar), 122.3 (Ar), 119.5 (Ar). HRMS (EI) calcd for $C_{14}H_{10}S$: 210.0503. Found: 210.0504. Anal. calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found C, 80.15; H, 4.91; S, 15.44.

1-Tosyl-2-phenylindole (22)

Compound **19** (39 mg, 0.11 mmol) was dissolved in dichloroethane (7 mL), and copper(II) triflate (12 mg, 0.035 mmol) was added. The mixture was heated at reflux for 48 h. After evaporation, the residue was purified by column chromatography (30:1, hexanes–EtOAc) to obtain pure **22** as a white waxy solid (20 mg, 52%): R_f 0.21 (20:1, hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.30–8.34 (m, 1H, Ar), 7.48–7.54 (m, 2H, Ar), 7.40–7.46 (m, 4H, Ar), 7.36–7.39 (m, 1H, Ar), 7.25–7.30 (m, 3H, Ar), 7.04 (d, 2H, J = 8.6 Hz, Ar), 6.55 (s, 1H, Ar), 2.33 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 144.5 (Ar), 142.1 (Ar), 138.3 (Ar), 134.7 (Ar), 132.4 (Ar), 130.5 (Ar), 131.6 (Ar), 130.3 (2, Ar), 129.2 (2, Ar), 128.6 (Ar), 127.5 (2, Ar), 126.8 (2, Ar), 124.8 (Ar), 124.3 (Ar), 120.7 (Ar), 116.7 (Ar), 113.6 (Ar), 21.6 (CH_3). HRMS (EI) calcd for $C_{21}H_{17}NO_2S$: 347.0980. Found: 347.0981. Anal. calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03; S, 9.23. Found C, 72.58; H, 5.17; N, 3.76; S, 9.25.

2-Phenylindole (23)

This compound was synthesized as an amphorous off-white solid from **15** in 74% yield by following the same procedure used for the synthesis of **20**: R_f 0.57 (4:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.32 (br s, 1H, NH), 7.65–7.70 (m, 3H, Ar), 7.44–7.49 (m, 2H, Ar), 7.40–7.5243 (m, 1H, Ar), 7.33–7.37 (m, 1H, Ar), 7.20–7.24 (m, 1H, Ar), 7.14–7.18 (m, 1H, Ar), 6.85 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 137.9 (Ar), 136.9 (Ar), 132.4 (Ar), 129.3 (Ar), 129.0 (2, Ar), 127.7 (Ar), 125.2 (2, Ar), 122.4 (Ar), 120.7 (Ar), 120.3 (Ar), 110.9 (Ar), 100.0 (Ar). HRMS (EI) calcd for $C_{14}H_{11}N$: 193.0891. Found: 193.0892. Anal. calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found C, 87.27; H, 5.79; N, 7.33.

3-(2-Phenylbenzofuran-3-yl)-prop-2-yn-1-ol (24)

To a solution of piperidine (3 mL), $PdCl_2(PPh_3)_2$ (2 mg, 5 mol%), **13** (21 mg, 0.064 mmol), and propargyl alcohol (5 mg, 0.1 mmol) was added CuI (1 mg, 10 mol%). The mixture was stirred at room temperature for 5 h. The reaction was then quenched by the addition of a satd aqueous NH_4Cl solution

and the resulting solution was extracted with Et_2O. The organic fractions were dried (Na_2SO_4), filtered, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (6:1 hexanes–EtOAc) to afford **24** (12 mg, 73%) as a brownish amorphous solid: R_f 0.29 (4:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.24–8.28 (m, 2H, Ar), 7.66–7.69 (m, 1H, Ar), 7.46–7.52 (m, 3H, Ar), 7.38–7.43 (m, 1H, Ar), 7.28–7.36 (m, 2H, Ar), 4.70 (s, 2H, OCH_2), 2.15 (br s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 156.7 (Ar), 153.4 (Ar), 130.0 (2, Ar), 129.3 (Ar), 128.7 (2, Ar), 126.0 (2, Ar), 125.4 (Ar), 123.4 (Ar), 120.2 (Ar), 111.2 (Ar), 98.4 (Ar), 94.8 (≡C), 77.6 (≡C), 52.0 (OCH_2). HRMS (EI) calcd for $C_{17}H_{12}O_2$: 248.0837. Found: 248.0838. Anal. calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found C, 82.05; H, 4.86.

3-(2-Phenylbenzothiophen-3-yl)-prop-2-yn-1-ol (25)

To a solution of piperidine (4 mL), $PdCl_2(PPh_3)_2$ (28 mg, 5 mol%), **14** (254 mg, 0.759 mmol), and propargyl alcohol (64 mg, 1.1 mmol) was added CuI (15 mg, 10 mol%). The mixture was stirred at room temperature for 12 h and the reaction was then quenched by the addition of a satd aqueous NH_4Cl solution, and the resulting solution was extracted with Et_2O. The organic fractions were dried (Na_2SO_4), filtered, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (6:1 hexanes–EtOAc) to afford **25** (162 mg, 81%) as a off-white amorphous solid: R_f 0.56 (2:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.92–8.02 (m, 3H, Ar), 7.78–7.84 (m, 1H, Ar), 7.36–7.52 (m, 5H, Ar), 4.62 (s, 2H, OCH_2), 1.82 (br s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 147.0 (Ar), 141.1 (Ar), 137.5 (Ar), 133.6 (Ar), 128.8 (Ar), 128.7 (2, Ar), 128.4 (2, Ar), 125.3 (Ar), 125.0 (Ar), 123.2 (Ar), 122.0 (Ar), 112.8 (Ar). 92.4 (≡C), 80.2 (≡C), 51.9 (OCH_2). HRMS (EI) calcd for $C_{17}H_{12}OS$: 264.0609. Found: 264.0610. Anal. calcd for $C_{17}H_{12}OS$: C, 77.24; H, 4.58; S, 12.13. Found C, 77.15; H, 4.68; S, 12.17.

3-(1-Tosyl-2-phenylindol-3-yl)-prop-2-yn-1-ol (26)

To a solution of piperidine (0.75 mL), DMF (0.25 mL), $PdCl_2(PPh_3)_2$ (11 mg, 20 mol%), **15** (38 mg, 0.079 mmol), and propargyl alcohol (7 mg, 0.1 mmol) was added CuI (2 mg, 10 mol%). The mixture was stirred at 100 °C in a microwave reactor for 2 h, the reaction was then quenched by the addition of a satd aqueous NH_4Cl solution, and the resulting solution was extracted with Et_2O. The organic fractions were dried (Na_2SO_4), filtered, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (3:1 hexanes–EtOAc) to afford **26** (17 mg, 52%) as a brownish oil: R_f 0.34 (2:1 hexanes–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.30–8.33 (m, 1H, Ar), 7.52–7.60 (m, 3H, Ar), 7.38–7.48 (m, 4H, Ar), 7.31–7.36 (m, 1H, Ar), 7.23–7.27 (m, 2H, Ar), 7.03–7.07 (m, 2H, Ar), 4.40 (s, 2H, OCH_2), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 144.9 (Ar), 143.8 (Ar), 137.0 (Ar), 134.6 (Ar), 131.1 (2, Ar), 130.7 (Ar), 130.5 (Ar), 129.4 (2, Ar), 129.2 (Ar), 127.4 (2, Ar), 126.8 (2, Ar), 125.8 (Ar), 124.7 (Ar), 120.0 (Ar), 116.5 (Ar), 107.3 (Ar), 92.6 (≡C), 77.6 (≡C), 51.7 (OCH_2), 21.5 (CH_3). HRMS (EI) calcd for $C_{24}H_{19}O_3NS$: 401.1086. Found: 401.1083. Purity: > 99%.

3-(2-Phenylindol-3-yl)-prop-2-yn-1-ol (27)

This compound was synthesized as a brown oil from **26** in 45% yield by following the same procedure used for the synthesis of **16**: R_f 0.30 (5:1 toluene–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.43 (br s, 1H, NH), 7.96–7.98 (m, 2H, Ar), 7.74–7.76 (m, 1H, Ar), 7.48–7.52 (m, 2H, Ar), 7.38–7.42 (m, 2H, Ar), 7.24–7.28 (m, 1H, Ar), 7.20–7.23 (m, 1H, Ar), 4.62 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 140.3 (Ar), 135.7 (Ar), 131.8 (Ar), 130.8 (Ar), 129.4 (2, Ar), 128.9 (Ar), 126.9 (2, Ar), 123.9 (Ar), 121.4 (Ar), 120.0 (Ar), 111.5 (Ar), 92.2 (Ar), 80.0 (≡C), 66.6 (≡C), 52.3 (OCH_2). HRMS (EI) calcd for $C_{17}H_{13}NO$: 249.0997. Found: 247.0998.

2-Propargyl 4-*O*-acetyl-3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside (29) and **2-Propargyl 4-*O*-acetyl-3-azido-2,3,6-trideoxy-α-L-*ribo*-hexopyranoside (30)**

Compound **28** (3.9g, 15 mmol), crushed activated 4Å molecular sieves (500 mg) and propargyl alcohol (1.7 g, 30 mmol) were suspended in anhydrous CH_2Cl_2 (60 mL). The mixture was stirred for 5–10 min at room temperature and then cooled to -10 °C. BF_3•Et_2O (3.91 mL, 30.8 mmol) was added dropwise via syringe. After adding BF_3•Et_2O, the reaction mixture was warmed to 0 °C. Once the starting material was fully consumed (within 0.5 h), the reaction mixture was quenched by the addition of K_2CO_3 (3.33 g), and then H_2O (120 mL), satd $NaHCO_3$ solution (120 mL) and CH_2Cl_2 (250 mL) were added. The organic layer was separated, washed with brine, and was dried (Na_2SO_4), filtered and concentrated. The crude product was purified by column chromatography (15:1 → 8:1, hexanes–EtOAc) to give pure **29** (2.11 g, 55%) and **30** (0.172 g, 4.5%) as colorless oils. In addition, a mixture of the two β isomers (**31** and **32**) and some **30** was collected as clear oil (0.98 g, 25%). (**29**): R_f 0.32 (8:1 hexanes–EtOAc); IR: *v* 3281 (≡C–H), 2103 (N=N=N), 1744 (C=O) cm^{-1}; $[\alpha]_D^{23}$ –189.0 (*c* 4.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.02 (br d, 1H, $J_{1,2a}$ = 3.4 Hz, H-1), 4.66 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 4.21 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.16 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 3.86 (ddd, 1H, $J_{2a,3}$ = 12.4 Hz, $J_{3,4}$ = 9.8 Hz, $J_{2e,3}$ = 5.0 Hz, H-3), 3.80 (dq, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 2.44 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.18 (ddd, 1H, $J_{2a,2e}$ = 13.3 Hz, $J_{2e,3}$ = 5.0 Hz, $J_{1,2e}$ = 1.1 Hz, H-2e), 2.11 (s, 3H, O=CCH$_3$), 1.75 (ddd, 1H, $J_{2a,2e}$ = 13.3 Hz, $J_{2a,3}$ = 12.4 Hz, $J_{1,2a}$ = 3.4 Hz, H-2a), 1.15 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.0 (C=O), 95.1 (C-1), 78.9 (<u>C</u>≡CH), 75.3 (C-4), 74.6 (C≡<u>C</u>H), 66.4 (C-5), 57.5 (C-3), 54.3 (OCH$_2$), 34.9 (C-2), 20.8 (O=C<u>C</u>H$_3$), 17.3 (C-6). HRMS (ESI) calcd for (M+Na) $C_{11}H_{15}N_3O_4Na$: 276.0955. Found: 276.0955. Anal. calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found C, 52.40; H, 5.85; N, 16.50.

(**30**): R_f 0.44 (4:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.01 (dd, 1H, $J_{1,2a}$ = 4.0 Hz, $J_{1,2e}$ = 1.5 Hz, H-1), 4.67 (dd, 1H, $J_{4,5}$ = 9.6 Hz, $J_{3,4}$ = 3.6 Hz, H-4), 4.25 (d, 2H, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.20 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 4.11 (ddd, 1H, $J_{3,4}$ = $J_{2a,3}$ = $J_{2e,3}$ = 3.6 Hz, H-3), 2.42 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.00–2.15 (m, 5H, O=CCH$_3$, H-2a, H-2e), 1.18 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.1 (C=O), 93.8 (C-1), 79.1 (<u>C</u>≡CH), 74.5 (C≡<u>C</u>H), 73.9 (C-4),

62.2 (C-5), 55.7 (C-3), 54.5 (OCH_2), 32.8 (C-2), 20.7 (O=C<u>C</u>H_3), 17.2 (C-6). HRMS (ESI) calcd for (M+Na) $C_{11}H_{15}N_3O_4Na$: 276.0955. Found: 276.0953.

2-Propargyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside (33)

Compound **29** (1.52 g, 6.01 mmol) was dissolved in CH_3OH (70 mL). To this solution was added K_2CO_3 (0.36 g, 2.6 mmol), and then the reaction mixture was stirred for 12 h. The solvent was evaporated and the residue was suspended in water (100 mL), extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was concentrated and the resulting residue was purified by column chromatography (4:1 hexanes–EtOAc) to acquire pure **33** as a colorless oil (1.27 g, 99%); R_f 0.44 (4:1 hexanes–EtOAc); IR *v* 3425 (O–H), 3293 (≡C–H), 2104 (N=N=N) cm^{-1}; $[\alpha]_D^{23}$ –160.0 (*c* 3.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 5.02 (br d, 1H, $J_{1,2a}$ = 3.4 Hz, H-1), 4.22 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.17 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 3.76 (ddd, 1H, $J_{2a,3}$ = 12.3 Hz, $J_{3,4}$ = 9.5 Hz, $J_{2e,3}$ = 5.0 Hz, H-3), 3.69 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.14 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 2.44 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.41 (br s, 1H, OH), 2.19 (ddd, 1H, $J_{2a,2e}$ = 13.2 Hz, $J_{2e,3}$ = 5.0 Hz, $J_{1,2e}$ = 1.2 Hz, H-2e), 1.74 (ddd, 1H, $J_{2a,2e}$ = 13.2 Hz, $J_{2a,3}$ = 12.3 Hz, $J_{1,2a}$ = 3.4 Hz, H-2a), 1.29 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 95.1 (C-1), 79.0 (<u>C</u>≡CH), 75.8 (C-4), 74.6 (C≡<u>C</u>H), 68.2 (C-5), 60.2 (C-3), 54.2 (OCH_2), 34.7 (C-2), 17.6 (C-6). HRMS (EI) calcd for $C_9H_{13}N_3O_3$: 211.0957. Found: 211.0960. Anal. calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found C, 51.22; H, 6.13; N, 19.77.

2-Propargyl 4-*O*-acetyl-3-azido-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside (34)

To a solution of compound **33** (128 mg, 0.611 mmol) in 19:1 CH_2Cl_2–pyridine (16.8 mL) at -15 °C was added the solution of Tf_2O (triflic anhydride) (0.438 mL, 2.58 mmol) in CH_2Cl_2 (3.4 mL). After stirring for 45 min while keeping the temperature below -5 °C, TLC showed the starting material was gone and a new spot (R_f 0.61, 4:1 hexanes–EtOAc) appeared. The reaction mixture was then extracted with ice-cold 1M HCl aqueous solution and water, dried with Na_2SO_4, filtered, and concentrated to yield an

orange liquid. The product was immediately dissolved in dry CH_3CN (10 mL) and *n*-Bu_4NOAc (366 mg, 1.22 mmol) was added. After stirring at 40 °C for 40 min, the solvent was removed under vacuum. The residue was purified by column chromatography (4:1 hexanes–EtOAc) to yield pure **34** (132 mg, 86%) as a pale yellow oil. R_f 0.39 (4:1 hexanes–EtOAc); IR *v* 3279 (≡C–H), 2104 (N=N=N), 1744 (C=O) cm^{-1}; $[\alpha]_D^{23}$ –161.4 (*c* 4.4, CH_2Cl_2); ^1H NMR (500 MHz, CD_3OD, δ_H) 5.16 (br s, 2H, H-1, H-4), 4.22 (2 d, 2H, *J* = 2.4 Hz, $OC\underline{H}_2C{\equiv}CH$), 4.02 (br q, 1H, $J_{5,6}$ = 6.5 Hz, H-5), 3.86 (ddd, 1H, $J_{2a,3}$ = 12.8 Hz, $J_{2e,3}$ = 4.8 Hz, $J_{3,4}$ = 3.0 Hz, H-3), 2.45 (t, 1H, *J* = 2.4 Hz, $OCH_2C{\equiv}C\underline{H}$), 2.18 (s, 3H, $O{=}CCH_3$), 2.10 (ddd, 1H, $J_{2a,2e} = J_{2a,3}$ = 12.8 Hz, $J_{1,2a}$ = 3.3 Hz, H-2a), 1.56 (br dd, 1H, $J_{2a,2e}$ = 12.8 Hz, $J_{2e,3}$ = 4.8 Hz, H-2e), 1.14 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.4 (C=O), 95.8 (C-1), 79.0 ($\underline{C}{\equiv}CH$), 74.6 ($C{\equiv}\underline{C}H$), 70.0 (C-4), 65.6 (C-5), 54.5 (OCH_2), 54.4 (C-3), 29.2 (C-2), 20.7 ($O{=}C\underline{C}H_3$), 16.6 (C-6). HRMS (ESI) calcd for (M+Na) $C_{11}H_{15}N_3O_4Na$: 276.0955. Found: 276.0956. Anal. calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found C, 52.53; H, 5.99; N, 16.93.

2-Propargyl 3-azido-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside (35)

Compound **34** (81 mg, 0.32 mmol) was dissolved in CH_3OH (6 mL), K_2CO_3 (31 mg, 0.23 mmol) added and then the reaction mixture was stirred for 24 h. The solvent was evaporated and the residue was purified by column chromatography (3:1 hexanes–EtOAc) to acquire pure **35** as a pale yellow thin oil (64 mg, 94%); R_f 0.26 (3:1 hexanes–EtOAc); IR *v* 3462 (O–H), 3294 (≡C–H), 2100 (N=N=N) cm^{-1}; $[\alpha]_D^{23}$ –169.7 (*c* 2.3, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 5.10 (br d, 1H, $J_{1,2a}$ = 3.8 Hz, H-1), 4.19 (s, 2H, $OC\underline{H}_2C{\equiv}CH$), 3.92 (br q, 1H, $J_{5,6}$ = 6.5 Hz, H-5), 3.79 (ddd, 1H, $J_{2a,3}$ = 13.0 Hz, $J_{2e,3}$ = 5.0 Hz, $J_{3,4}$ = 2.8 Hz, H-3), 3.68 (br s, 1H, H-4), 2.44 (t, 1H, *J* = 2.4 Hz, $OCH_2C{\equiv}C\underline{H}$), 2.09 (ddd, 1H, $J_{2a,2e} = J_{2a,3}$ = 13.0 Hz, $J_{1,2a}$ = 3.8 Hz, H-2a), 2.01 (br s, 1H, OH), 1.93 (br dd, 1H, $J_{2a,2e}$ = 13.0 Hz, $J_{2e,3}$ = 5.0 Hz, H-2e), 1.26 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 95.8 (C-1), 79.1 ($\underline{C}{\equiv}CH$), 74.5 ($C{\equiv}\underline{C}H$), 69.6 (C-4), 66.4 (C-5), 56.8 (C-3), 54.5 (OCH_2), 28.3 (C-2), 16.6 (C-6). HRMS (ESI) calcd for (M+Na) $C_9H_{13}N_3O_3Na$: 234.0849. Found: 234.0848. Anal. calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found C, 50.75; H, 6.30; N, 19.19.

2-Propargyl 3-amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside (36)

To a solution of compound **35** (458 mg, 2.17 mmol) in THF (50 mL) and H_2O (2 mL) was added PPh_3 (1.14 g, 4.35 mmol), and the reaction was heated at reflux for 10 h. After cooling and concentration of the solution, the residue was purified by column chromatography on Iatrobeads (EtOAc → CH_3OH) to yield pure **36** (356 mg, 89%) as a white waxy solid: R_f 0.55 (100:1 CH_3OH–HOAc); IR *v* 3287.4 (≡C–H, O–H) cm^{-1}; $[\alpha]_D^{23}$ –191.8 (*c* 1.9, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 5.00 (br d, 1H, $J_{1,2a}$ = 3.4 Hz, H-1), 4.18 (d, 2H, *J* = 2.5 Hz, OC<u>H</u>$_2$C≡CH), 3.87 (br q, 1H, $J_{5,6}$ = 6.6 Hz, H-5), 3.42 (br d, 1H, $J_{3,4}$ = 2.5 Hz, H-4), 3.07 (ddd, 1H, $J_{2a,3}$ = 12.7 Hz, $J_{2e,3}$ = 5.0 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 2.79 (t, 1H, *J* = 2.5 Hz, OCH$_2$C≡C<u>H</u>), 1.67 (ddd, 1H, $J_{2a,2e}$ = $J_{2a,3}$ = 12.7 Hz, $J_{1,2a}$ = 3.4 Hz, H-2a), 1.74 (ddd, 1H, $J_{2a,2e}$ = 12.7 Hz, $J_{2e,3}$ = 5.0 Hz, $J_{1,2e}$ = 1.1 Hz, H-2e), 1.19 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6); ^{13}C NMR (100 MHz, CD_3OD, δ_C) 96.8 (C-1), 80.5 (<u>C</u>≡CH), 79.3 (C-4), 75.4 (C≡<u>C</u>H), 69.9 (C-5), 54.8 (OCH$_2$), 50.3 (C-3), 38.2 (C-2), 18.1 (C-6). HRMS (ESI) calcd for (M+H) $C_9H_{16}NO_3$: 186.1125. Found: 186.1123. Anal. calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found C, 58.18; H, 8.08; N, 7.67.

2-Propargyl 3-amino-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside (37)

To a solution of **33** (1.27 g, 6.01 mmol) in THF (80 mL) and H_2O (14 mL) was added PPh_3 (3.17 g, 12.1 mmol), and the reaction mixture was heated at reflux for 10 h. After concentration of the solution, the residue was purified by column chromatography on Iatrobeads (EtOAc → CH_3OH) to yield pure **37** (1.08 g, 97%) as a white amorphous solid: R_f 0.34 (CH_3OH); IR *v* 3341.0 (N–H), 3296.7 (≡C–H), 3090.3 (O–H) cm^{-1}; $[\alpha]_D^{23}$ –175.8 (*c* 0.80, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 4.96 (br d, 1H, $J_{1,2a}$ = 3.4 Hz, H-1), 4.18 (d, 2H, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 3.58 (dq, 1H, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 2.94 (ddd, 1H, $J_{2a,3}$ = 12.1 Hz, $J_{3,4}$ = 9.3 Hz, $J_{2e,3}$ = 4.6 Hz, H-3), 2.82 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, H-4), 2.79 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 1.98 (ddd, 1H, $J_{2a,2e}$ = 13.4 Hz, $J_{2e,3}$ = 4.6 Hz, $J_{1,2e}$ = 1.3 Hz, H-2e), 1.56 (ddd, 1H, $J_{2a,2e}$ = 13.4 Hz, $J_{2a,3}$ = 12.1 Hz, $J_{1,2a}$ = 3.4 Hz, H-2a), 1.21 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (100 MHz, CD_3OD, δ_C) 96.8 (C-1), 80.5 (<u>C</u>≡CH), 79.3 (C-4), 75.4 (C≡<u>C</u>H), 69.9 (C-5),

54.8 (OCH_2), 50.3 (C-3), 38.2 (C-2), 18.1 (C-6). HRMS (ESI) calcd for (M+H) $C_9H_{16}NO_3$: 186.1125. Found: 186.1124. Anal. calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found C, 58.19; H, 8.13; N, 7.77.

Methyl 4-*O*-acetyl-2,3,6-trideoxy-α-L-*erythro*-hexopyranoside (40α) and **Methyl 4-*O*-acetyl-2,3,6-trideoxy-β-L-*erythro*-hexopyranoside (40β)**

A solution of the mixture of **39α** and **39β** (282 mg, 1.52 mmol) in EtOAc (40 mL) was hydrogenated in the presence of 10% Pd/C (8 mg, 2.7% mass ratio) at room temperature and normal pressure. Once the starting material was fully consumed (about 3.5 h), the reaction mixture was filtered through a Celite pad and concentrated. The crude product was purified by column chromatography (8:1, hexanes–EtOAc) to acquire pure **40α** as a colorless oil and pure **40β** as a white amorphous solid (256 mg for **40α** and **40β** together, 90%, α:β = 4.6:1). (**40α**): R_f 0.64 (6:1 hexanes–EtOAc); IR: ν 1738 (C=O) cm^{-1}; $[\alpha]_D^{23}$ –192.4 (*c* 4.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 4.63 (br s, 1H, H-1), 4.44–4.52 (m, 1H, H-4), 3.77 (dq, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.37 (s, 3H, OCH_3), 2.05 (s, 3H, O=CCH_3), 1.86–1.94 (m, 1H, H-3e), 1.70–1.84 (m, 3H, H-2a, H-2e, H-3a), 1.15 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.2 (C=O), 97.3 (C-1), 73.5 (C-4), 66.3 (C-5), 54.5 (OCH_3), 29.0 (C-2), 24.0 (C-3), 21.1 (O=C<u>C</u>H_3), 17.8 (C-6). HRMS (ESI) calcd for (M+Na) $C_9H_{16}O_4Na$: 211.0941. Found: 211.0941. Anal. calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found C, 57.08; H, 8.74.

(**40β**): R_f 0.60 (6:1 hexanes–EtOAc); IR: ν 1731 (C=O) cm^{-1}; $[\alpha]_D^{23}$ +17.0 (*c* 1.4, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, δ_H) 4.42 (ddd, 1H, $J_{3a,4}$ = 10.4 Hz, $J_{4,5}$ = 9.1 Hz, $J_{3e,4}$ = 4.1 Hz, H-4), 4.36 (dd, 1H, $J_{1,2a}$ = 9.0 Hz, $J_{1,2e}$ = 2.2 Hz, H-1), 3.48 (dq, 1H, $J_{4,5}$ = 9.1 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.45 (s, 3H, OCH_3), 2.13 (dddd, 1H, $J_{3a,3e}$ = 13.0 Hz, $J_{2e,3e}$ = $J_{3e,4}$ = $J_{2a,3e}$ = 4.1 Hz, H-3e), 2.02 (s, 3H, O=CCH_3), 1.86 (dddd, 1H, $J_{2a,2e}$ = 13.0 Hz, $J_{2e,3e}$ = $J_{2e,3a}$ = 4.1 Hz, $J_{1,2e}$ = 2.2 Hz, H-2e), 1.59 (dddd, 1H, $J_{2a,2e}$ = $J_{2a,3a}$ = 13.0 Hz, $J_{1,2a}$ = 9.0 Hz, $J_{2a,3e}$ = 4.1 Hz, H-2a), 1.45 (dddd, 1H, $J_{3a,3e}$ = $J_{2a,3a}$ = 13.0 Hz, $J_{3a,4}$ = 10.4 Hz, $J_{2e,3a}$ = 4.1 Hz, H-3a), 1.20 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.2 (C=O), 102.4 (C-1), 73.1 (C-5), 72.9 (C-4), 56.2 (OCH_3), 29.9 (C-2), 27.1 (C-3), 21.1 (O=C<u>C</u>H_3), 18.1

(C-6). HRMS (ESI) calcd for (M+Na) $C_9H_{16}O_4Na$: 211.0941. Found: 209.0942. Anal. calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found C, 57.47; H, 8.55.

Methyl 2,3,6-trideoxy-α-L-*erythro*-hexopyranoside (42α) and **Methyl 2,3,6-trideoxy-β-L-*erythro*-hexopyranoside (42β)**

A mixture of compounds **40α** and **40β** (1.85 g, 9.84 mmol) was dissolved in CH_3OH (100 mL). To the above solution was added K_2CO_3 (0.54 g, 3.9 mmol), and then the reaction was stirred for 12 h. The solvent was evaporated and the residue was purified by column chromatography (2:1, hexanes–EtOAc) to acquire pure **42α** (0.73 g) and **42β** (0.09 g), and their mixture (0.49 g) as a colorless oil respectively (1.31 g, 91%, α:β = 5.1:1). (**42α**): R_f 0.22 (2:1 hexanes–EtOAc); IR: *v* 3434 (O–H) cm^{-1}; $[\alpha]_D^{23}$ –168.6 (*c* 1.7, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.60 (br s, 1H, H-1), 3.54 (dq, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.32 (s, 3H, OCH_3), 3.30–3.36 (m, 1H, H-4), 1.94 (br s, 1H, OH), 1.65–1.85 (m, 4H, H-2a, H-2e, H-3a, H-3e), 1.24 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 97.3 (C-1), 72.0 (C-4), 69.3 (C-5), 54.4 (OCH_3), 29.5 (C-2), 27.6 (C-3), 17.9 (C-6). HRMS (ESI) calcd for (M+Na) $C_7H_{14}O_3Na$: 169.0835. Found: 169.0834. Anal. calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found C, 57.64; H, 9.77.

(**42β**): R_f 0.17 (2–1 hexanes:EtOAc); IR: *v* 3411 (O–H) cm^{-1}; $[\alpha]_D^{23}$ +47.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.36 (dd, 1H, $J_{1,2a}$ = 9.2 Hz, $J_{1,2e}$ = 2.0 Hz, H-1), 3.48 (s, 3H, OCH_3), 3.25–3.32 (m, 2H, H-4, H-5), 2.03–2.08 (m, 1H, H-3e), 1.86–1.91 (m, 1H, H-2e), 1.53–1.66 (m, 2H, H-2a, OH), 1.43–1.52 (m, 1H, H-3a), 1.32 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 102.5 (C-1), 75.7 (C-5), 71.6 (C-4), 56.3 (OCH_3), 31.0 (C-2/C-3), 30.5 (C-3/C-2), 18.0 (C-6). HRMS (EI) calcd for $C_7H_{14}O_3$: 146.0943. Found: 146.0940. Anal. calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found C, 58.02; H, 9.76.

Methyl 4-azido-2,3,4,6-trideoxy-α-L-*threo*-hexopyranoside (43α) and **Methyl 4-azido-2,3,4,6-trideoxy-β-L-*threo*-hexopyranoside (43β)**

Compounds **42α** and **42β** (378 mg, 2.59 mmol) were dissolved in CH_2Cl_2 (20 mL), and Et_3N (1.08 mL, 7.77 mmol) was added. The solution was cooled to 0 °C and then mesyl chloride (0.40 mL, 5.2 mmol) was added dropwise. After stirring for 2 h, the reaction mixture was washed with 1N HCl, 1N NaOH and brine sequentially. The solution was dried over Na_2SO_4. After filtration, the solvent was evaporated and the acquired yellow oil was dissolved in DMF (7 mL). To this solution was added NaN_3 (933 mg, 14.4 mmol) and the reaction mixture was stirred at 110 °C for 24 h before cooling and extraction with Et_2O. The ether solution was dried (Na_2SO_4), filtered, and evaporated. The resulting residue was purified by column chromatography (20:1, hexanes–EtOAc) to acquire pure **43α** (230 mg) and **43β** (22 mg), and their mixture (83 mg) as colorless oils respectively (335 mg, 76%). (**43α**): R_f 0.24 (20:1 hexanes–EtOAc); IR: *v* 2098 cm^{-1} (N=N=N); $[\alpha]_D^{23}$ –71.9 (*c* 3.6, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.68 (br d, 1H, $J_{12a\ or\ 2e}$ = 2.7 Hz, H-1), 3.95 (dq, 1H, $J_{5,6}$ = 6.5 Hz, $J_{4,5}$ = 1.7 Hz, H-5), 3.42 (br s, 1H, H-4), 3.32 (s, 3H, OCH_3), 2.06–2.14 (m, 1H, H-3e), 1.84–1.95 (m, 2H, H-3a, H-2e), 1.51–1.57 (m, 1H, H-2a), 1.20 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 97.9 (C-1), 65.0 (C-5), 59.9 (C-4), 54.6 (OCH_3), 24.0 (C-2), 23.0 (C-3), 17.9 (C-6). HRMS (EI) calcd for $C_7H_{13}N_3O_2$: 171.1008. Found: 171.0993. Anal. calcd for $C_7H_{13}N_3O_2$: C, 49.11; H, 7.65; N, 24.54. Found C, 49.33; H, 8.00; N, 24.69.

(**43β**): R_f 0.13 (20:1 hexanes–EtOAc); IR: *v* 2096 cm^{-1} (N=N=N); $[\alpha]_D^{23}$ +164.1 (*c* 1.9, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.35 (m, 1H, H-1), 3.66 (dq, 1H, $J_{5,6}$ = 6.4 Hz, $J_{4,5}$ = 1.7 Hz, H-5), 3.48 (s, 3H, OCH_3), 3.36–3.40 (m, 1H, H-4), 2.11–2.17 (m, 1H, H-3e), 1.77–1.85 (m, 1H, H-3a), 1.65–1.75 (m, 2H, H-2a, H-2e), 1.30 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 102.6 (C-1), 72.7 (C-5), 59.0 (C-4), 55.9 (OCH_3), 26.8 (C-3), 25.8 (C-2), 17.9 (C-6). HRMS (ESI) calcd for (M+Na) $C_7H_{13}N_3O_2Na$: 194.0900. Found: 194.0901.

2-Propargyl 4-azido-2,3,4,6-trideoxy-α-L-*threo*-hexopyranoside (44α) and **2-Propargyl 4-azido-2,3,4,6-trideoxy-β-L-*threo*-hexopyranoside (44β)**

To a flask were added the mixture of **43α** and **43β** (200 mg, 1.17 mmol), crushed activated 4Å molecular sieves (100 mg), propargyl alcohol (0.41 mL, 7.0 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred for 10 min at room temperatu, cooled to -40 ºC, and then BF_3•Et_2O (0.37 mL, 2.9 mmol) was added dropwise via syringe. After adding the BF_3•Et_2O, the reaction mixture was warmed to -10 ºC. Once the starting material was fully consumed (about 4 h), the reaction mixture was quenched by the addition of K_2CO_3 (150 mg). Next, H_2O (5 mL), satd aqueous $NaHCO_3$ solution (5 mL) and CH_2Cl_2 (15 mL) were added. The organic layer was separated, washed with brine, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography (30:1, hexanes–EtOAc) to acquire pure **44α** and **44β** both as colorless oils (203 mg, 89%, α:β = 3.5:1). (**44α**): R_f 0.32 (20:1 hexanes–EtOAc); IR: *ν* 3297 (≡C–H), 2100 (N=N=N) cm^{-1}; $[\alpha]_D^{23}$ –109.0 (*c* 1.5, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.60 (br d, 1H, $J_{1,2a \text{ or } 2e}$ = 3.5 Hz, H-1), 4.22 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.17 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.00 (dq, 1H, $J_{5,6}$ = 6.5 Hz, $J_{4,5}$ = 1.7 Hz, H-5), 3.45 (br s, 1H, H-4), 2.41 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.10–2.18 (m, 1H, H-3e), 1.87–2.00 (m, 2H, H-3a, H-2e), 1.58–1.63 (m, 1H, H-2a), 1.20 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 95.9 (C-1), 79.5 (<u>C</u>≡CH), 74.6 (C≡<u>C</u>H), 65.6 (C-5), 59.8 (C-4), 54.2 (OCH_2), 23.8 (C-2), 22.9 (C-3), 17.8 (C-6). HRMS (EI) calcd for $C_9H_{13}N_3O_2$ (loss of –OCH_2C≡CH): 140.0824. Found: 140.0828. Anal. calcd for $C_7H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.52. Found C, 55.85; H, 7.02; N, 21.74.

(**44β**): R_f 0.22 (20:1 hexanes–EtOAc); IR: *ν* 3297 (≡C–H), 2098 (N=N=N) cm^{-1}; $[\alpha]_D^{23}$ +208.6 (*c* 0.9, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 4.66 (dd, 1H, $J_{1,2a}$ = 8.8 Hz, $J_{1,2e}$ = 3.1 Hz, H-1), 4.38 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.34 (dd, 1H, *J* = 15.7 Hz, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 3.68 (dq, 1H, $J_{5,6}$ = 6.3 Hz, $J_{4,5}$ = 1.7 Hz, H-5), 3.40 (br s, 1H, H-4), 2.40 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.13–2.19 (m, 1H, H-3e), 1.68–1.88 (m, 3H, H-2a, H-2e, H-3a), 1.29 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 99.1 (C-1), 79.3 (<u>C</u>≡CH), 74.3 (C≡<u>C</u>H), 72.9 (C-5), 59.0 (C-4), 54.6 (OCH_2), 26.8 (C-3), 25.7 (C-2), 17.8 (C-6). HRMS (ESI) calcd for (M+Na) $C_9H_{13}N_3O_2Na$: 218.0900. Found: 218.0901.

2-Propargyl 4-amino-2,3,4,6-trideoxy-α-L-*threo*-hexopyranoside (45)

To a solution of compound **44α** (423 mg, 2.17 mmol) in THF (25 mL) and H_2O (0.39 mL) was added PPh_3 (0.85 g, 3.3 mmol), and the reaction was stirred for 10 h under reflux. After cooling and evaporation, the residue was purified by column chromatography (EtOAc → CH_3OH) to yield pure **45** (313 mg, 85%) as a foamy white solid: R_f 0.39 (5:1 CH_2Cl_2–CH_3OH); IR: *v* 3392 (N–H), 3295 (≡C–H), 3257 (N–H), 2118 (C≡C) cm^{-1}; $[\alpha]_D^{23}$ –156.1 (*c* 3.5, CH_3OH); ^1H NMR (500 MHz, CD_3OD, δ_H) 4.60 (br d, 1H, $J_{1,2a\text{ or }2e}$ = 3.6 Hz, H-1), 4.20 (d, 2H, *J* = 2.4 Hz, OC<u>H</u>$_2$C≡CH), 4.00 (dq, 1H, $J_{5,6}$ = 6.7 Hz, $J_{4,5}$ = 1.5 Hz, H-5), 2.80 (t, 1H, *J* = 2.4 Hz, OCH$_2$C≡C<u>H</u>), 2.71 (br s, 1H, H-4), 2.00–2.09 (m, 1H, H-3e), 1.88–1.96 (m, 1H, H-2e), 1.58–1.64 (m, 1H, H-3a), 1.45–1.51 (m, 1H, H-2a), 1.10 (d, 3H, $J_{5,6}$ = 6.7 Hz, H-6); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 97.1 (C-1), 80.7 (<u>C</u>≡CH), 75.4 (C≡<u>C</u>H), 67.6 (C-5), 54.8 (OCH_2), 49.2 (C-4), 26.7 (C-3), 24.1 (C-2), 17.7 (C-6). HRMS (ESI) calcd for (M+H) $C_9H_{16}NO_2$: 170.1176. Found: 170.1177. Anal. calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found C, 63.99; H, 9.01; N, 7.90.

3-(2-Phenyl-benzo[*b*]furan-3-yl)-prop-2-ynyl 4-*O*-acetyl-2,3,6-trideoxy-α-L-*erythro*-hexopyranoside (46)

Compound **24** (97.9 mg, 0.39 mmol), compound **40** (110.3 mg, 0.59 mmol), and crushed activated 4Å molecular sieves (30 mg) were suspended in anhydrous CH_2Cl_2 (5 mL). The mixture was stirred for 5–10 min at room temperature and then cooled to -10 °C. BF_3•Et_2O (102 μL, 0.8 mmol) was added dropwise via syringe. After adding BF_3•Et_2O, the reaction mixture was warmed to 0 °C. Once the starting material was fully consumed, the reaction mixture was quenched by the addition of K_2CO_3 (0.1 g), and then H_2O (10 mL), satd $NaHCO_3$ solution (5 mL) and CH_2Cl_2 (20 mL) were added. The organic layer was separated, washed with brine, and was dried (Na_2SO_4), filtered and concentrated. The crude product was purified by column chromatography (10:1, hexanes–EtOAc) giving pure **46** as a yellow paste (77.3 mg, 49%). (**46**): R_f 0.46 (4:1 hexanes–EtOAc); IR: *v* 2222 (C≡C), 1737 (C=O) cm^{-1}; $[\alpha]_D$ –108.0 (*c* 5.6, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.26–8.30 (m, 2H, Ar), 7.66–7.70 (m, 1H, Ar),

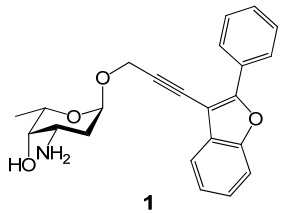
7.47–7.53 (m, 3H, Ar), 7.39–7.43 (m, 1H, Ar), 7.28–7.36 (m, 2H, Ar), 5.13 (br s, 1H, H-1), 4.64 (s, 2H, OC$\underline{H}_2$C≡C), 4.52–4.58 (m, 1H, H-4), 3.93 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 2.06 (s, 3H, O=CCH_3), 1.83–2.01 (m, 4H, H-2a, H-2e, H-3a, H-3e), 1.20 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.2 (C=O), 156.8 (Ar), 153.4 (Ar), 129.9(9) (Ar), 129.9(6) (Ar), 129.2 (Ar), 128.6 (2, Ar), 126.0 (2, Ar), 125.3 (Ar), 123.4 (Ar), 120.3 (Ar), 111.2 (Ar), 98.5 (Ar), 95.0 (C-1), 92.6 (≡C), 77.8 (≡C), 73.4 (C-4), 67.1 (C-5), 55.0 (OCH_2), 29.0 (C-2), 24.1 (C-3), 21.2 (O=C$\underline{C}H_3$), 17.9 (C-6). HRMS (ESI) calcd for (M+Na) $C_{25}H_{24}O_5Na$: 427.1516. Found: 427.1517. Anal. calcd for $C_{25}H_{24}O_5$: C, 74.24; H, 5.98. Found C, 74.50; H, 6.33.

3-(2-Phenyl-benzo[*b*]thiophen-3-yl)-prop-2-ynyl 4-*O*-acetyl-2,3,6-trideoxy-α-L-*erythro*-hexopyranoside (47)

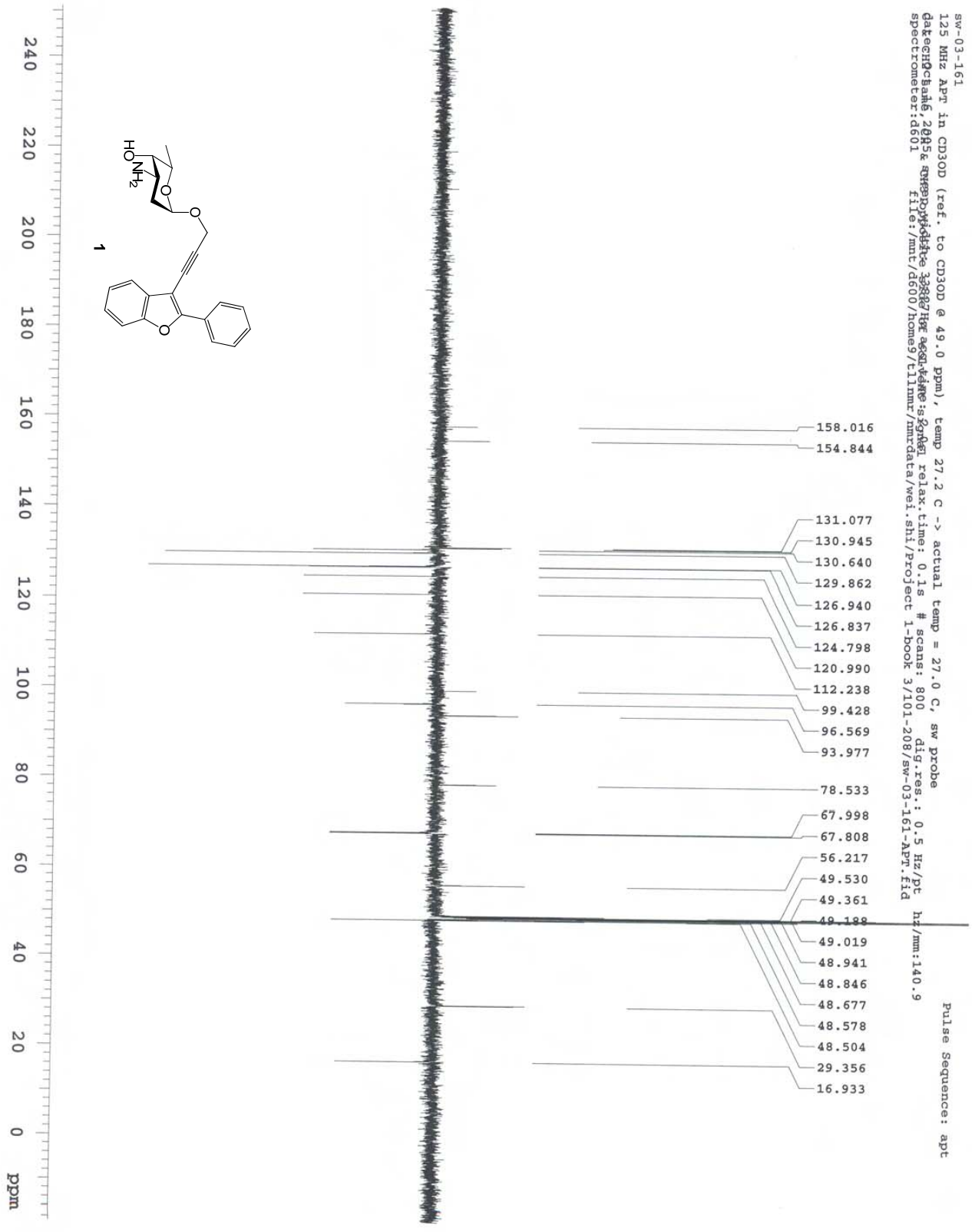
Compound **47** was synthesized from **25** (124.2 mg, 0.47 mmol) and **40** (133.2 mg, 0.71 mmol) in 43% yield by following the same procedure used for the synthesis of **46**. (**47**): white needle-like solid after recrystallization from hexanes–Et_2O (2:1), m.p.: 89–91 °C; R_f 0.36 (6:1 hexanes–EtOAc); IR: *ν* 2216 (C≡C), 1736 (C=O) cm^{-1}; $[\alpha]_D$ –120.2 (*c* 1.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 7.96–8.00 (m, 2H, Ar), 7.92–7.96 (m, 1H, Ar), 7.79–7.82 (m, 1H, Ar), 7.36–7.50 (m, 5H, Ar), 5.08 (br s, 1H, H-1), 4.58 (s, 2H, OC$\underline{H}_2$C≡C), 4.50–4.57 (m, 1H, H-4), 3.89 (dq, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 2.06 (s, 3H, O=CCH_3), 1.80–2.00 (m, 4H, H-2a, H-2e, H-3a, H-3e), 1.17 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 170.2 (C=O), 146.9 (Ar), 141.1 (Ar), 137.5 (Ar), 133.7 (Ar), 128.8 (Ar), 128.7 (2, Ar), 128.4 (2, Ar), 125.2 (Ar), 124.9 (Ar), 123.3 (Ar), 122.0 (Ar), 112.9 (Ar), 94.8 (C-1), 90.2 (≡C), 80.4 (≡C), 73.4 (C-4), 67.0 (C-5), 54.8 (OCH_2), 29.0 (C-2), 24.0 (C-3), 21.2 (O=C$\underline{C}H_3$), 17.8 (C-6). HRMS (ESI) calcd for (M+Na) $C_{25}H_{24}O_4SNa$: 443.1288. Found: 443.1289. Anal. calcd for $C_{25}H_{24}O_4S$: C, 71.40; H, 5.75; S, 7.63. Found C, 71.34; H, 5.80; S, 7.41.

sw-03-161
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Oct 16 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-161.fid

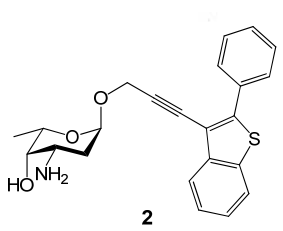
Pulse Sequence: s2pul



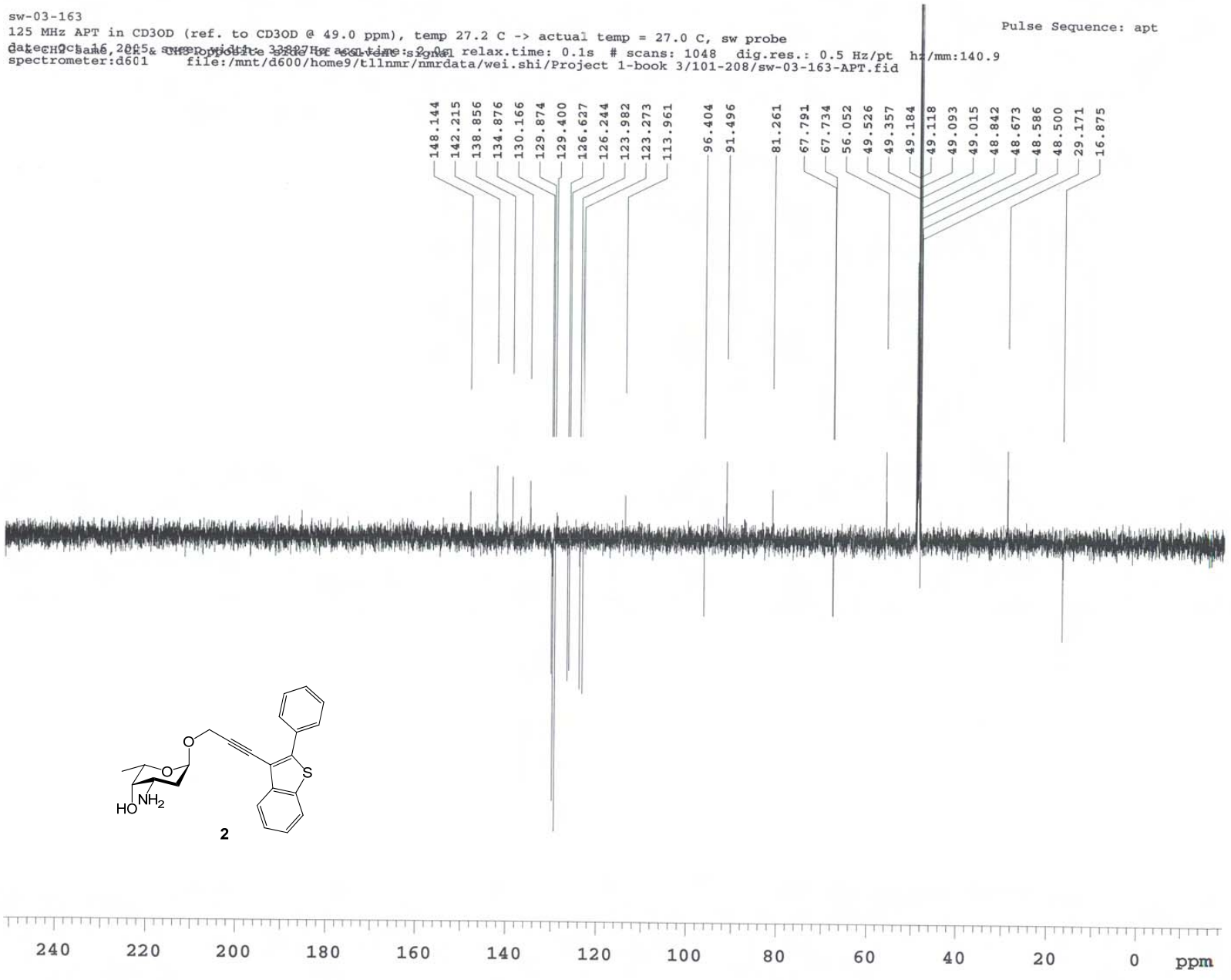
1


sw-03-161
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
spectrometer:d601
file:/mnt/d600/home9/tlinmr/nmrdata/wei.shi/project 1-book 3/101-208/sw-03-161-APT.fid
Pulse Sequence: apt
158.016
154.844
131.077
130.945
130.640
129.862
126.940
126.837
124.798
120.990
112.238
99.428
96.569
93.977
78.533
67.998
67.808
56.217
49.530
49.361
49.188
49.019
48.941
48.846
48.677
48.578
48.504
29.356
16.933
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

sw-03-163
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
Pulse Sequence: s2pul
date: Oct 16 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-163.fid



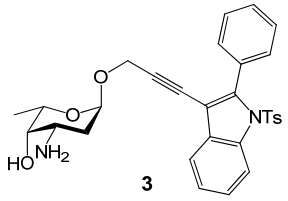
2


sw-03-163
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-163-APT.fid
Pulse Sequence: apt
148.144
142.215
138.856
134.876
130.166
129.874
129.400
126.637
126.244
123.982
123.273
113.961
96.404
91.496
81.261
67.791
67.734
56.052
49.526
49.357
49.184
49.118
49.093
49.015
48.842
48.673
48.586
48.500
29.171
16.875
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

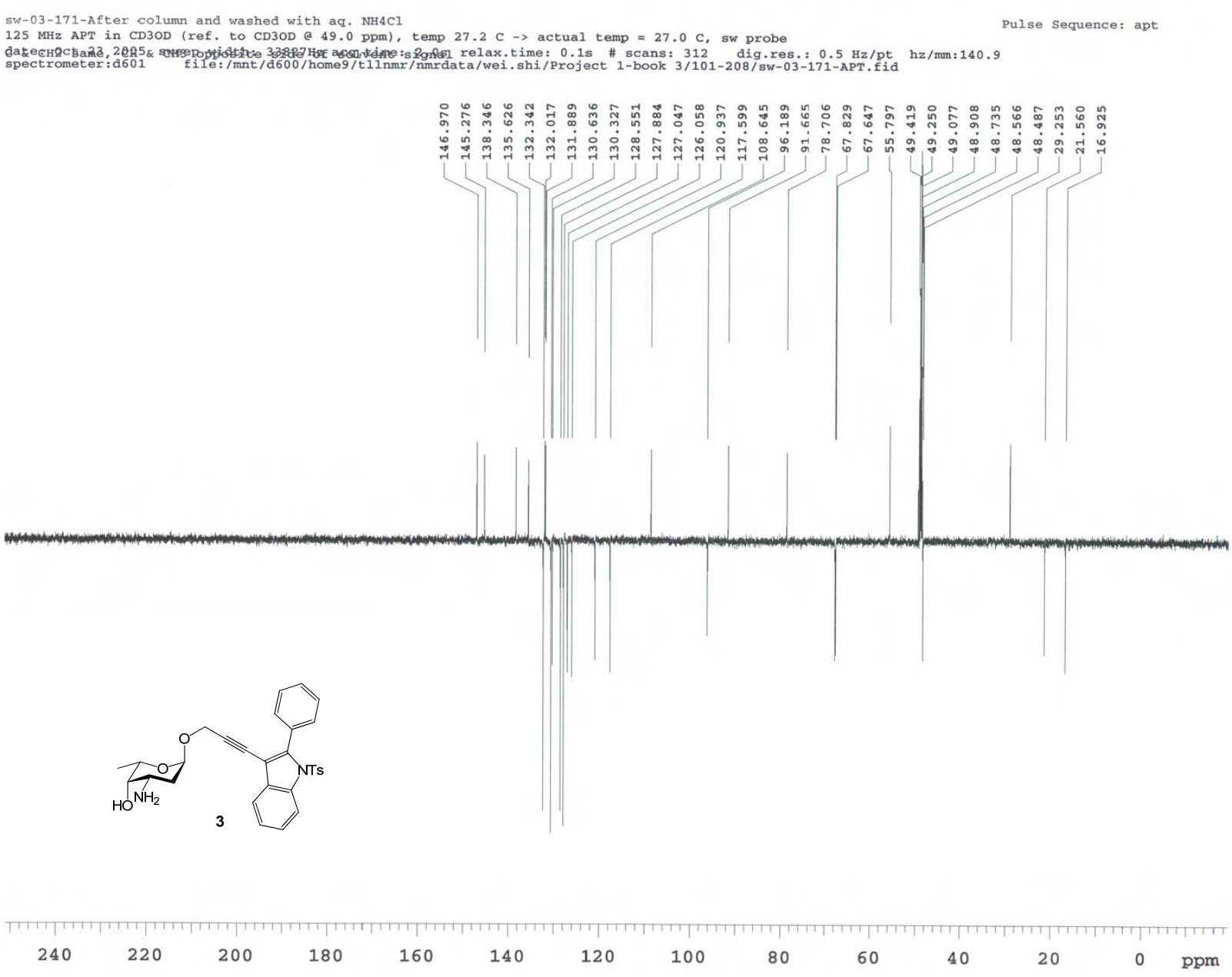
2

sw-03-171-After column and washed with aq. NH4Cl
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Oct 23 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-171.fid

Pulse Sequence: s2pul

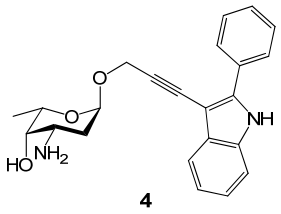


3

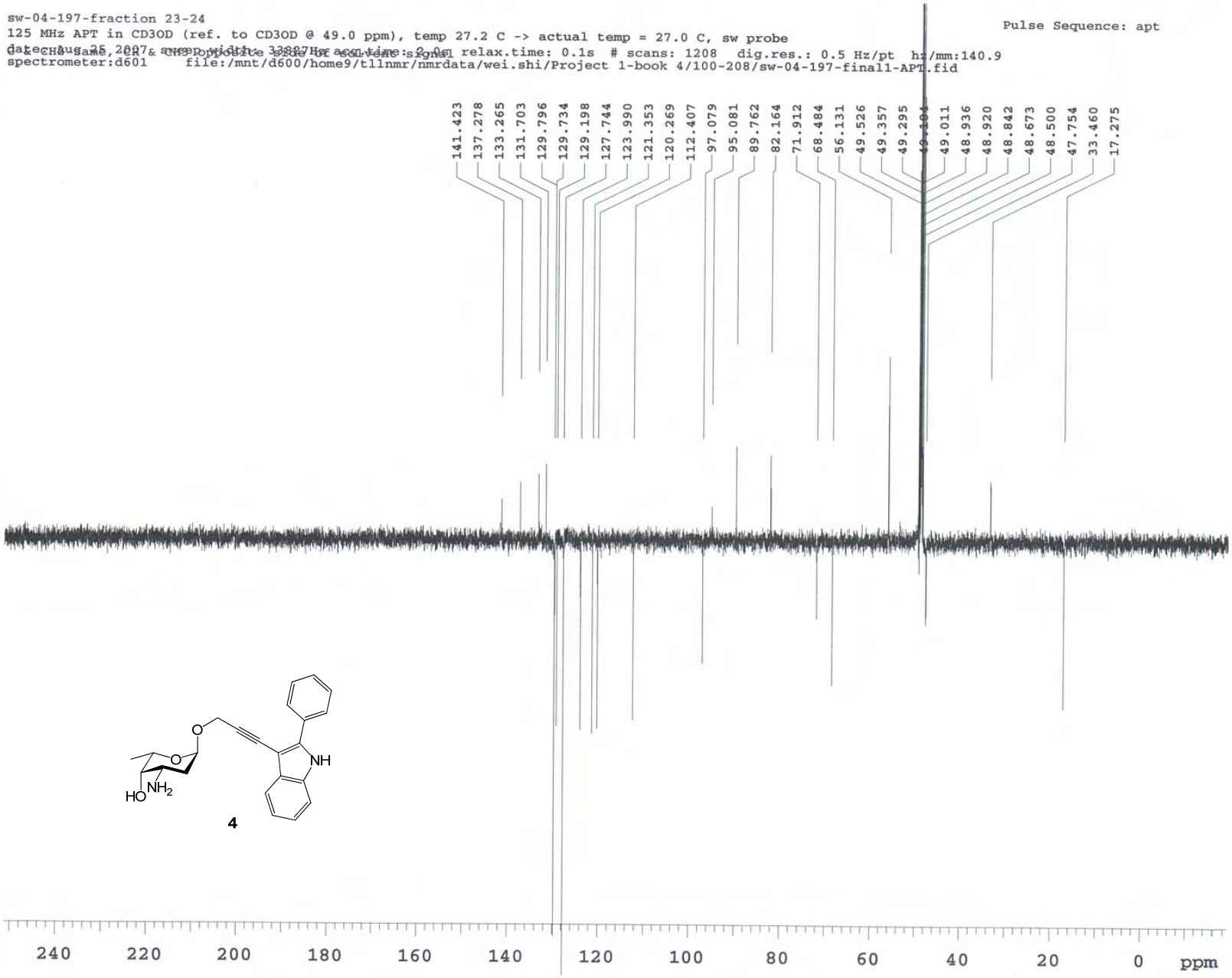

sw-03-171-After column and washed with aq. NH4Cl
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-171-APT.fid
146.970
145.276
138.346
135.626
132.342
132.017
131.889
130.636
130.327
128.551
127.884
127.047
126.058
120.937
117.599
108.645
96.189
91.665
78.706
67.829
67.647
55.797
49.419
49.250
49.077
48.908
48.735
48.566
48.487
29.253
21.560
16.925
O
O
NTs
HO
NH2
3
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

sw-04-197-fraction 23-24
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Aug 25 2007 sweep width: 6001Hz acq.time: 3.0s relax.time: 2.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-197-final.fid

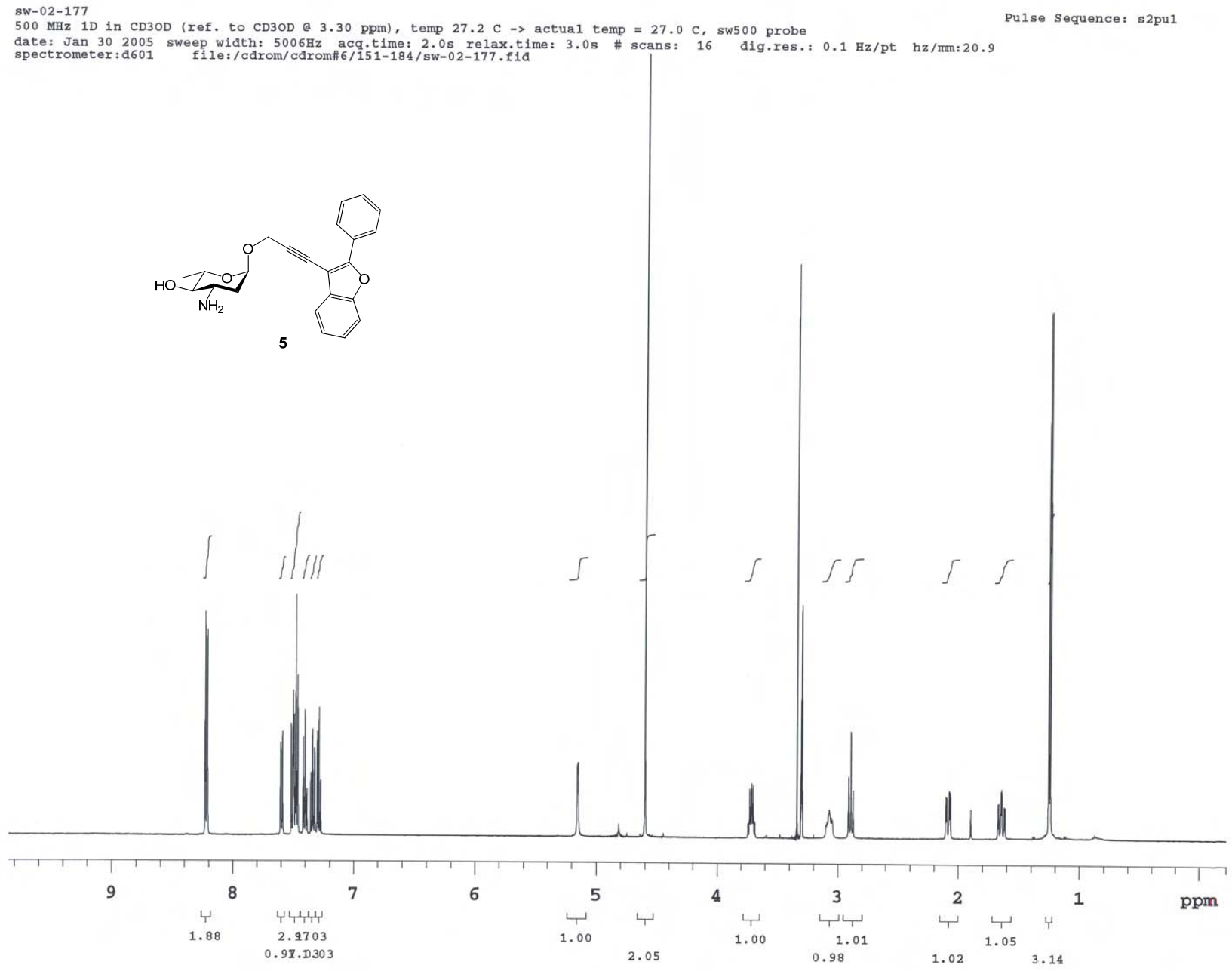
Pulse Sequence: s2pul

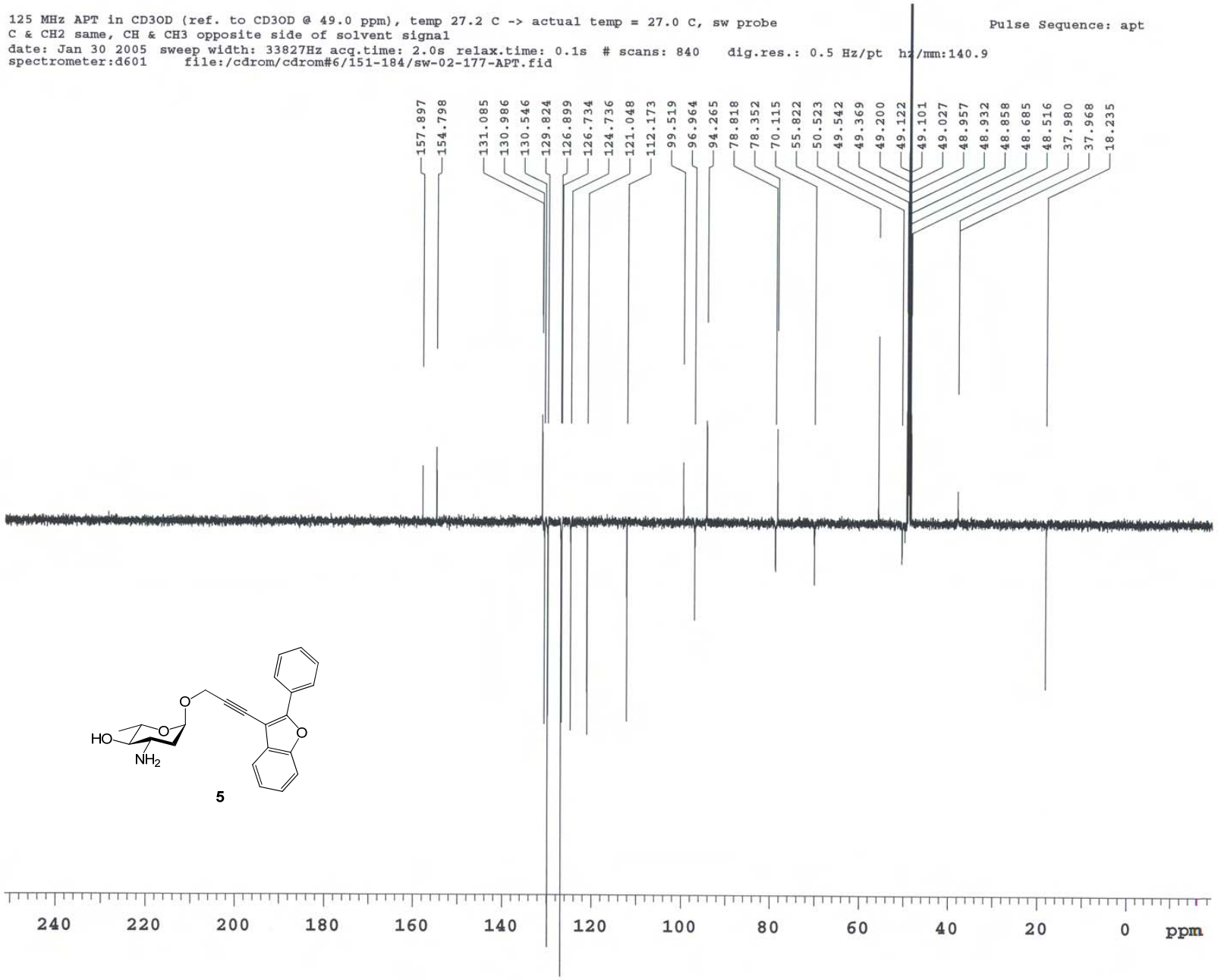


4


sw-04-197-fraction 23-24
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-197-final1-APT.fid
Pulse Sequence: apt
141.423
137.278
133.265
131.703
129.796
129.734
129.198
127.744
123.990
121.353
120.269
112.407
97.079
95.081
89.762
82.164
71.912
68.484
56.131
49.526
49.357
49.295
49.011
48.936
48.920
48.842
48.673
48.500
47.754
33.460
17.275
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
O
NH
HO
NH2

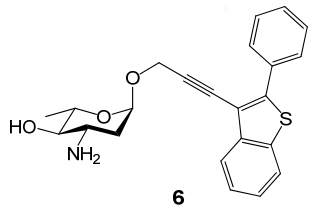
4


sw-02-177
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
Pulse Sequence: s2pul
date: Jan 30 2005 sweep width: 5006Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
spectrometer:d601 file:/cdrom/cdrom#6/151-184/sw-02-177.fid
HO
O
O
NH2
O
O
5
9
8
7
6
5
4
3
2
1
ppm
1.88
2.97
1.03
1.00
2.05
1.00
0.98
1.01
1.02
1.05
3.14

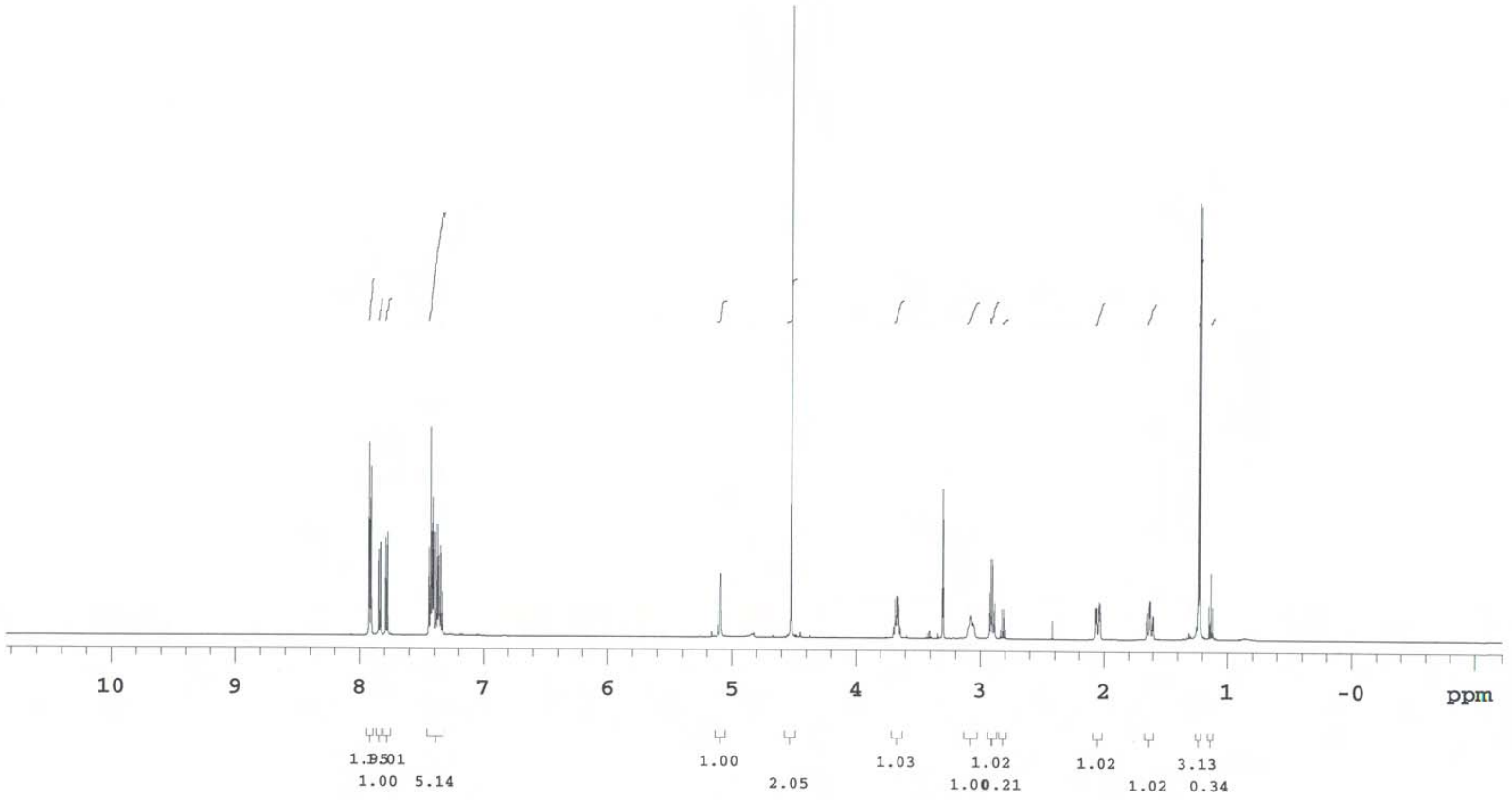

125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jan 30 2005 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 840 dig.res.: 0.5 Hz/pt hz/mm:140.9
spectrometer:d601 file:/cdrom/cdrom#6/151-184/sw-02-177-APT.fid
Pulse Sequence: apt
157.897
154.798
131.085
130.986
130.546
129.824
126.899
126.734
124.736
121.048
112.173
99.519
96.964
94.265
78.818
78.352
70.115
55.822
50.523
49.542
49.369
49.200
49.122
49.101
49.027
48.957
48.932
48.858
48.685
48.516
37.980
37.968
18.235
HO
O
O
O
NH2
5
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

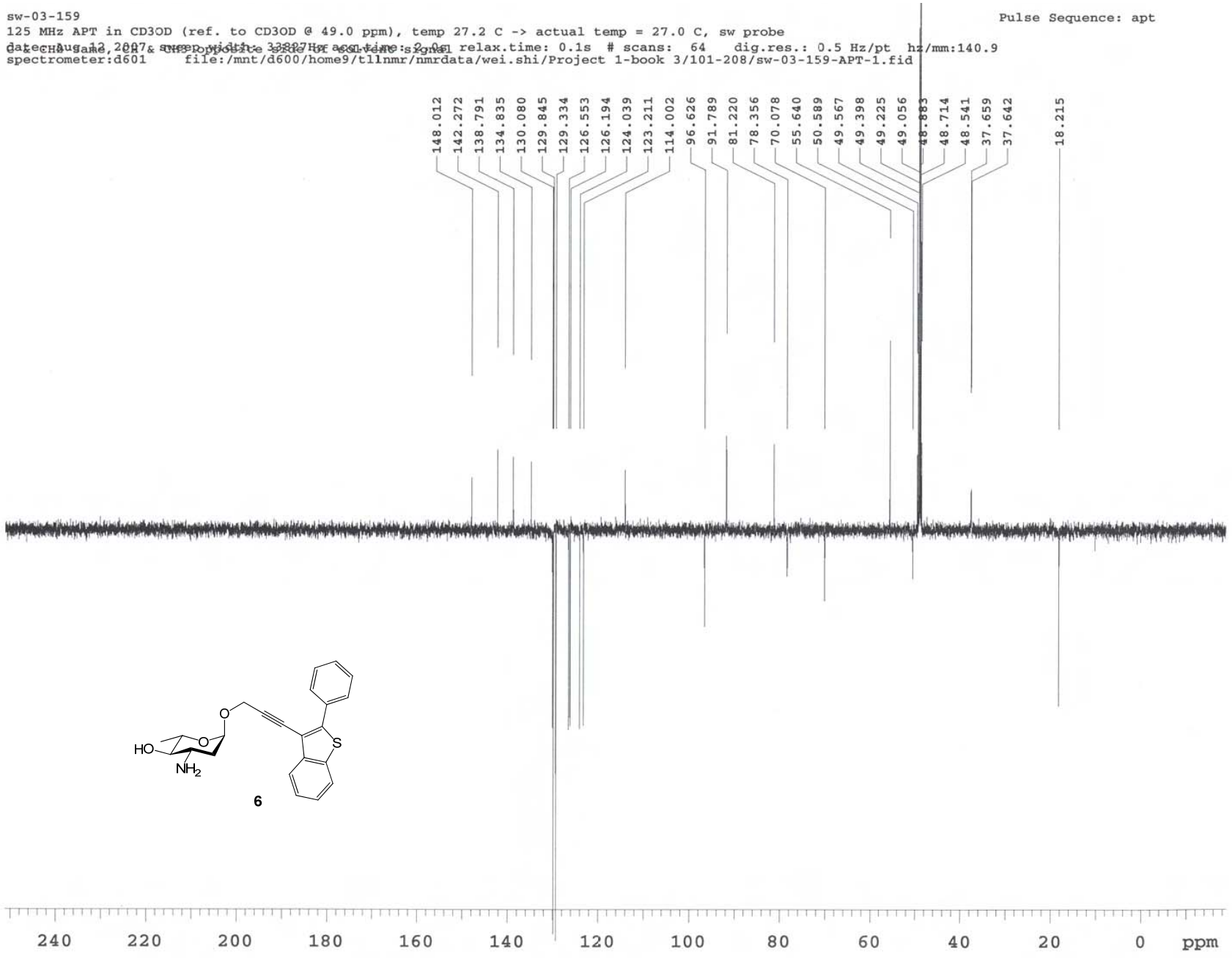
sw-03-159-High Vaccum 2 days after methanol evaporation
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Aug 12 2007 sweep width: 6001Hz acq.time: 3.0s relax.time: 2.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-159-1.fid

Pulse Sequence: s2pul



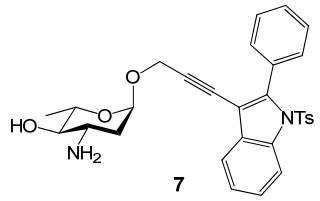
6



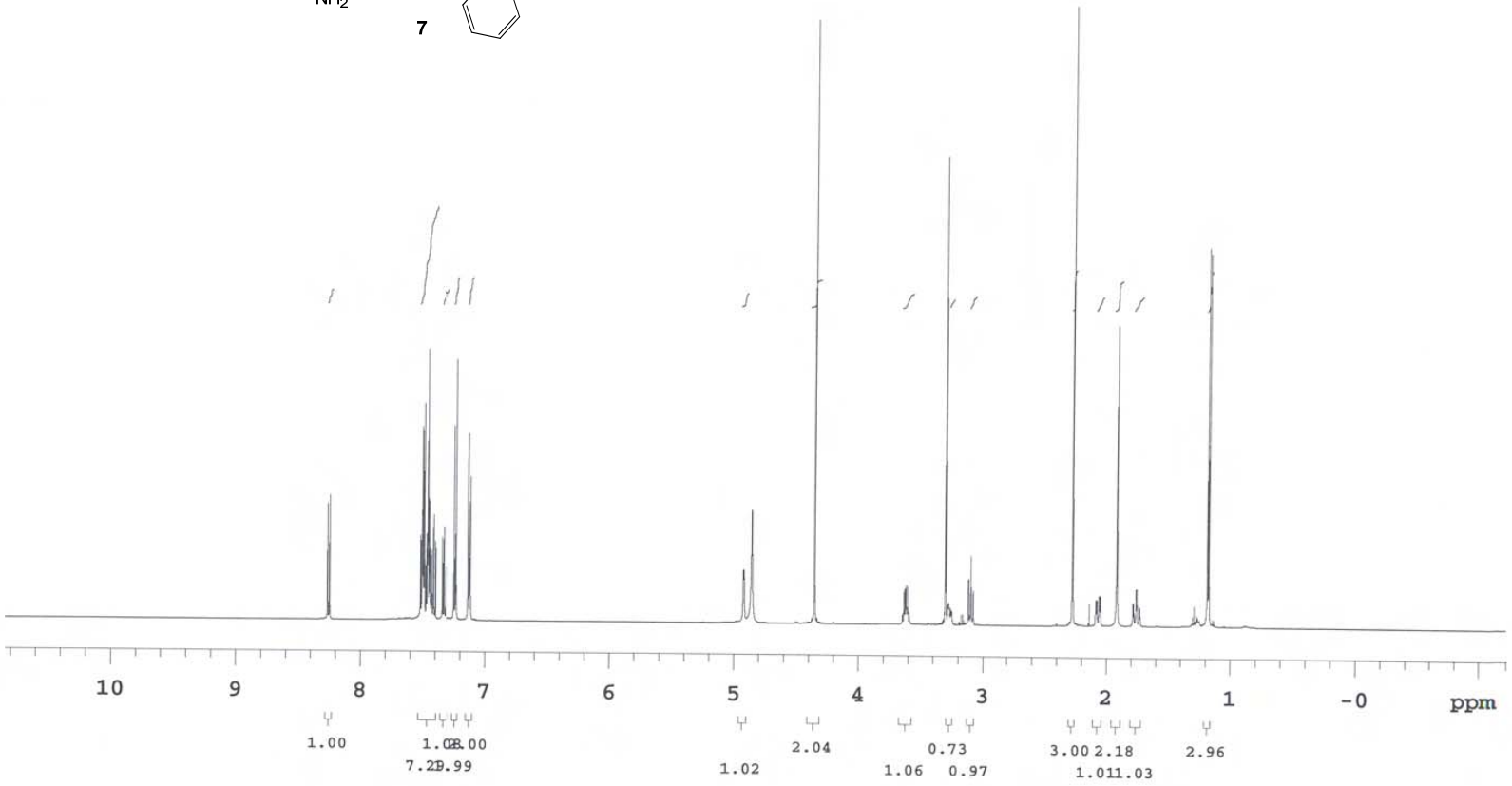

sw-03-159
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date: Aug 12 2007 sweep width: 32827Hz acq.time: 2.0s relax.time: 0.1s # scans: 64 dig.res.: 0.5 Hz/pt hz/mm:140.9
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-159-APT-1.fid
Pulse Sequence: apt
148.012
142.272
138.791
134.835
130.080
129.845
129.334
126.553
126.194
124.039
123.211
114.002
96.626
91.789
81.220
78.356
70.078
55.640
50.589
49.567
49.398
49.225
49.056
48.883
48.714
48.541
37.659
37.642
18.215
HO
O
O
NH2
S
6
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

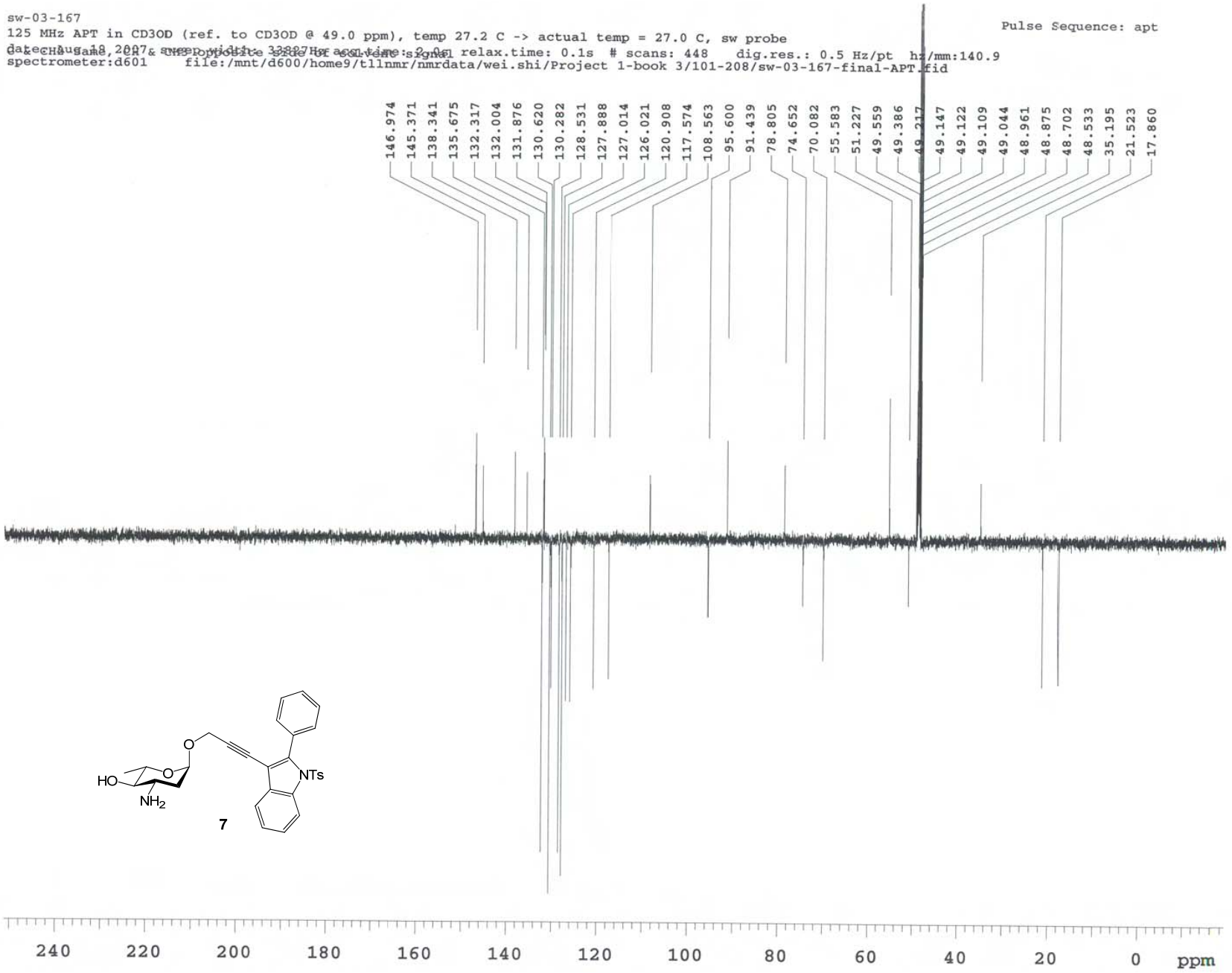
sw-03-167
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Aug 19 2007 sweep width: 6001Hz acq.time: 3.0s relax.time: 2.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-167-final.fid

Pulse Sequence: s2pul



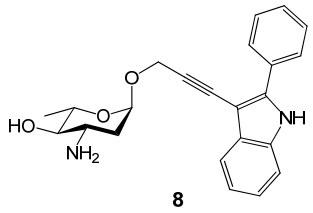
7



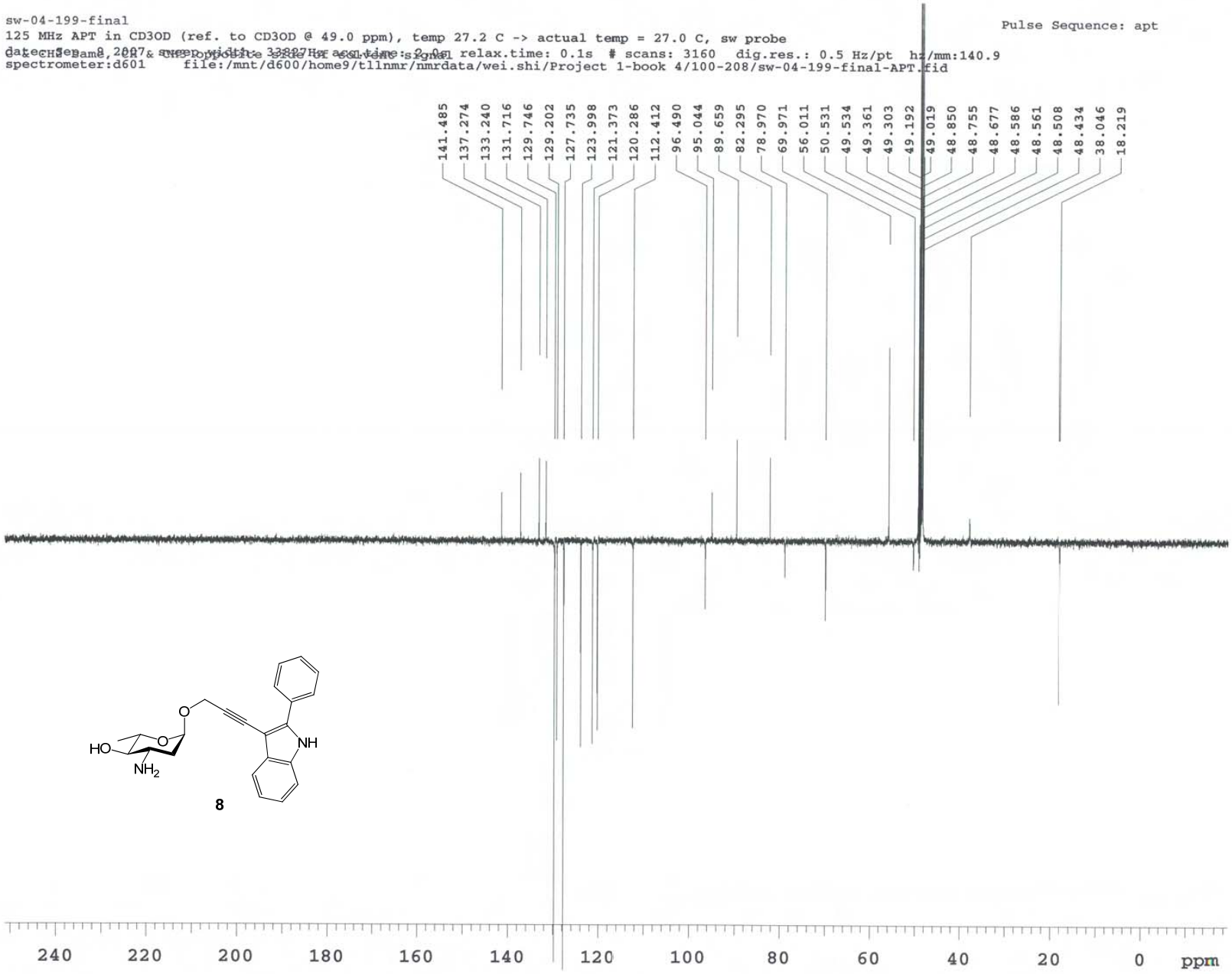

sw-03-167
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-167-final-APT.fid
146.974
145.371
138.341
135.675
132.317
132.004
131.876
130.620
130.282
128.531
127.888
127.014
126.021
120.908
117.574
108.563
95.600
91.439
78.805
74.652
70.082
55.583
51.227
49.559
49.386
49.217
49.147
49.122
49.109
49.044
48.961
48.875
48.702
48.533
35.195
21.523
17.860
HO
O
O
NH2
NTs
7
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

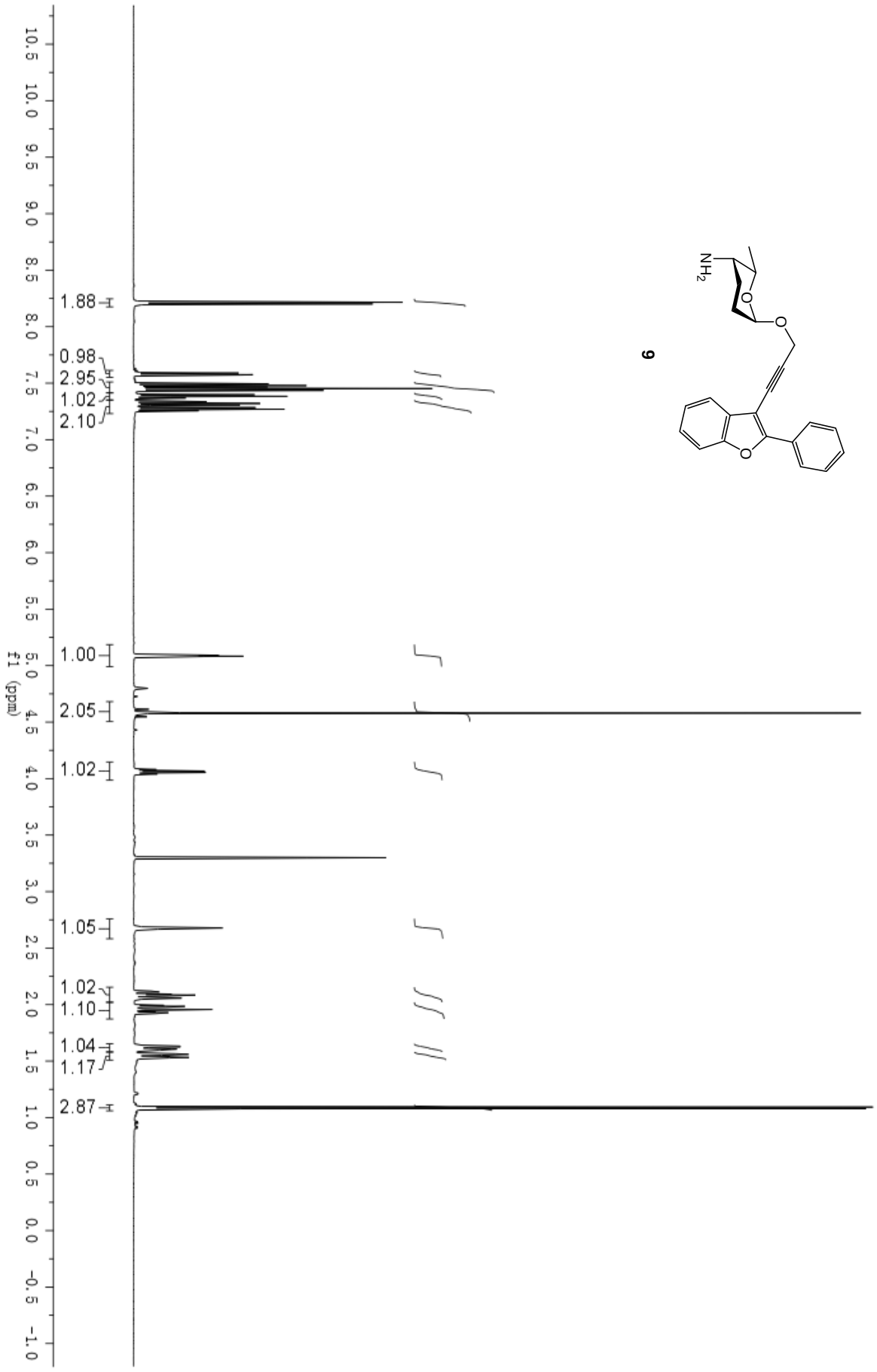
sw-04-199-final
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Sep 9 2007 sweep width: 6001Hz acq.time: 3.0s relax.time: 2.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-199-final.fid

Pulse Sequence: s2pul

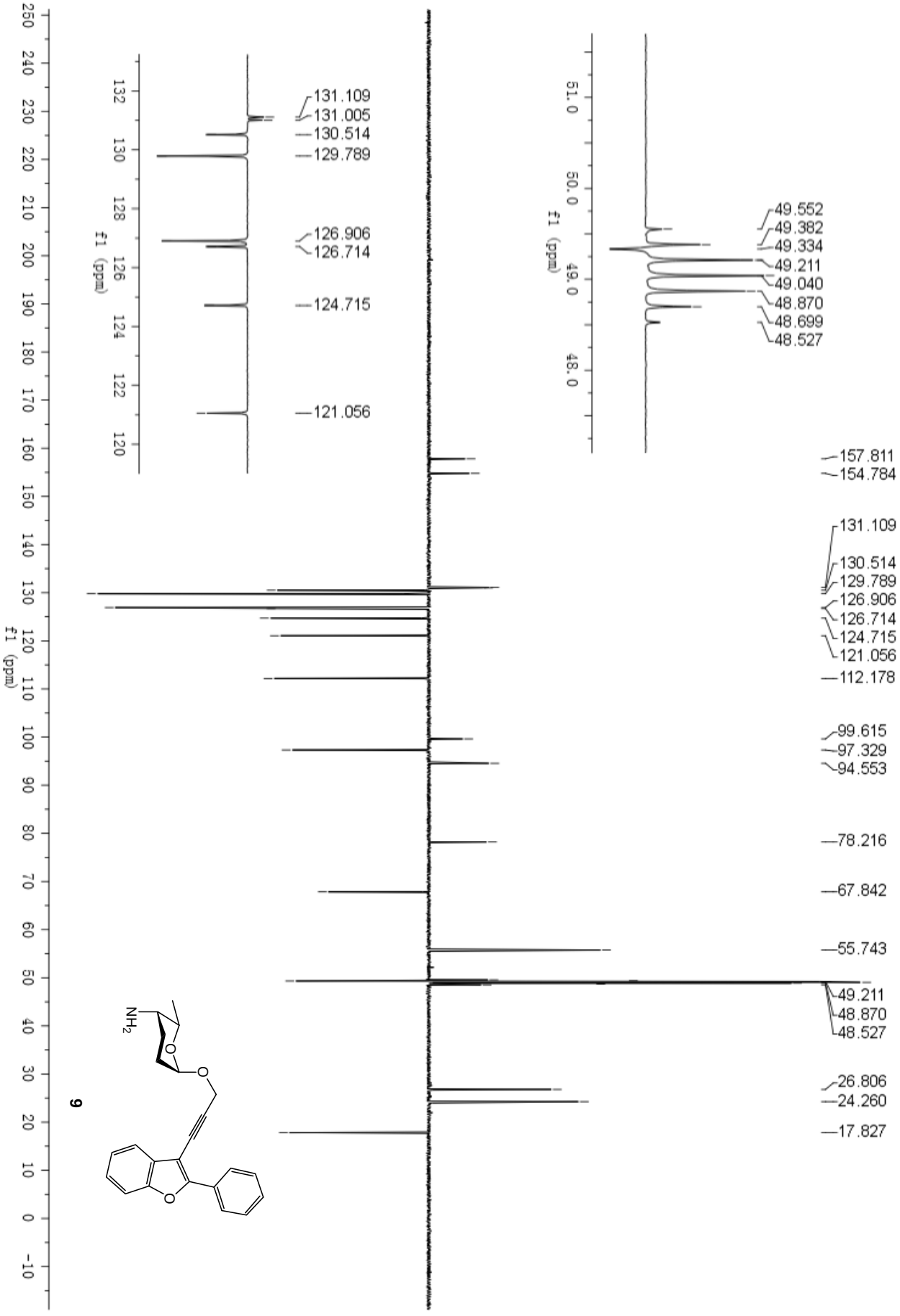


8

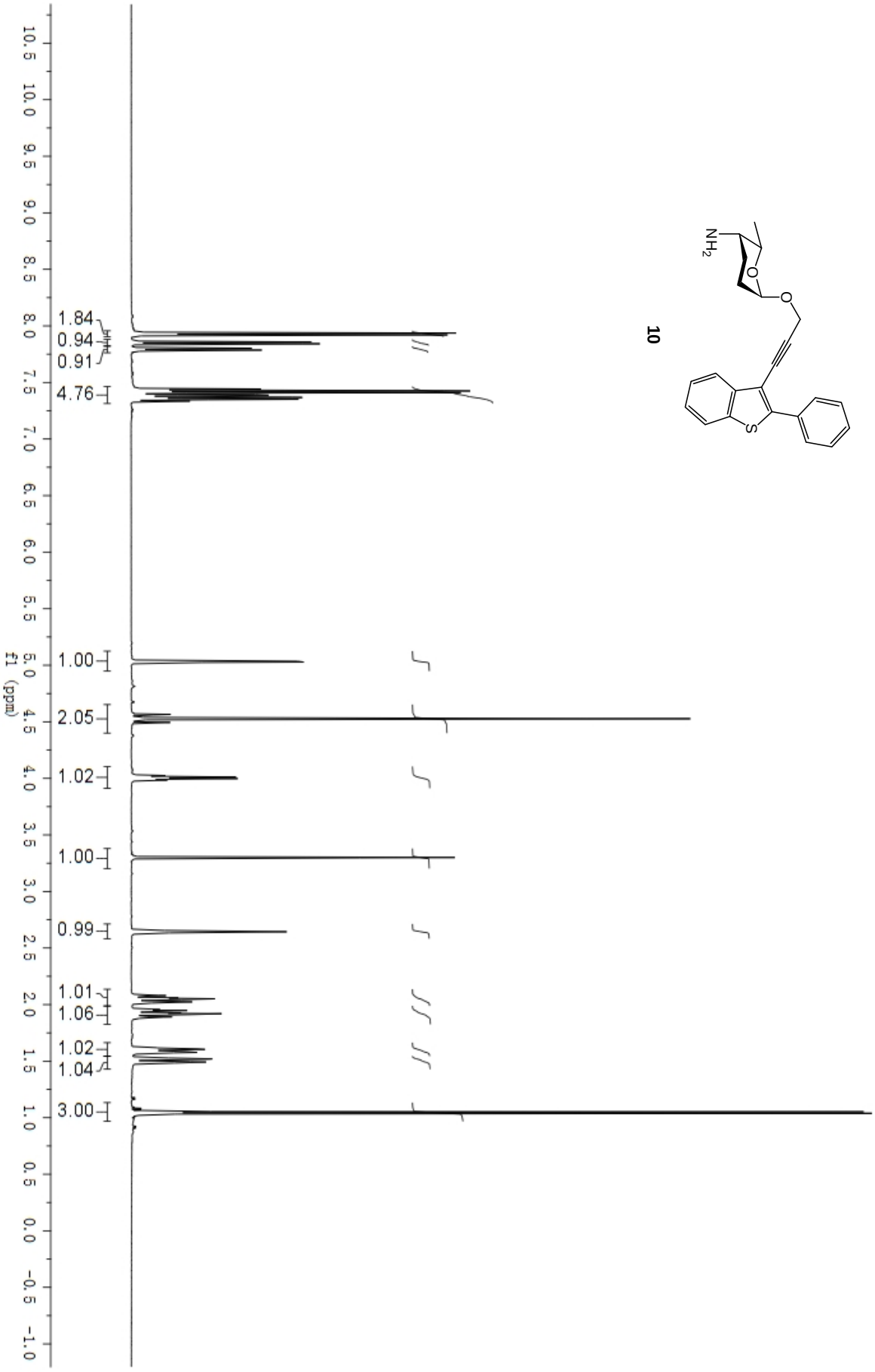

sw-04-199-final
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-199-final-APT.fid
Pulse Sequence: apt
141.485
137.274
133.240
131.716
129.746
129.202
127.735
123.998
121.373
120.286
112.412
96.490
95.044
89.659
82.295
78.970
69.971
56.011
50.531
49.534
49.361
49.303
49.192
49.019
48.850
48.755
48.677
48.586
48.561
48.508
48.434
38.046
18.219
HO
NH2
O
O
NH
8
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


1.88
0.98
2.95
1.02
2.10
1.00
2.05
1.02
1.05
1.02
1.10
1.04
1.17
2.87
f1 (ppm)
NH2
O
O
O

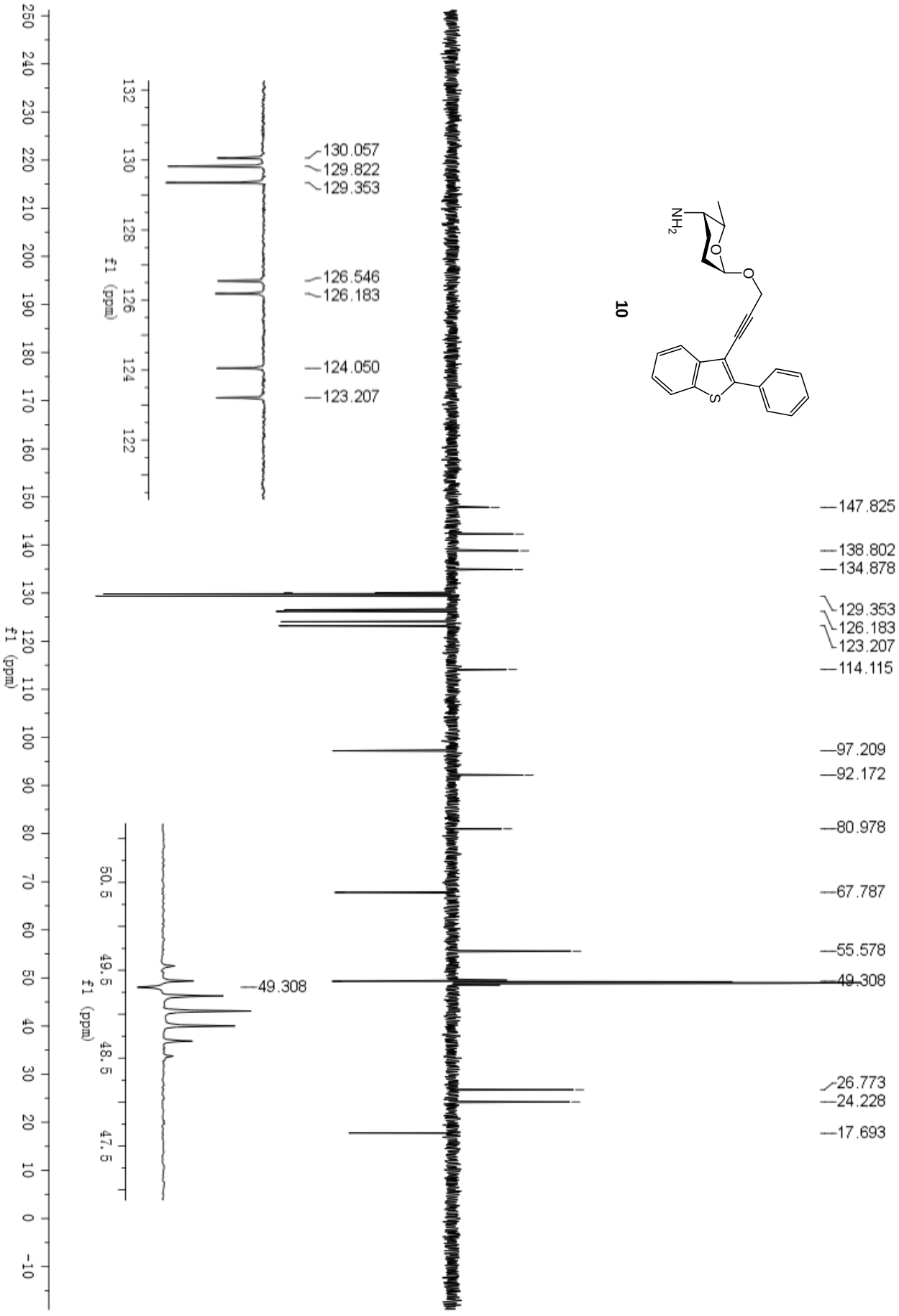
6

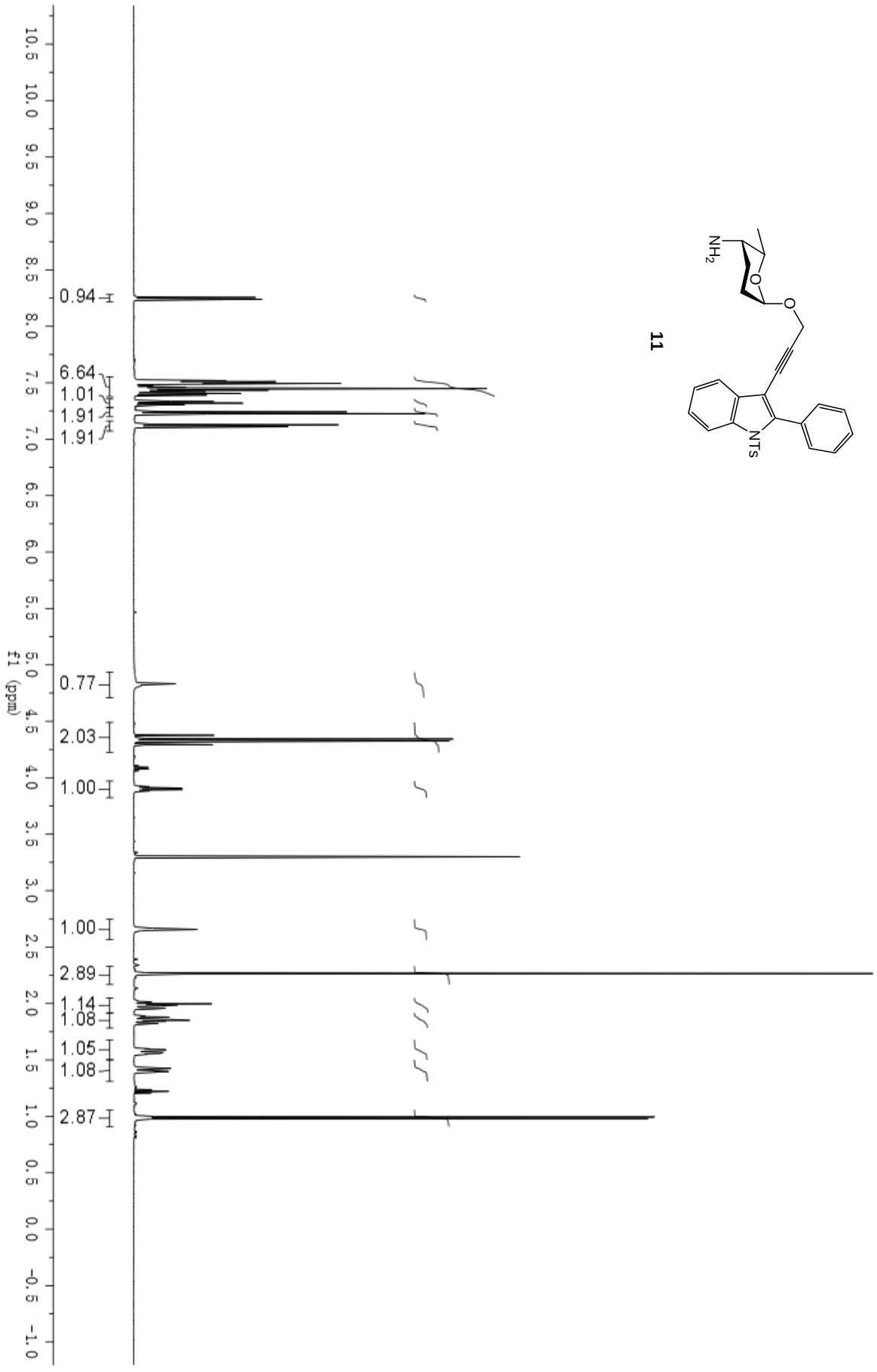

157.811
154.784
131.109
130.514
129.789
126.906
126.714
124.715
121.056
112.178
99.615
97.329
94.553
78.216
67.842
55.743
49.211
48.870
48.527
26.806
24.260
17.827
131.109
131.005
130.514
129.789
126.906
126.714
124.715
121.056
49.552
49.382
49.334
49.211
49.040
48.870
48.699
48.527
f1 (ppm)
NH2
O
O
O

6


1.84
0.94
0.91
4.76
1.00
2.05
1.02
1.00
0.99
1.01
1.06
1.02
1.04
3.00
f1 (ppm)
NH2
O
O
S

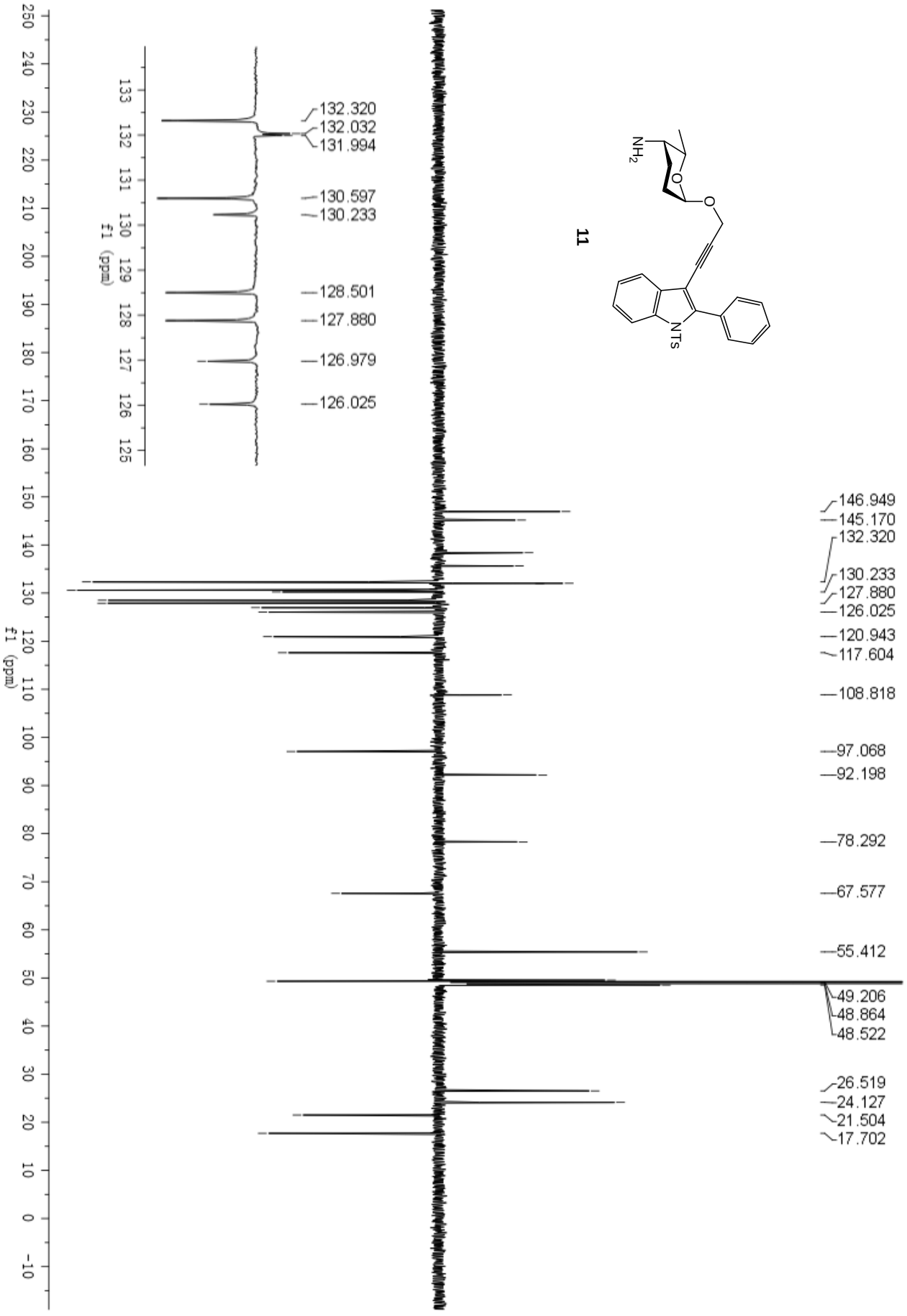
10

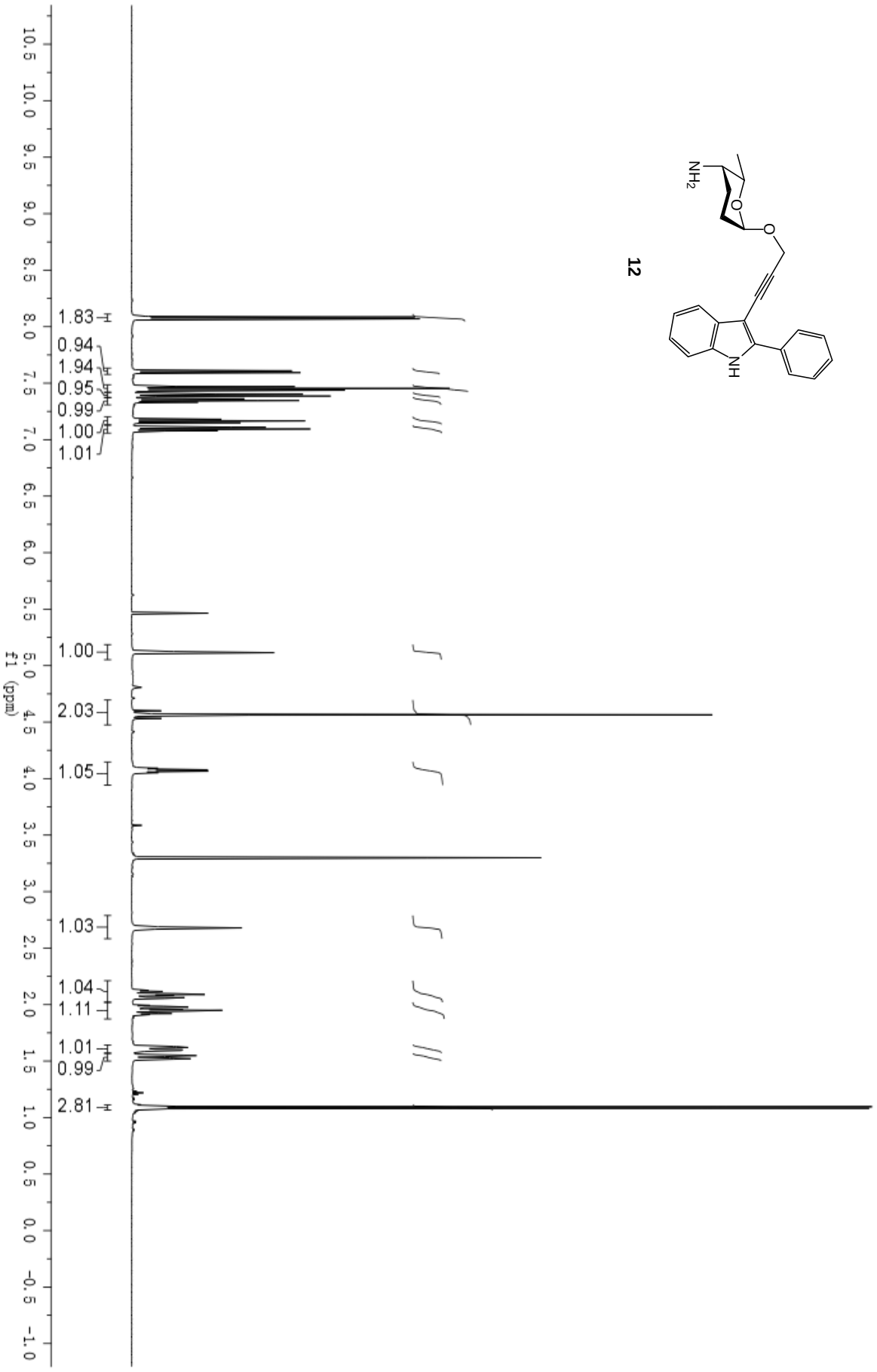

10
NH2
O
O
S
147.825
138.802
134.878
129.353
126.183
123.207
114.115
97.209
92.172
80.978
67.787
55.578
49.308
26.773
24.228
17.693
130.057
129.822
129.353
126.546
126.183
124.050
123.207
49.308
f1 (ppm)

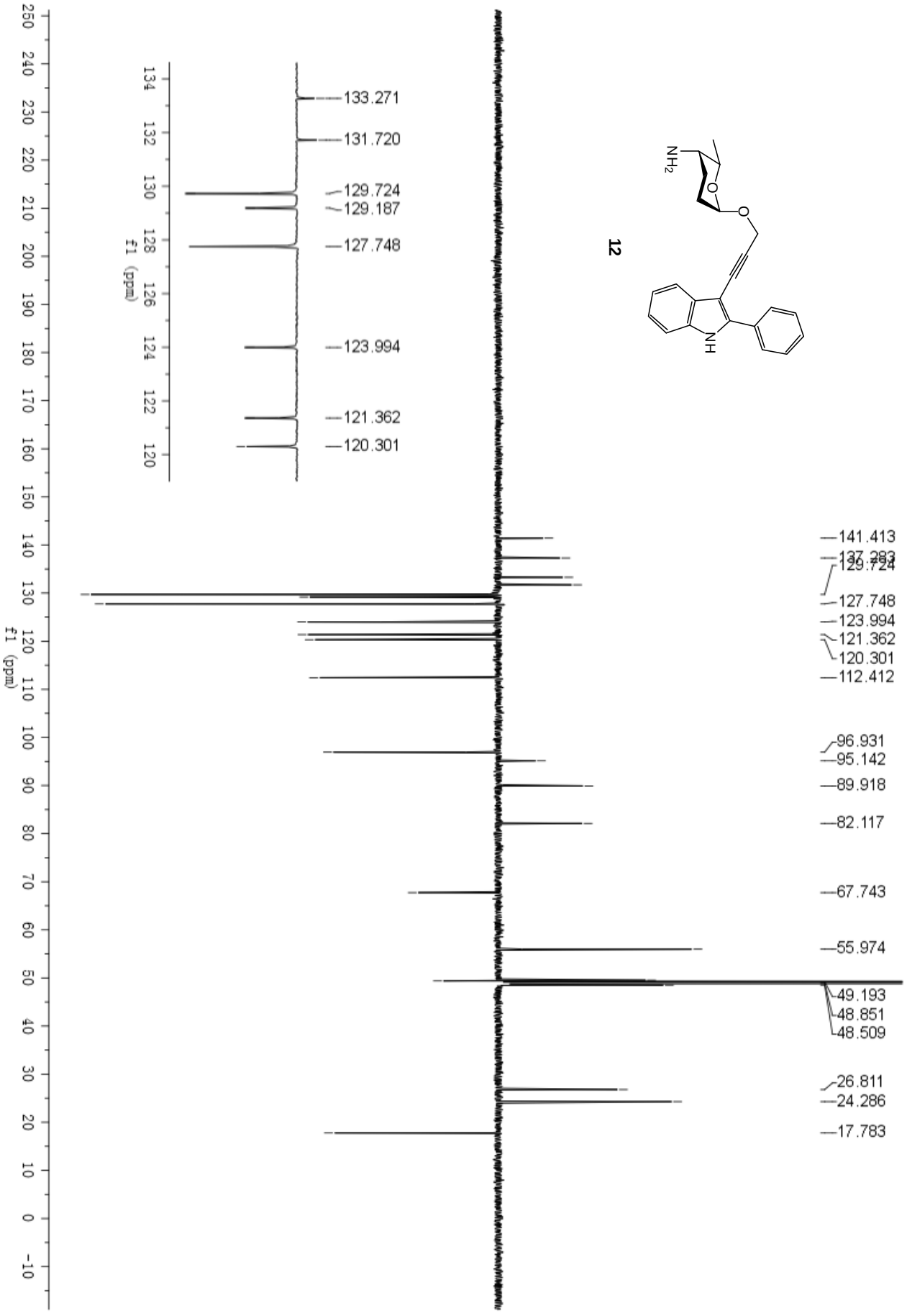

0.94
6.64
1.01
1.91
1.91
0.77
2.03
1.00
1.00
2.89
1.14
1.08
1.05
1.08
2.87
f1 (ppm)

NH2
O
O
NTs

11


11
NH2
O
O
NTs
132.320
132.032
131.994
130.597
130.233
128.501
127.880
126.979
126.025
146.949
145.170
132.320
130.233
127.880
126.025
120.943
117.604
108.818
97.068
92.198
78.292
67.577
55.412
49.206
48.864
48.522
26.519
24.127
21.504
17.702
f1 (ppm)


12
NH2
O
O
NH
1.83
0.94
1.94
0.95
0.99
1.00
1.01
1.00
2.03
1.05
1.03
1.04
1.11
1.01
0.99
2.81
f1 (ppm)


133.271
131.720
129.724
129.187
127.748
123.994
121.362
120.301
f1 (ppm)
141.413
129.724
127.748
123.994
121.362
120.301
112.412
96.931
95.142
89.918
82.117
67.743
55.974
49.193
48.851
48.509
26.811
24.286
17.783
f1 (ppm)
NH2
O
O
NH
12

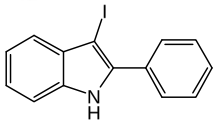
sw-04-127

Pulse Sequence: s2pul

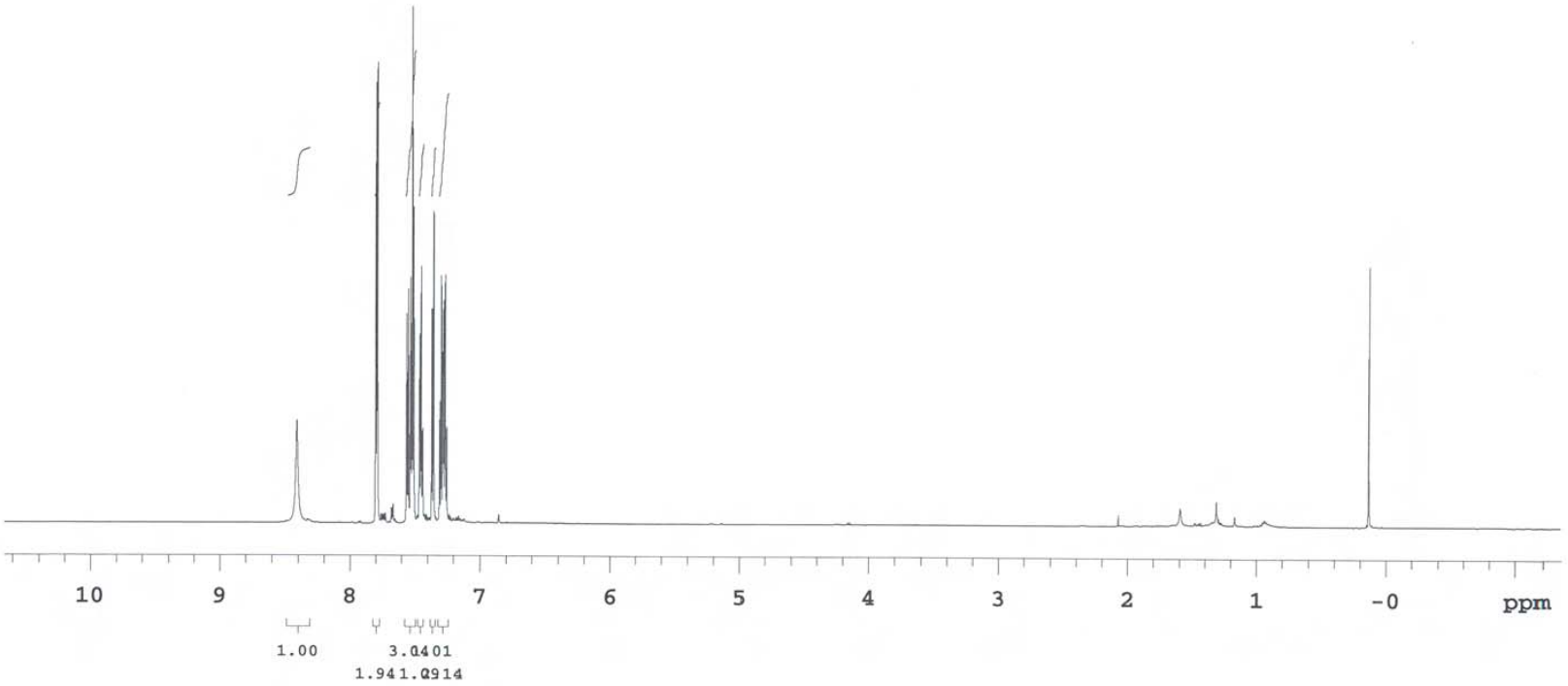
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 28.0 C -> actual temp = 27.0 C, id600 probe

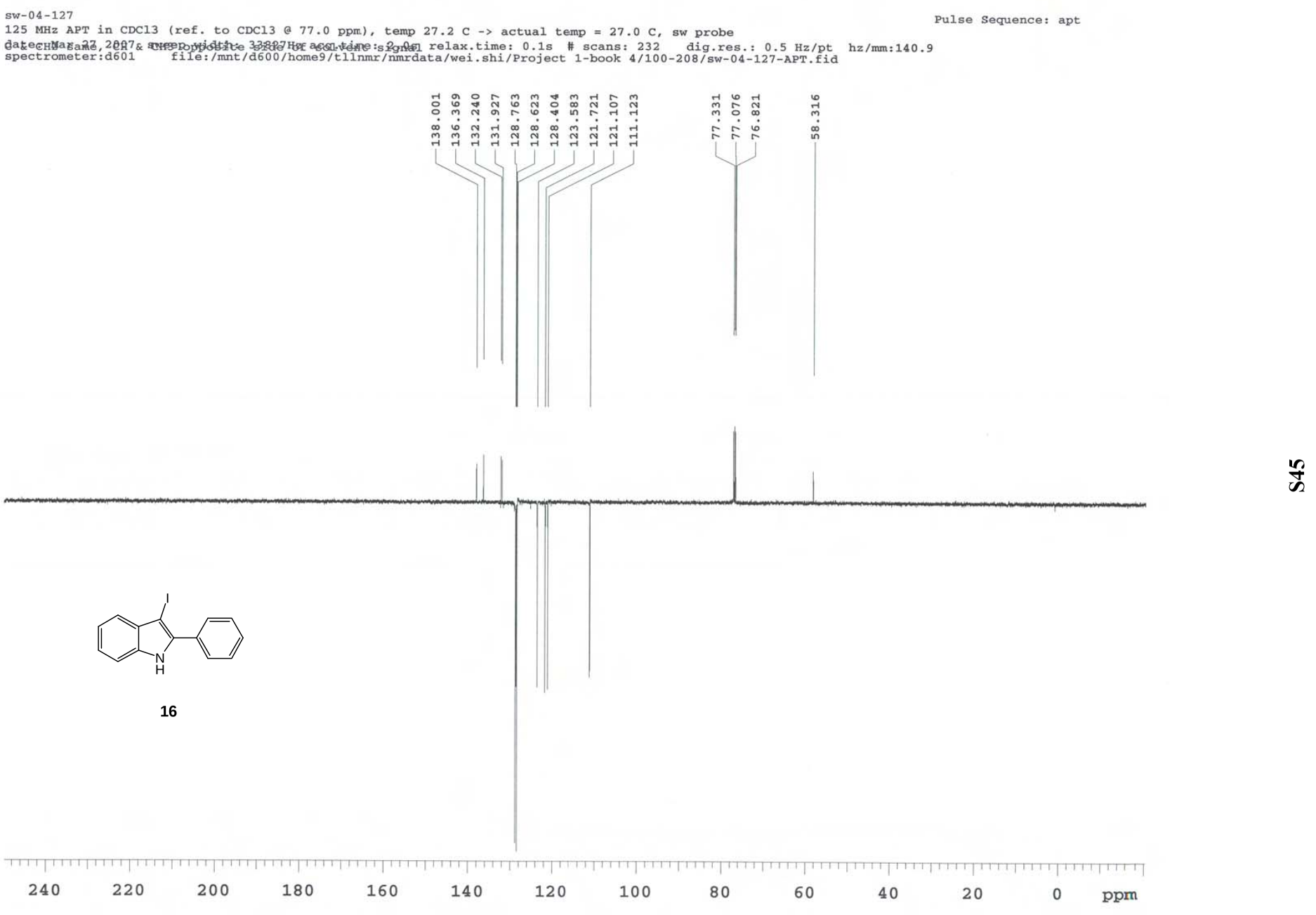
date: Mar 27 2007 sweep width: 7201Hz acq.time: 5.0s relax.time: 0.1s # scans: 8 dig.res.: 0.1 Hz/pt hz/mm:30.0

spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-127.fid



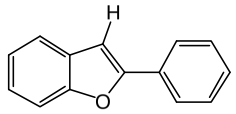
16



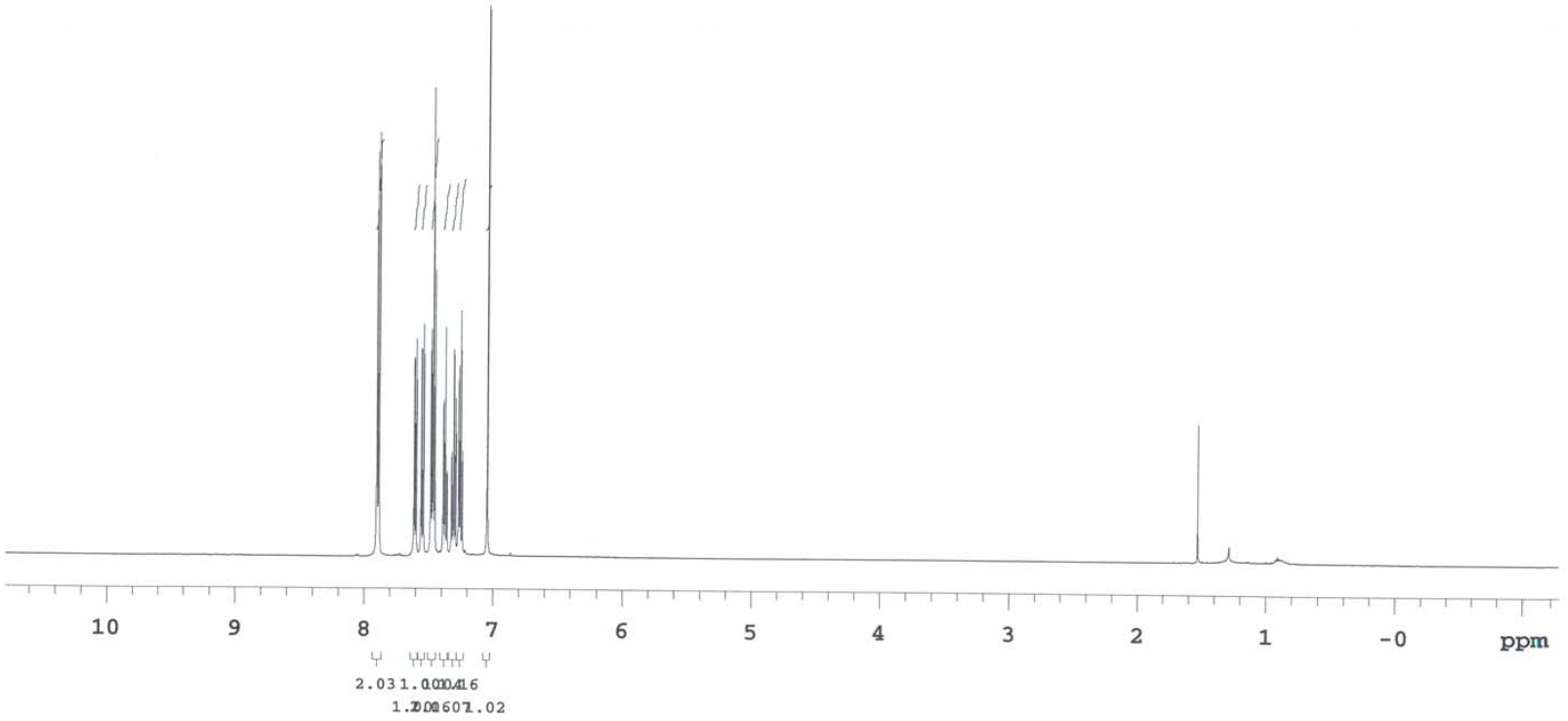

sw-04-127
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-127-APT.fid
138.001
136.369
132.240
131.927
128.763
128.623
128.404
123.583
121.721
121.107
111.123
77.331
77.076
76.821
58.316
I
N
H
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

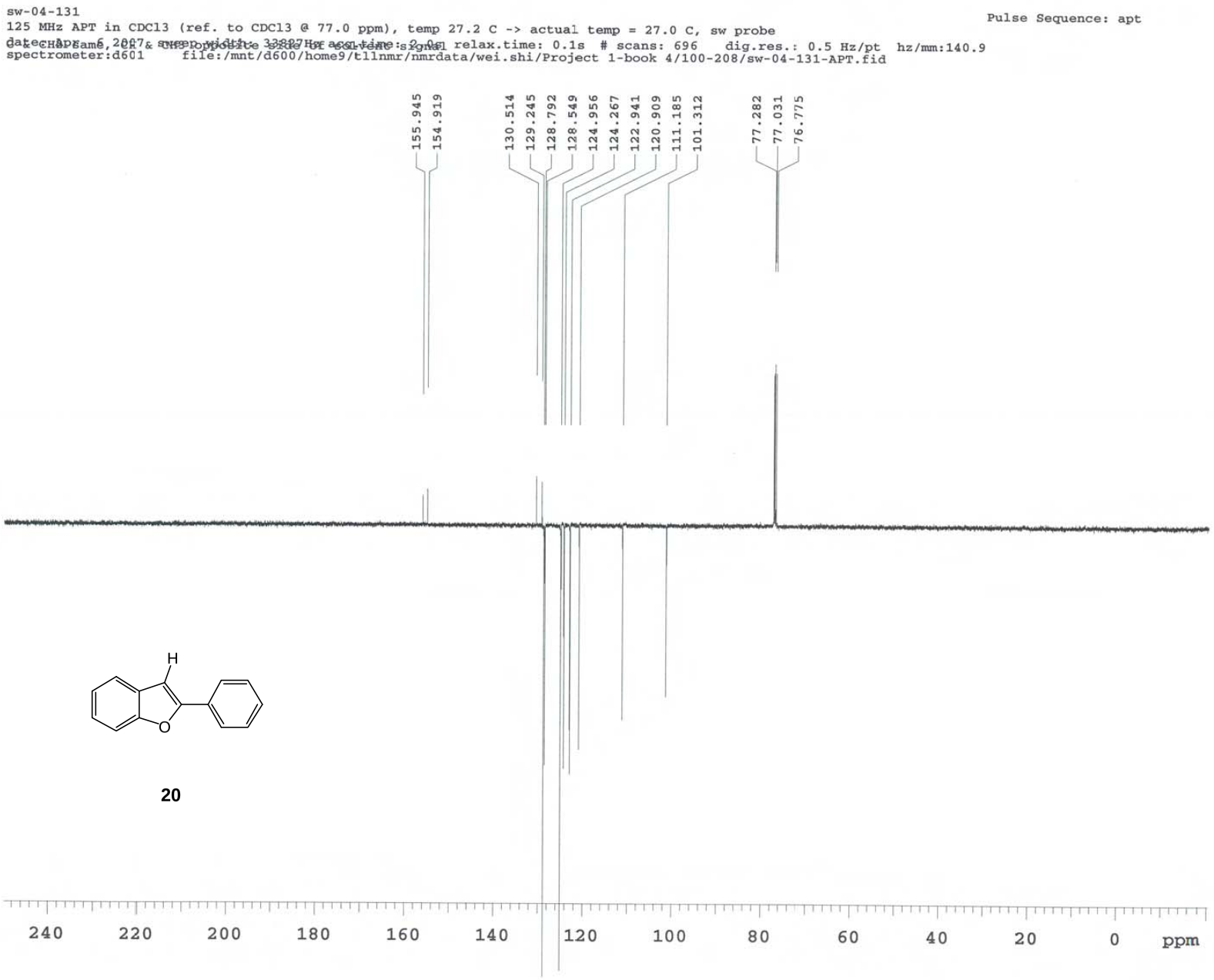
16

sw-04-131
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
Pulse Sequence: s2pul
date: Apr 6 2007 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-131.fid



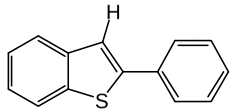
20



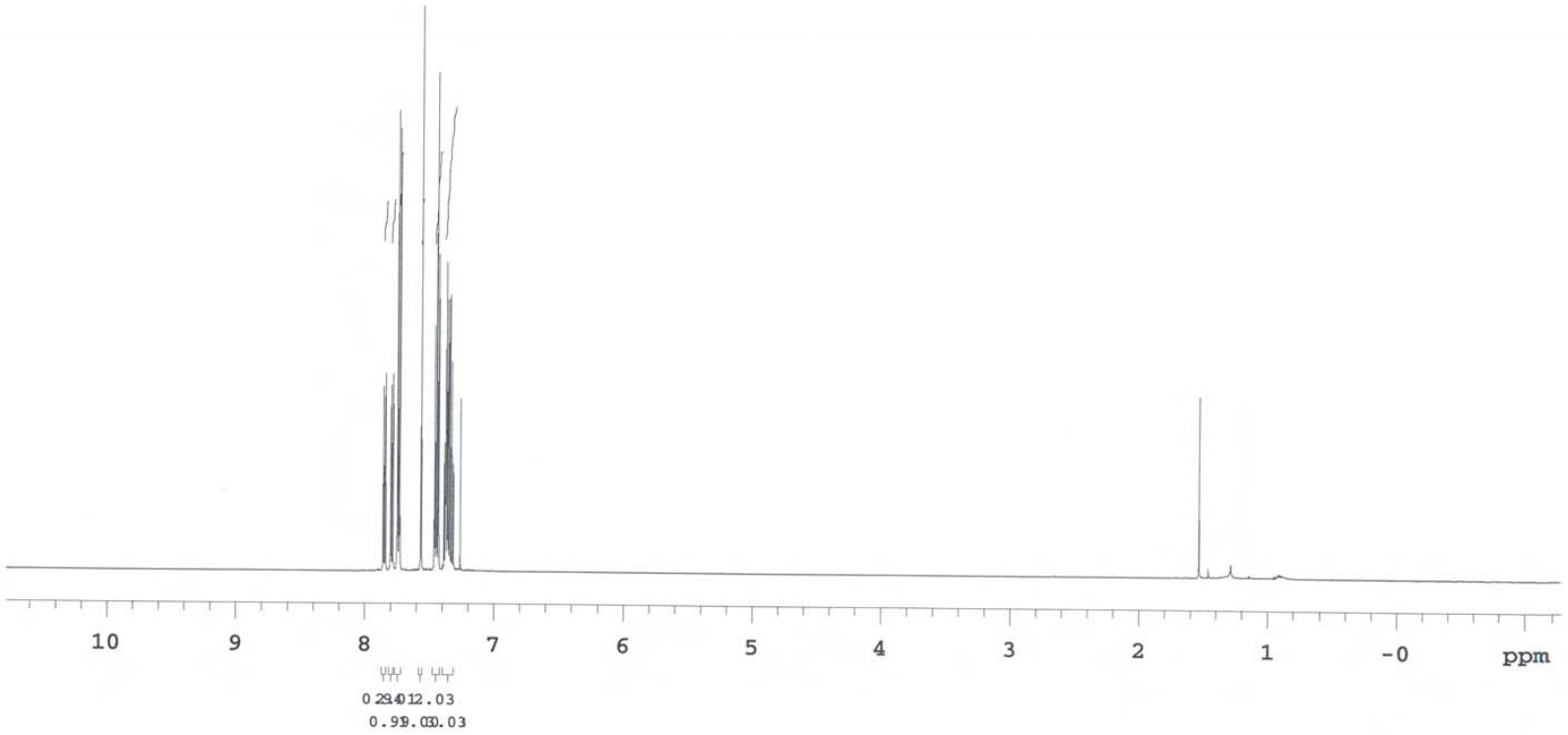

sw-04-131
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-131-APT.fid
155.945
154.919
130.514
129.245
128.792
128.549
124.956
124.267
122.941
120.909
111.185
101.312
77.282
77.031
76.775
H
O
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

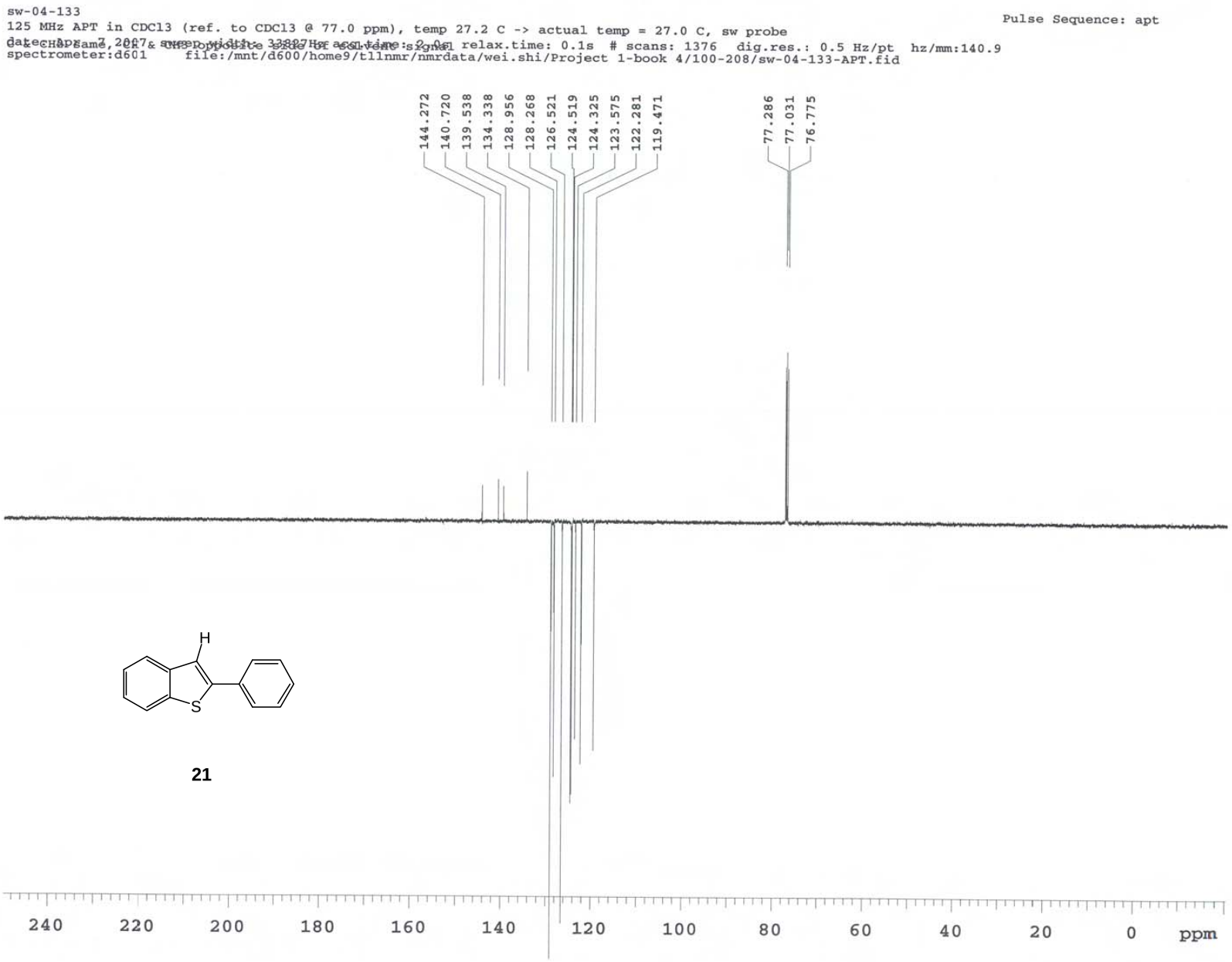
20

sw-04-133
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
Pulse Sequence: s2pul
date: Apr 7 2007 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-133.fid

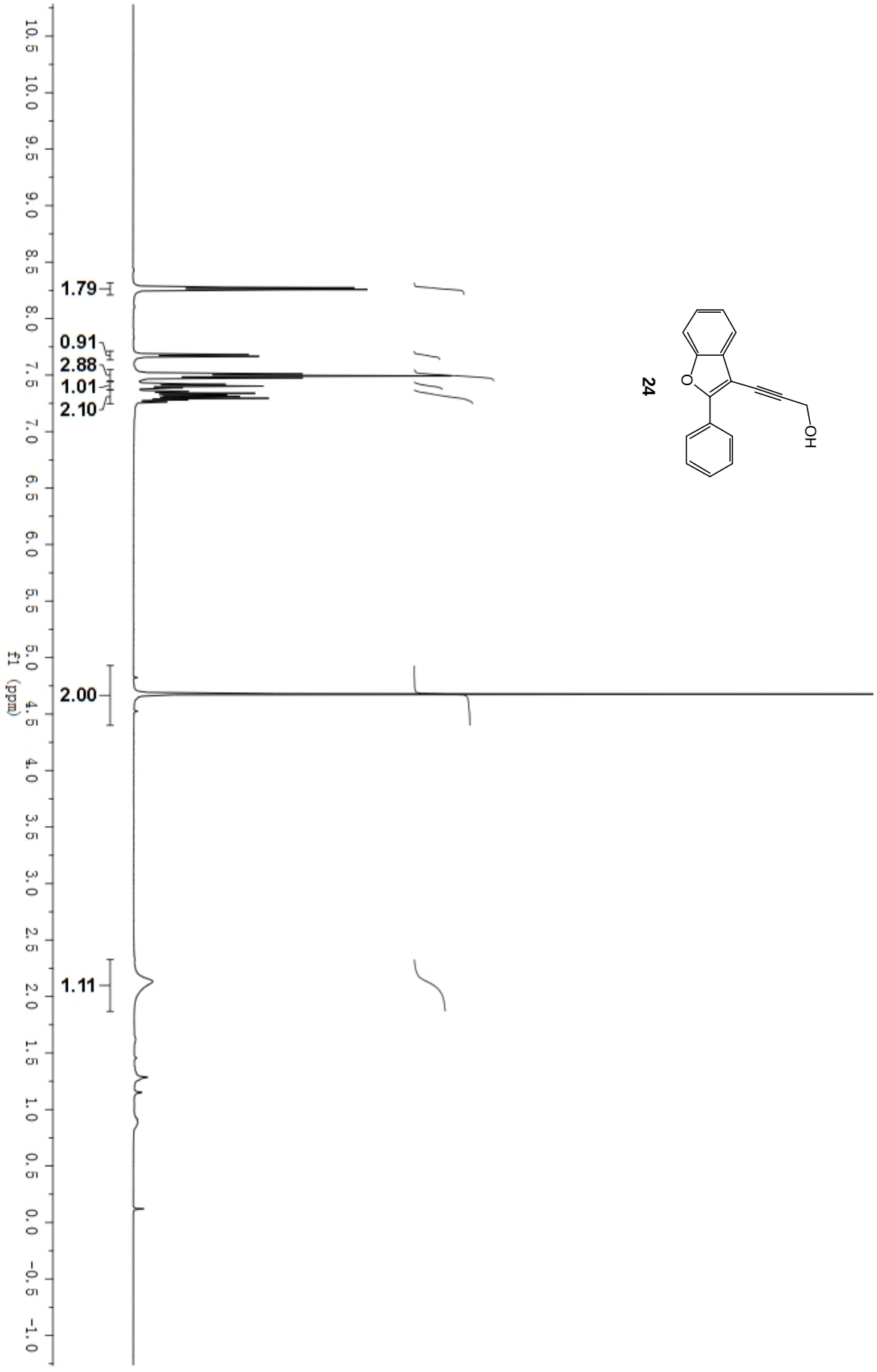


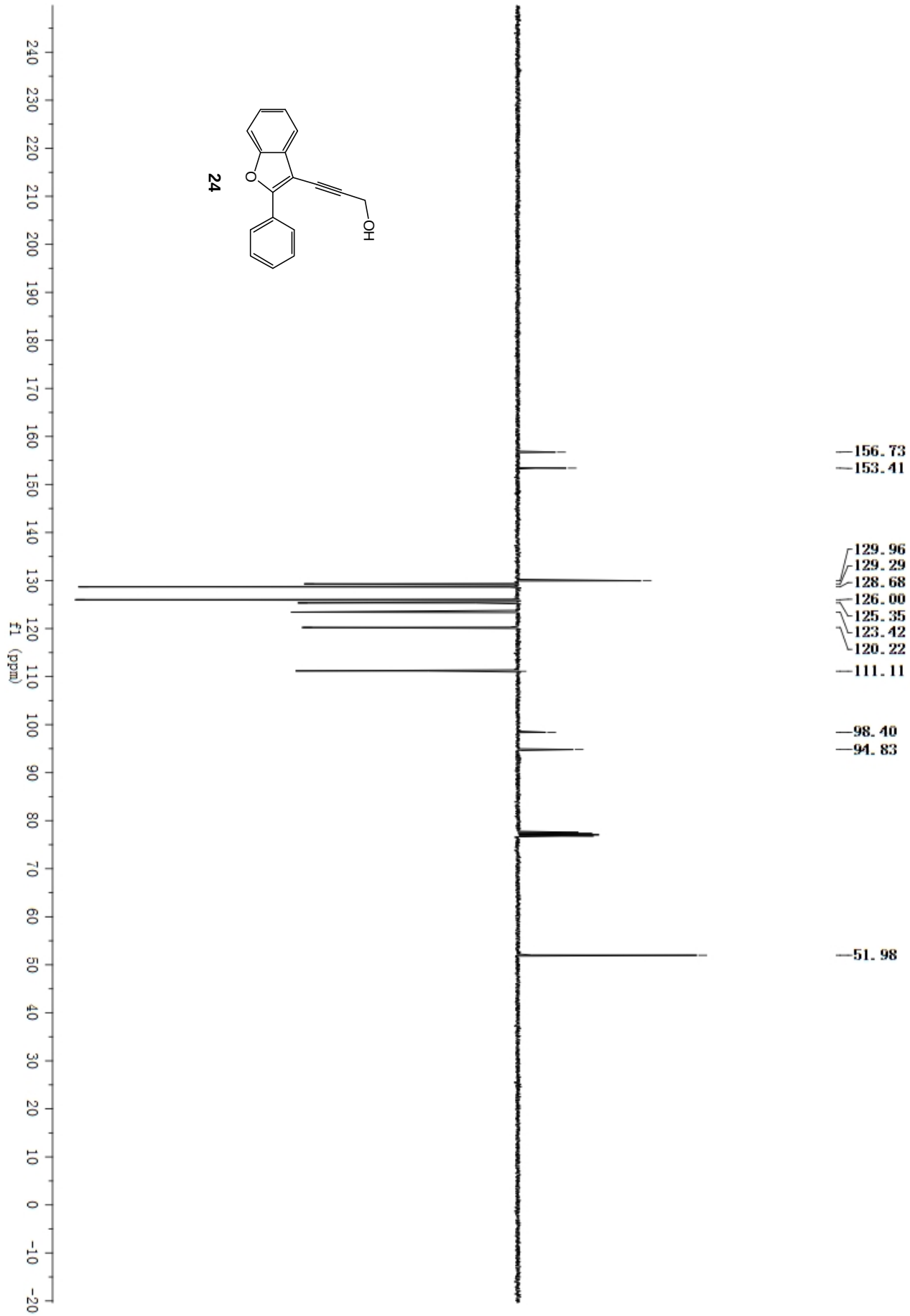
21




sw-04-133
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-133-APT.fid
144.272
140.720
139.538
134.338
128.956
128.268
126.521
124.519
124.325
123.575
122.281
119.471
77.286
77.031
76.775
H
S
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

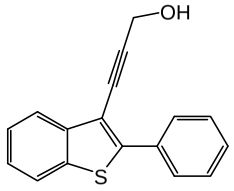
21


1.79
0.91
2.88
1.01
2.10
2.00
1.11
f1 (ppm)
24
O
OH

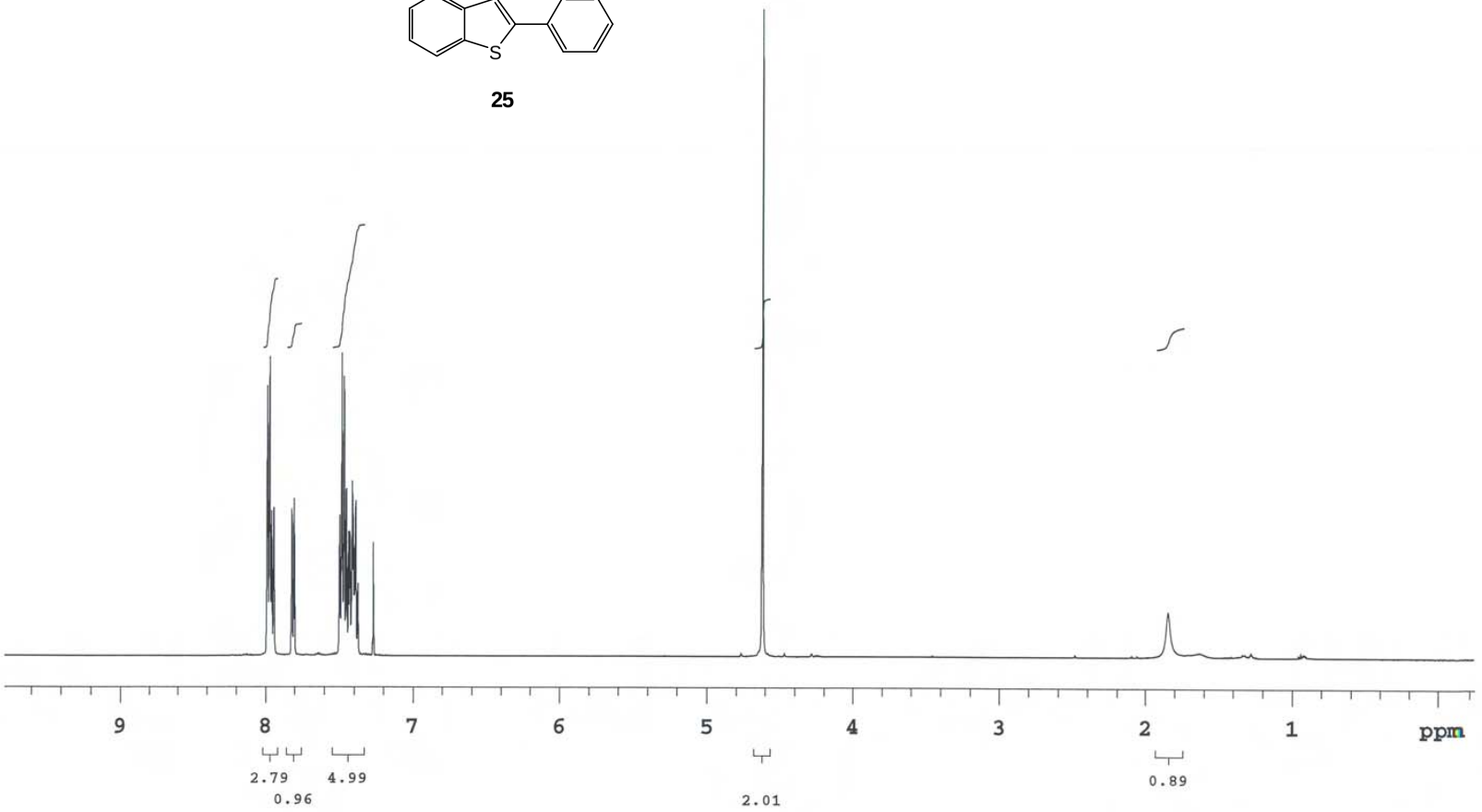

24
OH
156.73
153.41
129.96
129.29
128.68
126.00
125.35
123.42
120.22
111.11
98.40
94.83
51.98
f1 (ppm)

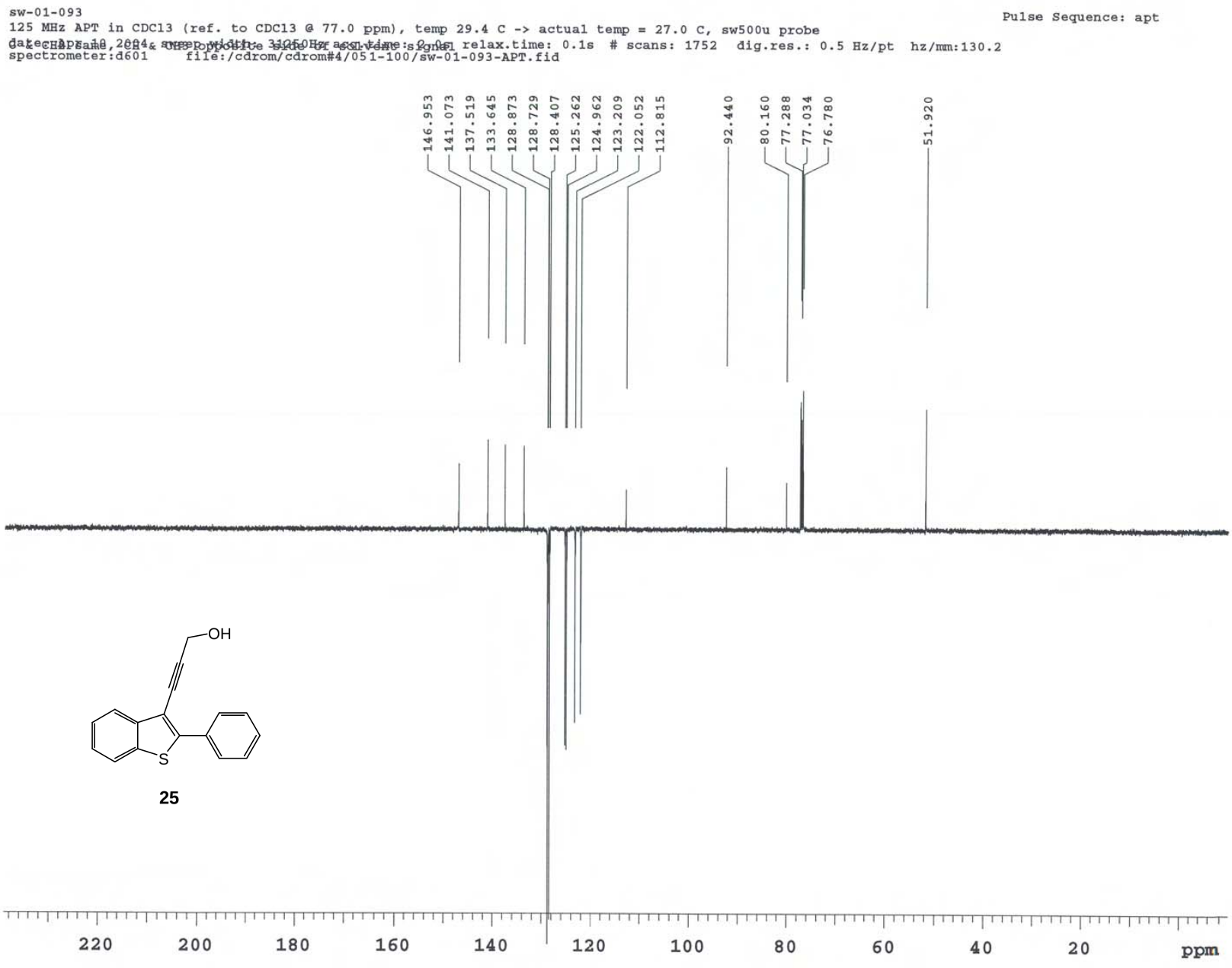
sw-01-093
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.24 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
date: Apr 10 2004 sweep width: 5001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.8
spectrometer:d601 file:/cdrom/cdrom#4/051-100/sw-01-093.fid

Pulse Sequence: s2pul



25

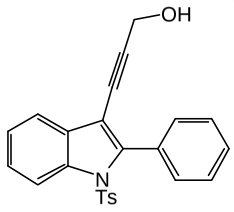



sw-01-093
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe
Pulse Sequence: apt
spectrometer:d601 file:/cdrom/cdrom#4/051-100/sw-01-093-APT.fid
146.953
141.073
137.519
133.645
128.873
128.729
128.407
125.262
124.962
123.209
122.052
112.815
92.440
80.160
77.288
77.034
76.780
51.920
OH
S
220
200
180
160
140
120
100
80
60
40
20
ppm

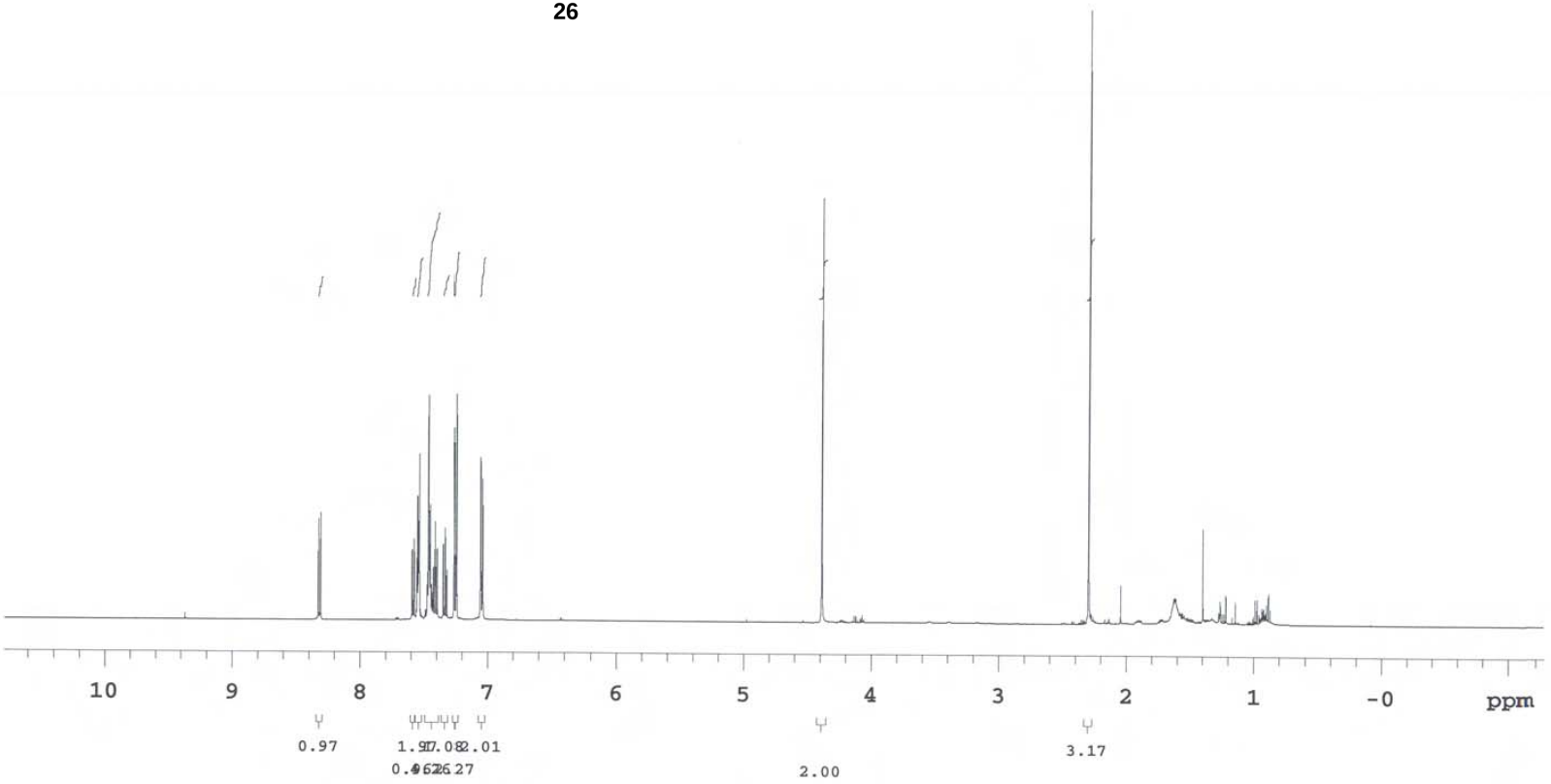
25

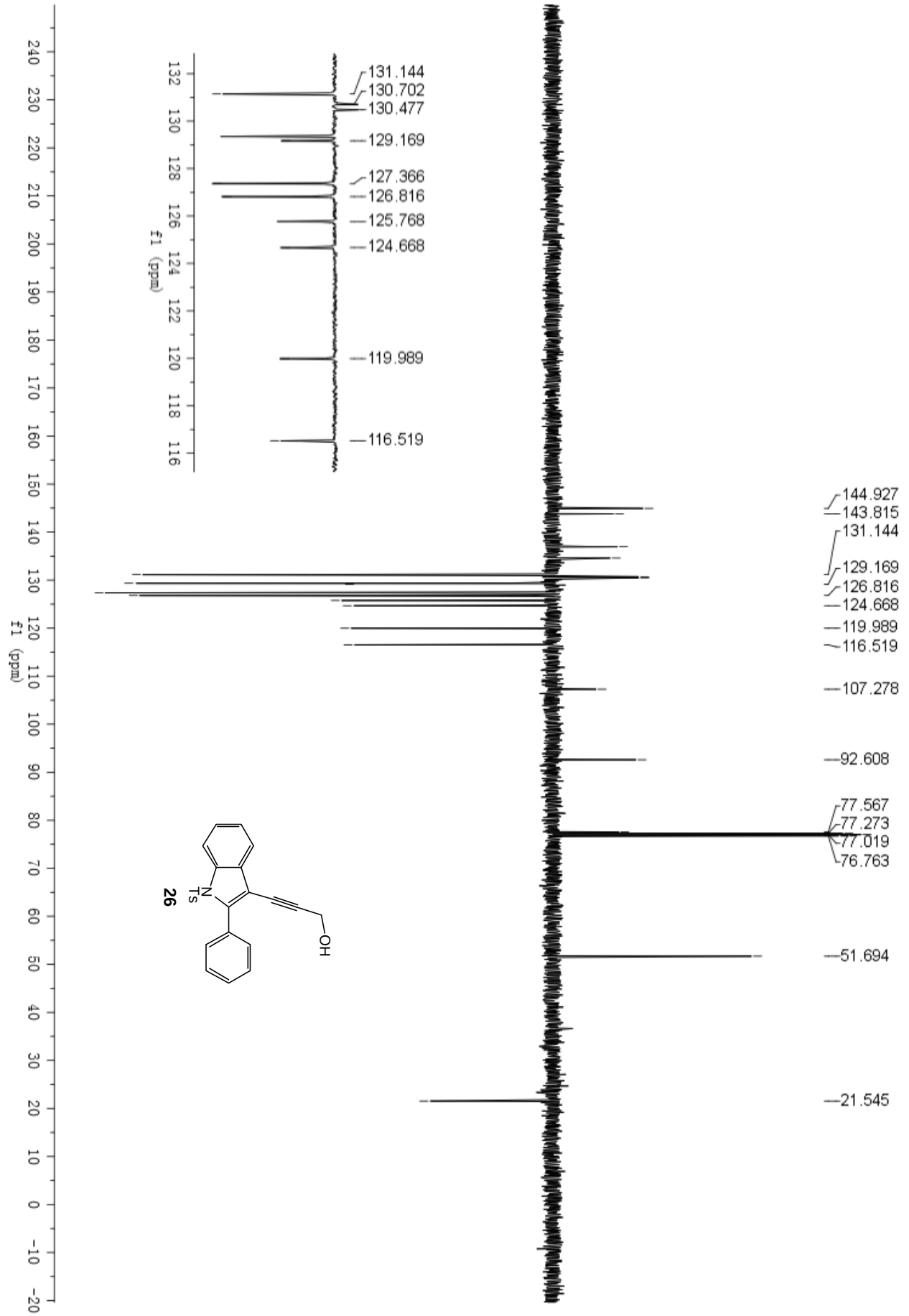
sw-04-155
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Apr 30 2007 sweep width: 6001Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-155.fid

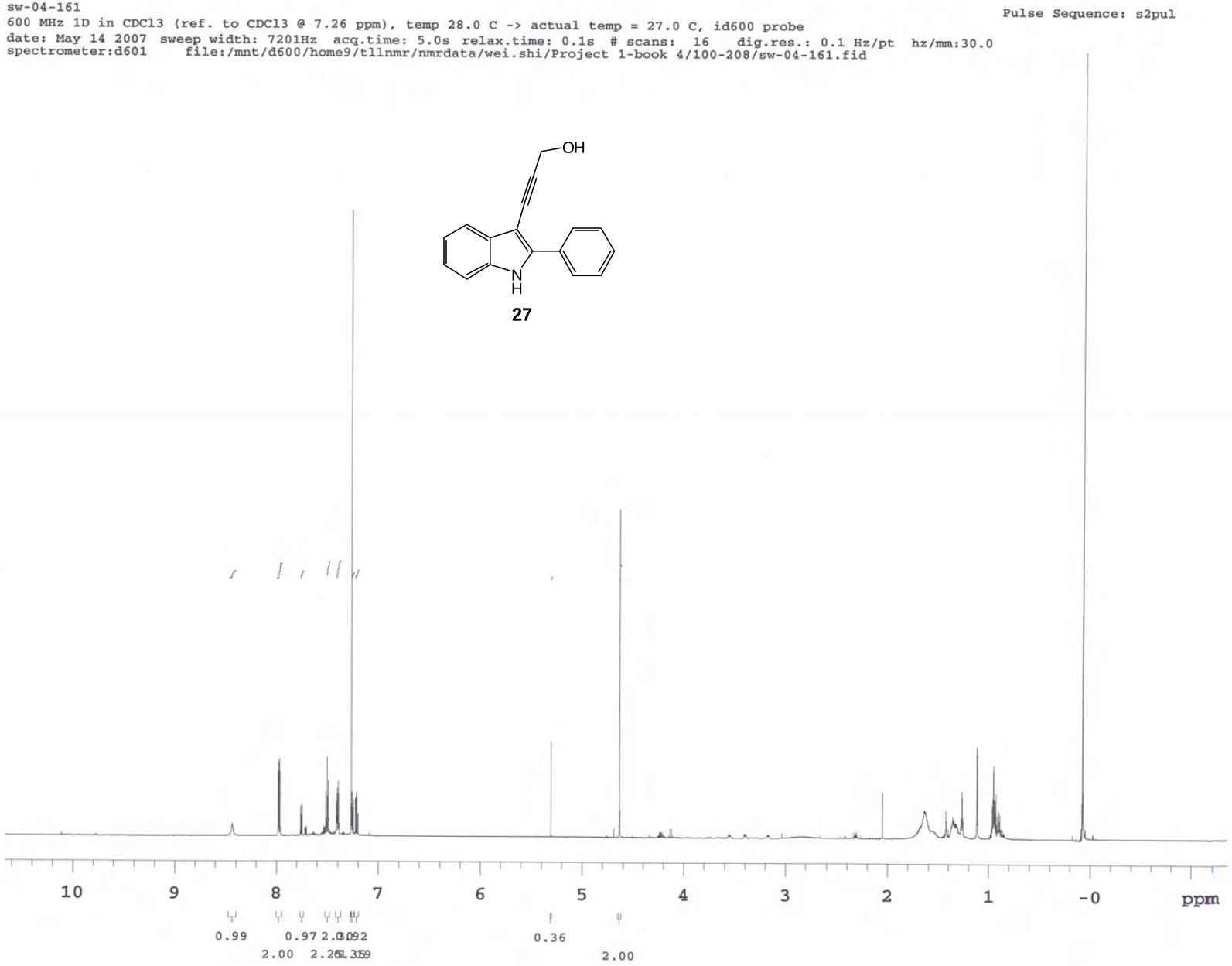
Pulse Sequence: s2pul

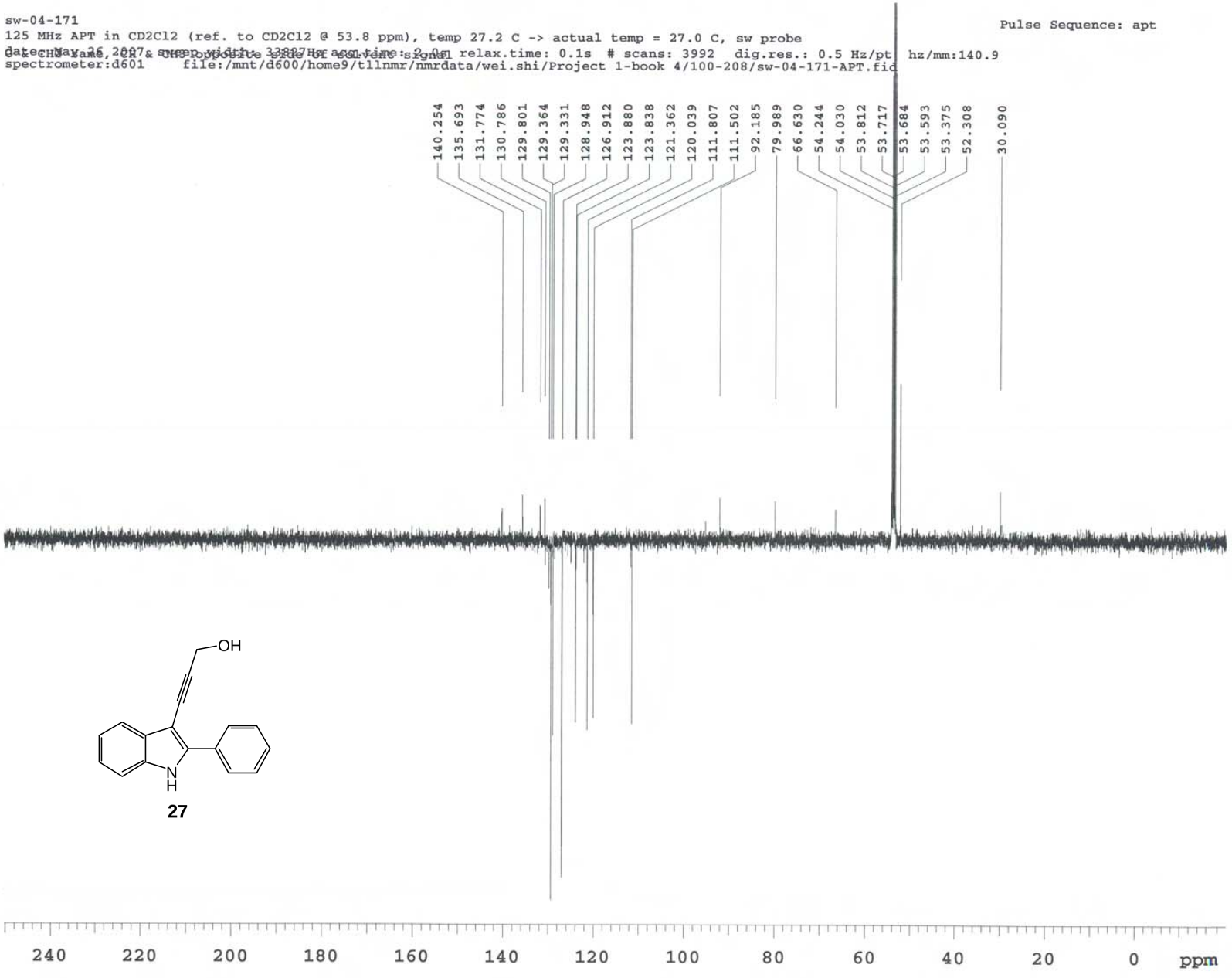


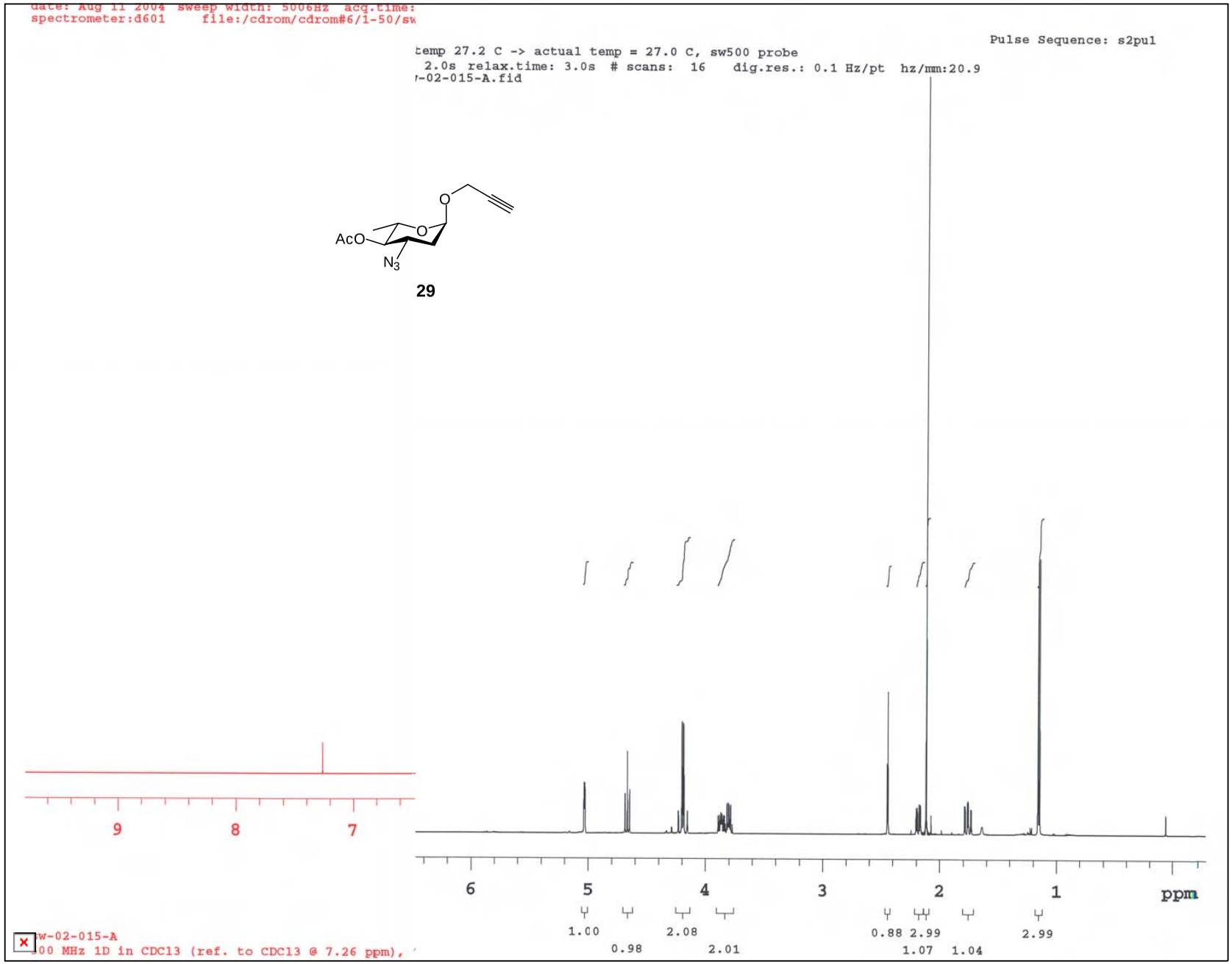
26

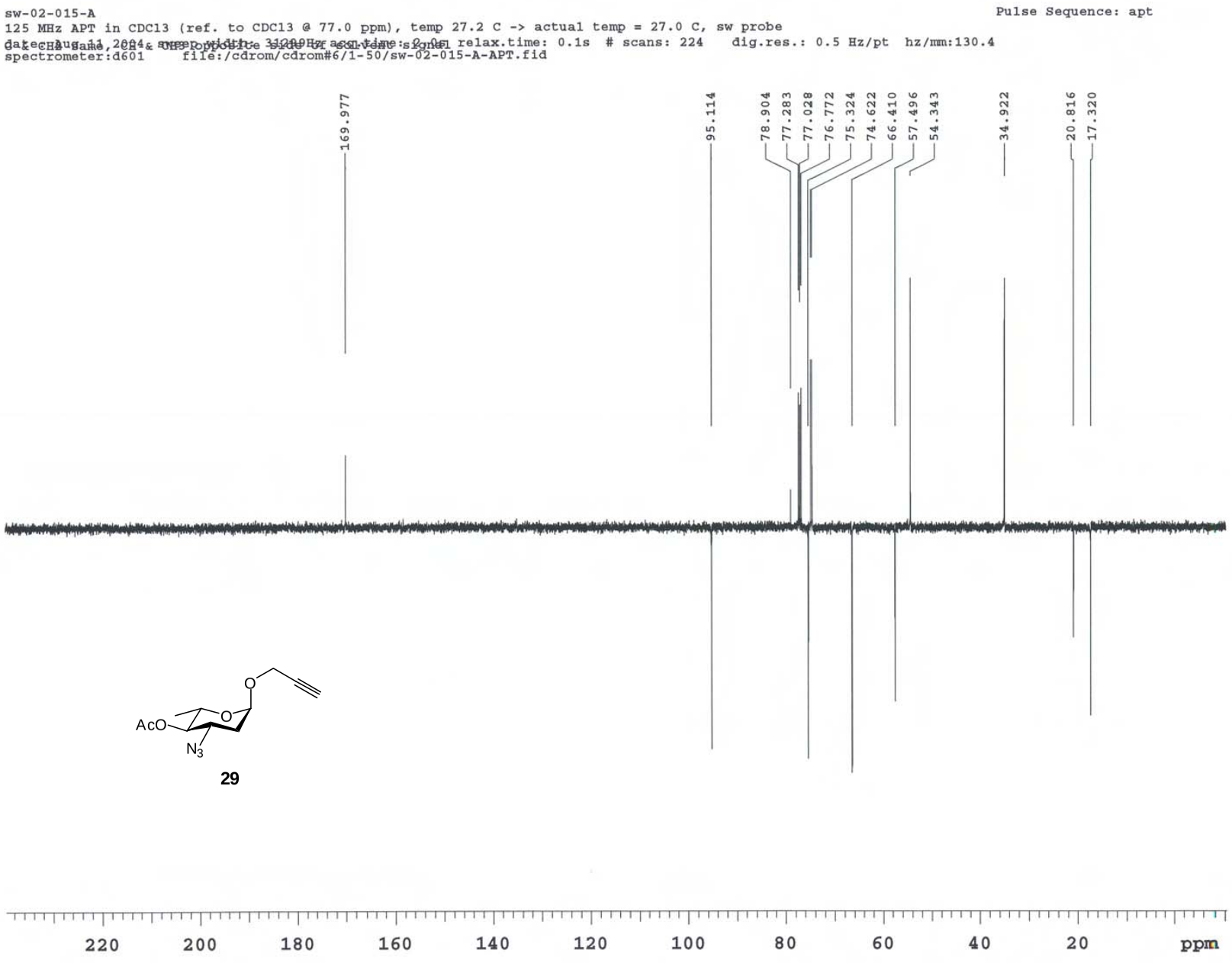



131.144
130.702
130.477
129.169
127.366
126.816
125.768
124.668
119.989
116.519
f1 (ppm)
144.927
143.815
131.144
129.169
126.816
124.668
119.989
116.519
107.278
92.608
77.567
77.273
77.019
76.763
51.694
21.545
f1 (ppm)
26
Ts
N
OH


sw-04-161
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 28.0 C -> actual temp = 27.0 C, id600 probe
date: May 14 2007 sweep width: 7201Hz acq.time: 5.0s relax.time: 0.1s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:30.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-161.fid
Pulse Sequence: s2pul
OH
N
H
27
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.99
0.97
0.36
2.00
2.00


sw-04-171
125 MHz APT in CD2Cl2 (ref. to CD2Cl2 @ 53.8 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date:May 26 2017 sweep width: 33897Hz acq.time:2.0s relax.time: 0.1s # scans: 3992 dig.res.: 0.5 Hz/pt hz/mm:140.9
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 4/100-208/sw-04-171-APT.fid
Pulse Sequence: apt
140.254
135.693
131.774
130.786
129.801
129.364
129.331
128.948
126.912
123.880
123.838
121.362
120.039
111.807
111.502
92.185
79.989
66.630
54.244
54.030
53.812
53.717
53.684
53.593
53.375
52.308
30.090
OH
N
H
27
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

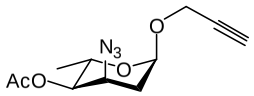

spectrometer:d601
file:/cdrom/cdrom#6/1-50/sw
Pulse Sequence: s2pul
temp 27.2 C -> actual temp = 27.0 C, sw500 probe
2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
-02-015-A.fid
AcO
O
O
N3
29
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
2.08
2.01
0.88
2.99
1.07
1.04
2.99
w-02-015-A
00 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm),


sw-02-015-A
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date:Aug 11 2004 sweep width: 31289Hz acq.time: 2.0s relax.time: 0.1s # scans: 224 dig.res.: 0.5 Hz/pt hz/mm:130.4
d1 & CH3 same, CH & CH2 opposite side of solvent signal
spectrometer:d601 file:/cdrom/cdrom#6/1-50/sw-02-015-A-APT.fid
Pulse Sequence: apt
169.977
95.114
78.904
77.283
77.028
76.772
75.324
74.622
66.410
57.496
54.343
34.922
20.816
17.320
AcO
O
O
N3
220
200
180
160
140
120
100
80
60
40
20
ppm

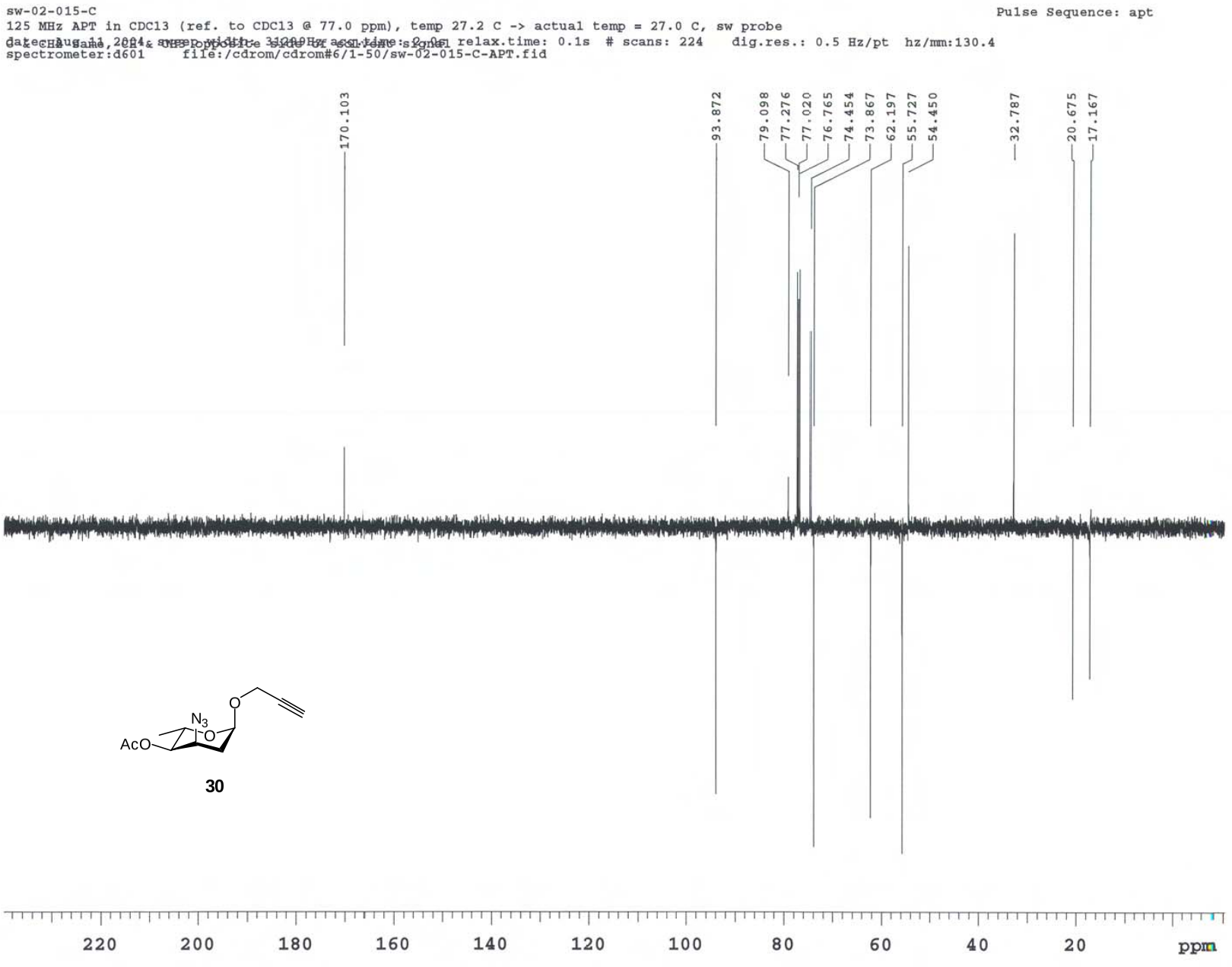
29

sw-02-015-C
500 MHz 1D in CDC13 (ref. to CDC13 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Aug 11 2004 sweep width: 5006Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
spectrometer:d601 file:/cdrom/cdrom#6/1-50/sw-02-015-C.fid

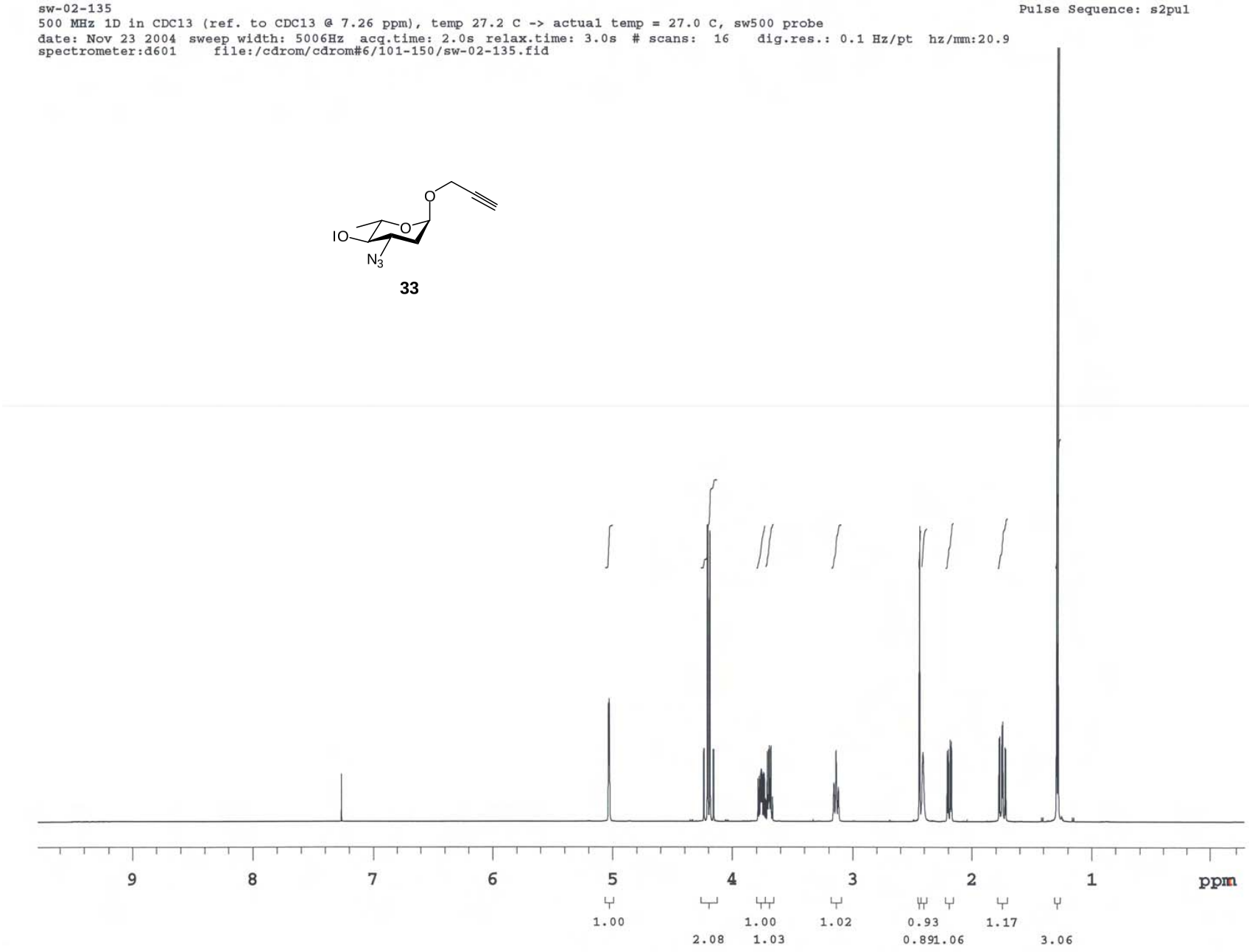
Pulse Sequence: s2pul



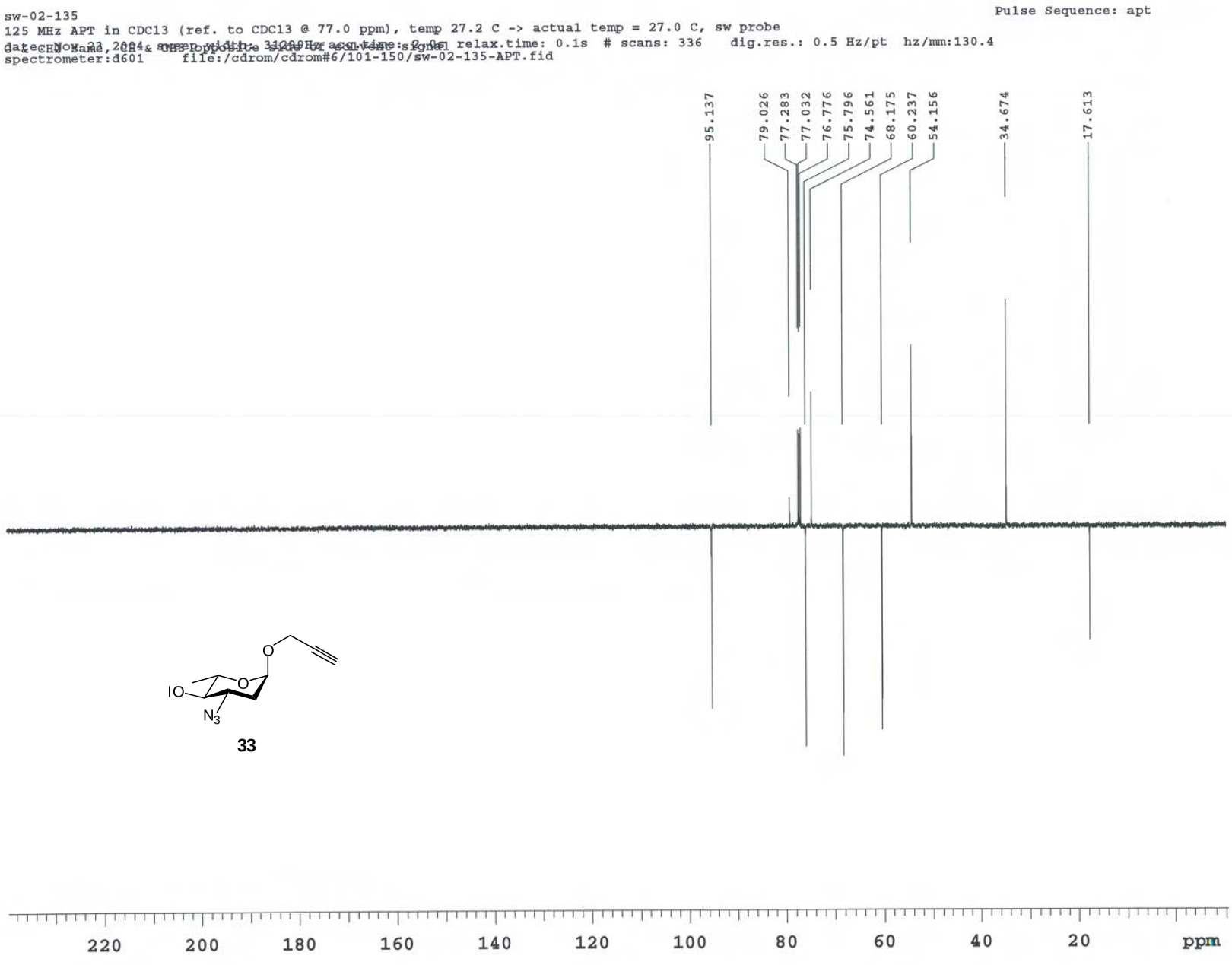
30


sw-02-015-C
Pulse Sequence: apt
125 MHz APT in CDC13 (ref. to CDC13 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
relax.time: 0.1s # scans: 224 dig.res.: 0.5 Hz/pt hz/mm:130.4
spectrometer:d601 file:/cdrom/cdrom#6/1-50/sw-02-015-C-APT.fid
170.103
93.872
79.098
77.276
77.020
76.765
74.454
73.867
62.197
55.727
54.450
32.787
20.675
17.167
AcO
N3
O
O
220
200
180
160
140
120
100
80
60
40
20
ppm

30

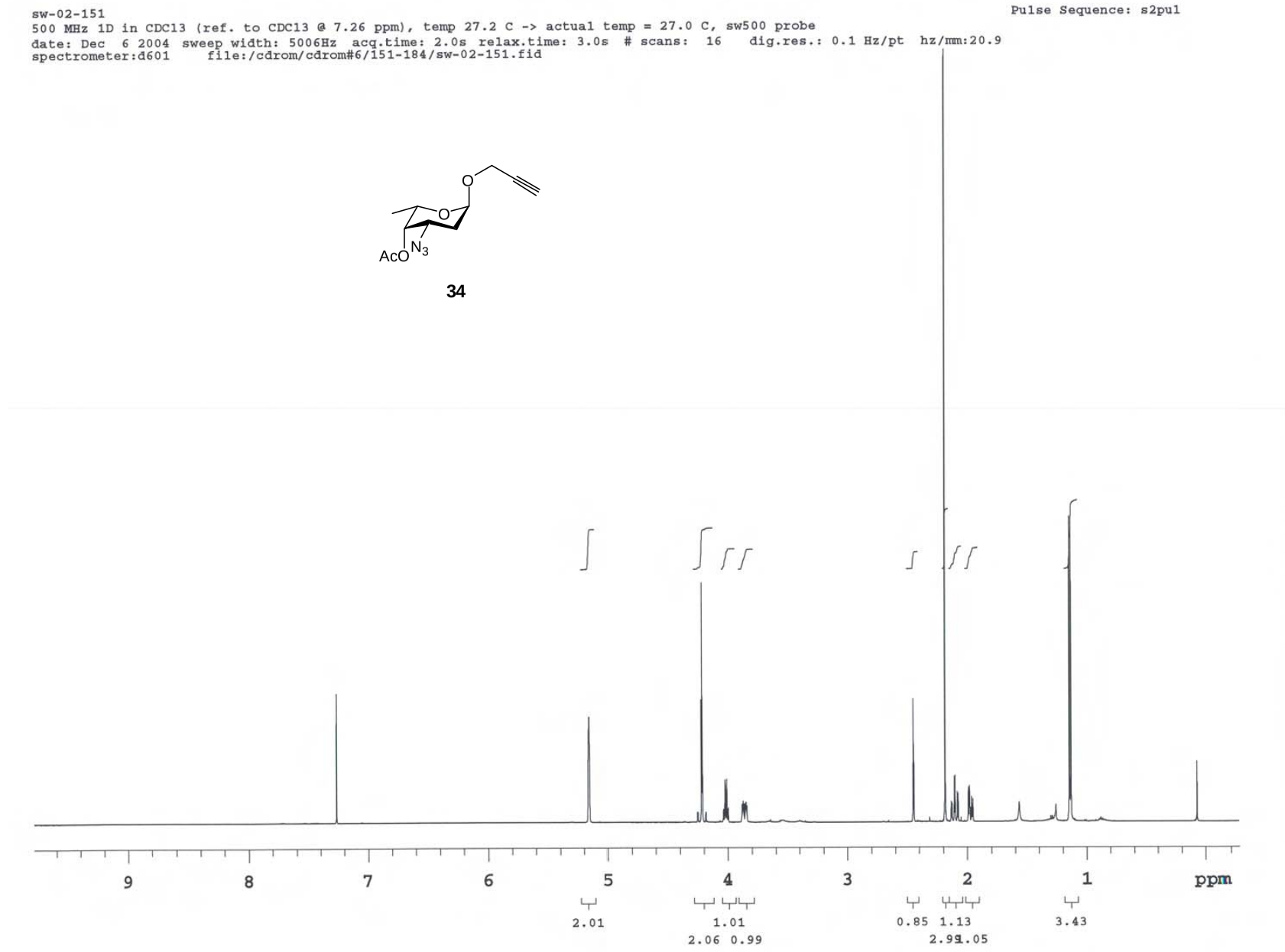

sw-02-135
Pulse Sequence: s2pul
500 MHz 1D in CDC13 (ref. to CDC13 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Nov 23 2004 sweep width: 5006Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
spectrometer:d601 file:/cdrom/cdrom#6/101-150/sw-02-135.fid
O
O
IO
N3
9
8
7
6
5
4
3
2
1
ppm
1.00
2.08
1.00
1.03
1.02
0.93
0.89
1.06
1.17
3.06

33

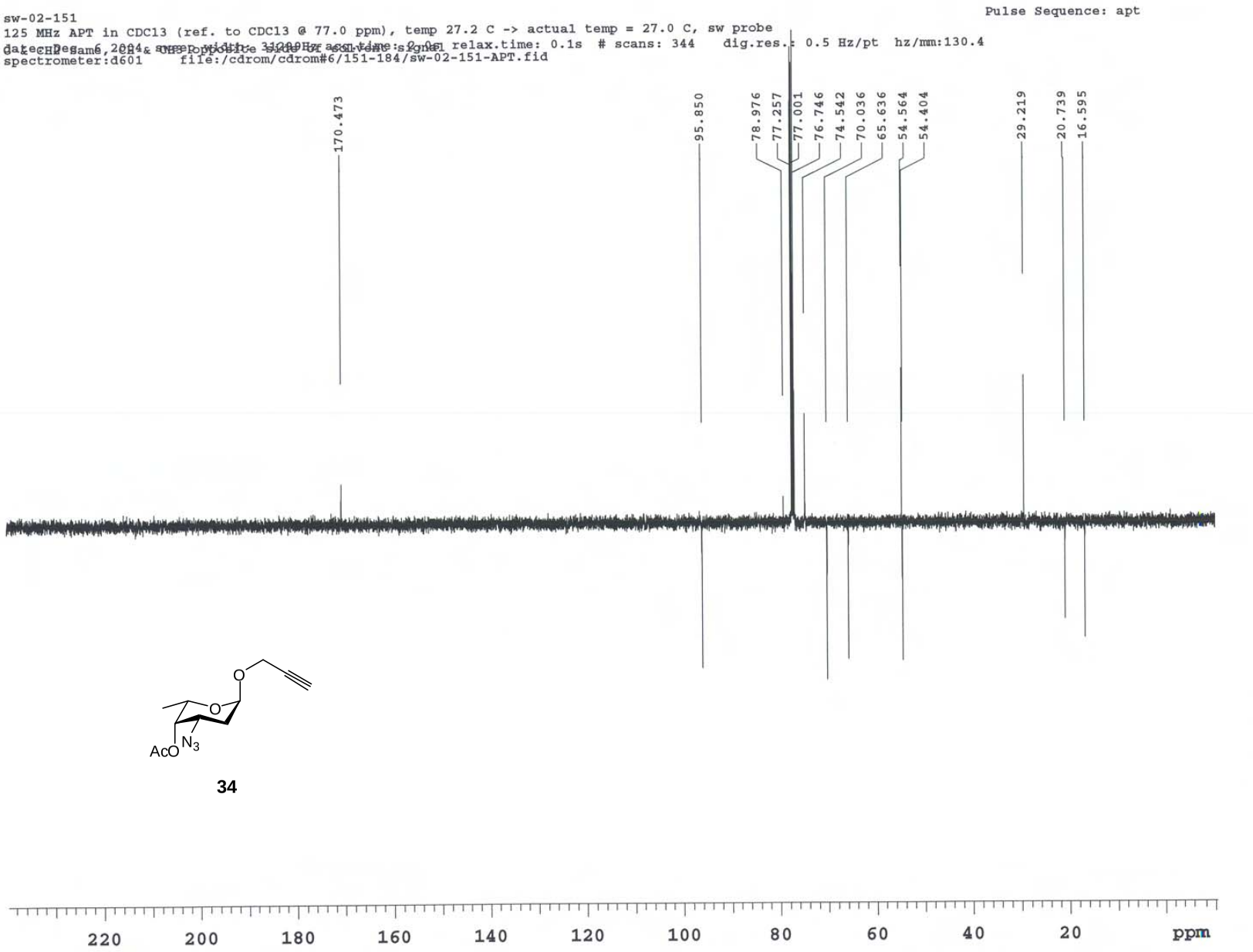

sw-02-135
Pulse Sequence: apt
125 MHz APT in CDC13 (ref. to CDC13 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date:Nov 23 2004 sweep width: 31009Hz acq.time: 2.0s relax.time: 0.1s # scans: 336 dig.res.: 0.5 Hz/pt hz/mm:130.4
d1 & CHD same, d1 & CHD=probe safe for solvent signal
spectrometer:d601 file:/cdrom/cdrom#6/101-150/sw-02-135-APT.fid
95.137
79.026
77.283
77.032
76.776
75.796
74.561
68.175
60.237
54.156
34.674
17.613
220
200
180
160
140
120
100
80
60
40
20
ppm

O
IO
O
N3

33

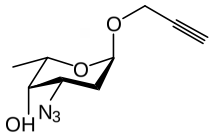

sw-02-151
Pulse Sequence: s2pul
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Dec 6 2004 sweep width: 5006Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
spectrometer:d601 file:/cdrom/cdrom#6/151-184/sw-02-151.fid
O
O
AcO
N3
9
8
7
6
5
4
3
2
1
ppm
2.01
1.01
2.06 0.99
0.85
1.13
2.99 1.05
3.43

34

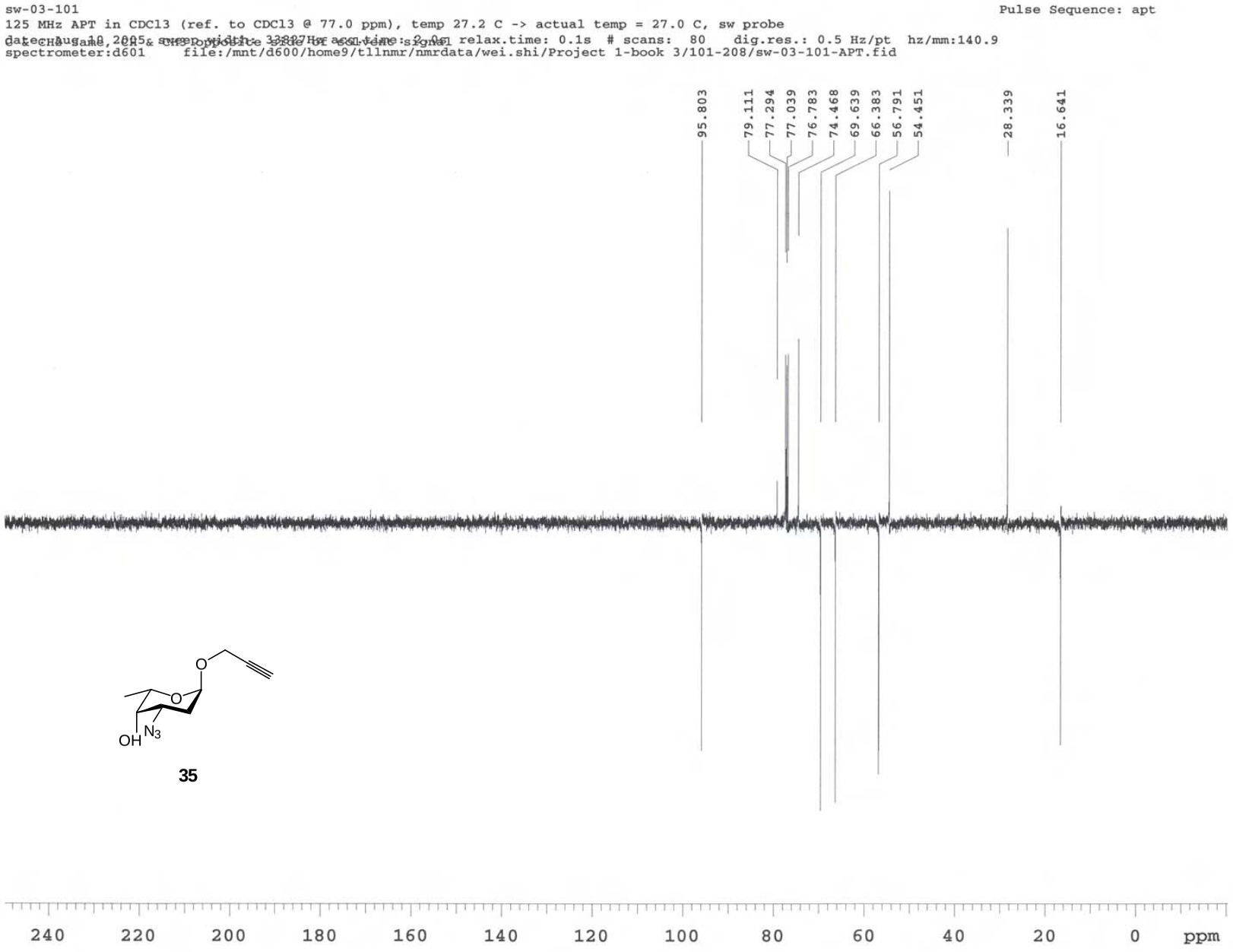

sw-02-151
125 MHz APT in CDC13 (ref. to CDC13 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date Dec 6 2014 sweep width: 31000Hz acq.time: 2.0s relax.time: 0.1s # scans: 344 dig.res.: 0.5 Hz/pt hz/mm:130.4
spectrometer:d601 file:/cdrom/cdrom#6/151-184/sw-02-151-APT.fid
Pulse Sequence: apt
170.473
95.850
78.976
77.257
77.001
76.746
74.542
70.036
65.636
54.564
54.404
29.219
20.739
16.595
O
O
AcO
N3
220
200
180
160
140
120
100
80
60
40
20
ppm

34

sw-03-101 Pulse Sequence: s2pul
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Aug 10 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 1 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-101.fid

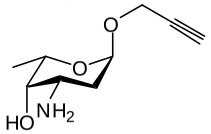


35

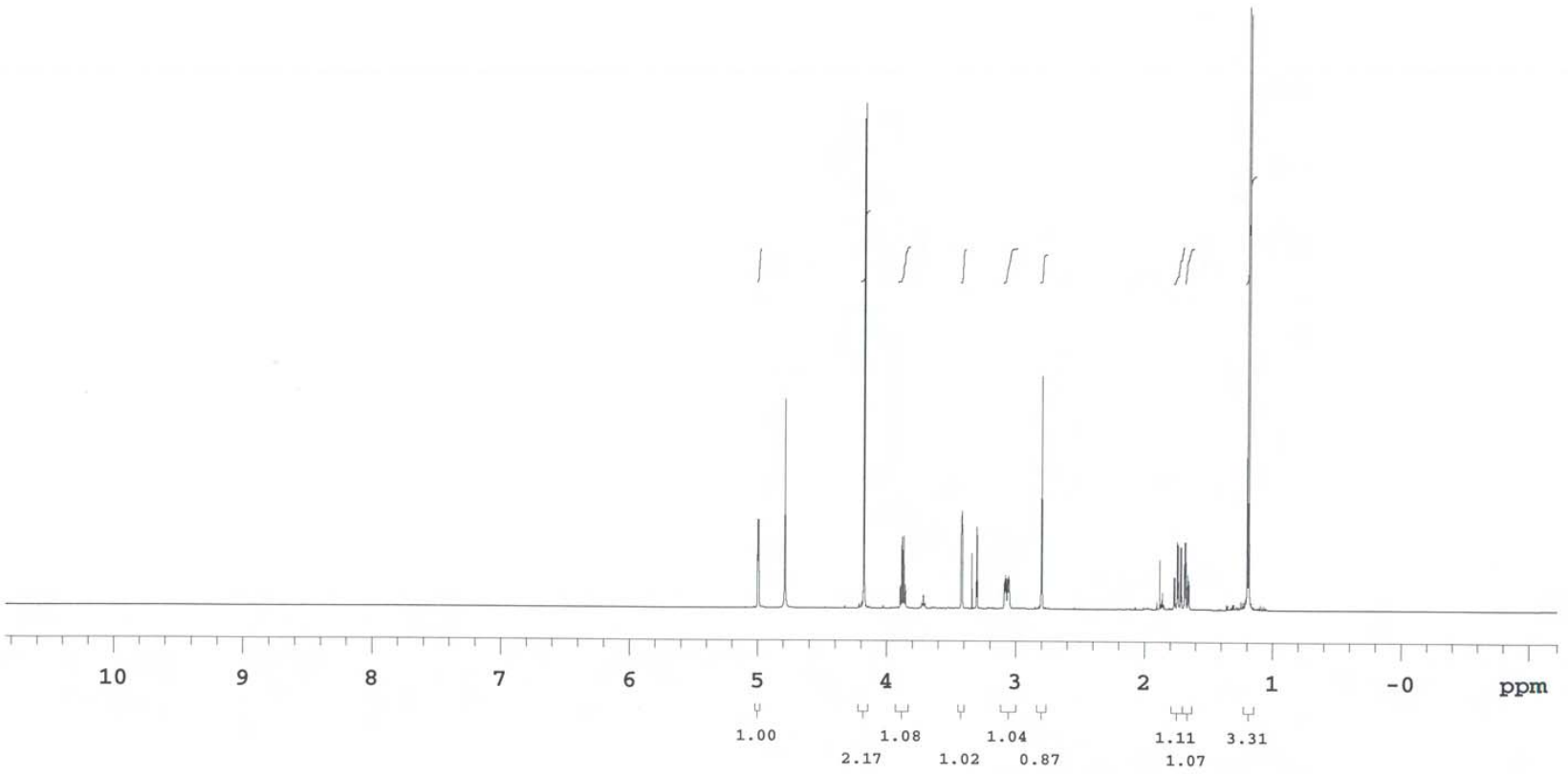

sw-03-101
Pulse Sequence: apt
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
date:Aug 10 2005 sweep width: 33897Hz acq.time: 2.0s relax.time: 0.1s # scans: 80 dig.res.: 0.5 Hz/pt hz/mm:140.9
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-101-APT.fid
95.803
79.111
77.294
77.039
76.783
74.468
69.639
66.383
56.791
54.451
28.339
16.641
O
O
OH
N3
35
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

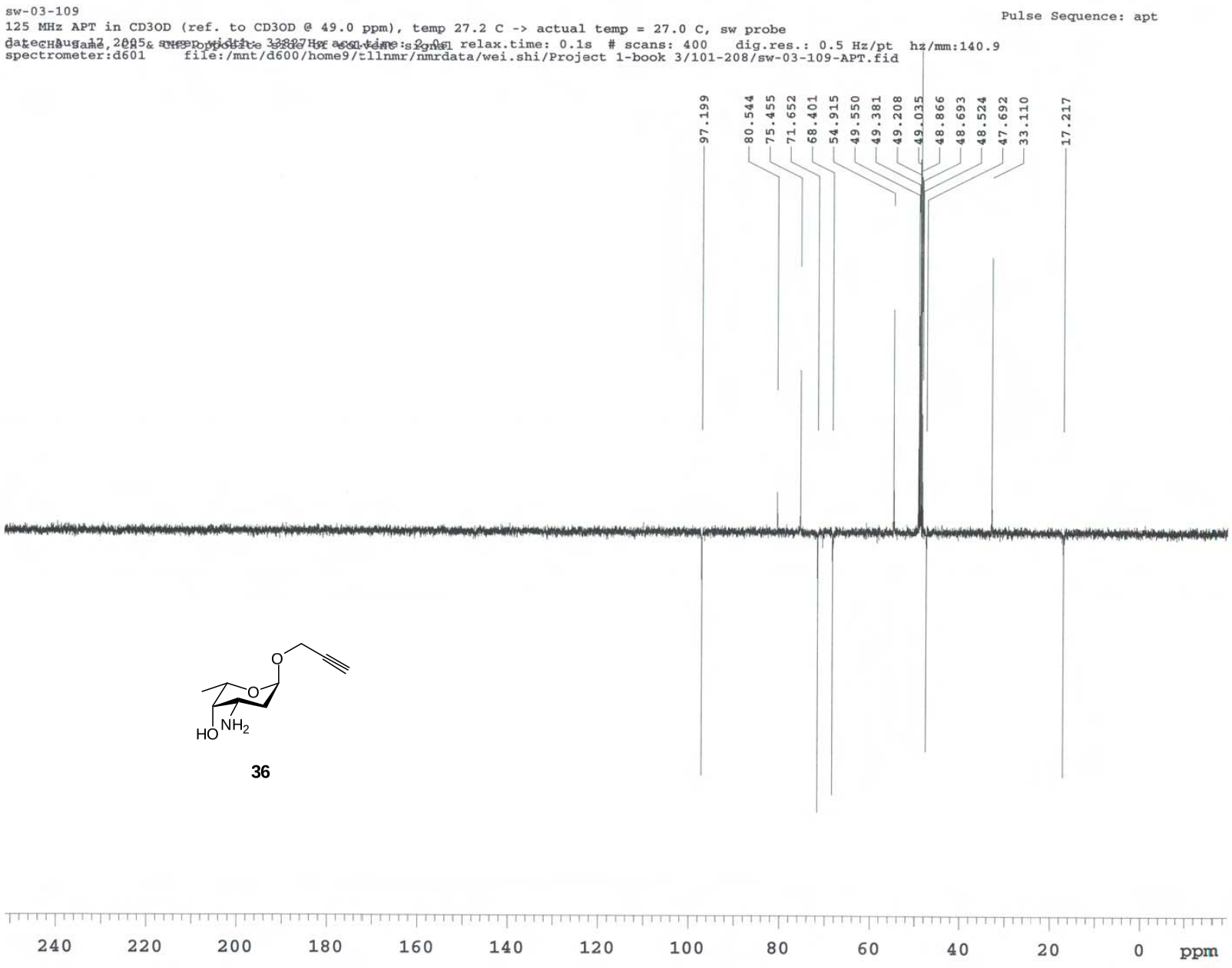
sw-03-147
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Oct 3 2005 sweep width: 6001Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:25.0
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-147.fid

Pulse Sequence: s2pul



36

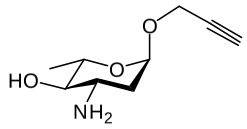



sw-03-109
125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
Pulse Sequence: apt
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Project 1-book 3/101-208/sw-03-109-APT.fid
97.199
80.544
75.455
71.652
68.401
54.915
49.550
49.381
49.208
49.035
48.866
48.693
48.524
47.692
33.110
17.217
O
O
HO
NH2
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

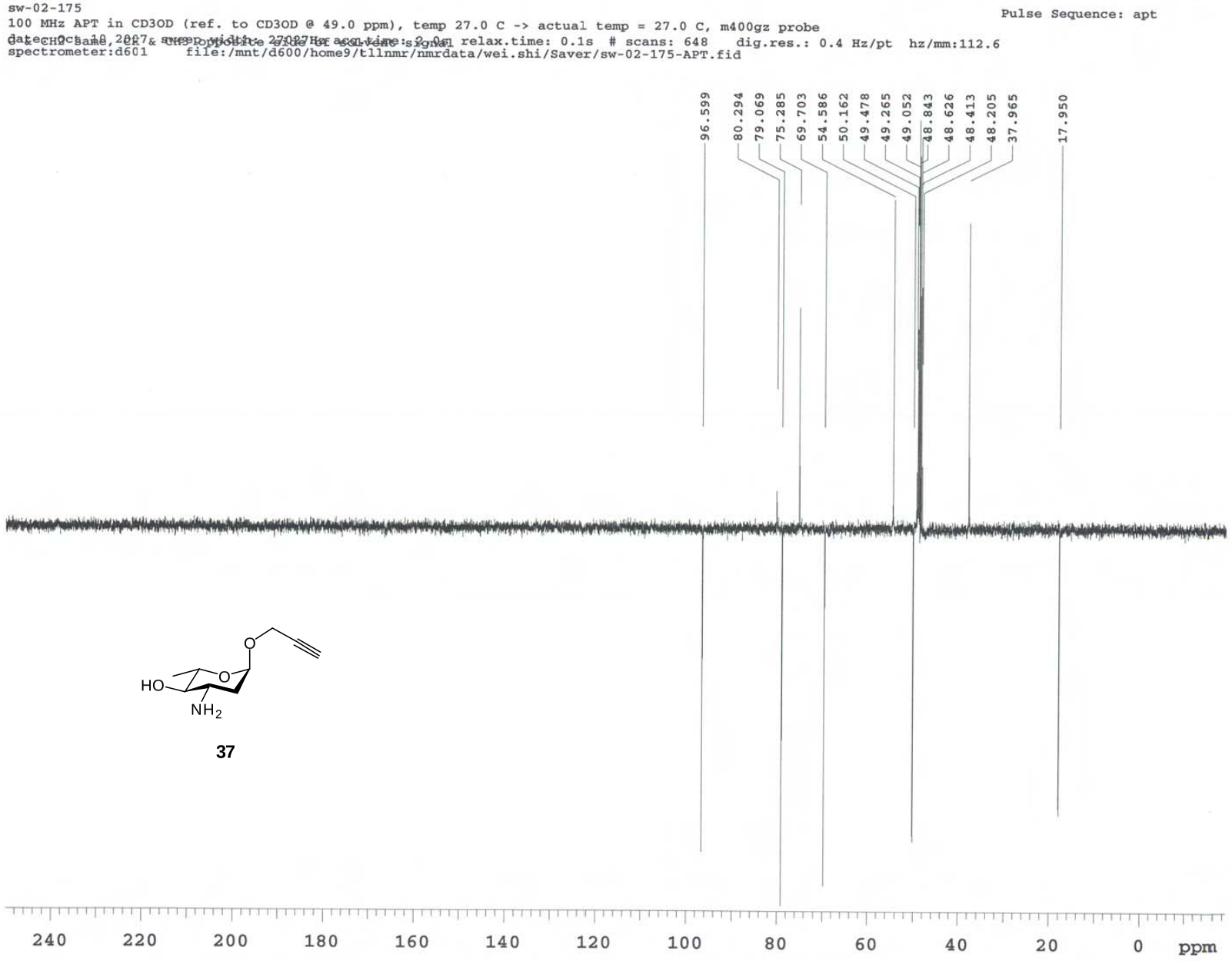
36

sw-02-175
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Jan 15 2005 sweep width: 5006Hz acq.time: 2.0s relax.time: 3.0s # scans: 16 dig.res.: 0.1 Hz/pt hz/mm:20.9
spectrometer:d601 file:/cdrom/cdrom#6/151-184/sw-02-175.fid

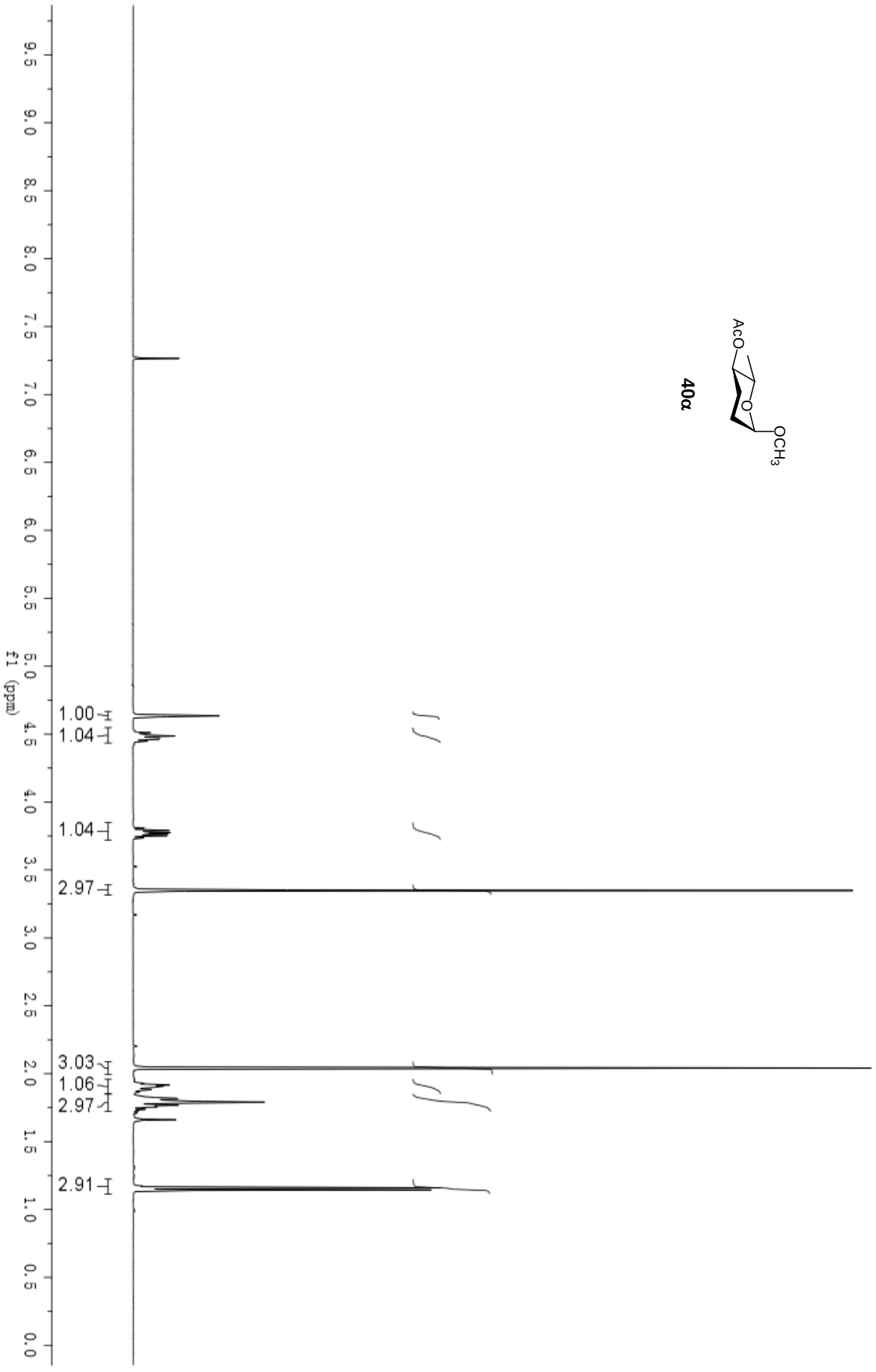
Pulse Sequence: s2pul

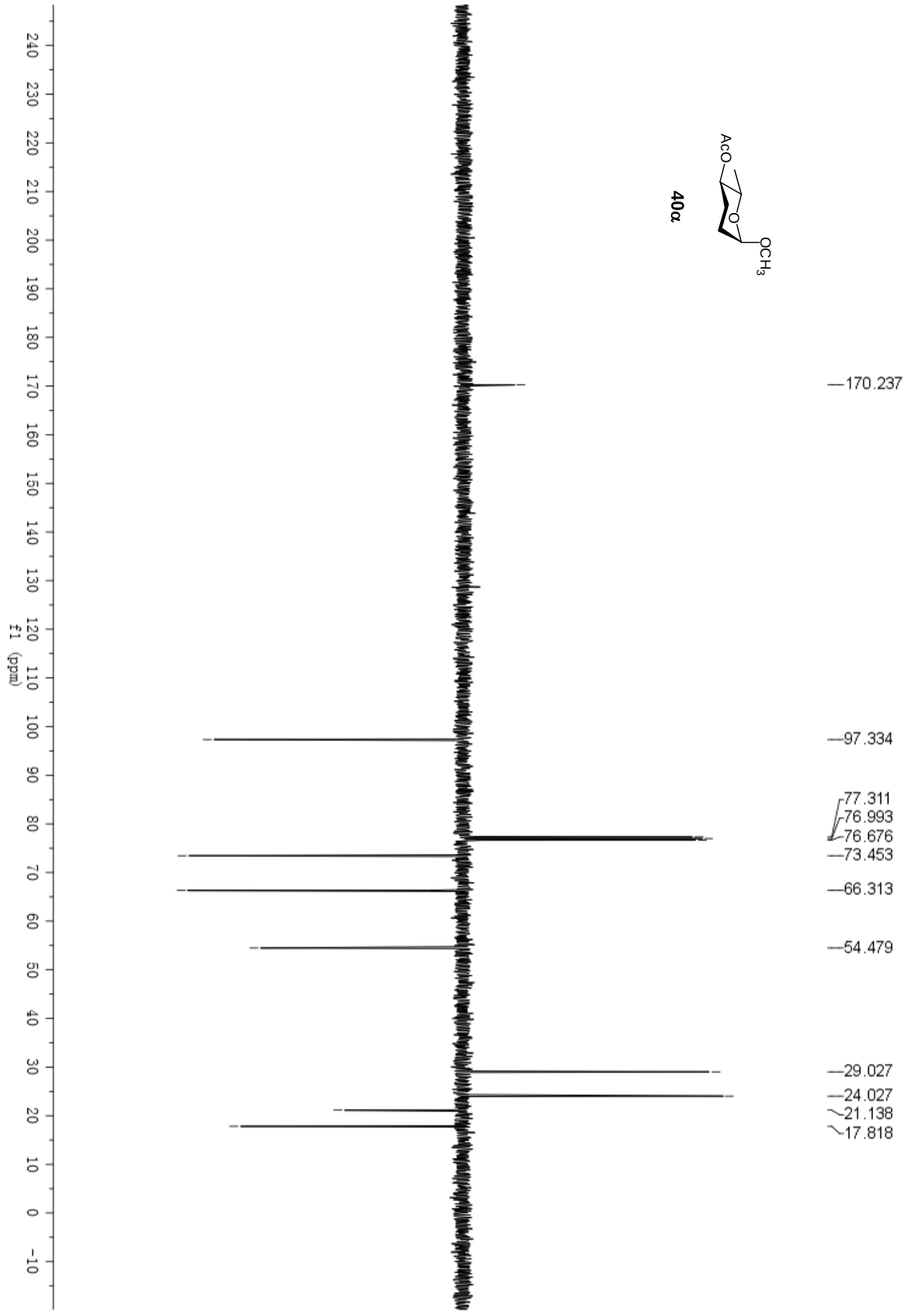


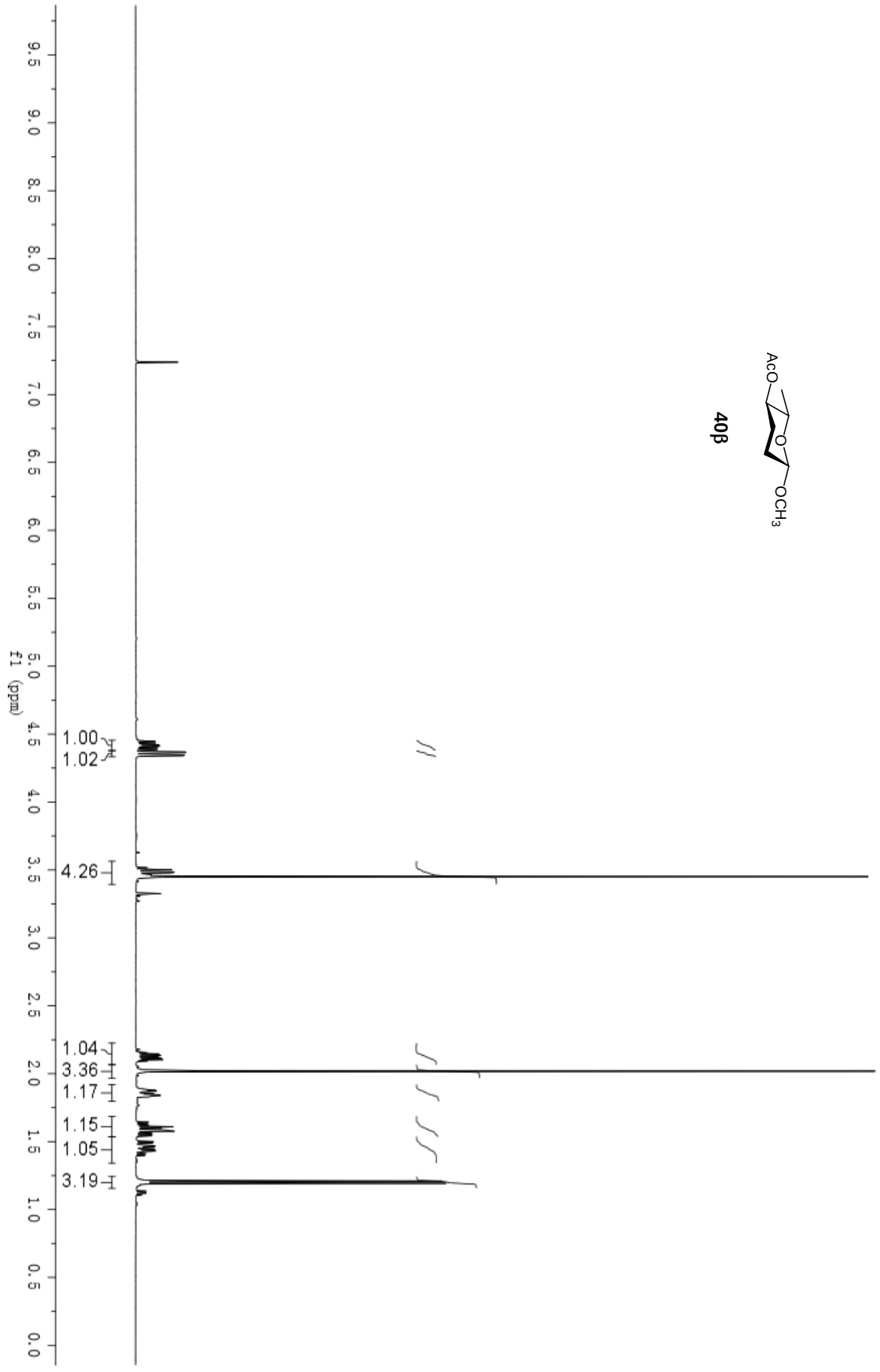
37

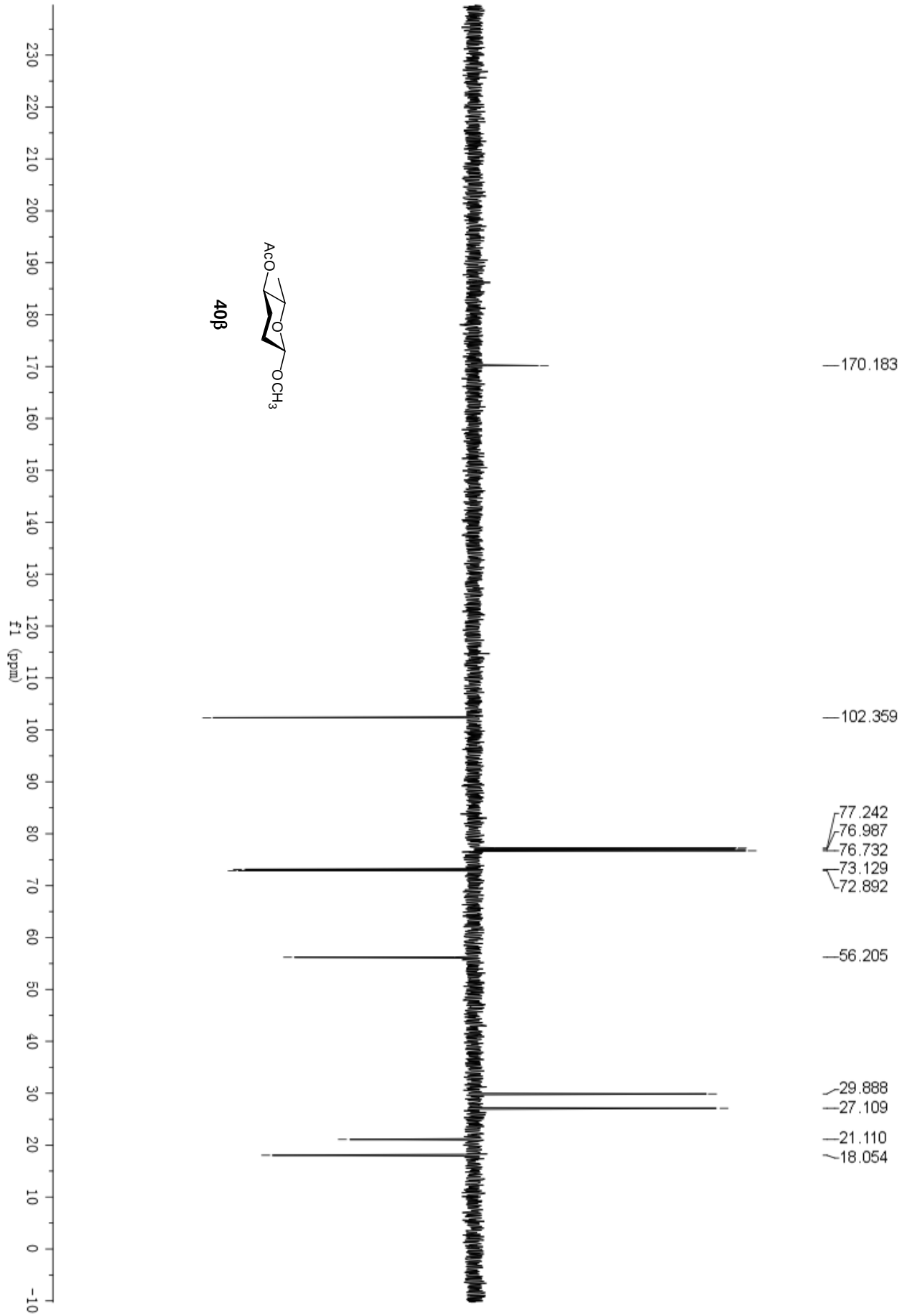

sw-02-175
100 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
Pulse Sequence: apt
date: Oct 10 2007 sweep width: 27027Hz acq.time: 2.0s relax.time: 0.1s # scans: 648 dig.res.: 0.4 Hz/pt hz/mm:112.6
spectrometer:d601 file:/mnt/d600/home9/tllnmr/nmrdata/wei.shi/Saver/sw-02-175-APT.fid
96.599
80.294
79.069
75.285
69.703
54.586
50.162
49.478
49.265
49.052
48.843
48.626
48.413
48.205
37.965
17.950
HO
O
O
NH2
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

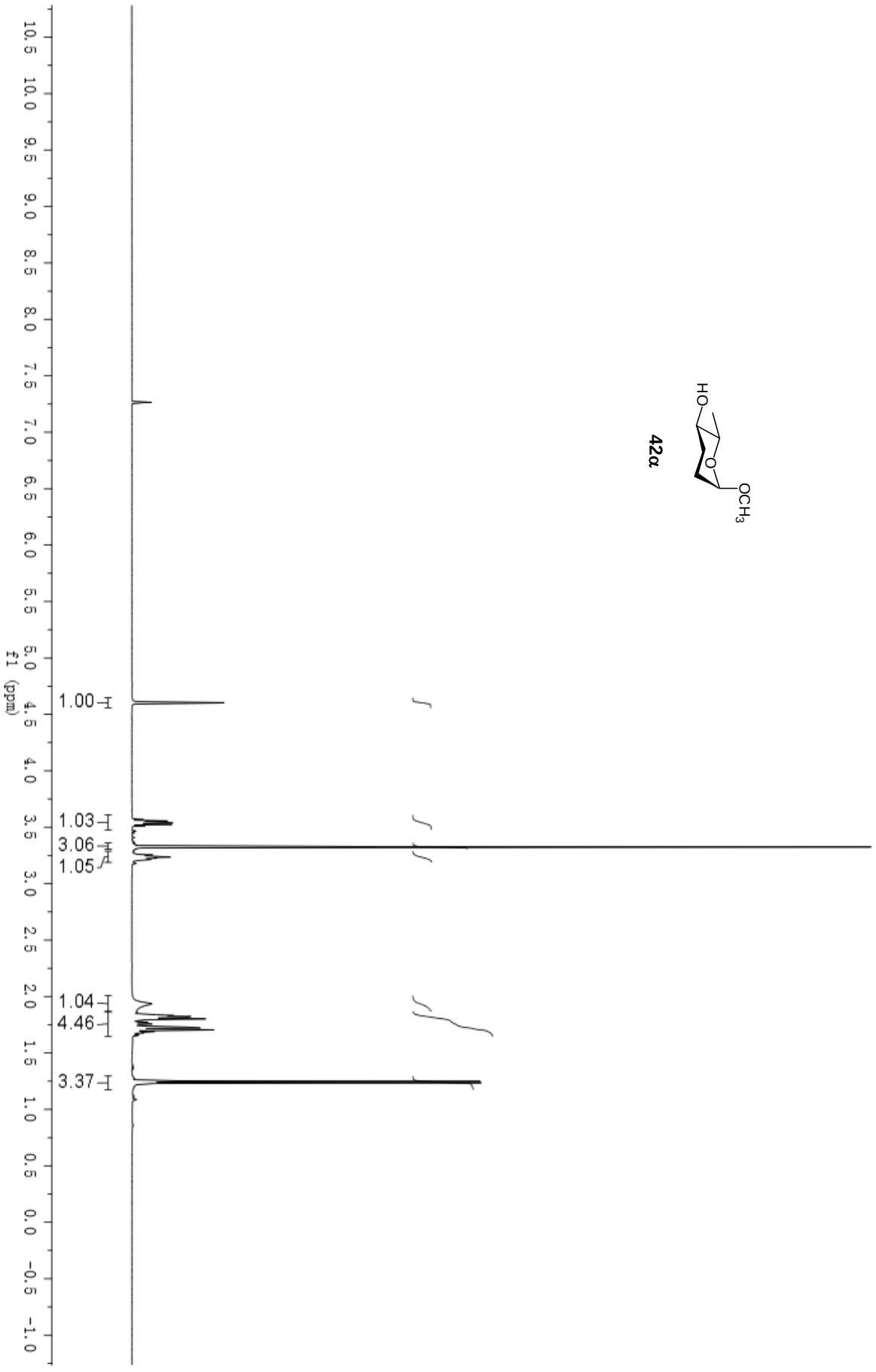
37

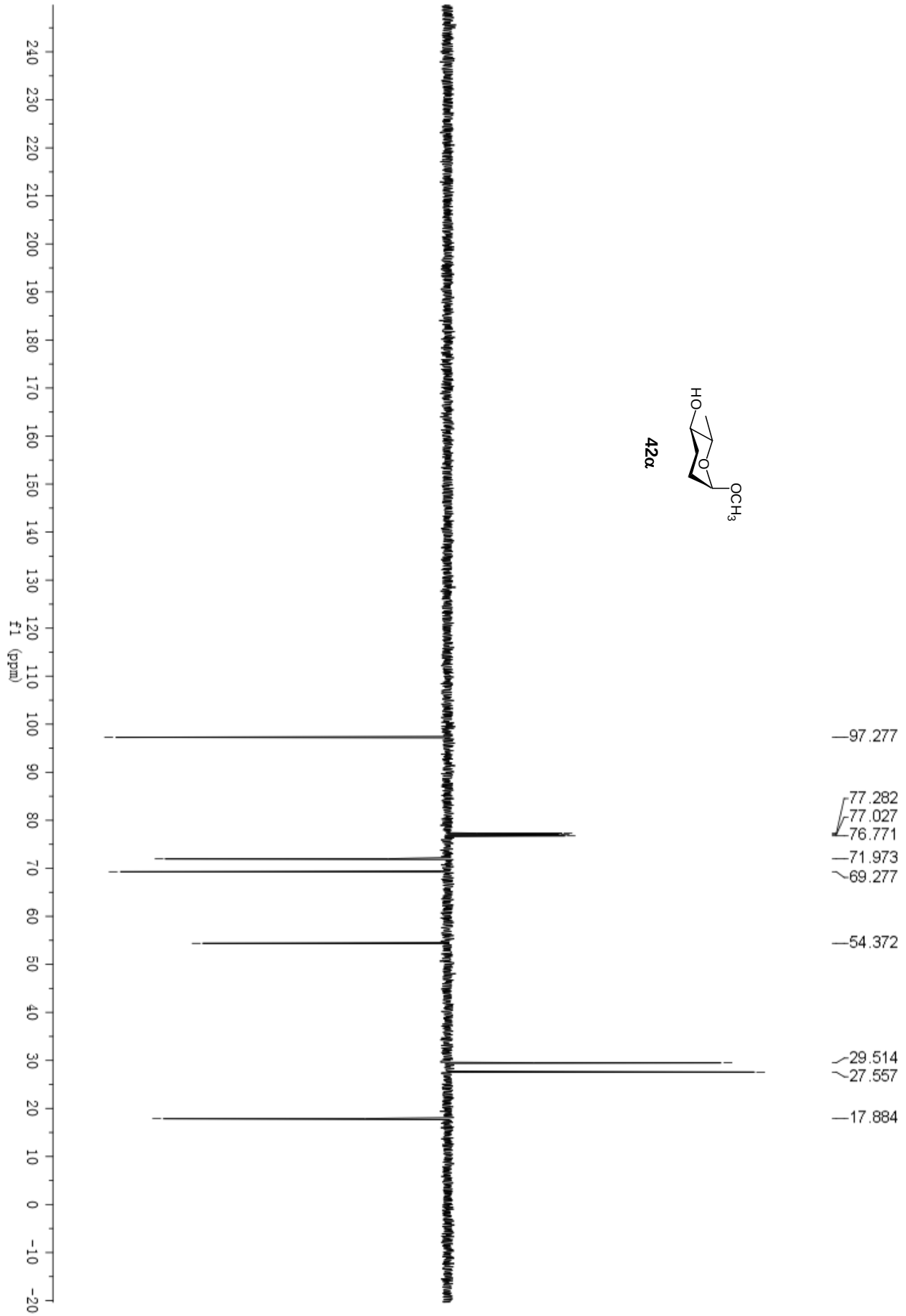

AcO
O
OCH3
40α
f1 (ppm)
1.00
1.04
1.04
2.97
3.03
1.06
2.97
2.91


AcO
OCH3
40α
170.237
97.334
77.311
76.993
76.676
73.453
66.313
54.479
29.027
24.027
21.138
17.818
f1 (ppm)

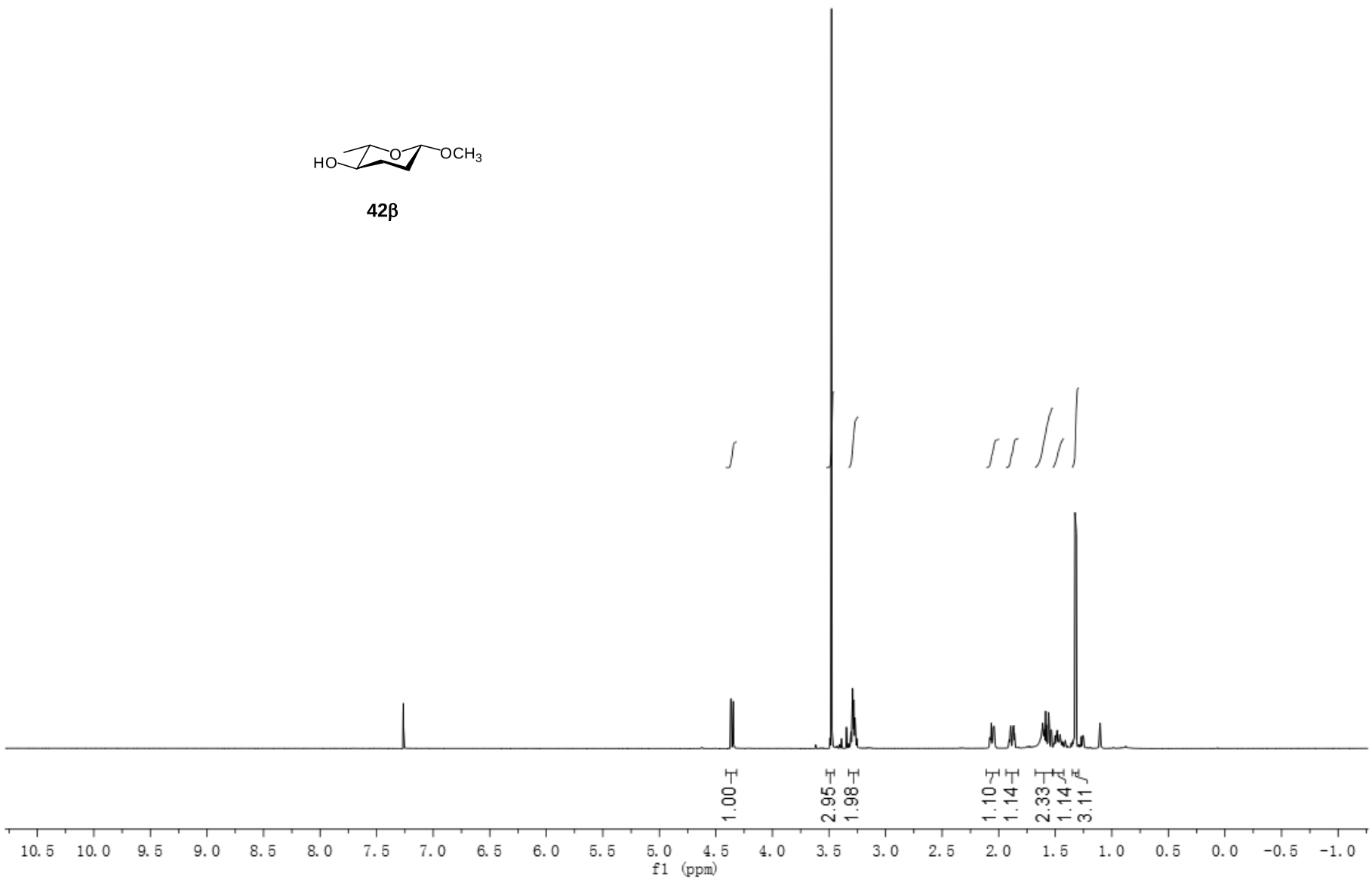

40β
AcO
O
OCH3
f1 (ppm)
1.00
1.02
4.26
1.04
3.36
1.17
1.15
1.05
3.19

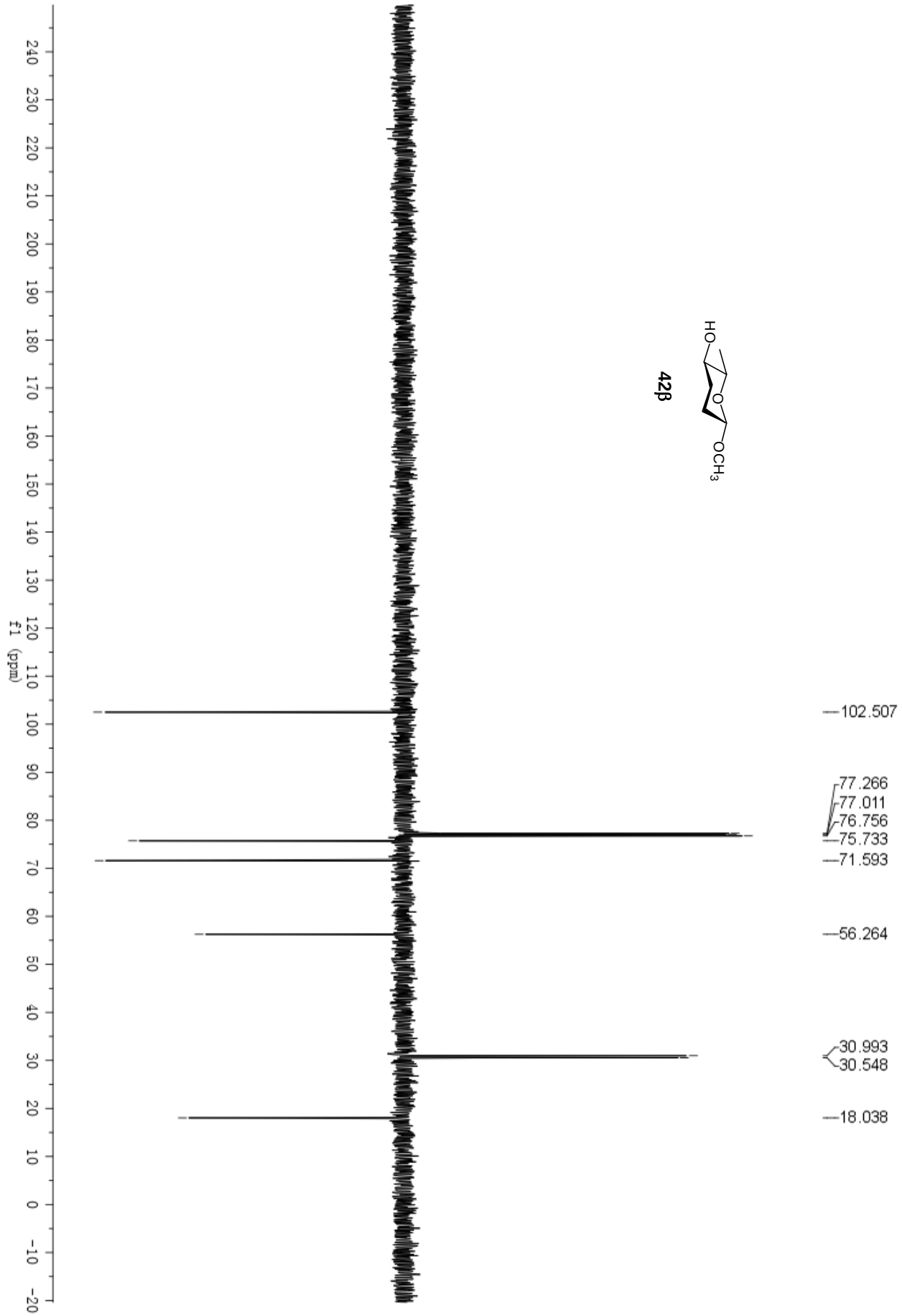

AcO
O
OCH3
40β
170.183
102.359
77.242
76.987
76.732
73.129
72.892
56.205
29.888
27.109
21.110
18.054
f1 (ppm)

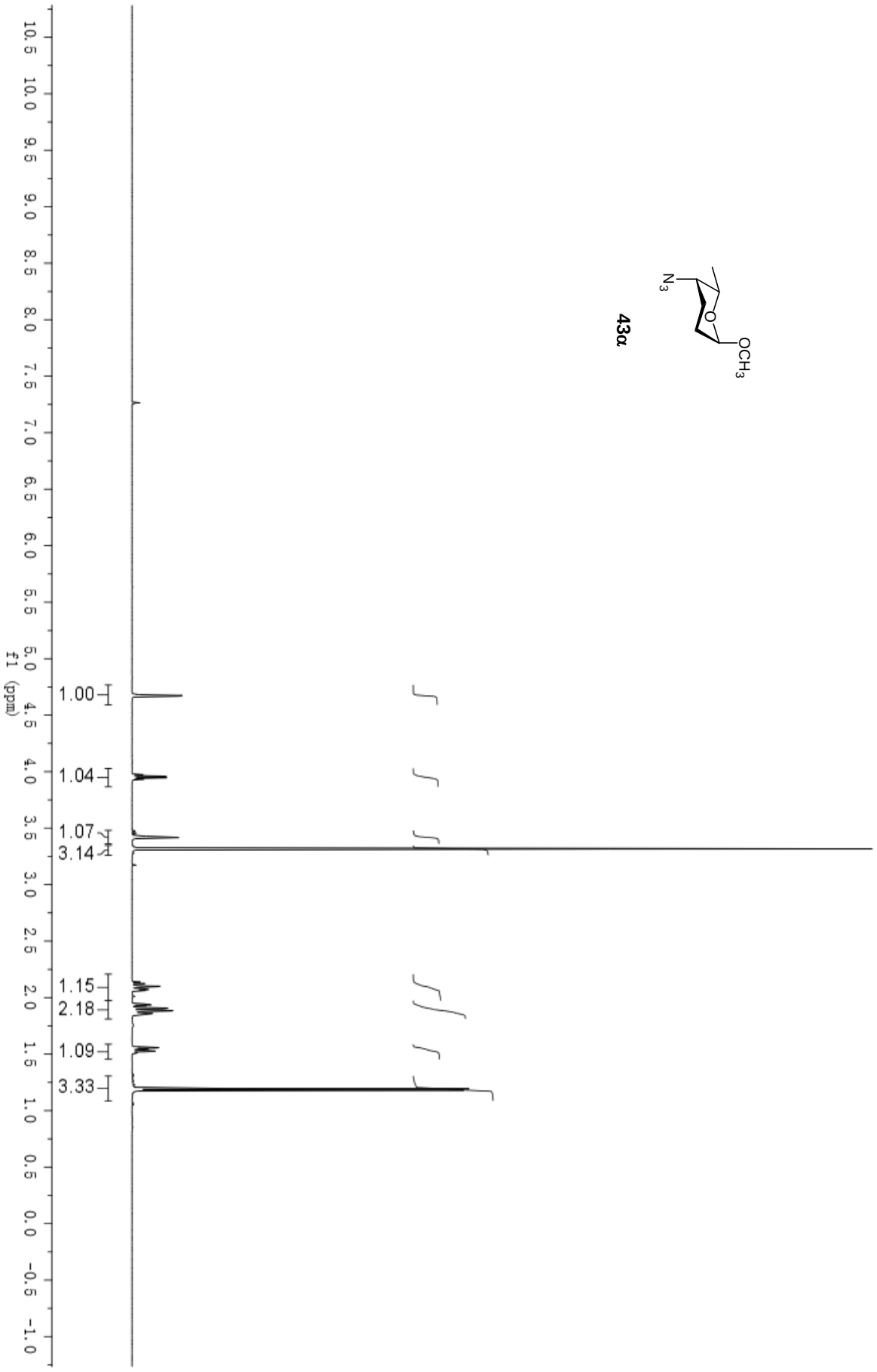

42α
HO
O
OCH3
f1 (ppm)
1.00
1.03
3.06
1.05
1.04
4.46
3.37

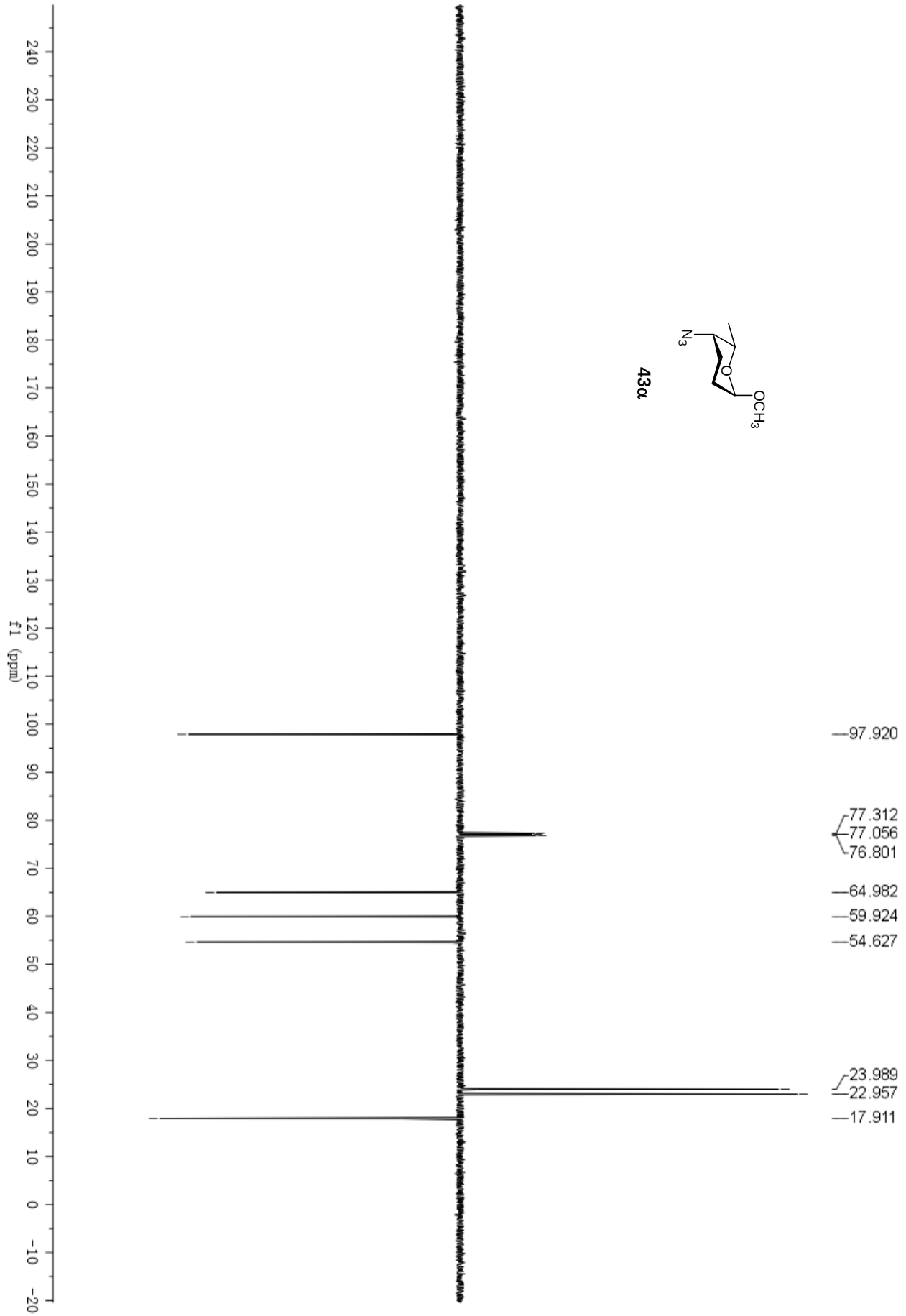

f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
97.277
77.282
77.027
76.771
71.973
69.277
54.372
29.514
27.557
17.884
HO
O
OCH3

42α

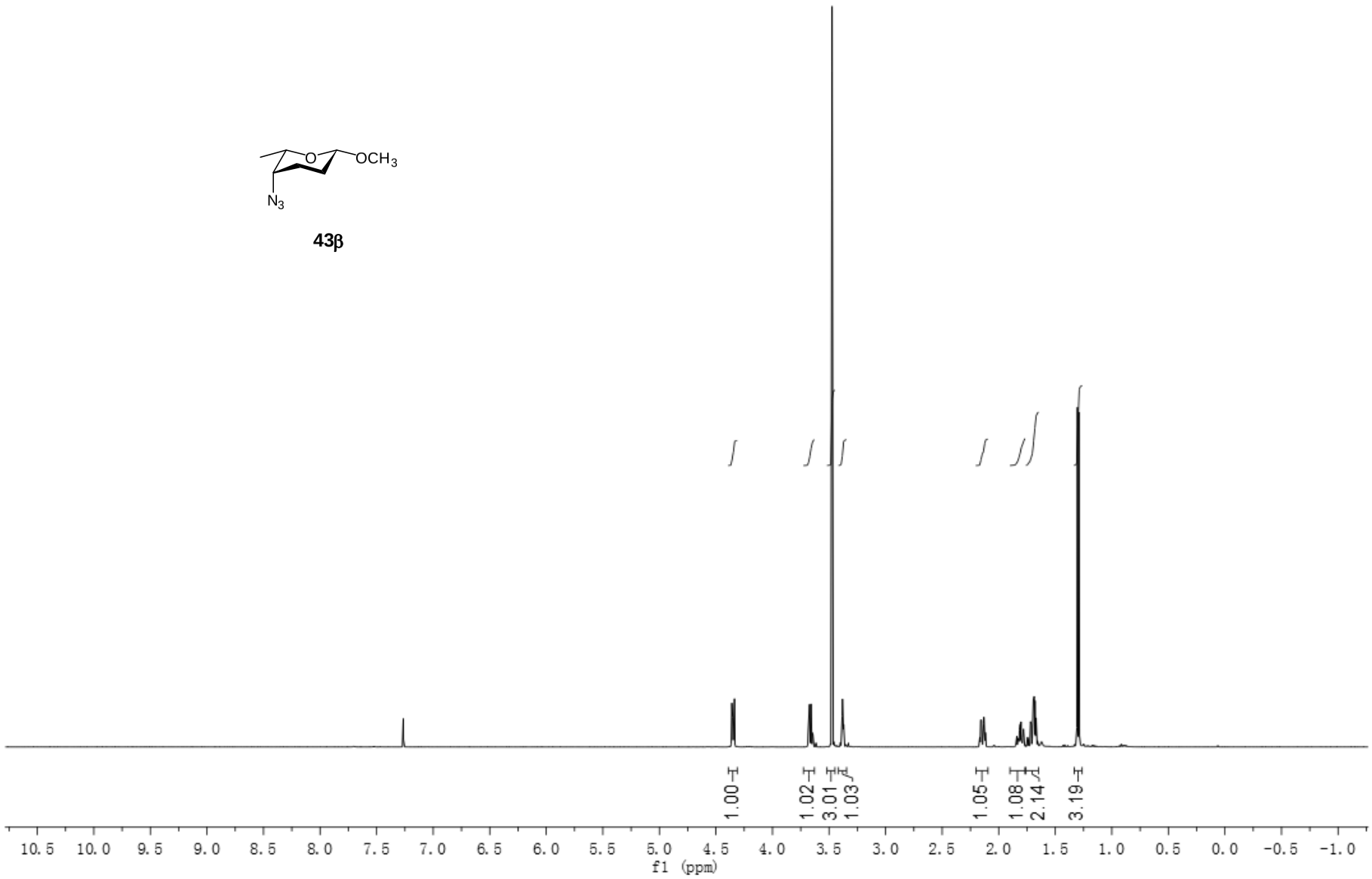

HO
O
OCH3
42β
1.00
2.95
1.98
1.10
1.14
2.33
1.14
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

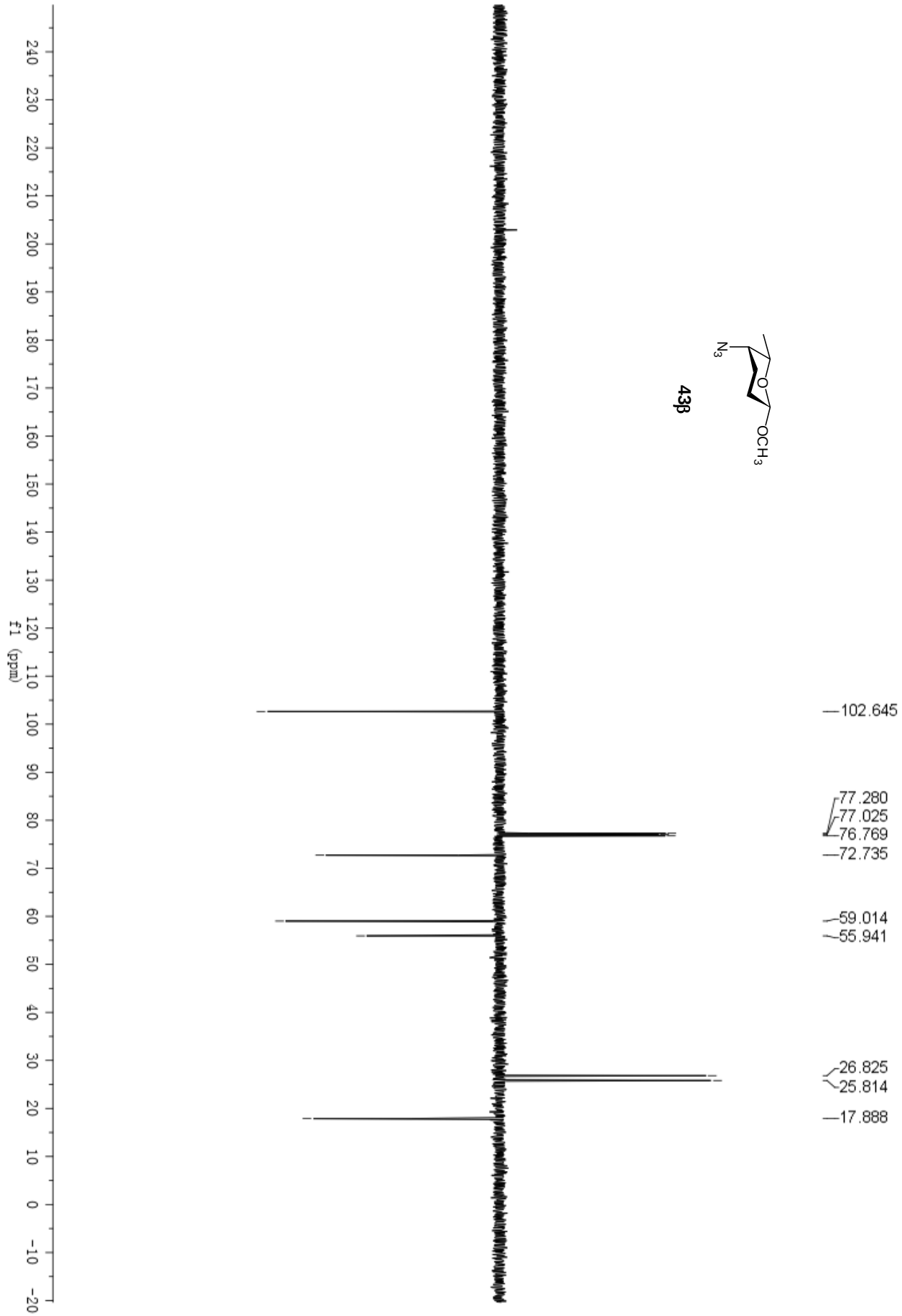

HO
O
OCH3
42β
102.507
77.266
77.011
76.756
75.733
71.593
56.264
30.993
30.548
18.038
f1 (ppm)

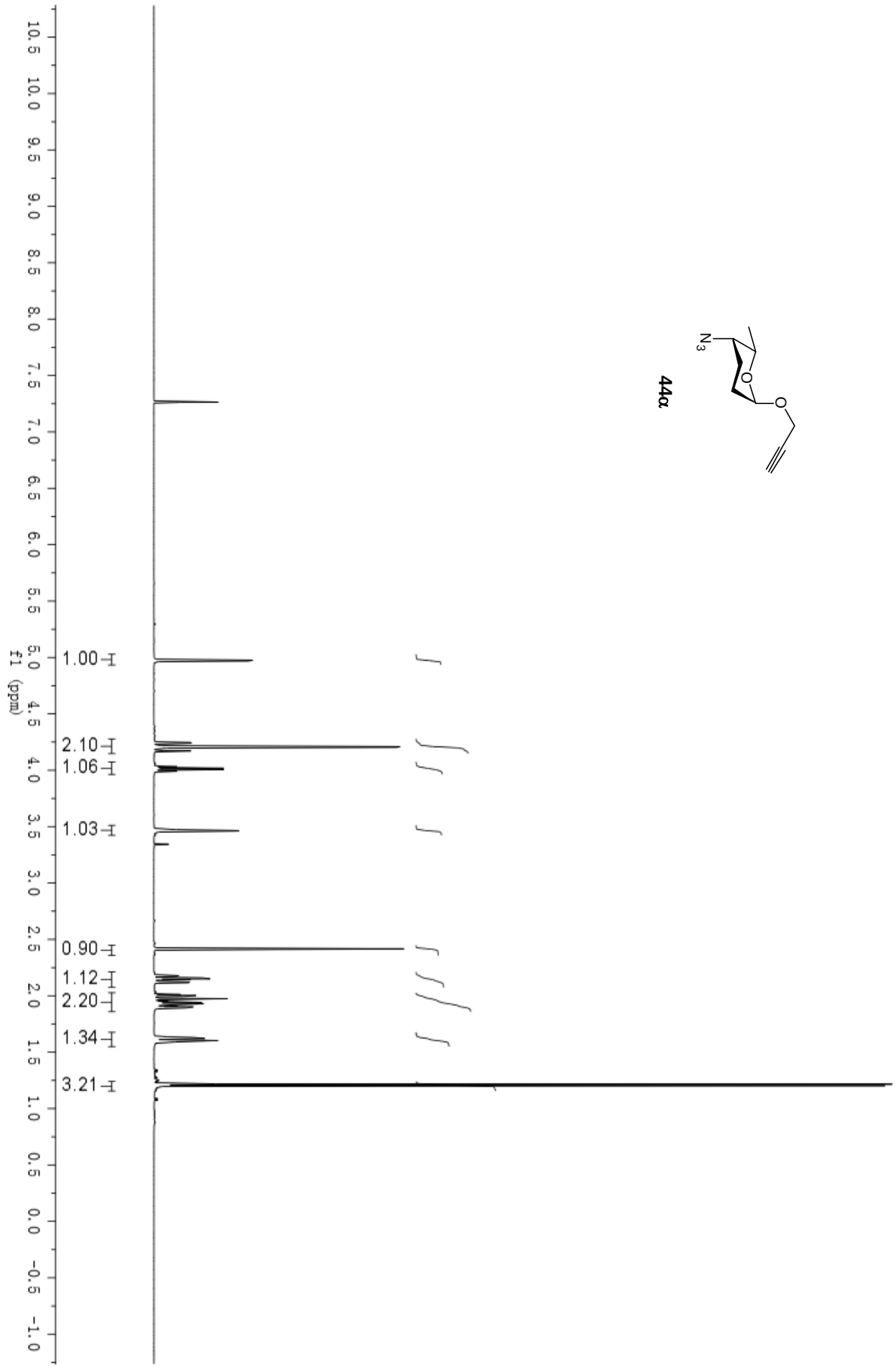

43α
N3
O
OCH3
f1 (ppm)
1.00
1.04
1.07
3.14
1.15
2.18
1.09
3.33


f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
97.920
77.312
77.056
76.801
64.982
59.924
54.627
23.989
22.957
17.911
N3
O
OCH3

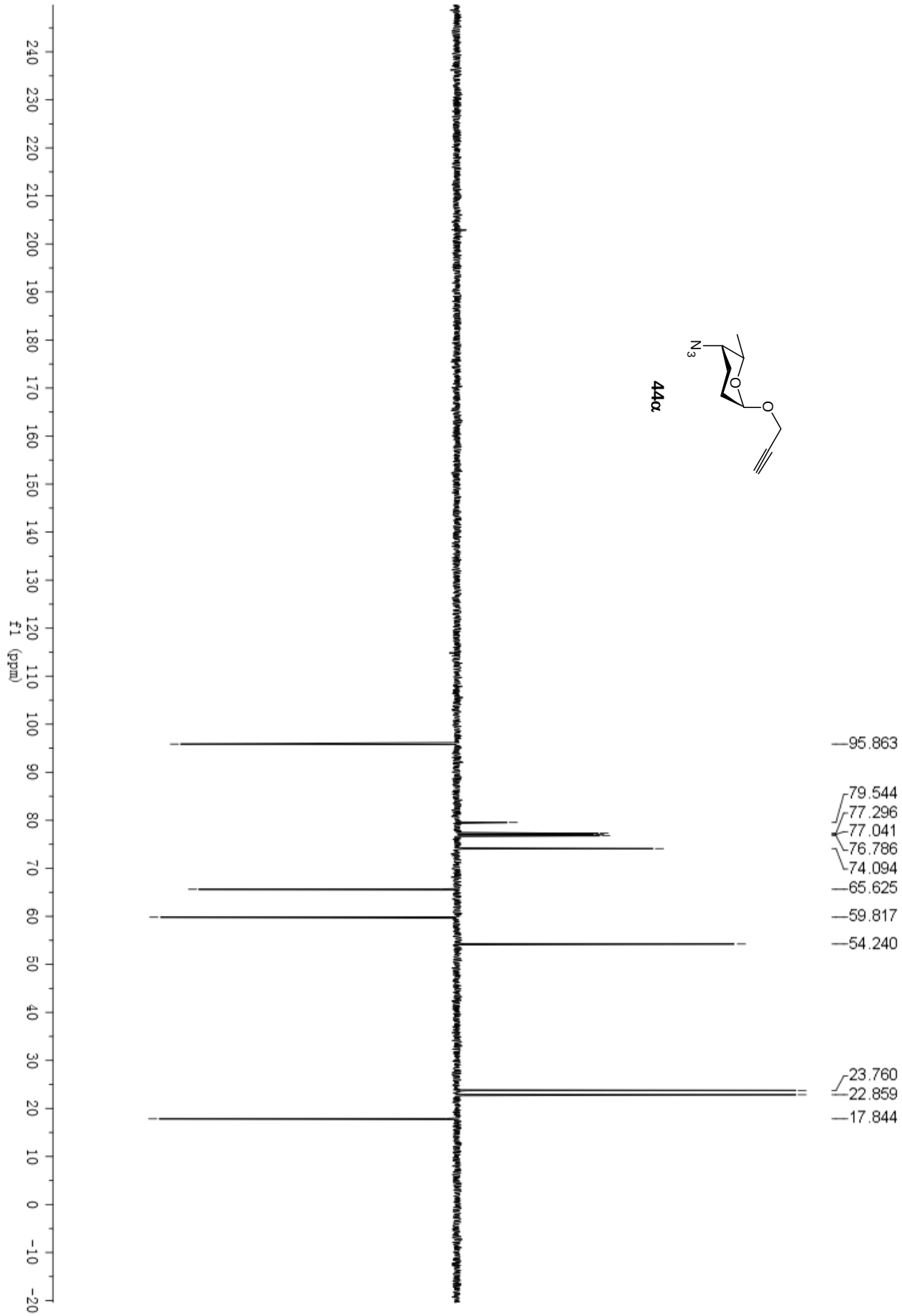
43α

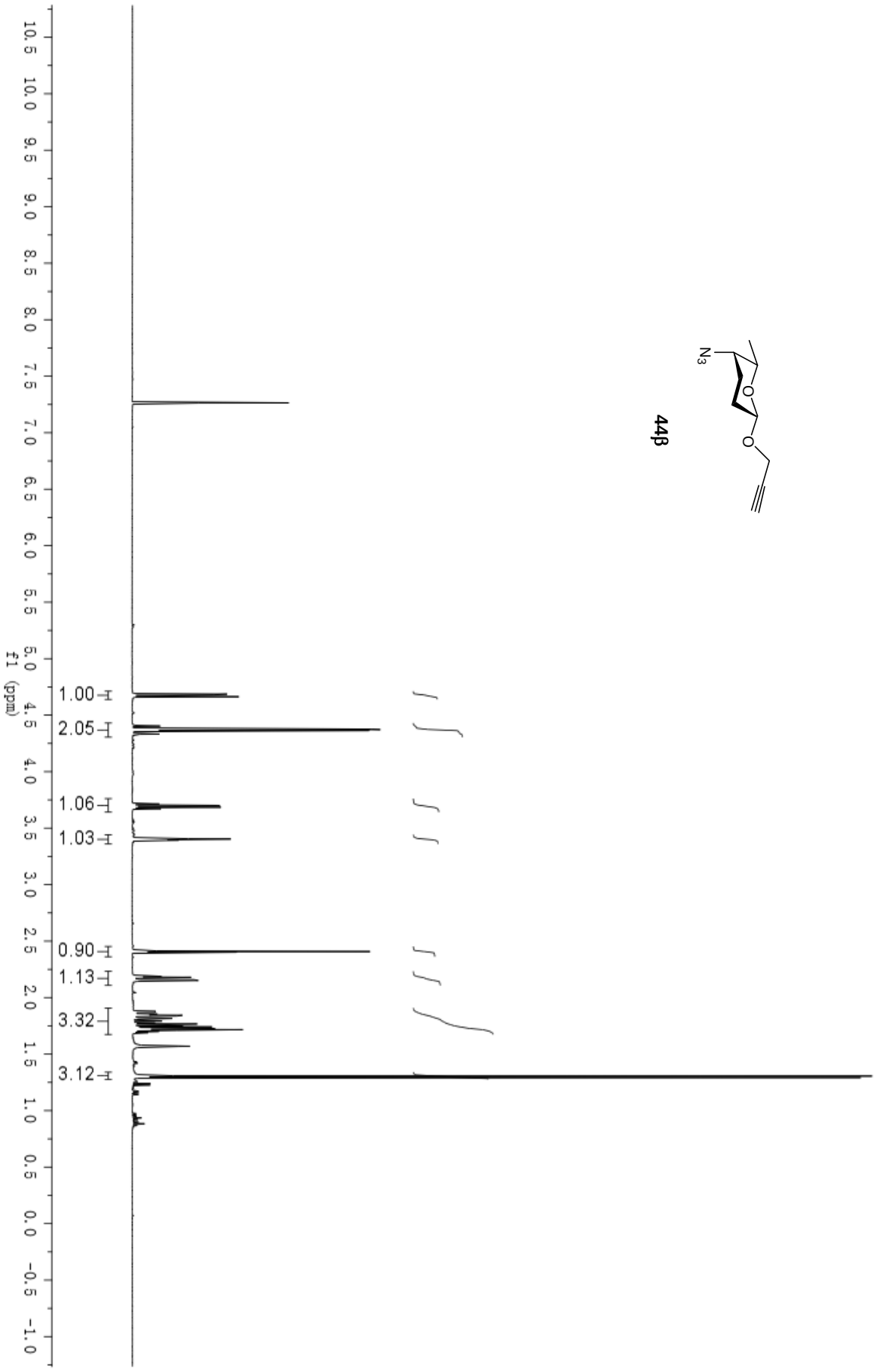

OCH3
O
N3
43β
1.00
1.02
3.01
1.03
1.05
1.08
2.14
3.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

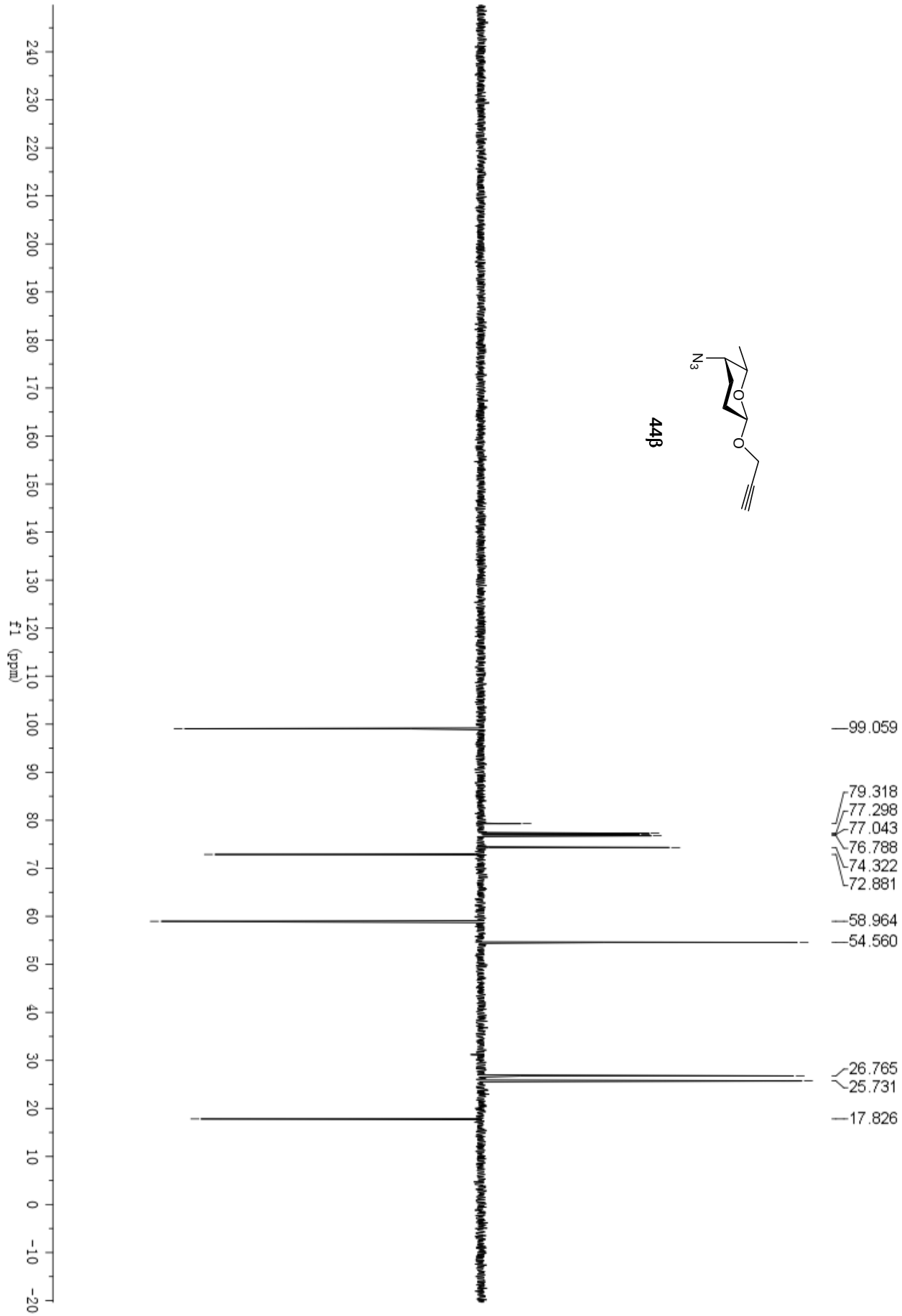

43β
N3
O
OCH3
102.645
77.280
77.025
76.769
72.735
59.014
55.941
26.825
25.814
17.888
f1 (ppm)

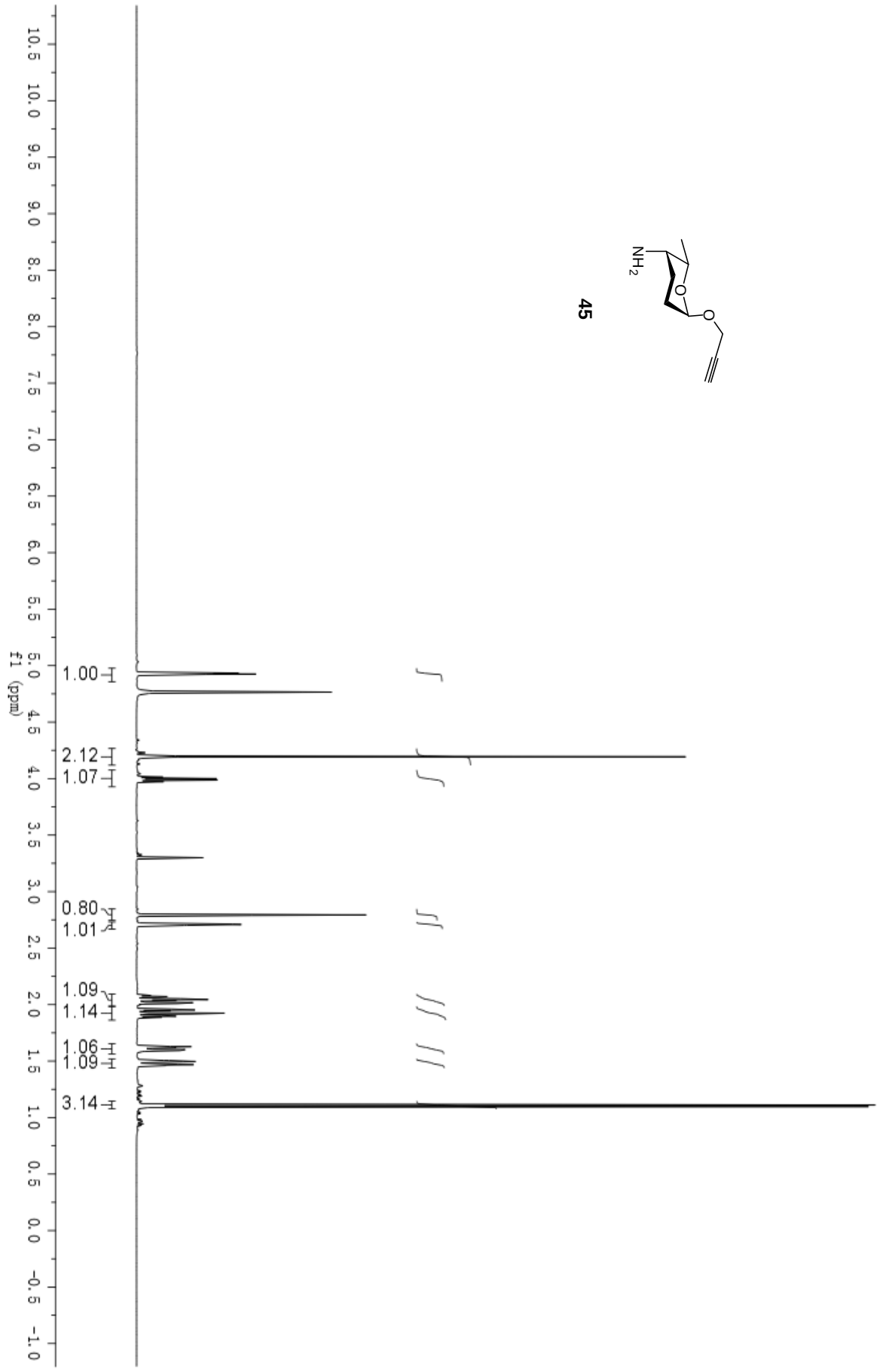

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
1.00
2.10
1.06
1.03
0.90
1.12
2.20
1.34
3.21
N3
O
O

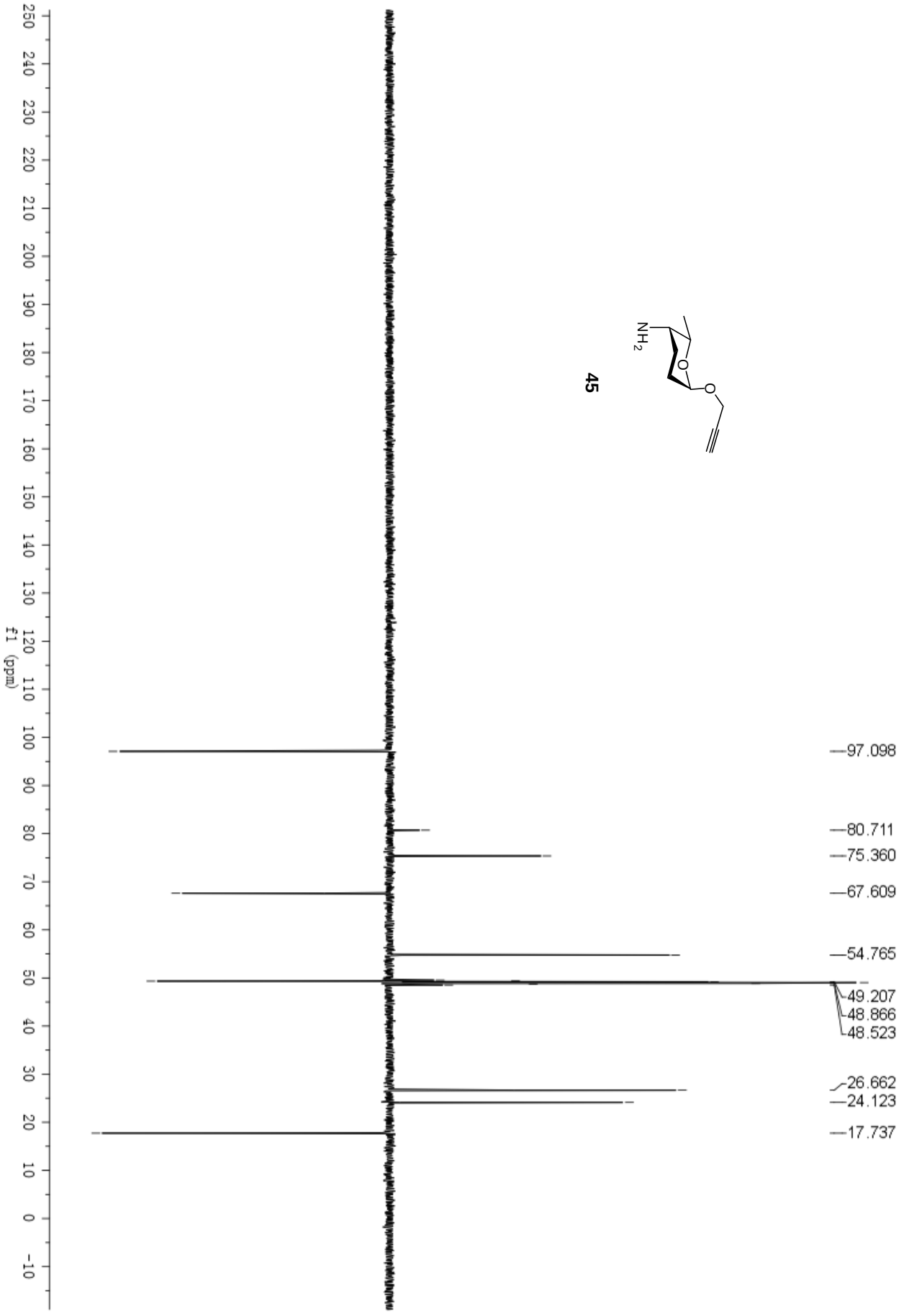
44α

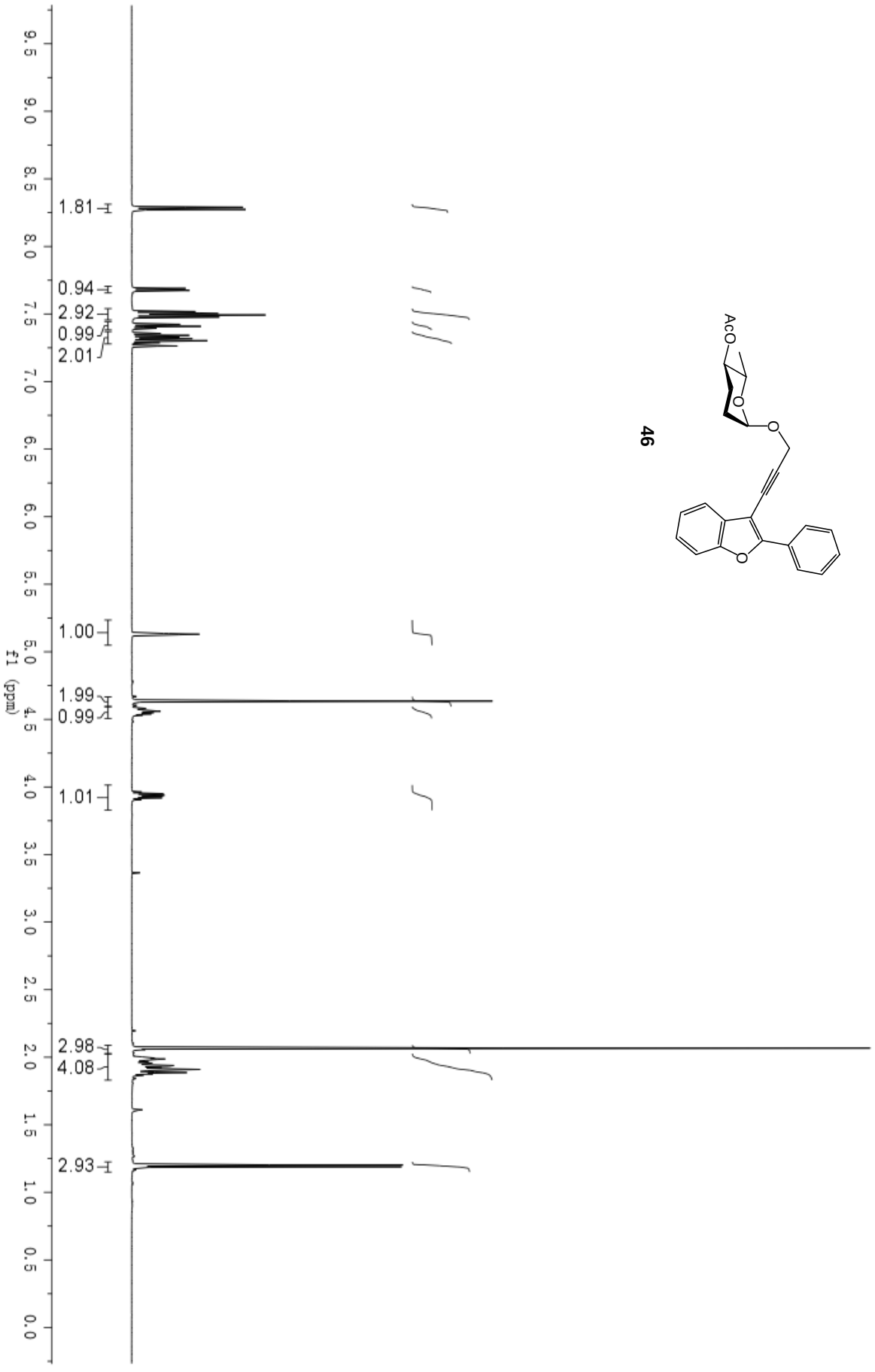

95.863
79.544
77.296
77.041
76.786
74.094
65.625
59.817
54.240
23.760
22.859
17.844
f1 (ppm)
44α


44β
N3
O
O
f1 (ppm)
1.00
2.05
1.06
1.03
0.90
1.13
3.32
3.12

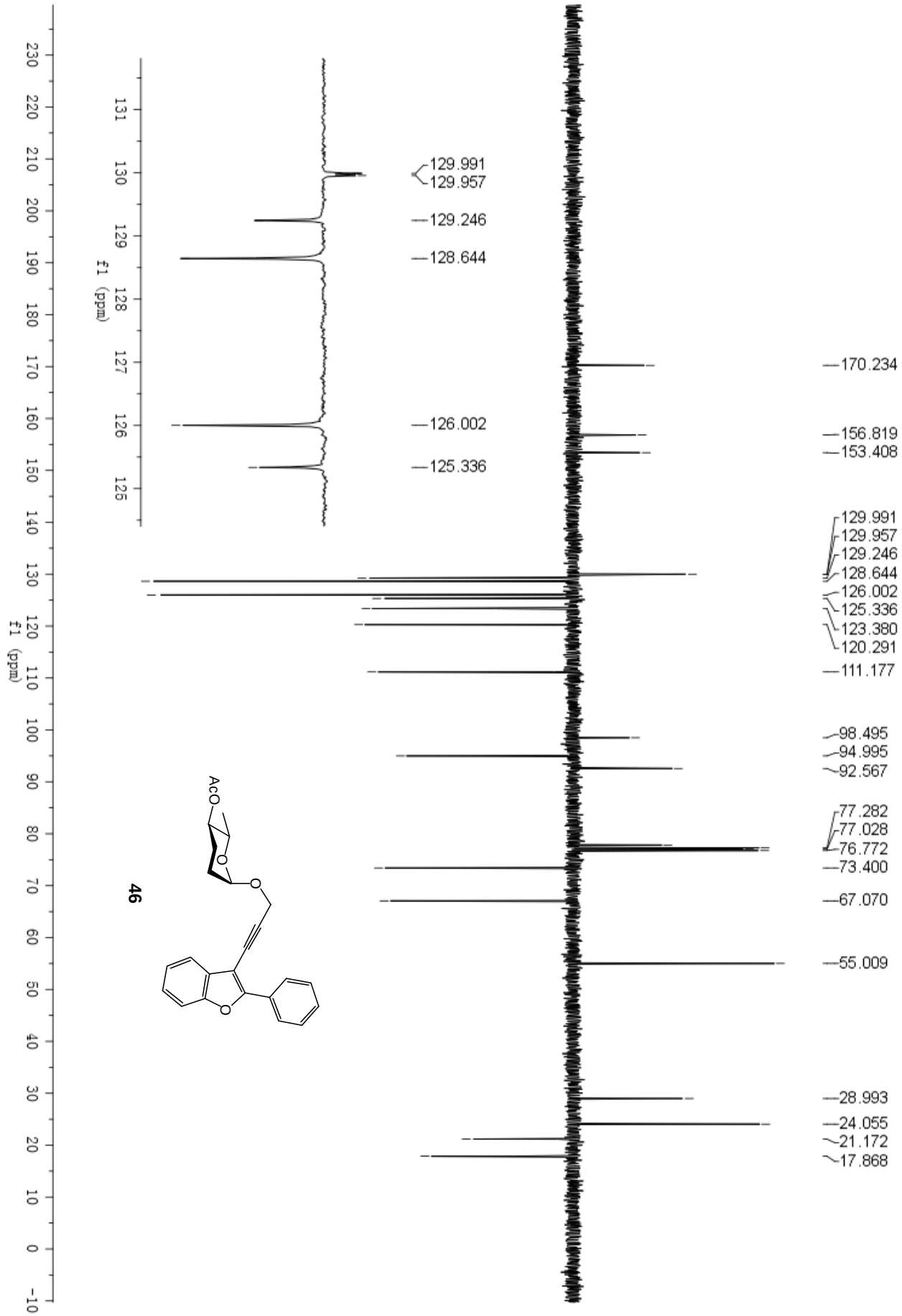

44β
N3
O
O
99.059
79.318
77.298
77.043
76.788
74.322
72.881
58.964
54.560
26.765
25.731
17.826
f1 (ppm)

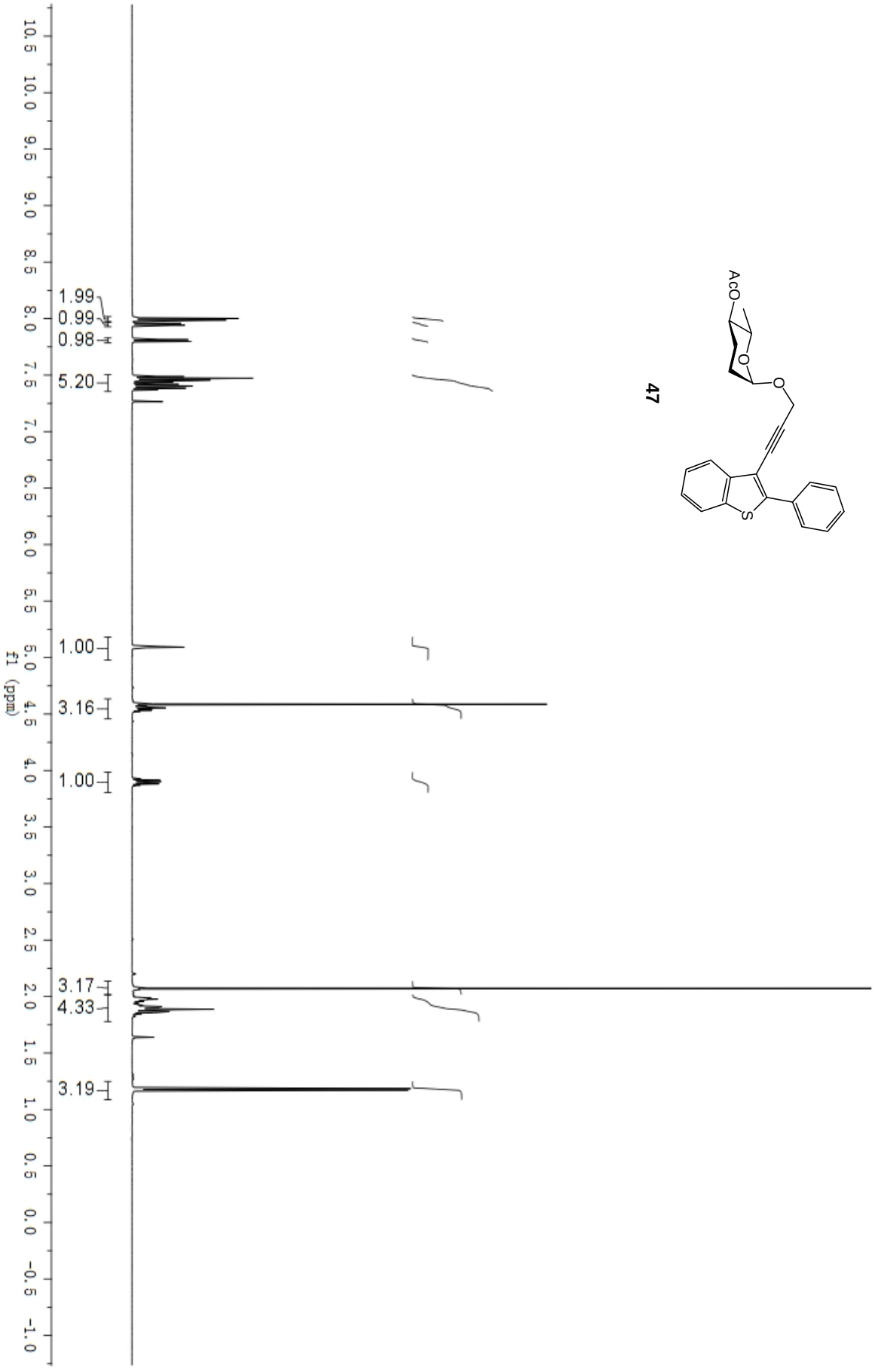

45
NH2
O
O
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
1.00
2.12
1.07
0.80
1.01
1.09
1.14
1.06
1.09
3.14


45
NH2
O
O
97.098
80.711
75.360
67.609
54.765
49.207
48.866
48.523
26.662
24.123
17.737
f1 (ppm)

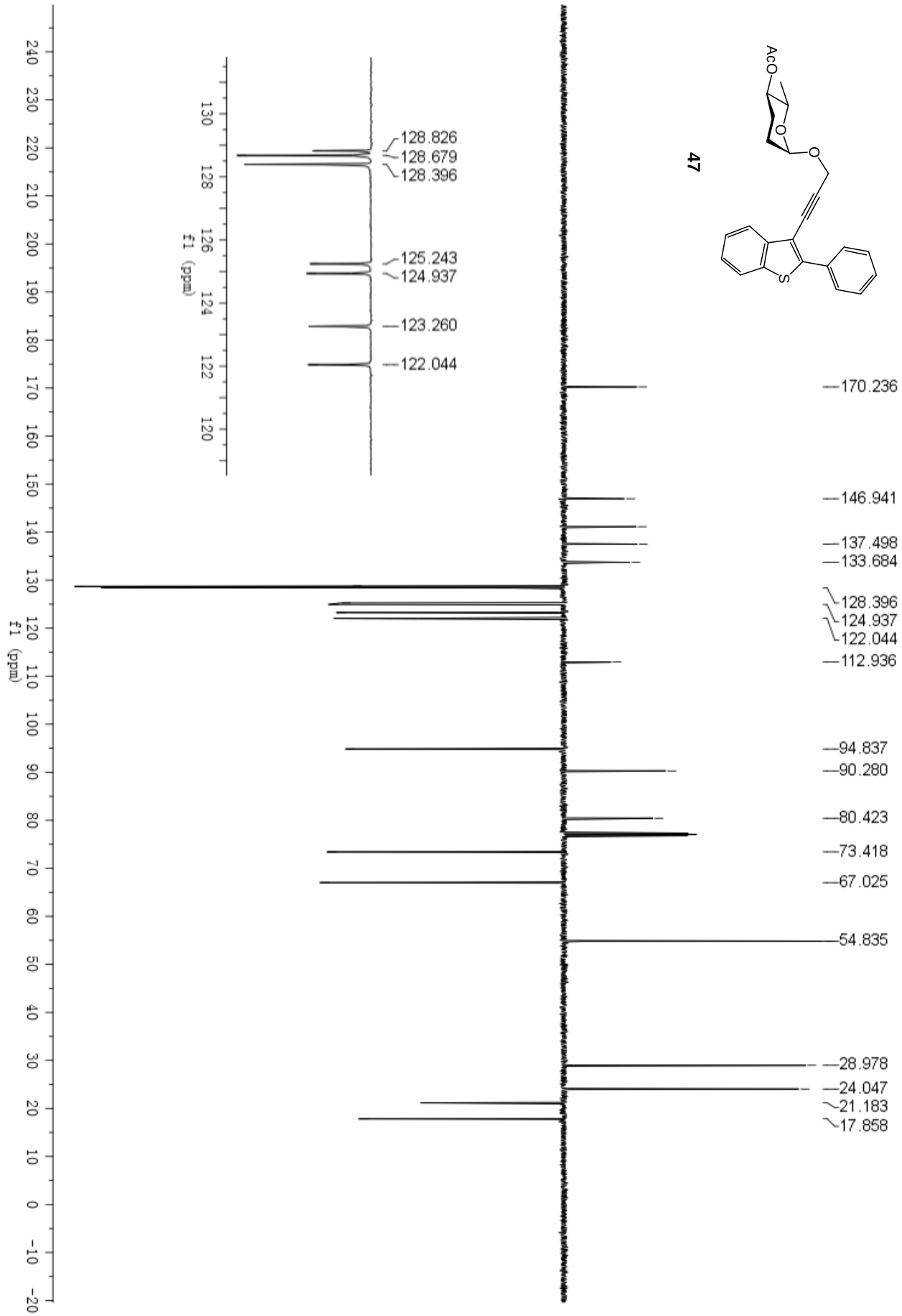


46


f1 (ppm)
129.991
129.957
129.246
128.644
126.002
125.336
170.234
156.819
153.408
129.991
129.957
129.246
128.644
126.002
125.336
123.380
120.291
111.177
98.495
94.995
92.567
77.282
77.028
76.772
73.400
67.070
55.009
28.993
24.055
21.172
17.868
AcO
O
O
O
46



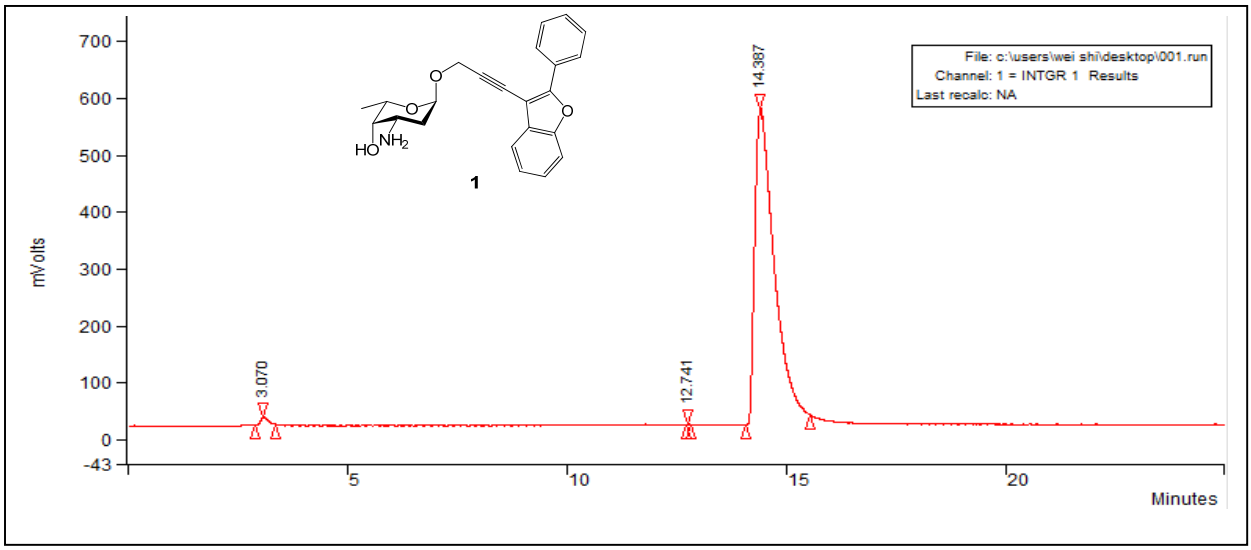
47


47
AcO
O
O
S
128.826
128.679
128.396
125.243
124.937
123.260
122.044
170.236
146.941
137.498
133.684
128.396
124.937
122.044
112.936
94.837
90.280
80.423
73.418
67.025
54.835
28.978
24.047
21.183
17.858
f1 (ppm)

HPLC Analysis of test compounds
HPLC: VARIAN ProStar Model 701
Column: VARIAN Polaris 5 C8-A 250x4.6 mm
Detector: ELSD

Gradient of HPLC eluents

	0 min	2 min	5 min	20 min	21 min	25 min
25 mM NH_4OAc Buffer, pH = 5.3 (%)	60	60	40	40	60	60
CH_3CN (%)	40	40	60	60	40	40

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Print Date: Mon Dec 03 13:55:04 2007                Page 1 of 1

Title        :
Run File     : c:\users\wei shi\desktop\001.run
Method File  : C:\star\Methods\Wei\Mannose.mth
Sample ID    : Manual Sample

Injection Date: 2007/12/3 13:00     Calculation Date: 2007/12/3 13:25

Operator     : Wei                    Detector Type: ProStar/Dynamax (2 Volts)
Workstation:                          Bus Address  : 24
Instrument : Instrument #1            Sample Rate  : 5.00 Hz
Channel    : 1 = INTGR 1              Run Time     : 24.987 min

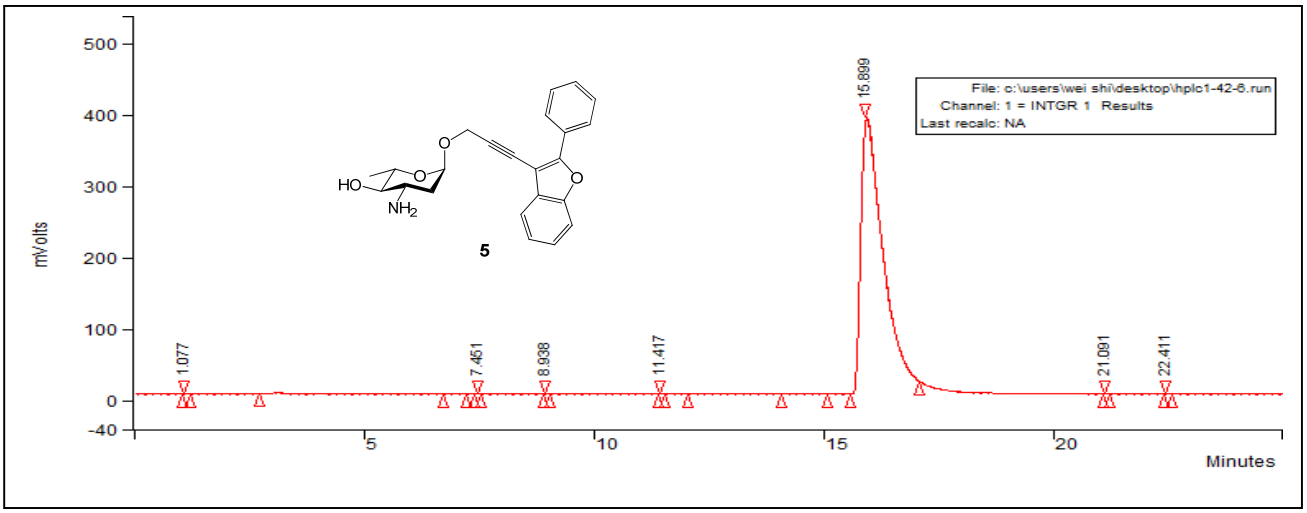
** LC Workstation Version 6.30 ** 02868-26D0-AE7-0234 **

Run Mode          : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
```

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.9944	3.070	0.000	168790	BB	12.5	
2		0.0383	12.741	0.000	6497	BB	2.8	
3		98.9673	14.387	0.000	16798884	BB	27.7	
	Totals:	100.0000		0.000	16974171			

Gradient of HPLC eluents

	0 min	2 min	5 min	20 min	21 min	25 min
25 mM NH_4OAc Buffer, pH = 5.3 (%)	60	60	40	40	60	60
CH_3CN (%)	40	40	60	60	40	40

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Print Date: Fri Dec 07 19:38:41 2007                Page 1 of 1

Title          :
Run File       : c:\users\wei shi\desktop\hplc1-42-6.run
Method File    : C:\star\Methods\Wei\Mannose.mth
Sample ID      : Manual Sample

Injection Date: 2007/12/5 19:35     Calculation Date: 2007/12/5 20:00

Operator    : Wei                    Detector Type: ProStar/Dynamax (2 Volts)
Workstation:                         Bus Address  : 24
Instrument  : Instrument #1          Sample Rate  : 5.00 Hz
Channel     : 1 = INTGR 1            Run Time     : 24.987 min

** LC Workstation Version 6.30 ** 02868-26D0-AE7-0234 **

Run Mode          : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
```

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.0665	1.077	0.000	8350	BB	3.0	
2		0.0680	7.451	0.000	8547	BB	7.7	
3		0.0633	8.938	0.000	7951	BB	0.0	
4		0.0611	11.417	0.000	7680	BB	3.5	
5		99.6070	15.899	0.000	12513063	BB	30.1	
6		0.0673	21.091	0.000	8448	BB	4.3	
7		0.0669	22.411	0.000	8399	BB	9.2	
	Totals:	100.0001		0.000	12562438			

Sample figure from the FID assays of compound **1** – **4**