Electronic Supplementary Material (ESI) for Medicinal Chemistry Communications.

Supporting Information for:

Sulfonium Ions as Inhibitors of the Mycobacterial Galactofuranosyltransferase GlfT2

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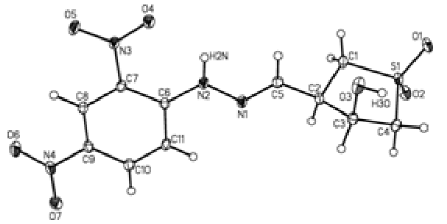
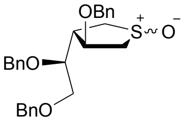
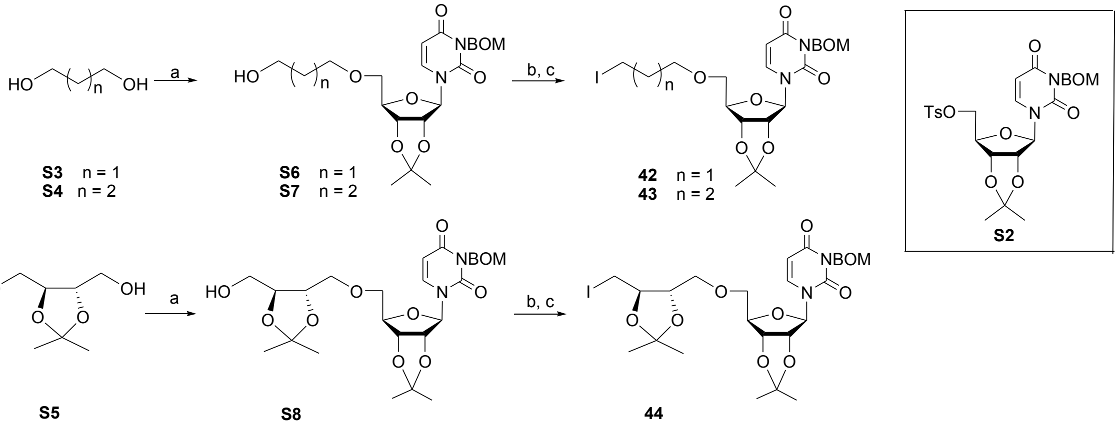


Fig. S1 Crystal structure of **29**.



S1

Fig. S2 Sulfoxide byproduct **S1**.



Scheme S1 *Reagents and conditions:* (a) **S2**, NaH, DMF, **S6**: 36%; **S7**: 52%; **S8**: 57%; (b) MsCl, Et_3N, CH_2Cl_2; (c) NaI, Acetone, **42**: 65%; **43**: 61%; **44**: 35%.

Preparation of iodides

Most of these alkyl halides were either commercially available or could be obtained via iodination of the corresponding commercially available alcohol using literature methods.[S1] However, the uridine-based compounds **42**–**44** required additional synthetic effort. Their preparation started with, 2',3'-*O*-isopropylidene-5'-*O*-tosyl-3-(benzyloxymethyl)uridine (**S2**).[S2] As illustrated in Scheme 5, reaction of **S1** with 10 equivalents of diol **S3**, **S4** or **S5** and 1.2 equivalents of NaH in DMF afforded **S6**, **S7** and **S8** in 36%, 52% and 57% yield, respectively. Attempts to improve the yield of this displacement reaction by changing the ratio of the starting materials or the sequence reagent addition were unsuccessful. Compounds **S6** and **S7** were treated with MsCl to form the corresponding mesylates, which were subsequently heated with NaI at 50 °C to give iodides **42** and **43** in moderate yield (~60%). More vigorous conditions were required to convert **S8** into the required iodide, presumably due to steric hindrance arising from the isoproylidene moiety. After mesylation of **S8**, the intermediate was combined with freshly fused NaI in a sealed vessel and heated at 80 °C for 4 h, leading to **44** in 37% yield. Unreacted mesylate was also detected after the reaction. However the yield could not be improved by elongation of the reaction time or by raising the reaction temperature.

Experimental

All reagents were purchased from commercial sources and were used without further purification. Solvents used in reactions were pre-dried by PURESOLV-400 System from Innovative Technology Inc. All reactions were monitored by TLC on silica gel G-25 UV254 (0.25 mm, Macherey–Nagel). Spots were detected under UV light and/or by charring with acidified ethanolic anisaldehyde. Solvents were evaporated under reduced pressure and below 50 ºC (water bath). Column chromatography was performed on silica gel 60 (40–60 μm). The ratio between silica gel and crude product ranged from 100:1 to 20:1 (w/w). Iatrobeads refers to a beaded silica gel 6RS-8060, which was manufactured by Iatron laboratories (Tokyo). ^{1}H NMR spectra were recorded on VARIAN INOVA-NMR spectrometers at 400, 500 or 600 MHz and chemical shifts are referenced to $CDCl_3$ (7.26, $CDCl_3$) or CD_3OD (4.78, CD_3OD). ^{13}C NMR APT spectra were recorded at 100 or 125 MHz, and chemical shifts are referenced to $CDCl_3$ (77.23, $CDCl_3$) or CD_3OD (48.9, CD_3OD). ^{1}H NMR data are reported as though they are first order, and the peak assignments are made by 2D-NMR spectroscopy (^{1}H–^{1}H COSY and HMQC). HRMS-ESI spectra were recorded on samples suspended in THF or CH_3OH and added NaCl. Optical rotations were measured on Perkin-Elmer 241 Polarimeter with sodium D line (589 nm) and are in units of deg·mL (dm·g)$^{-1}$.

(*3R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)tetrahydrothiophene 1,1-dioxide (25):

To a solution of **21** (0.50 g, 1.15 mmol) in CH_2Cl_2 (15 mL) was added *m*-CPBA, (77%, 0.62 g, 2.76 mmol) at rt and the mixture was stirred for 20 min. The solution was diluted with CH_2Cl_2, and washed with NaOH (1 M). The organic layer was then washed with brine, dried (Na_2SO_4) and concentrated. The resulting residue was purified by chromatography (EtOAc–Hexane 1:4) to give **25** (0.50 g, 94%) as a colorless oil: R_f = 0.29 (EtOAc–Hexane 1:3); $[\alpha]_D^{20}$ –62.7 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 15H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.56–4.48 (m, 2H), 4.38–4.32 (m, 2H), 4.26 (d, *J* = 11.7 Hz, 1H), 4.20 (ddd, *J* = 7.8, 7.8, 7.8 Hz, 1H), 3.95 (ddd, *J* = 2.5, 5.0, 5.0 Hz, 1H), 3.56–3.47 (m, 2H), 3.39 (dd, *J* = 7.8, 13.1 Hz, 1H), 3.25 (m, 2H), 2.99 (dd, *J* = 7.8, 13.1 Hz, 1H), 2.70 (dddd, *J* = 2.5, 7.8, 9.4, 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.6, 136.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 74.4, 73.5, 73.4, 72.6, 72.4, 70.6, 56.1, 51.4, 45.5; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{27}H_{30}O_5SNa$: 489.1706, found: 489.1704.

(3*R*,4*R*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)tetrahydrothiophene 1,1-dioxide (26): To a solution of tetrahedrothiophene **22** (25.3 mg, 0.061 mmol) in CH_2Cl_2 (3 mL) was added *m*-CPBA (77%, 34.1 mg, 1.53 mmol) at rt and the mixture was stirred for 20 min. The solution was then diluted with CH_2Cl_2, and washed with NaOH (1 M). The organic layer was washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (EtOAc–Hexane 1:4) to give **26** as a colorless oil (26.6 mg, 94%): $R_f = 0.22$ (EtOAc–Hexane 1:3); $[\alpha]_D^{20}$ –66.4 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.24 (m, 15H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.59–4.56 (m, 3H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.29 (d, *J* = 11.4 Hz, 1H), 3.88 (ddd, *J* = 3.7, 3.7, 9.7 Hz, 1H), 3.65 (dd, *J* = 3.7, 10.7 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 3.39 (dd, *J* = 3.7, 10.7 Hz, 1H), 3.14–3.04 (m, 3H), 2.87 (dddd, *J* = 2.9, 7.2, 9.7, 13.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 137.6, 136.9, 128.6, 128.5, 127.7, 127.6, 127.5, 76.0, 75.2, 73.5, 72.2, 71.1, 69.5, 59.9, 51.6, 44.8; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{27}H_{30}O_5SNa$: 489.1706, found: 489.1702.

(3*R*,4*S*)-3-(hydroxyl)-4-((*S*)-1,2-dihydroxyethyl)tetrahydrothiophene 1,1-dioxide (27): To a solution of **25** (110 mg, 0.2 mmol) in CH_3OH (5 mL) and CH_2Cl_2 (1 mL) was added HOAc (10 μL) and Pd–C (10%, 10 g). The reaction mixture was stirred under a H_2 atmosphere for 48 h at rt. The solution was filtered and the filtrate was concentrated to give **27** as a colorless oil (48 mg, 98%): $R_f = 0.22$ (CH_2Cl_2–CH_3OH 9:1); $[\alpha]_D^{20}$ –56.9 (*c* = 2.6, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 4.42 (ddd, *J* = 7.9, 7.9, 7.9 Hz, 1H), 3.97 (ddd, *J* = 3.2, 6.0, 6.0 Hz, 1H), 3.52–3.31 (m, 3H), 3.26 (dd, *J* = 8.0, 13.3 Hz, 1H), 3.14 (dd, *J* = 11.2, 13.3 Hz, 1H), 2.99 (dd, *J* = 7.9, 13.3 Hz, 1H), 2.47 (dddd, *J* = 3.2, 7.9, 8.0, 11.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 69.7, 69.1, 66.0, 59.3, 52.6, 48.3; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_6H_{12}O_5SNa$: 219.0298, found: 219.0298.

(3*R*,4*R*)-3-(hydroxyl)-4-((*S*)-1,2-dihydroxyethyl)tetrahydrothiophene1,1-dioxide (28): To a solution of **26** (0.39 g, 0.8 mmol) in CH_3OH (15 mL) and CH_2Cl_2 (3 mL) was added HOAc

(50 μL) and Pd–C (10%, 40 mg). The solution was stirred under a H_2 atmosphere for 20 h at rt. The solution was filtered and the filtrate was concentrated to give **28** as a colorless oil (0.17 g, 98%): R_f = 0.20 (CH_2Cl_2–CH_3OH 9:1); $[\alpha]_D^{20}$ –31.6 (*c* 1.31 in CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ = 4.77 (dd, *J* = 3.3, 3.5 Hz, 1H), 3.82 (m, 1H), 3.62 (dd, *J* = 4.0, 11.5 Hz, 1H), 3.51 (dd, *J* = 5.1, 11.5 Hz, 1H), 3.39–3.19 (m, 2H), 3.12 (d, *J* = 10.3 Hz, 2H), 2.53 (dddd, *J* = 3.3, 10.3, 10.3, 10.3 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 71.3, 69.3, 66.0, 62.7, 52.1, 46.1; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_6H_{12}O_5SNa$: 219.0298, found: 219.0298.

(3*R*,4*R*)-3-(hydroxyl)-4-((2-(2,4-dinitrophenyl)hydrazinylidene)methyl)tetra-hydrothiophene 1,1-dioxide (29): To a solution of **28** (0.10 g, 0.51 mmol) in THF (3 mL) and H_2O (0.5 mL) was added $NaIO_4$ (0.16 g, 0.76 mmol) and $NaHCO_3$ (0.09 g, 1.0 mmol). The mixture was stirred for 30 min and then the precipitate was filtered. The filtrate was concentrated and the resulting residue was purified by chromatography (CH_2Cl_2–CH_3OH, 20:1). The product (R_f = 0.5 (CH_2Cl_2–CH_3OH, 9:1)) was dissolved in CH_3OH and was added a solution of (2,4-dinitrophenyl)hydrazine (1 M, 1 mL). After stirring for 10 min, the mixture was concentrated and the resulting residue was purified by chromatography (CH_2Cl_2–CH_3OH, 19:1) to give **29** as a yellow solid (51 mg, 30%). This solid was recrystallized from CH_3OH and acetone. R_f = 0.23 (CH_2Cl_2–CH_3OH, 19:1); mp: 89–90 °C; $[\alpha]_D^{20}$ +4.9 (*c* 0.1, acetone); ^1H NMR (500 MHz, CD_3COCD_3) δ 8.97 (d, *J* = 2.7 Hz, 1H), 8.39–8.36 (m, 1H), 8.09–8.06 (m, 2H), 4.98 (m, 1H), 3.64–3.59 (m, 2H), 3.44 (dd, *J* = 5.0, 13.8 Hz, 1H), 3.33 (m, 1H), 3.25 (dd, *J* = 1.6, 13.8, Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.7; 144.5, 136.8, 129.6, 129.0, 122.8, 116.4, 68.7, 60.7, 50.6, 44.9; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}N_4O_7SNa$: 367.0319, found: 367.0321.

2',3'-*O*-isopropylidene-5'-*O*-(3-hydroxylpropyl)-3-(benzyloxymethyl)uridine (S6): To a solution of **S2** (0.50 g, 0.9 mmol) and 1,3-propanediol (**S3**) (0.69 g, 9.0 mmol) in DMF (4 mL) at 0 ºC was added NaH (72 mg, 1.8 mmol, 60% in mineral oil). The solution was stirred at rt for 20 h and then was added water H_2O (10 mL). The mixture was extracted with Et_2O. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (EtOAc–Hexane 2:1) to give **S6** as a colorless oil (0.15 g, 36%): R_f = 0.14 (EtOAc–Hexane 2.5:1); $[\alpha]_D^{20}$ –3.3 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 1H), 7.38–7.23 (m, 5H), 5.77 (d, *J* = 1.9 Hz, 1H), 5.73 (d, *J* = 8.2 Hz, 1H), 5.50 (d, *J* = 9.7 Hz, 1H), 5.47 (d, *J* = 9.7 Hz, 1H), 4.81–4.77 (m, 2H), 4.70 (s, 2H), 4.37 (ddd, *J* = 3.0, 3.0, 4.5 Hz, 1H), 3.73–3.69 (m, 3H), 3.67–3.58 (m, 3H), 1.83–1.77 (m, 2H), 1.58 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6; 150.8, 139.9, 137.9, 128.3, 127.6, 114.1, 101.6, 94.4, 85.9, 85.2, 80.9, 72.3, 70.9, 70.3, 69.6, 60.6, 32.2, 27.2, 25.4; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{23}H_{30}N_2O_8Na$: 485.1894, found: 485.1894.

2’3’-*O*-isopropylidene-5’-*O*-(3-iodopropyl)-3-(benzyloxymethyl) uridine (42): To a solution of compound **S6** (150 mg, 0.32 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1 mL) and MsCl (43 mg, 0.38 mmol) at 0 ºC. The mixture was stirred for 30 min at rt and then was added H_2O (10 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give the crude mesylate. The mesylate was dissolved in acetone (10 mL) and then reacted with fresh fused NaI (70 mg, 0.47 mmol). The reaction was heated at 50 ºC for 4 h, cooled and concentrated. The crude product was purified by chromatography (EtOAc–Hexane 1:2) to give **42** as a colorless oil (121 mg, 65%): R_f = 0.11 (EtOAc–Hexane 1:2); $[\alpha]_D^{20}$ –6.0 (*c* 1.6, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 1H), 7.40–7.28 (m, 5H), 5.83 (d, *J* = 2.2 Hz, 1H), 5.76 (d, *J* = 8.1 Hz, 1H), 5.52 (d, *J* = 9.7 Hz, 1H), 5.49 (d, *J* = 9.7 Hz, 1H), 4.82 (dd, *J* = 3.0, 6.2 Hz, 1H), 4.78 (dd, *J* = 2.2, 6.2 Hz, 1H), 4.73 (s, 2H), 4.41 (ddd, *J* = 3.0, 3.1, 4.4 Hz, 1H), 3.76 (dd, *J* = 3.0, 10.5 Hz, 1H), 3.65 (dd, *J* = 4.4, 10.5 Hz, 1H), 3.59–3.56 (m, 2H), 3.22 (dd, *J* = 6.8, 6.8 Hz, 2H), 2.07–2.02 (m, 2H), 1.62 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6; 150.8, 139.6, 137.9, 128.2, 127.6, 114.1, 101.5, 94.2, 86.0, 85.4, 80.9, 72.3, 71.0, 70.9, 70.3, 32.8, 27.2, 25.4, 2.5; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{23}H_{30}N_2O_7I$: 595.0912, Found: 595.0912.

2’,3’-*O*-isopropylidene-5’-*O*-(4-hydroxylbutyl)-3-(benzyloxymethyl)uridine (S7): To a solution of **S1** (0.89 g, 1.6 mmol) and 1,4-butanediol (**S4**) (1.62 g, 19.4 mmol) in DMF (4 mL) at 0 ºC was added NaH (128 mg, 3.2 mmol, 60% in mineral oil). The reaction was stirred at rt for 20 h and then was added H_2O (10 mL). The mixture was extracted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by chromatography (EtOAc–Hexane 2:1) to give **S7** as a colorless oil (0.40 g, 52%): R_f = *0.*16 (EtOAc–Hexane 2.5:1); $[\alpha]_D^{20}$ –3.7 (*c* = 2.4, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.36–7.23 (m, 5H), 5.83 (s, 1H), 5.71 (d, *J* = 8.1 Hz, 1H), 5.59 (d, *J* = 9.8 Hz, 1H), 5.45 (d, *J* = 9.8 Hz, 1H), 4.78–4.74 (m, 2H), 4.70 (s, 2H), 4.38 (ddd, *J* = 2.6, 2.6, 3.9 Hz, 1H), 3.69 (dd, *J* = 2.6, 10.7 Hz, 1H), 3.61–3.57 (m, 3H), 3.59–3.46 (m, 2H), 1.64–1.55 (m, 4H), 1.57 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7; 150.9, 139.7, 137.9, 128.3, 127.6, 114.0, 101.4, 94.0, 85.9, 85.4, 80.9, 72.3, 71.6, 70.7, 70.3, 62.4, 29.5, 27.2, 26.2, 25.4; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{24}H_{32}N_2O_8Na$: 499.2051, found: 499.2046.

2’3’-*O*-isopropylidene-5’-*O*-(4-iodobutyl)-3-(benzyloxymethyl) uridine (43): To a solution of compound **S7** (140 mg, 0.29 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1 mL) and MsCl (40 mg, 0.35 mmol) at 0 ºC. The mixture was stirred for 30 min at rt and then was added H_2O (10 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give the crude mesylate. The mesylate was dissolved in acetone (10 mL) and was reacted with fresh fused NaI (65 mg, 0.44 mmol). The reaction was heated at 50 ºC for 4 h, cooled and concentrated. The crude product was purified by chromatography (EtOAc–Hexane 1:2) to give **43** as a colorless oil (105 mg, 61%): R_f = 0.17 (EtOAc–Hexane 1:2); $[\alpha]_D^{20}$ –7.4 (*c* = 0.6, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 1H), 7.36–7.23 (m, 5H), 5.82 (d, *J* = 1.9 Hz, 1H), 5.72 (d, *J* = 8.1 Hz, 1H), 5.49 (d, *J* = 9.8 Hz, 1H), 5.45 (d, *J* = 9.8 Hz, 1H), 4.77–4.73 (m, 2H), 4.69 (s, 2H), 4.37 (ddd, *J* = 2.3, 3.1, 3.9 Hz, 1H), 3.68 (dd, *J* = 2.3, 10.6

Hz, 1H), 3.58 (dd, *J* = 3.9, 10.6 Hz, 1H), 3.51–3.43 (m, 2H), 3.16 (dd, *J* = 6.7, 6.7 Hz, 2H), 1.86–1.80 (m, 2H), 1.68–1.62 (m, 2H), 1.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6; 150.9, 139.6, 137.9, 128.3, 127.6, 114.0, 101.5, 94.0, 85.9, 85.4, 80.9, 72.3, 70.8, 70.5, 71.4, 30.4, 30.1, 27.2, 25.4, 6.3; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{24}H_{32}N_2O_7I$: 587.1249, found: 587.1260.

2’3’-*O*-isopropylidene-5’-*O*-((2*S*,3*S*)-2,3-*O*-isopropylidene-2,3,4-trihydroxyl-butyl)-3-(benzyloxymethyl) uridine (S8): To a solution of **S1** (0.61 g, 1.09 mmol) and **S5** (1.77 g, 10.9 mmol) in DMF (3 mL) was added NaH (66 mg, 1.63 mmol, 60% in mineral oil) at 0 ºC. The reaction mixture was then warmed to rt, stirred overnight and was added H_2O (10 mL). The mixture was extracted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by chromatography (EtOAc–Hexane 2:1) to give **S8** as a colorless oil (0.340 g, 57 %): R_f = 0.29 (EtOAc–Hexane 2.5:1); $[\alpha]_D^{20}$ –9.6 (*c* 1.9, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.2 Hz, 1H), 7.37–7.23 (m, 5H), 5.80 (d, *J* = 2.1 Hz, 1H), 5.74 (d, *J* = 8.2 Hz, 1H), 5.49 (d, *J* = 9.7 Hz, 1H), 5.45 (d, *J* = 9.7 Hz, 1H), 4.82–4.76 (m, 2H), 4.70 (s, 2H), 4.33 (ddd, *J* = 3.2, 3.2, 4.4 Hz, 1H), 4.04 (ddd, *J* = 4.9, 4.9, 8.3 Hz, 1H), 3.87 (ddd, *J* = 4.2, 4.2, 8.3 Hz, 1H), 3.79–3.75 (m, 2H), 3.71 (dd, *J* = 4.5, 10.7 Hz, 1H), 3.66–3.63 (m, 3H), 1.58 (s, 3H), 1.41 (s, 6H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 162.6; 150.9, 140.1, 137.9, 128.3, 127.6, 114.0, 109.5, 101.9, 94.0, 85.6, 84.8, 80.7, 78.6, 76.4, 72.3, 71.9, 71.4, 70.3, 62.1, 27.2, 27.1, 27.0, 25.4; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{27}H_{36}N_2O_{10}Na$: 571.2262, found: 571.2265.

2’3’-*O*-isopropylidene-5’-*O*-((2*S*,3*R*)-4-iodo-2,3-*O*-isopropylidene-2,3-dihydr-oxyl-butyl)-3-(benzyloxymethyl) uridine (44): To a solution of compound **S8** (340 mg, 0.62 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1 mL) and MsCl (85 mg, 0.74 mmol) at 0 ºC. The mixture was stirred for 30 min at rt and then was added H_2O (10 mL). The solution was extracted with Et_2O and the organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give the crude mesylate. The mesylate was dissolved in acetone (10 mL) and then reacted with fresh fused NaI (140 mg, 0.93 mmol) in a sealed vessel at 80 ºC for 4 h, cooled and concentrated. The iodide was purified by chromatography (EtOAc–Hexane 1:2) to give **44** as a colorless oil (141 mg, 35%): $R_f = 0.43$ (EtOAc–Hexane 1:1); $[\alpha]_D^{20}$ –11.6 ($c = 2.0$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, $J = 8.2$ Hz, 1H), 7.38–7.24 (m, 5H), 5.84 (d, $J = 2.6$ Hz, 1H), 5.75 (d, $J = 8.2$ Hz, 1H), 5.50 (d, $J = 9.7$ Hz, 1H), 5.46 (d, $J = 9.7$ Hz, 1H), 4.82 (dd, $J = 3.3$, 6.3 Hz, 1H), 4.79 (dd, $J = 2.5$, 6.3 Hz, 1H), 4.70 (s, 2H), 4.35 (ddd, $J = 3.1$, 3.3, 4.4 Hz, 1H), 3.93 (ddd, $J = 3.9$, 5.6, 7.3 Hz, 1H), 3.85 (ddd, $J = 5.5$, 5.5, 7.3 Hz, 1H), 3.80 (dd, $J = 3.1$, 10.7 Hz, 1H), 3.75 (dd, $J = 3.9$, 10.6 Hz, 1H), 3.73 (dd, $J = 4.4$, 10.7 Hz, 1H), 3.67 (dd, $J = 5.6$, 10.6 Hz, 1H), 3.29 (d, $J = 5.5$ Hz, 2H), 1.59 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6; 150.9, 140.0, 137.9, 128.3, 127.6, 114.3, 109.9, 102.0, 93.8, 85.6, 84.8, 80.8, 80.3, 76.9, 72.3, 72.1, 71.5, 70.3, 27.4, 27.3, 27.2, 25.4, 5.8; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{27}H_{35}N_2O_9INa$: 681.1280, found: 681.1285.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-propyl-tetrahydro-1*H*-thiophenium tetrafluoroborate (45): Using the general procedure for preparation of sulfonium ions, compound **21** (69 mg, 0.16 mmol) was treated with **30** (27.2 mg, 0.16 mmol) and $AgBF_4$ (32 mg, 0.16 mmol) to give **45** as a colorless oil (65 mg, 73%): $R_f = 0.69$ (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{30}H_{37}O_3S$: 477.2458, found: 477.2459. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-propyl-tetrahydro-1*H*-thiophenium chloride (46): Using the general procedure for the benzyl deprotection, **45** (44 mg, 0.078 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **46** as a 70:30 mixture of inseparable stereoisomers as a colorless oil (13 mg, 72%): $R_f = 0.06$ (CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 4.74 (dd, $J = 2.0$, 2.0 Hz, 0.7H), 4.67 (ddd, $J = 5.4$, 5.6, 5.6 Hz, 0.3H), 3.89–3.75 (m, 2H), 3.66–3.61 (m, 1H), 3.57–3.34 (m, 6H), 3.05 (dddd, $J =$

1.6, 2.1, 4.8, 6.6 Hz, 0.7H), 2.66 (dddd, *J* = 2.6, 6.0, 6.0, 8.6 Hz, 0.3H), 1.90–1.82 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 80.0; 77.2, 70.9, 70.0, 66.1, 65.3, 53.8, 52.9, 50.3, 49.4, 48.1, 45.5, 42.9, 40.2, 20.5, 20.2, 13.1, 13.0; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_9H_{19}O_3S$: 207.1049, found: 207.1050.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-propyl-tetrahydro-1*H*-thiophenium tetrafluoroborate (47): Using the general procedure for the preparation of sulfonium ions, **21** (69 mg, 0.16 mmol) was treated with **31** (38.2 mg, 0.16 mmol) and $AgBF_4$ (31 mg, 0.16 mmol) to give **47** as a colorless oil (76 mg, 77%): R_f = 0.70 (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{35}H_{47}O_3S$: 547.3240, found: 547.3245. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-octyl-tetrahydro-1*H*-thiophenium chloride (48): Using the general procedure for the benzyl deprotection, **47** (76 mg, 0.12 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst ($Cl^–$ form) to give **48** as a 70:30 mixture of inseparable stereoisomers as a colorless oil (32 mg, 86%): R_f 0.06 (CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 4.74 (dd, *J* = 1.9, 1.9 Hz, 0.7H), 4.67 (ddd, *J* = 5.5, 5.7, 5.7 Hz, 0.3H), 3.89–3.74 (m, 2H), 3.66–3.61 (m, 1H), 3.57–3.30 (m, 6H), 2.97 (dddd, *J* = 1.7, 3.3, 4.8, 6.6 Hz, 0.7H), 2.66 (m, *J* = 2.3, 5.9, 5.9, 8.6 Hz, 0.3H), 1.87–1.77 (m, 2H), 1.52–1.45 (m, 2H), 1.49–1.35 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 80.0; 77.2, 70.9, 70.0, 66.1, 65.3, 53.8, 51.6, 50.3, 48.1, 46.9, 43.7, 42.9, 40.2, 32.9, 30.1, 30.0, 29.5, 29.4, 26.8, 26.5, 14.4; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{14}H_{29}O_3S$: 277.1832, found: 277.1832.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-isobutyl-tetrahydro-1*H*-thiophenium tetrafluoroborate (49): Using the general procedure for the preparation of sulfonium ions, **21** (77 mg, 0.18 mmol) was reacted with **32** (34 mg, 0.18 mmol) and $AgBF_4$ (35 mg, 0.18 mmol) to give **49** as a colorless oil (24.3 mg, 24%): R_f = 0.70 (CH_2Cl_2–CH_3OH, 9:1);

HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{31}H_{39}O_3S$: 491.2614, found: 491.2617. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-isobutyl-tetrahydro-1*H*-thiophenium chloride (50): Using the general procedure for the benzyl deprotection, **49** (45 mg, 0.078 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **50** as a 70:30 mixture of inseparable stereoisomers as a colorless foam (18 mg, 88%): R_f = 0.06 (CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 4.74 (dd, *J* = 2.0, 2.0 Hz, 0.7H), 4.68 (ddd, *J* = 5.2, 5.2, 5.2 Hz, 0.3H), 3.92 (dd, *J* = 1.8, 12.2 Hz, 0.7H,), 3.86–3.78 (m, 1.3H), 3.66–3.33 (m, 7H), 3.06 (dddd, *J* = 1.7, 3.2, 4.9, 6.6 Hz, 0.7H), 2.69 (dddd, *J* = 2.4, 5.6, 5.6, 8.4 Hz, 0.3H), 2.20–2.08 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, CD_3OD) δ 80.0; 77.4, 70.9, 70.0, 66.0, 65.3, 55.3, 53.9, 52.1, 51.6, 50.9, 48.9, 43.5, 40.9, 27.7, 27.6, 21.9, 21.7; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{10}H_{21}O_3S$: 221.1206, found: 221.1207.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-cyclohexylmethyl-tetrahydro-1*H*-thiophenium tetrafluoroborate (51): Using the general procedure for the preparation of sulfonium ions, **21** (86 mg, 0.20 mmol) was reacted with iodide **33** (45 mg, 0.20 mmol) and $AgBF_4$ (38 mg, 0.20 mmol) to give **51** as a colorless oil (10 mg, 8%): R_f = 0.34 (CH_2Cl_2–CH_3OH, 19:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{34}H_{43}O_3S$: 531.2927, found: 531.2925. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-cyclohexylmethyl-tetra-hydro-1*H*-thiophenium chloride (52): Using the general procedure for the benzyl deprotection, **51** (8 mg, 0.13 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **52** as a colorless foam as a 91:9 ratio of isomers (3.3 mg, 100%): R_f = 0.06 (CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 4.73 (dd, *J* = 2.0, 2.0 Hz, 1H), 3.90 (dd, *J* = 1.8, 12.2 Hz, 1H), 3.78 (dd, *J* = 3.9, 12.5 Hz, 1H), 3.62 (ddd, *J* = 1.4, 5.6, 6.9 Hz, 1H), 3.46 (dd, *J* = 6.8, 12.2 Hz, 1H), 3.42 (dd, *J* = 6.7, 11.2 Hz, 1H,), 3.38 (dd, *J* = 7.1, 12.6 Hz, 1H), 3.34–3.31 (m, 3H), 3.05 (dddd, *J* = 1.9, 3.4, 3.4, 6.8 Hz, 1H), 1.91–1.77 (m, 4H), 1.72–1.69 (m, 1H), 1.40–1.32 (m, 2H), 1.28–1.18 (m, 2H), 1.17–1.11 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 80.0; 70.9, 65.3, 54.1, 53.9, 50.9, 43.5, 36.5, 33.2, 33.0, 26.8, 26.7; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{13}H_{25}O_3S$: 261.1519, found: 261.1517.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(2-methoxyethyl)-tetrahydro-1*H*-thiophenium tetrafluoroborate (53): Using the general procedure for the preparation of sulfonium ions, **21** (61 mg, 0.14 mmol) was reacted with **34** (28.7 mg, 0.15 mmol) and $AgBF_4$ (30 mg, 0.15 mmol) to give **53** as a colorless oil (66 mg, 81%): R_f = 0.70 (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{30}H_{37}O_4S$: 493.2407, found: 493.2402. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(2-methoxyethyl)-tetrahydro-1*H*-thiophenium chloride (54): Using the general procedure for the benzyl deprotection, **53** (38 mg, 0.065 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **54** as a 70:30 mixture of inseparable stereoisomers as a colorless foam (14 mg, 83%): R_f = 0.06 (CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ = 4.73 (dd, *J* = 2.0, 2.0 Hz, 0.7H), 4.67 (ddd, *J* = 5.0, 5.0, 5.0 Hz, 0.3H), 3.90–3.61 (m, 7H), 3.57–3.47 (m, 3H), 3.44–3.41 (m, 4H), 3.03 (dddd, *J* = 1.7, 3.3, 5.0, 7.0 Hz, 0.7H), 2.68 (dddd, *J* = 2.3, 5.3, 5.3, 8.2 Hz, 0.3H); ^{13}C NMR (125 MHz, CD_3OD) δ 80.0; 77.4, 70.8, 70.0, 68.7, 68.4, 66.0, 65.3, 59.4, 53.7, 51.5, 51.2, 49.4, 47.8, 44.7, 43.9, 41.1; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_9H_{19}O_4S$: 223.0999, found: 223.0997.

((3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(8-methoxyoctyl)-tetraydro-1*H*-thiophenium tetrafluoroborate (55): Using the general procedure for the preparation of sulfonium ions, **21** (103 mg, 0.24 mmol) was reacted with **35** (80 mg, 0.29 mmol) and $AgBF_4$

(46 mg, 0.24 mmol) to give **55** as a colorless oil (152 mg, 97%): $R_f = 0.70$ (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{36}H_{49}O_4S$: 577.3346, found: 577.3345. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(8-methoxyoctyl)-tetrahydro-1*H*-thiophenium chloride (56): Using the general procedure for the benzyl deprotection, **55** (100 mg, 0.15 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give product **56** as a 70:30 mixture of inseparable stereoisomers as a colorless foam (32 mg, 55%): $R_f = 0.06$ (CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 4.74 (dd, *J* = 2.0, 2.0 Hz, 0.7H), 4.67 (ddd, *J* = 5.7, 5.7, 5.7 Hz, 0.3H), 3.89–3.75 (m, 2H), 3.66–3.61 (m, 1H), 3.57–3.36 (m, 8H), 3.30 (s, 3H), 2.97 (dddd, *J* = 1.6, 3.1, 5.6, 6.5 Hz, 0.7H), 2.66 (dddd, *J* = 2.3, 5.9, 5.9, 8.5 Hz, 0.3H), 1.87–1.78 (m, 2H), 1.58–1.46 (m, 4H), 1.40–1.35 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 80.0; 77.2, 73.8, 70.9, 70.0, 66.1, 65.3, 58.8, 53.8, 51.6, 50.3, 48.1, 46.9, 43.7, 42.9, 40.2, 30.5, 30.0, 29.9, 29.3, 27.0, 26.7, 26.5; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{15}H_{31}O_4S$: 307.1937, found: 307.1934.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(3-benzyloxypropyl)-tetrahydro-1*H*-thiophenium tetrafluoroborate (57): Using the general procedure for the preparation of sulfonium ions, compound **21** (70 mg, 0.16 mmol) was reacted with **36** (50 mg, 0.18 mmol) and $AgBF_4$ (35 mg, 0.18 mmol) to give **57** as a colorless oil (52 mg, 48%): $R_f = 0.67$ (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{37}H_{43}O_4S$: 583.2877, found: 583.2881. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(3-hydroxpropyl)-tetra-hydro-1*H*-thiophenium chloride (58): Using the general procedure for the benzyl deprotection, **57** (63 mg, 0.09 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **58** as a 70:30 mixture of stereoisomers as a colorless foam (23 mg, 94%): $R_f = 0.05$ (CH_3OH); ^{1}H

NMR (500 MHz, CD_3OD) δ 4.73 (m, 0.7H), 4.67 (ddd, *J* = 5.1, 5.1, 5.1 Hz, 0.3H), 3.90–3.38 (m, 11H), 3.06–3.04 (m, 0.7H), 2.66 (dddd, *J* = 2.2, 6.1, 8.4, 11.4 Hz, 0.3H), 2.08–2.03 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 78.2, 74.5, 70.2, 69.3, 65.1, 64.7, 64.1, 60.2, 52.0, 49.9, 49.1, 45.6, 43.7, 42.8, 41.8, 39.9, 28.6, 28.3; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_9H_{19}O_4S$: 223.0999, found: 223.0999.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(8-benzyloxyoctyl)-tetrahydro-1*H*-thiophenium tetrafluoroborate (59): Using the general procedure for the preparation of sulfonium ions, **21** (80 mg, 0.18 mmol) was reacted with **37** (75 mg, 0.22 mmol) and $AgBF_4$ (42 mg, 0.22 mmol) to give **59** as a colorless oil (123 mg, 90%): R_f = 0.38 (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{42}H_{53}O_4S$: 653.3659, found: 653.3659. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(8-hydroxyoctyl)-tetrahydro-1*H*-thiophenium chloride (60): Using the general procedure for the benzyl deprotection, **59** (123 mg, 0.17 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst (Cl^- form) to give **60** as a 75:25 mixture of inseparable stereoisomers as a colorless foam (43 mg, 79%): R_f = 0.06 (CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 4.74 (dd, *J* = 2.0, 2.0 Hz, 0.75H), 4.67 (ddd, *J* = 5.6, 5.6, 5.6 Hz, 0.25H), 3.89–3.84 (m, 1H), 3.81–3.74 (m, 1H), 3.65–3.61 (m, 1H), 3.50–3.35 (m, 8H), 3.05 (dddd, *J* = 1.6, 3.1, 5.6, 6.5 Hz, 0.75H), 2.68 (dddd, *J* = 2.4, 5.9, 5.9, 8.5 Hz, 0.25H), 1.87–1.78 (m, 2H), 1.55–1.47 (m, 4H), 1.43–1.35 (m, 6H); ^{13}C NMR (125 MHz, CD_3O) δ 80.0; 77.2, 70.9, 70.0, 66.1, 65.3, 62.9, 53.8, 51.6, 50.3, 48.1, 46.9, 43.8, 42.9, 40.2, 33.7, 30.2, 30.0, 29.9, 29.4, 29.3, 26.8, 26.5; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{14}H_{29}O_4S$: 293.1781, found: 193.1783.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(12-benzyloxy-dodecyl)-tetrahydro-1*H*-thiophenium tetrafluoroborate (61): Using the general procedure for the preparation of sulfonium ions, compound **21** (80 mg, 0.18 mmol) was reacted with **38** (89 mg, 0.22 mmol) and $AgBF_4$ (42 mg, 0.22 mmol) to give **61** as a colorless oil (116 mg, 81%): R_f = 0.38 (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{46}H_{61}O_4S$: 709.4285, found: 709.4288. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(12-hydroxydodecyl)-tetrahydro-1*H*-thiophenium chloride (62): Using the general procedure for the benzyl deprotection, **61** (116 mg, 0.15 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst ($Cl^–$ form) to give **62** as a 60:40 ratio of inseparable stereoisomers as a colorless foam (39 mg, 70%): R_f = 0.06 (CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 4.74 (dd, *J* = 2.0, 2.0 Hz, 0.6H), 4.67 (ddd, *J* = 5.6, 5.6, 5.6 Hz, 0.4H), 3.89–3.84 (m, 1H), 3.82–3.74 (m, 1H), 3.66–3.61 (m, 1H), 3.54–3.34 (m, 8H), 3.05 (dddd, *J* = 1.9, 3.3, 4.7, 6.8 Hz, 0.6H), 2.68 (dddd, *J* = 2.4, 5.0, 5.0, 8.5 Hz, 0.4H), 1.86–1.77 (m, 2H), 1.55–1.45 (m, 4H), 1.40–1.28 (m, 14H); ^{13}C NMR (100 MHz, CD_3OD) δ 80.0; 77.2, 70.9, 70.0, 66.1, 65.3, 63.0, 53.8, 51.6, 50.3, 48.1, 46.9, 43.8, 42.9, 40.2, 33.7, 30.7, 30.6, 30.4, 30.1, 29.5, 29.4, 26.9, 26.8, 26.6; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{18}H_{37}O_4S$: 349.2407, found: 349.2407.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(2-phenethyl)-tetrahydro-1*H*-thiophenium tetrafluoroborate (63): Using the general procedure for the preparation of sulfonium ions, **21** (75 mg, 0.17 mmol) was reacted with **41** (32 mg, 0.18 mmol) and $AgBF_4$ (34 mg, 0.18 mmol) to give **63** as an colorless oil (34 mg, 32%): R_f = 0.70 (CH_2Cl_2–CH_3OH, 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{35}H_{39}O_3S$: 539.2614, found: 539.2615. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(2-phenethyl)-tetrahydro-1*H*-thiophenium chloride (64): Using the general procedure for the benzyl deprotection, **63** (34 mg, 0.054 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst ($Cl^–$ form) to give **64** as a

70:30 mixture of inseparable stereoisomers as a colorless foam (15 mg, 91%): R_f = 0.06 (CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.39–7.27 (m, 5H), 4.71 (dd, *J* = 1.9, 1.9 Hz, 0.7H), 4.65 (ddd, *J* = 5.1, 5.1, 5.2 Hz, 0.3H), 3.84–3.34 (m, 9.6H), 3.18 (dd, *J* = 7.4, 7.4 Hz, 1.4H), 2.97 (m, 0.7H), 2.66 (dddd, *J* = 2.0, 5.2, 5.2, 7.5 Hz, 0.3H); ^{13}C NMR (125 MHz, CD_3OD) δ 138.3; 130.2, 129.8, 128.6, 80.0, 77.5, 70.8, 70.0, 65.9, 65.3, 53.8, 51.6, 50.5, 48.4, 45.4, 43.7, 43.1, 40.4, 32.8, 32.6; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{14}H_{21}O_3S$: 269.1206, found: 269.1202.

(*S*)-1-((3*S*,4*R*)-4-hydroxytetrahydrothiophen-3-yl)ethane-1,2-diol (65): Ammonia (20 mL) was condensed at –78 ºC and a solution of **21** (0.16 g, 0.37 mmol) in THF (6 mL) was added. To this mixture was then added sodium metal (0.5 g, 22 mmol) and CH_3OH (30 μL). The reaction was stirred for 1 h at –78 ºC and then was added CH_3OH (10 mL). The solution was then warmed to rt, neutralized with HOAc and concentrated. The resulting residue was purified by chromatography (CH_2Cl_2–CH_3OH 9:1) to give **65** as a colorless oil (54.0 mg, 90%): R_f = 0.27 (CH_2Cl_2–CH_3OH 9:1); $[\alpha]_D^{20}$ –9.2 (*c* = 1.7, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 4.22 (ddd, *J* = 6.0, 7.7, 7.7 Hz, 1H), 3.72 (ddd, *J* = 5.0, 5.0, 6.7 Hz, 1H), 3.56 (dd, *J* = 5.0, 11.3 Hz, 1H), 3.51 (dd, *J* = 6.7, 11.3 Hz, 1H), 2.94 (dd, *J* = 6.0, 10.5 Hz, 1H), 2.88 (dd, *J* = 8.8, 10.6 Hz, 1H), 2.82 (dd, *J* = 7.6, 10.6 Hz, 1H), 2.68 (dd, *J* = 7.7, 10.5 Hz, 1H), 2.87 (dddd, *J* = 5.0, 7.6, 7.7, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 76.2, 71.6, 66.4, 52.6, 37.3, 27.9; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_6H_{12}O_3SNa$: 187.0399, found: 187.0400.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(4-benzyl)-tetrahydro-1*H*-thiophenium bromide (66): To a solution of **65** (11 mg, 0.07 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (0.5 mL) was added benzyl bromide **39** (14 mg, 0.08 mmol). The mixture was stirred at 50 ºC for 5 h, cooled to rt and then concentrated. The residue was purified by chromatography (CH_2Cl_2–CH_3OH 2:1) on Iatrobeads to give **66** as a colorless oil which is 70:30 mixture of inseparable stereoisomers (12.6 mg, 57%): $R_f = 0.06$ (CH_3OH); ^1H NMR (400 MHz, CD_3OD) δ 7.55–7.46 (m, 5H), 4.79 (dd, *J* = 2.0, 2.0 Hz, 0.7H), 4.77 (s, 1.4H), 4.74 (s, 0.6H), 4.65 (ddd, *J* = 5.7, 5.7, 5.7 Hz, 0.3H), 3.88 (ddd, *J* = 2.3, 5.7, 5.7 Hz, 0.3H,), 3.78 (dd, *J* = 1.9, 12.4 Hz, 0.7H,), 3.72–3.34 (m, 6H), 3.11 (dddd, *J* = 1.9, 3.4, 3.4, 6.8 Hz, 0.7H), 2.70 (dddd, *J* = 2.4, 5.9, 5.9, 8.4 Hz, 0.3H); ^{13}C NMR (100 MHz, CD_3OD) δ 131.6, 131.4, 131.3, 131.1, 131.0, 130.9, 130.8, 130.4, 80.2, 77.2, 70.8, 70.0, 66.1, 65.3, 53.9, 51.7, 50.9, 49.4, 47.8, 47.4, 42.7, 39.4; HRMS-ESI *m/z* $[M–Br]^+$ calcd for $C_{13}H_{19}O_3S$: 255.1049, found: 255.1047.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(4-nitrobenzyl)-tetrahydro-1*H*-thiophenium bromide (67): To a solution of **65** (10 mg, 0.061 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (1 mL) was added 4-nitrobenzyl bromide (**40**, 18 mg, 0.09 mmol). The mixture was stirred at 50 ºC for 18 h, cooled to rt and then concentrated. The resulting residue was purified by chromatography (CH_2Cl_2–CH_3OH 2:1) on Iatrobeads to give **67** as a yellowish oil which is a 70:30 mixture of inseparable stereoisomers (13.5 mg, 58%): $R_f = 0.06$ (CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 8.34–8.32 (m, 2H), 7.82–7.79 (m, 2H), 4.93–4.88 (m, 2H), 4.79 (dd, *J* = 2.0, 2.0 Hz, 0.7H), 4.67 (ddd, *J* = 5.4, 5.4, 5.4 Hz, 0.3H), 3.91–3.87 (m, 1H), 3.79–3.71 (m, 1.4H), 3.67–3.63 (m, 1.3H), 3.60–3.48 (m, 2H), 3.43–3.39 (m, 1.3H), 3.11 (dddd, *J* = 1.6,.3.2, 4.8, 6.5 Hz, 0.7H), 2.74 (dddd, *J* = 2.1, 5.6, 5.6, 7.8 Hz, 0.3H); ^{13}C NMR (125 MHz, CD_3OD) δ 138.3, 137.7, 132.8, 125.6, 80.3, 77.5, 70.8, 70.0, 66.2, 65.3, 54.1, 51.8, 50.1, 49.9, 48.8, 46.2, 43.4, 40.0; HRMS-ESI *m/z* $[M–Br]^+$ calcd for $C_{13}H_{18}NO_5S$: 300.0900, found: 300.0904.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(3-(2’3’-*O*-isopropyli-dene-3-(benzyloxymethyl)uridin-5-yl)propyl)-3-(benzyloxy)-tetrahydro-1*H*-thiophenium tetrafluoroborate (68): Using the general procedure for the preparation of sulfonium ions, **21** (80 mg, 0.18 mmol) was reacted with **42** (105 mg, 0.18 mmol) and $AgBF_4$ (35 mg, 0.18 mmol) to afford the product **68** as a colorless oil (53 mg, 30%): $R_f = 0.45$ (CH_3OH–CH_2Cl_2, 9:1);

HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{50}H_{59}N_2O_{10}S$: 879.3885, found: 879.3883. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(3-(uridin-5-yl-)propyl))-tetrahydro-1*H*-thiophenium chloride (69): Using the general procedure for benzyl deprotection, **68** (53 mg, 0.05 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst ($Cl^–$ form) to give **69** as a 80:20 inseparable mixture of stereoisomers as a colorless foam (14 mg, 55%): $R_f = 0.05$ (CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.87 (d, *J* = 8.1 Hz, 0.8H) 7.76 (d, *J* = 8.1 Hz, 0.2H), 5.83 (d, *J* = 4.1 Hz, 0.8H), 5.82 (d, *J* = 4.1 Hz, 0.2H), 5.76 (d, *J* = 8.1 Hz, 0.8H), 5.74 (d, *J* = 8.1 Hz, 0.2H), 4.73 (dd, *J* = 1.8, 2.0 Hz, 0.8H), 4.66 (dd, *J* = 5.4, 5.4 Hz, 0.2H), 4.20–4.07 (m, 3H), 3.91–3.37 (m, 13H), 3.03 (m, 0.8H), 2.58 (dddd, *J* = 2.4, 5.6, 5.6, 11.1 Hz, 0.2H), 2.20–2.13 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 166.1, 152.3, 142.5, 102.9, 91.5, 84.3, 80.0, 75.3, 71.6, 71.3, 70.9, 70.3, 70.0, 66.1, 65.3, 53.8, 51.6, 50.9, 50.4, 45.2, 43.5, 42.3, 40.8, 27.3, 27.1; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{18}H_{29}N_2O_9S$: 449.1588, found:449.1588.

(3*R*,4*S*)-3-(benzyloxy)-4-((*S*)-1,2-bis(benzyloxy)ethyl)-1-(3-(2'3'-*O*-isopropyli-dene-3-(benzyloxymethyl)uridin-5-yl)butyl)-3-(benzyloxy)-tetrahydro-1*H*-thiophenium tetrafluoroborate (70): Using the general procedure for the preparation of sulfonium ions, **21** (70 mg, 0.16 mmol) was reacted with **43** (95 mg, 0.16 mmol) and $AgBF_4$ (32 mg, 0.16 mmol to give the **70** as a colorless oil (62 mg, 39%): $R_f = 0.45$ ($CH_3OH–CH_2Cl_2$ 9:1); HRMS-ESI *m/z* $[M–BF_4]^+$ calcd for $C_{51}H_{61}N_2O_{10}S$: 893.4041, found: 893.4042. The compound used in the next step without further characterization.

(3*R*,4*S*)-3-((*S*)-1,2-dihydroxyethyl)-4-hydroxy-1-(3-(uridin-5-yl-)butyl))-tetrahydro-1*H*-thiophenium chloride (71): Using the general procedure for the benzyl deprotection, **70** (51 mg, 0.05 mmol) was treated with BCl_3 (1 M in CH_2Cl_2) and then Amberlyst ($Cl^–$ form) to give **71** as a colorless foam as 88:12 ratio of isomers (14 mg, 54%): $R_f = 0.05$ (CH_3OH); ^{1}H

NMR (300 MHz, CD_3OD) δ 7.90 (d, 1H, *J* = 8.1 Hz), 5.86 (d, *J* = 3.6 Hz, 1H), 5.70 (d, *J* = 8.1 Hz, 1H), 4.73 (dd, *J* = 2.0, 2.3 Hz, 1H), 4.17–4.07 (m, 3H, 3.88 (dd, *J* = 1.8, 12.3 Hz, 1H), 3.80–3.73 (m, 2H), 3.66–3.35 (m, 10H), 3.05 (m, 1H), 1.97–1.86 (m, 2H), 1.83–1.75 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 166.2, 152.3, 142.5, 102.6, 91.2, 84.6, 80.1, 75.7, 71.4, 71.3, 71.1, 70.9, 65.3, 53.9, 50.4, 46.7, 42.9, 29.3, 24.0; HRMS-ESI *m/z* $[M–Cl]^+$ calcd for $C_{19}H_{31}N_2O_9S$: 463.1745, found: 463.1742.

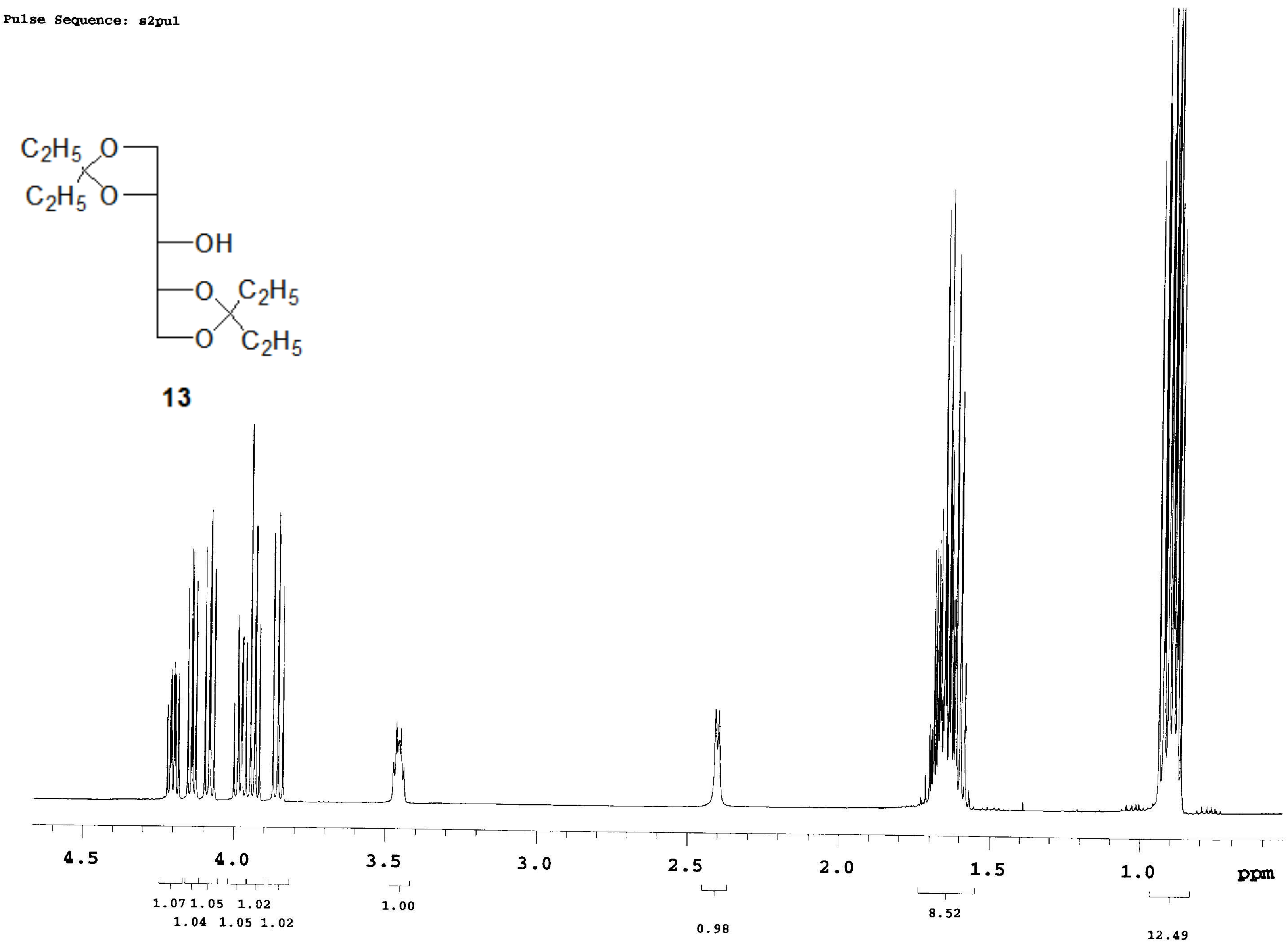
References

S1 S. Mohan, L. Sim, D. R. Rose and B. M. Pinto, *Carbohydr. Res.*, 2007, **342**, 901–912.

S2 R. Wang, D. H. Steensma, Y. Takaoka, J. W. Yun, T. Kajimoto and C. H. Wong, *Bioorg. Med. Chem.*, 1997, **5**, 661–672.

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

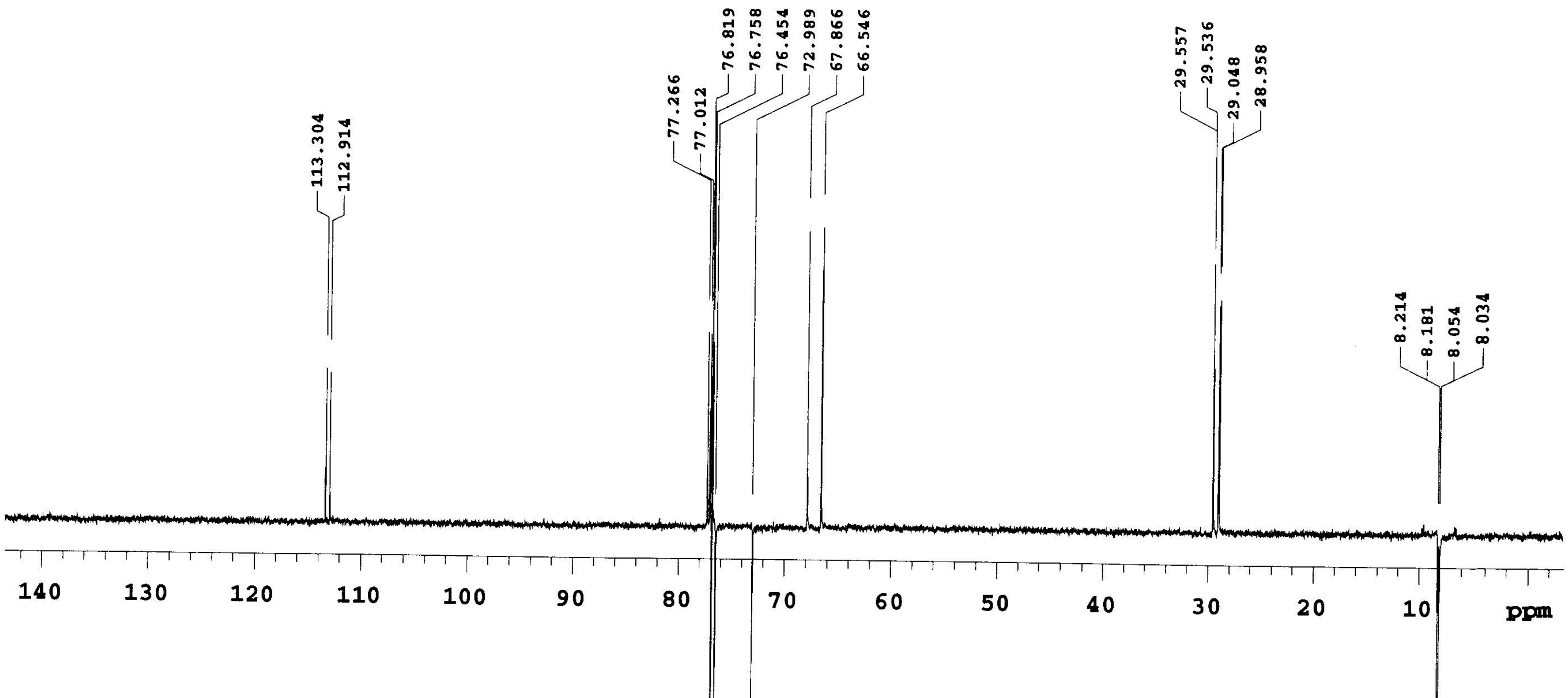
Pulse Sequence: s2pul

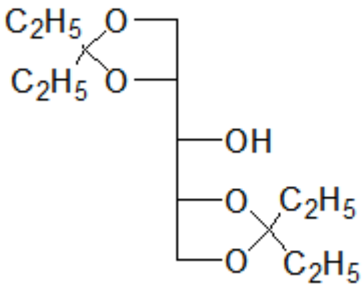


13

125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

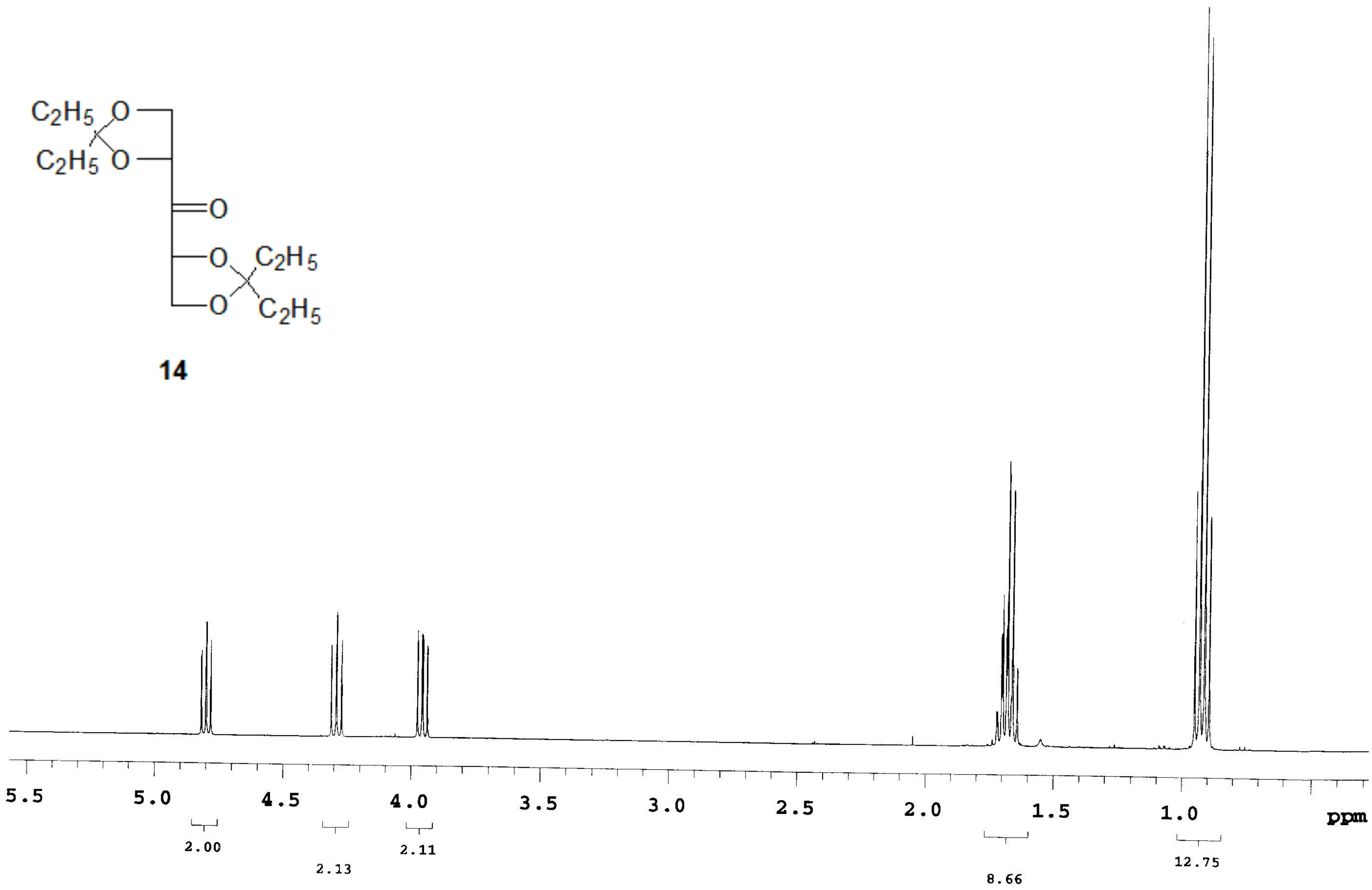




13

400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

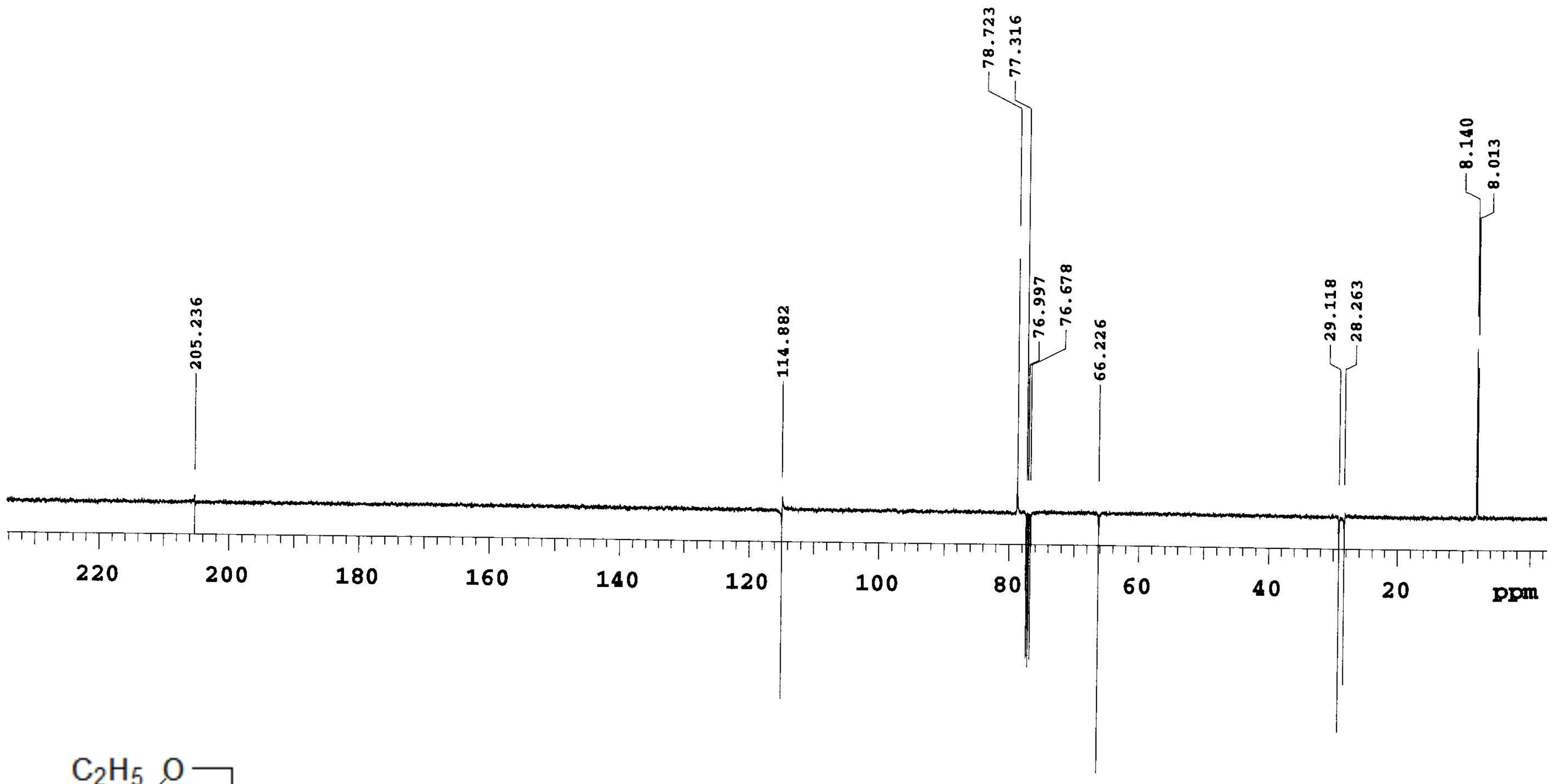
Pulse Sequence: s2pul

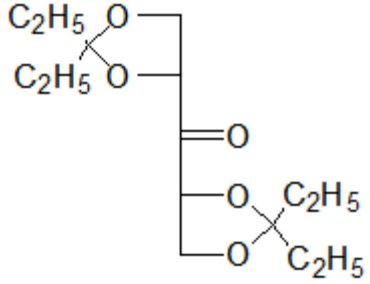


14

100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

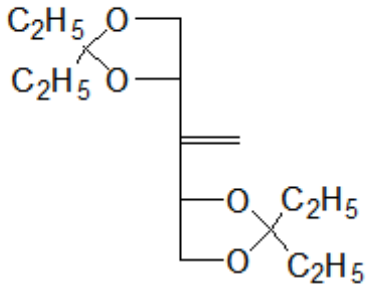




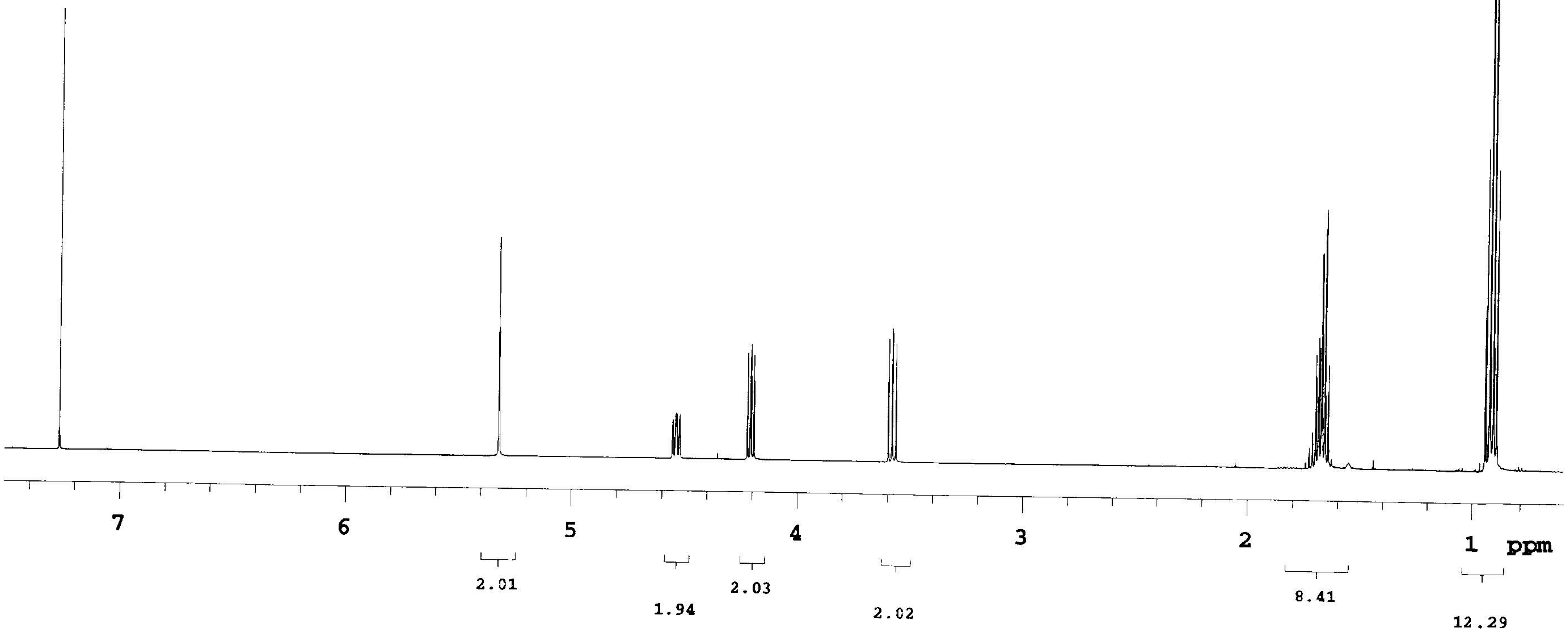
14

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

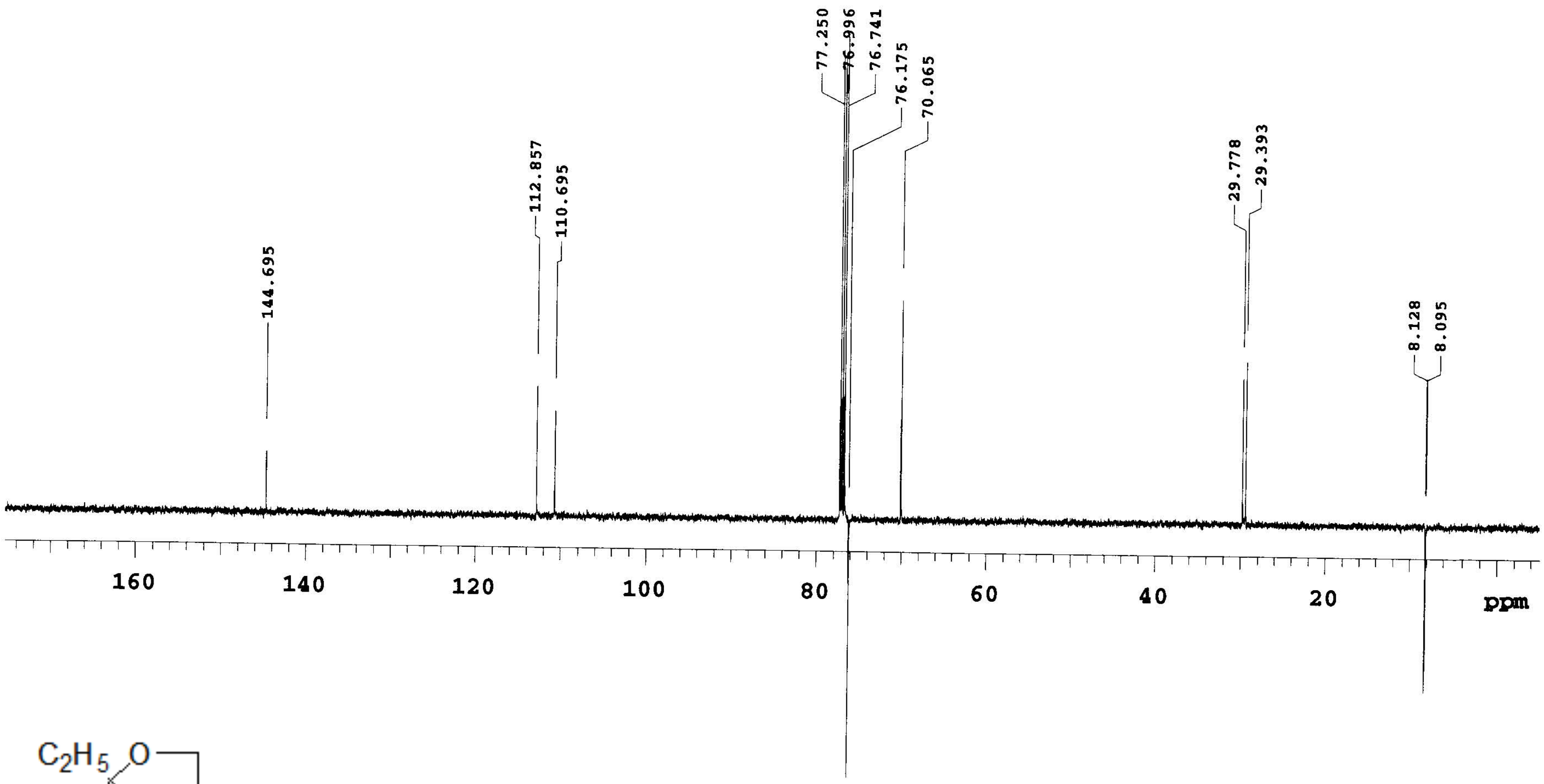


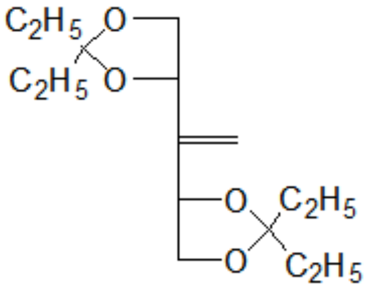
15



125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

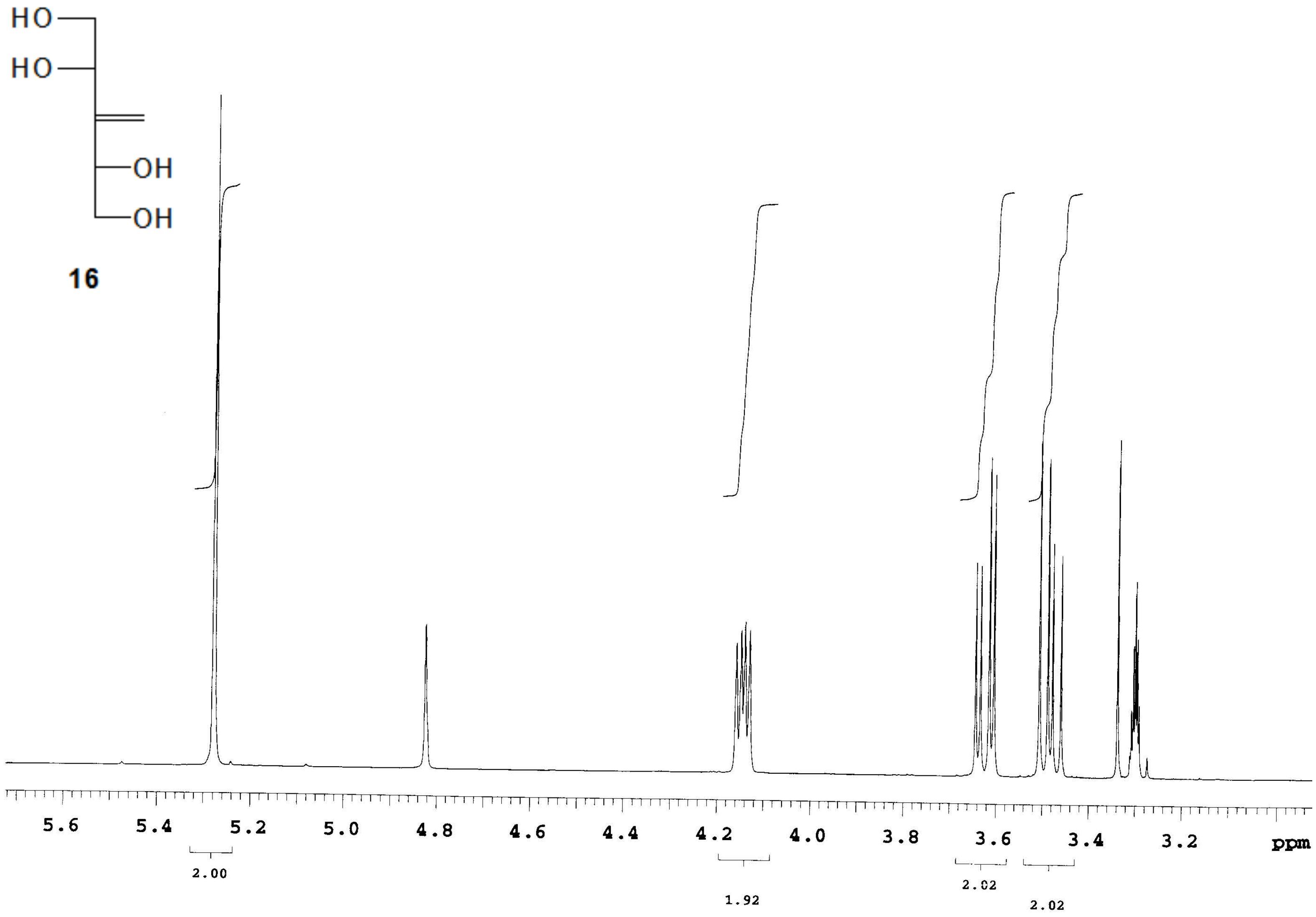




15

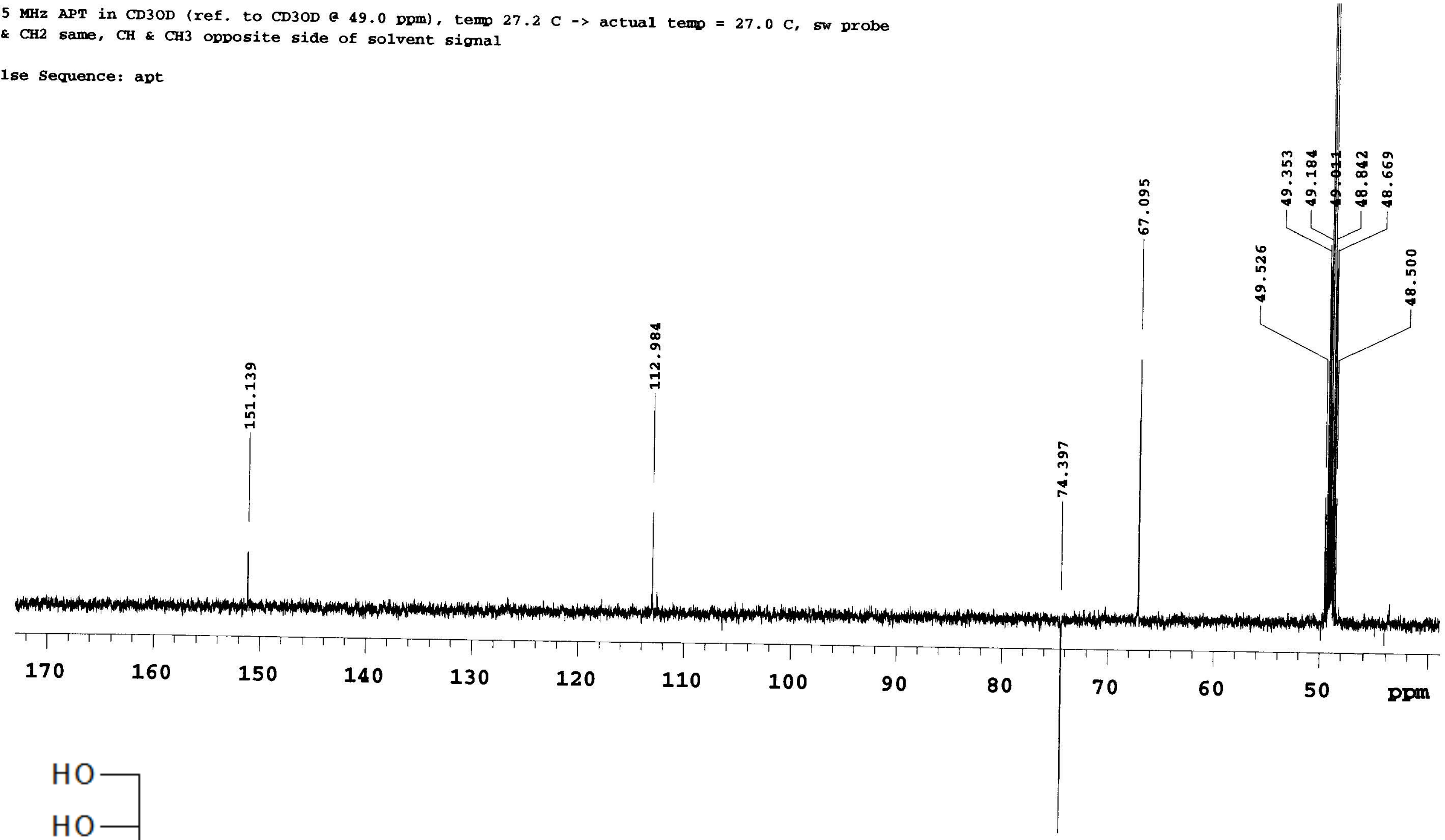
400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

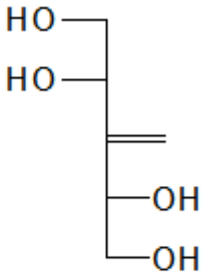
Pulse Sequence: s2pul


16

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

Pulse Sequence: apt

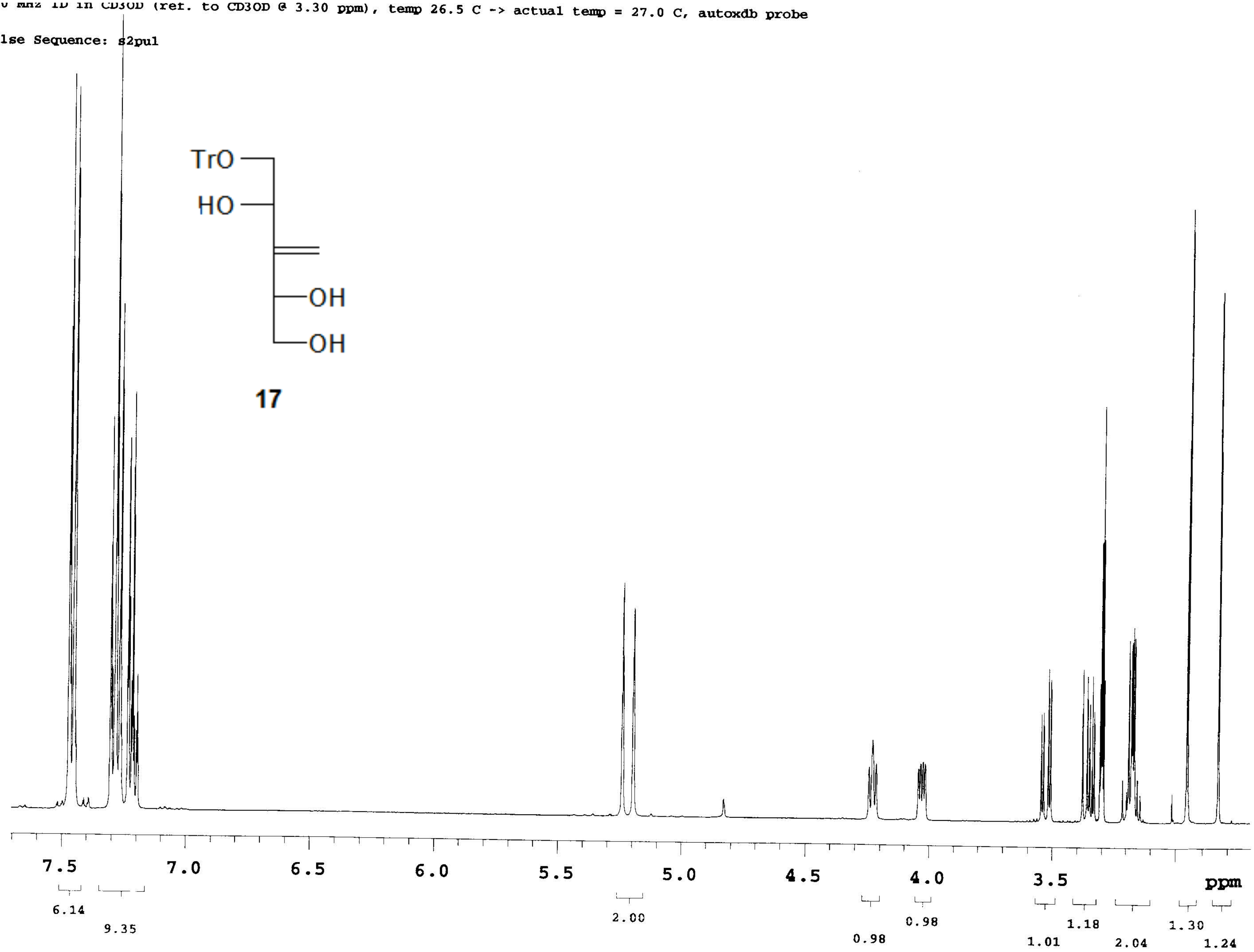




16

400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

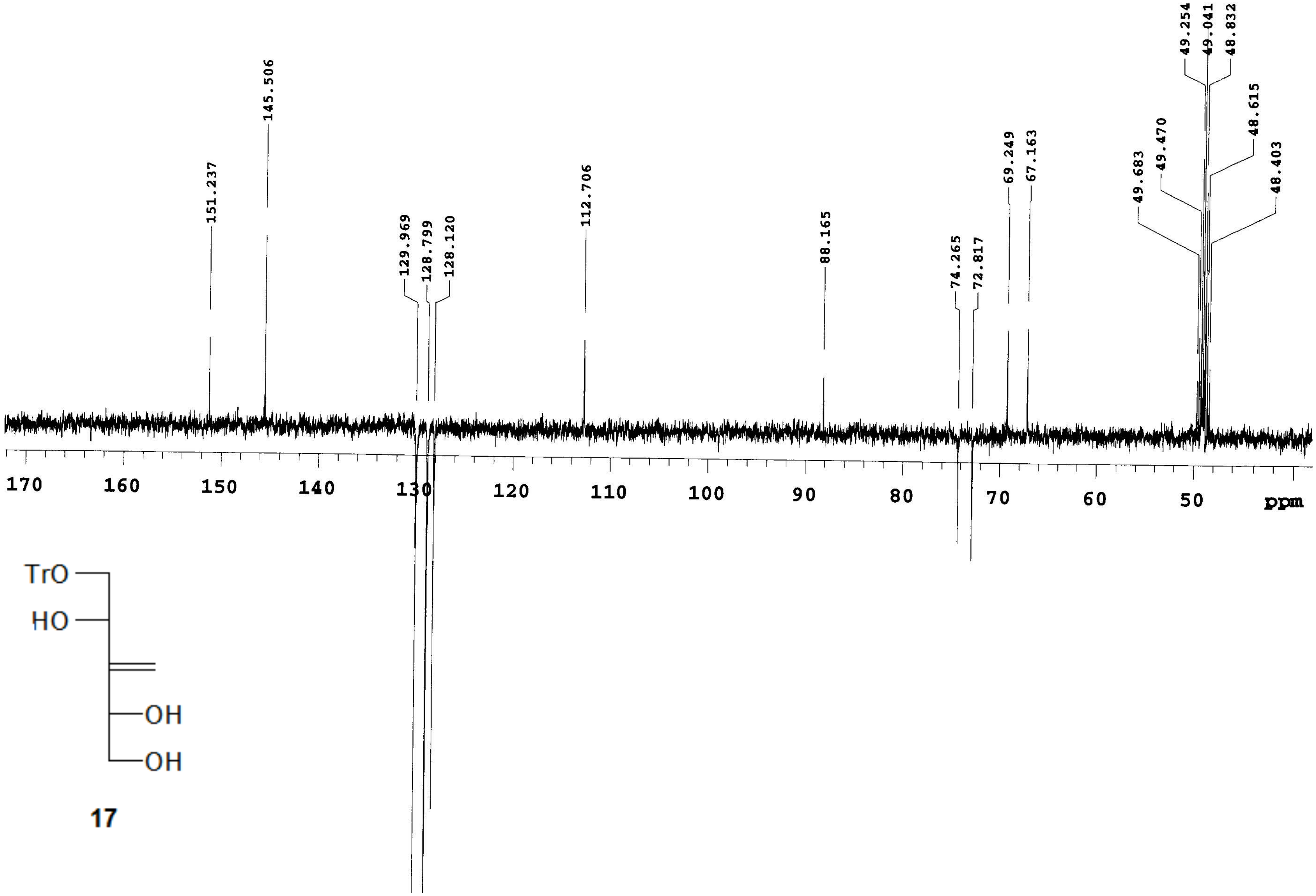
Pulse Sequence: s2pul



17

100 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

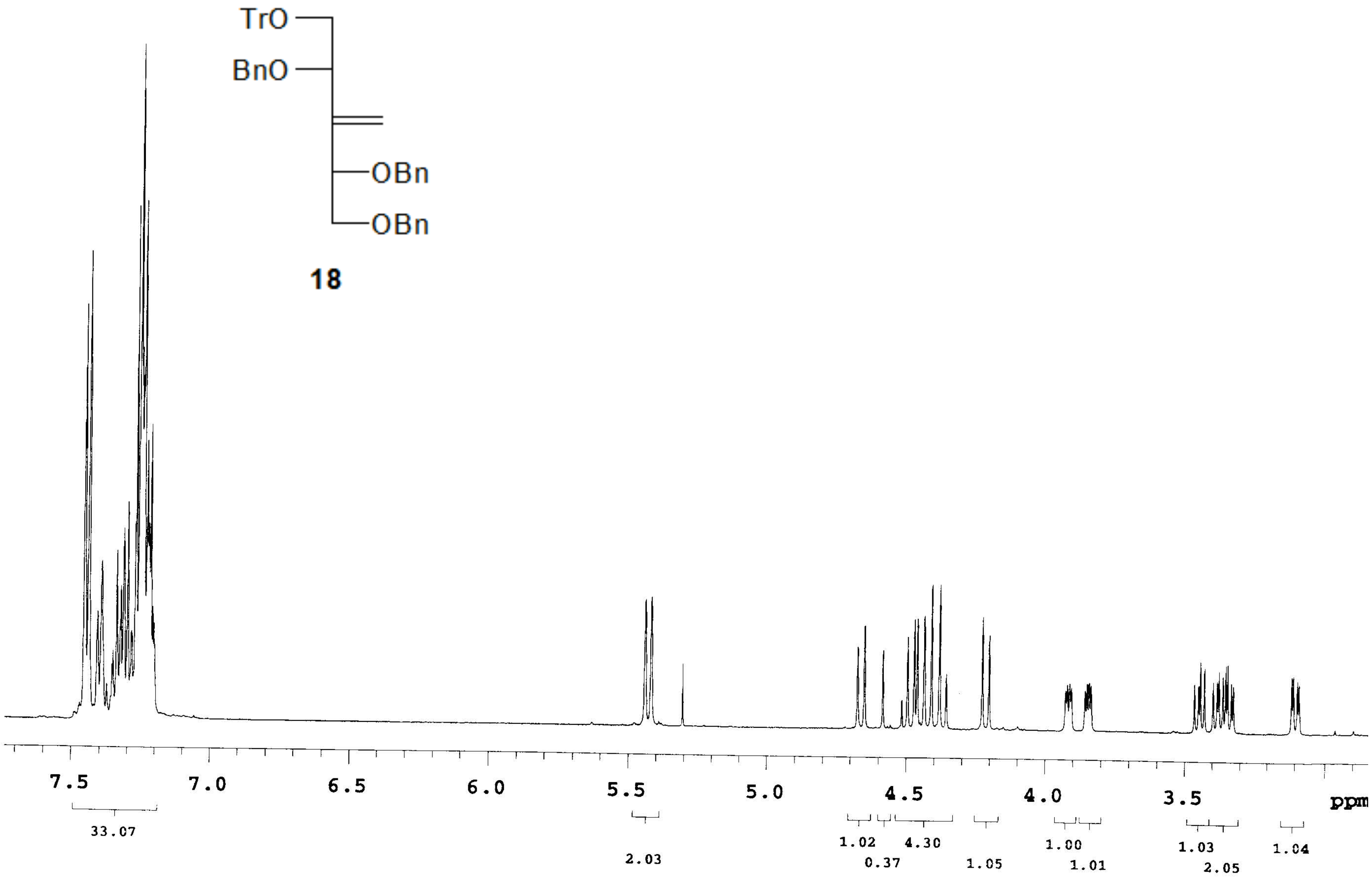
Pulse Sequence: apt



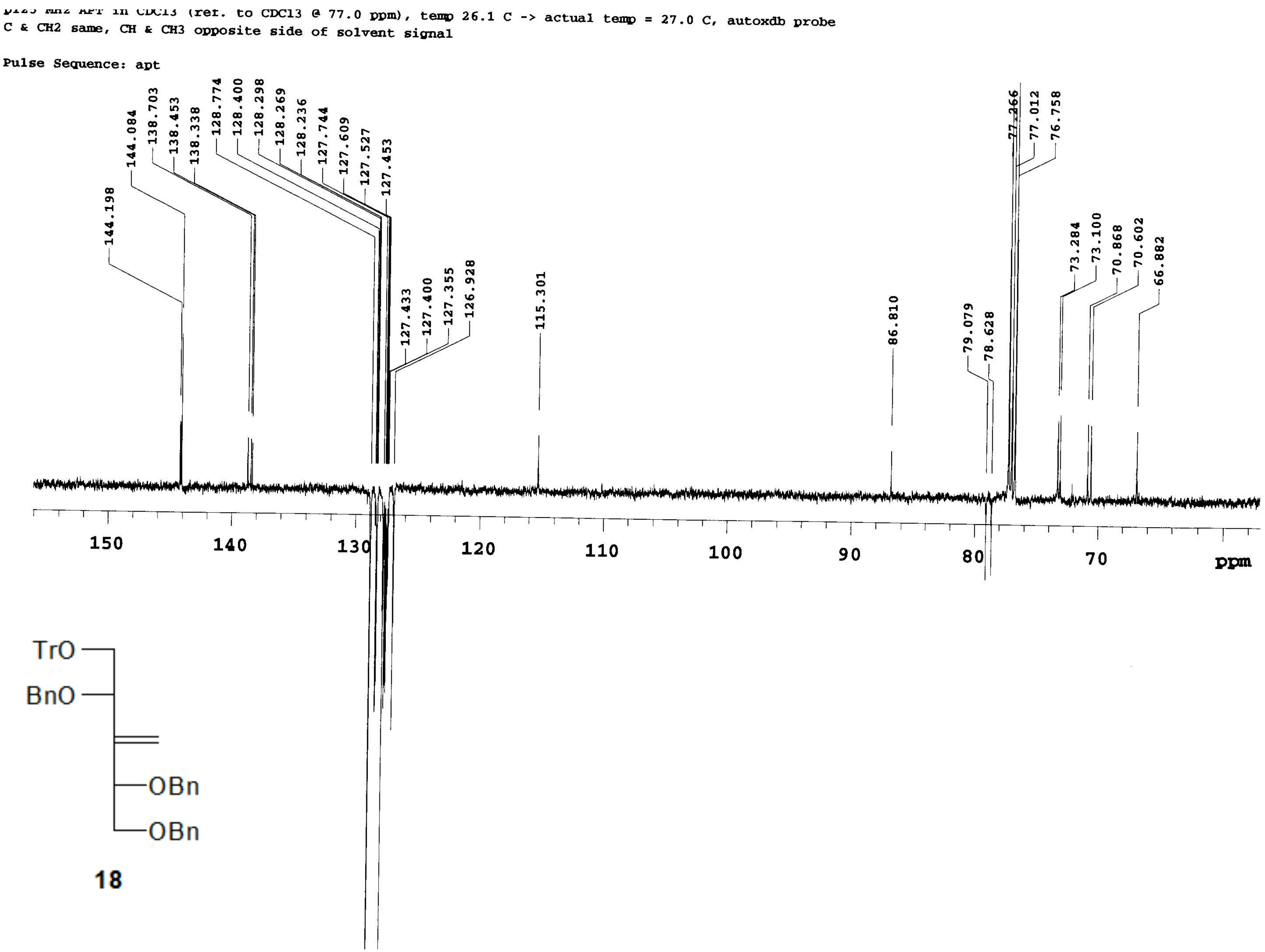
17

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul



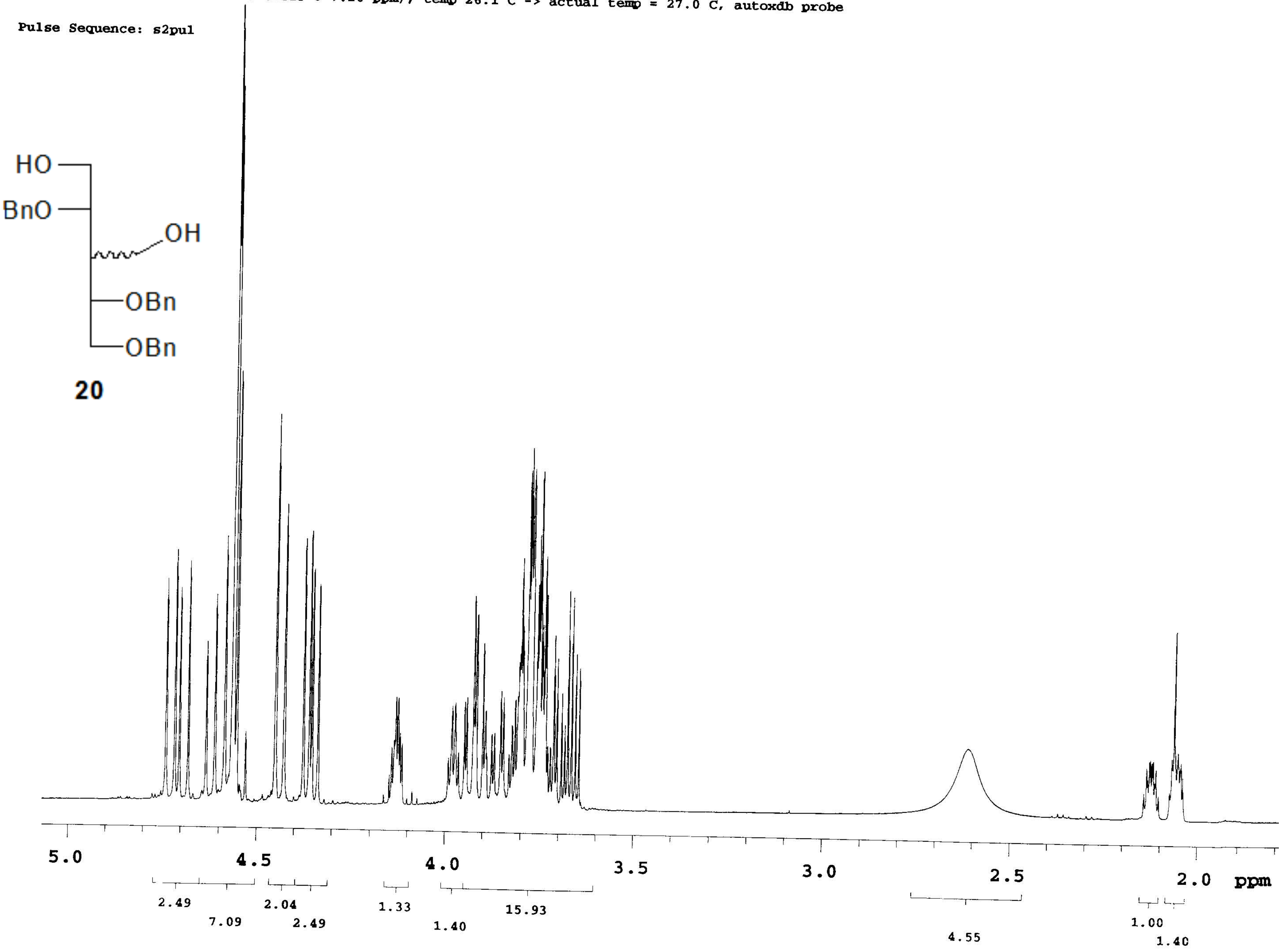
18


125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
144.198
144.084
138.703
138.453
138.338
128.774
128.400
128.298
128.269
128.236
127.744
127.609
127.527
127.453
127.433
127.400
127.355
126.928
115.301
86.810
79.079
78.628
77.266
77.012
76.758
73.284
73.100
70.868
70.602
66.882
150
140
130
120
110
100
90
80
70
ppm
TrO
BnO
OBn
OBn

18

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

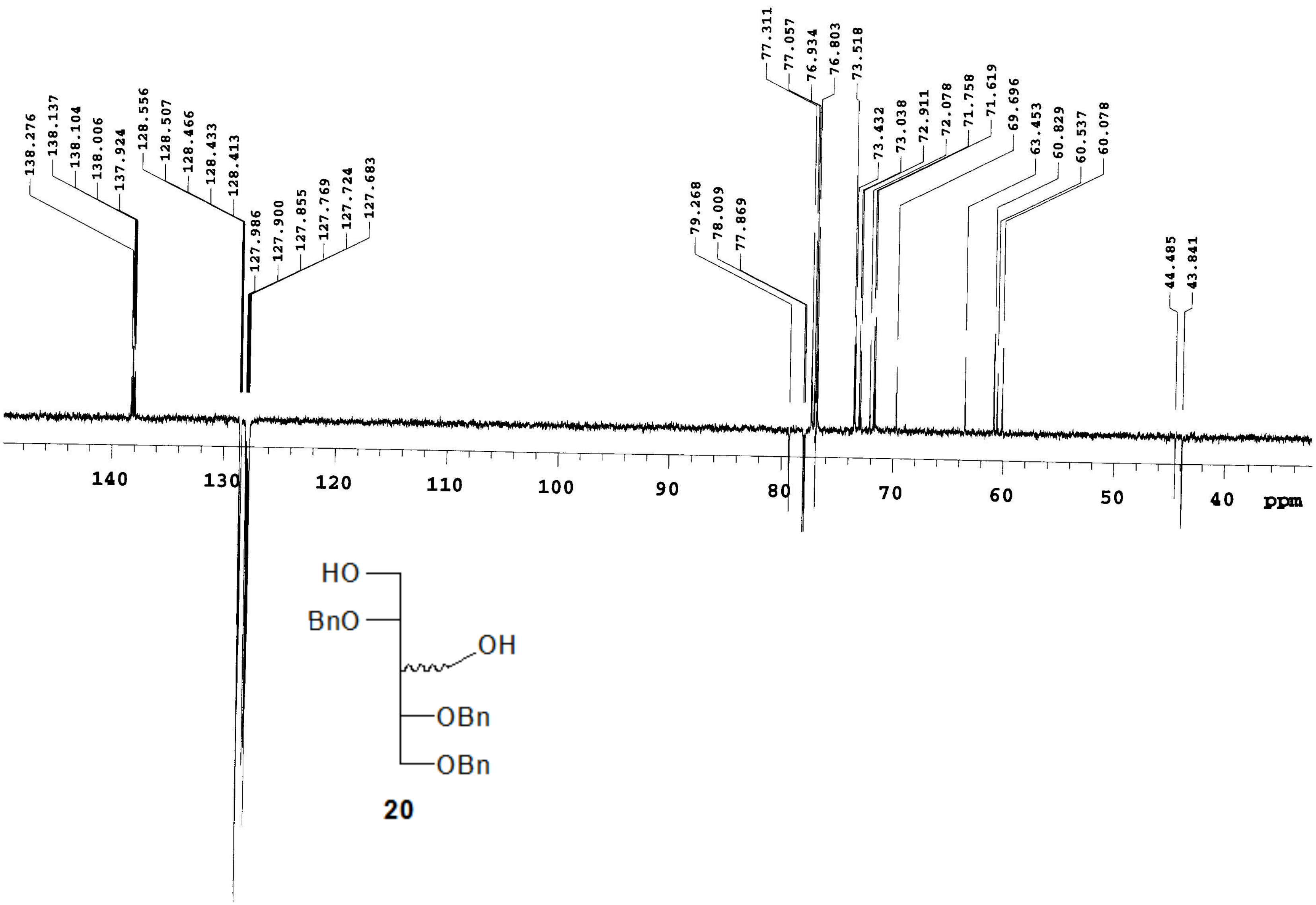
Pulse Sequence: s2pul



20

125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

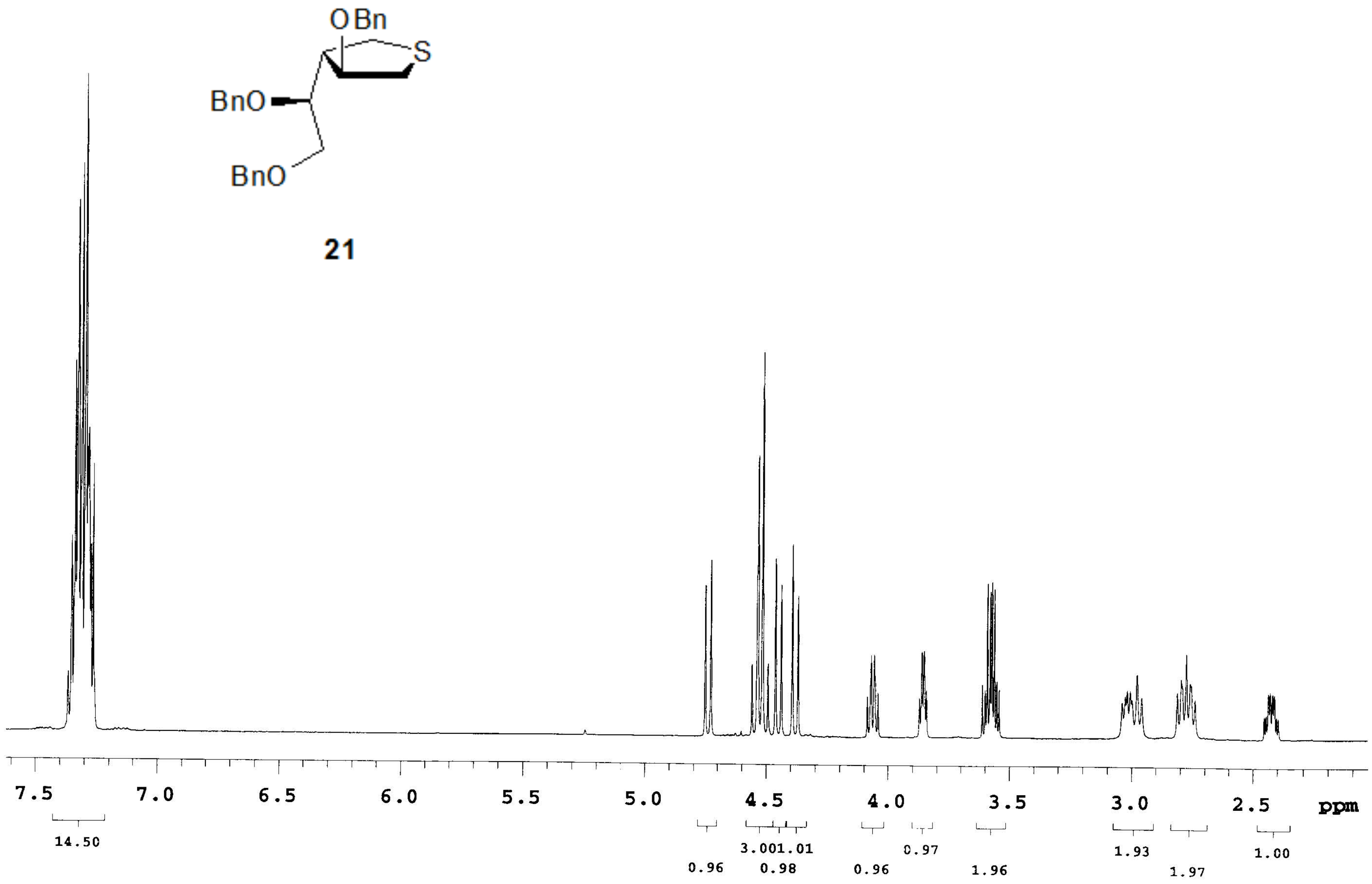
Pulse Sequence: apt



20

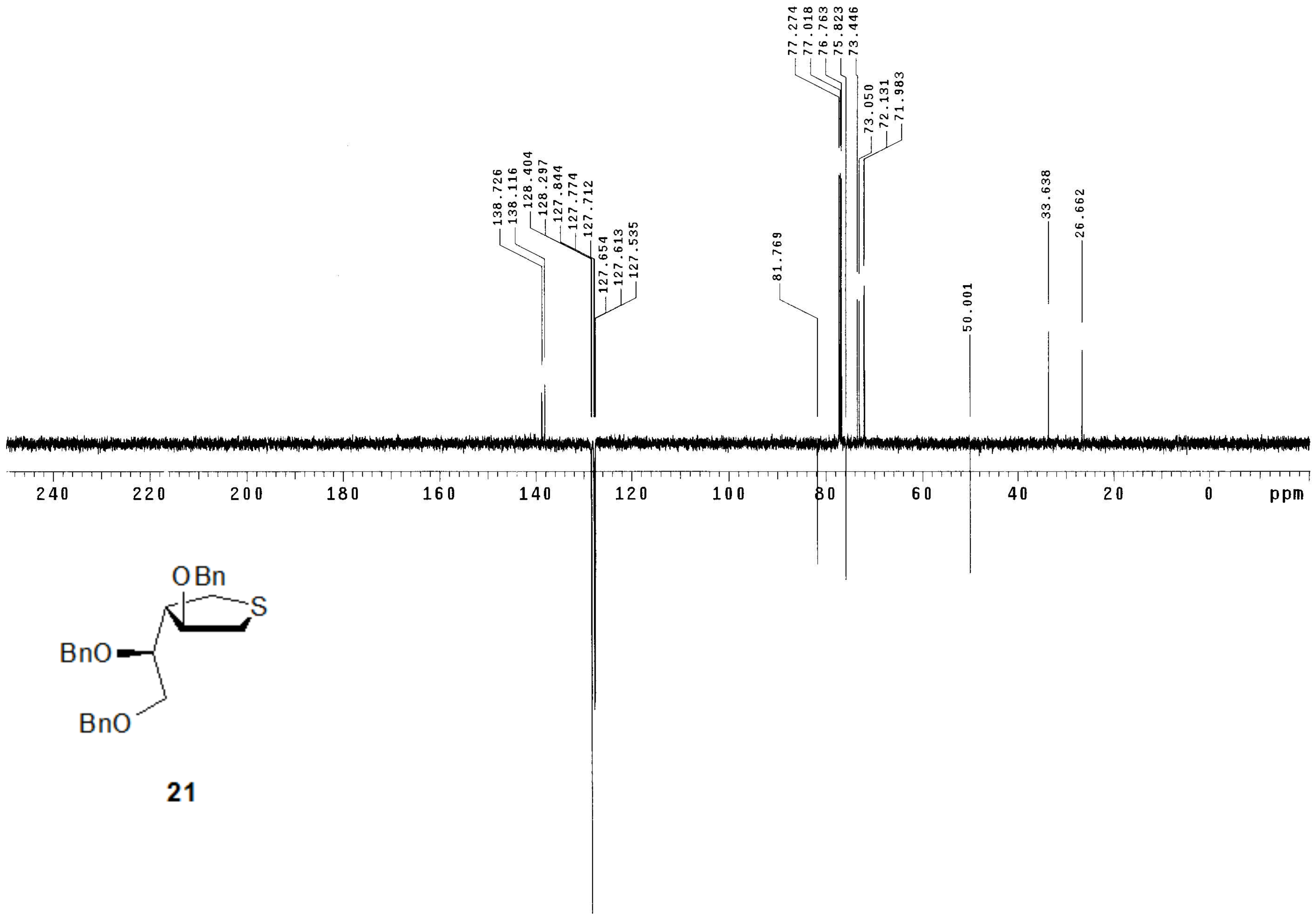
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

Pulse Sequence: s2pul



21

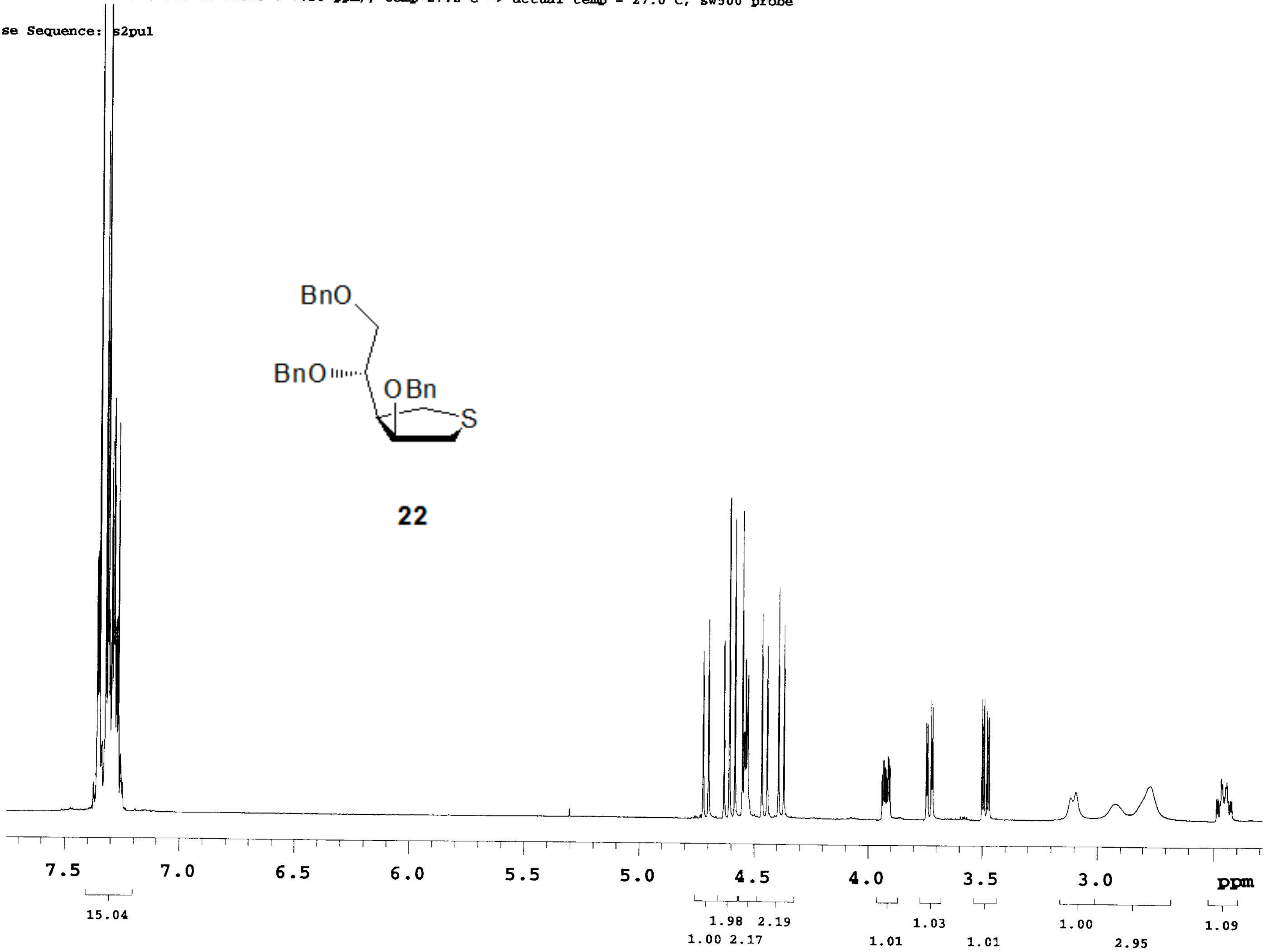
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal



21

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

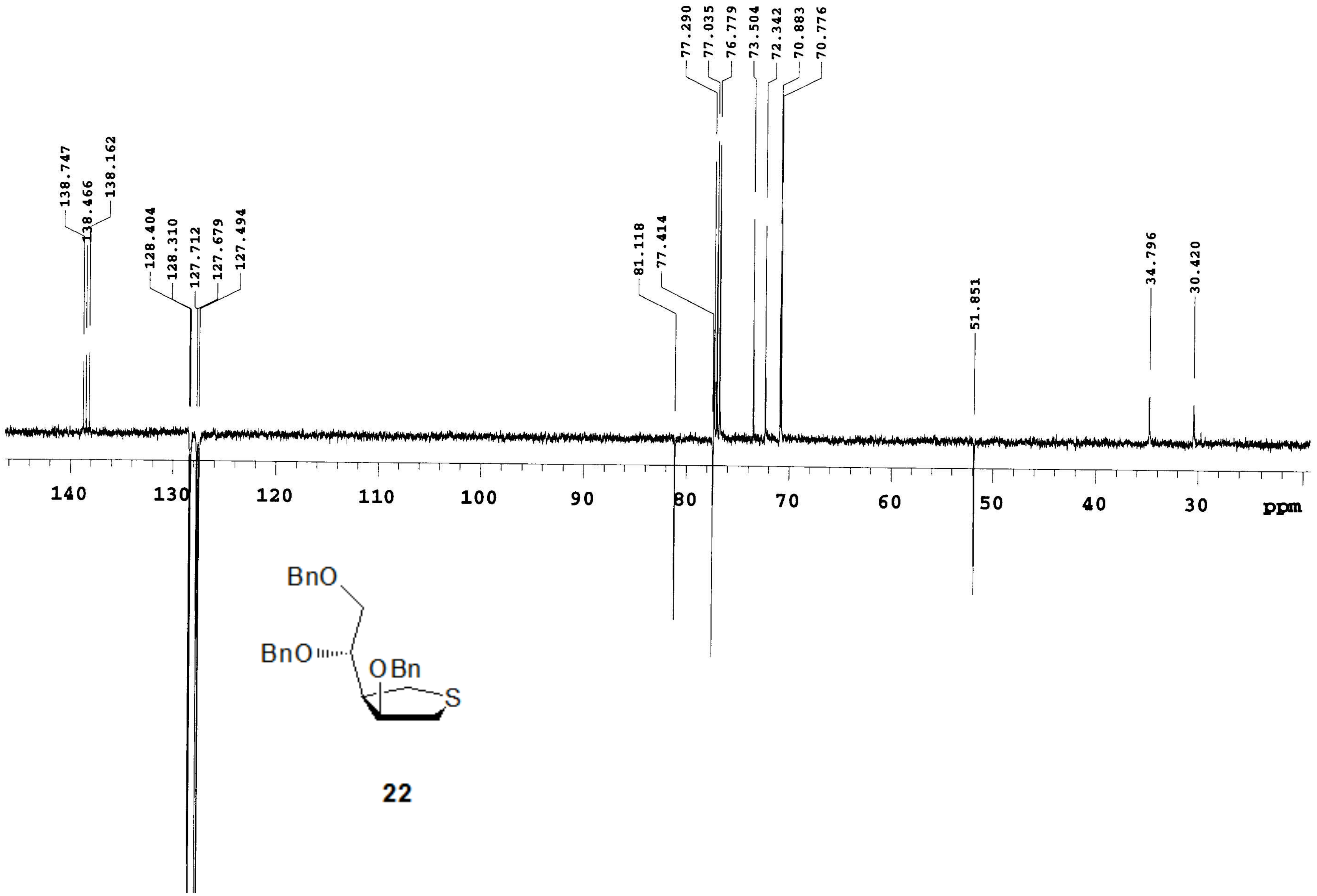
Pulse Sequence: s2pul



22

125 MHz APT in CDC13 (ref. to CDC13 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal

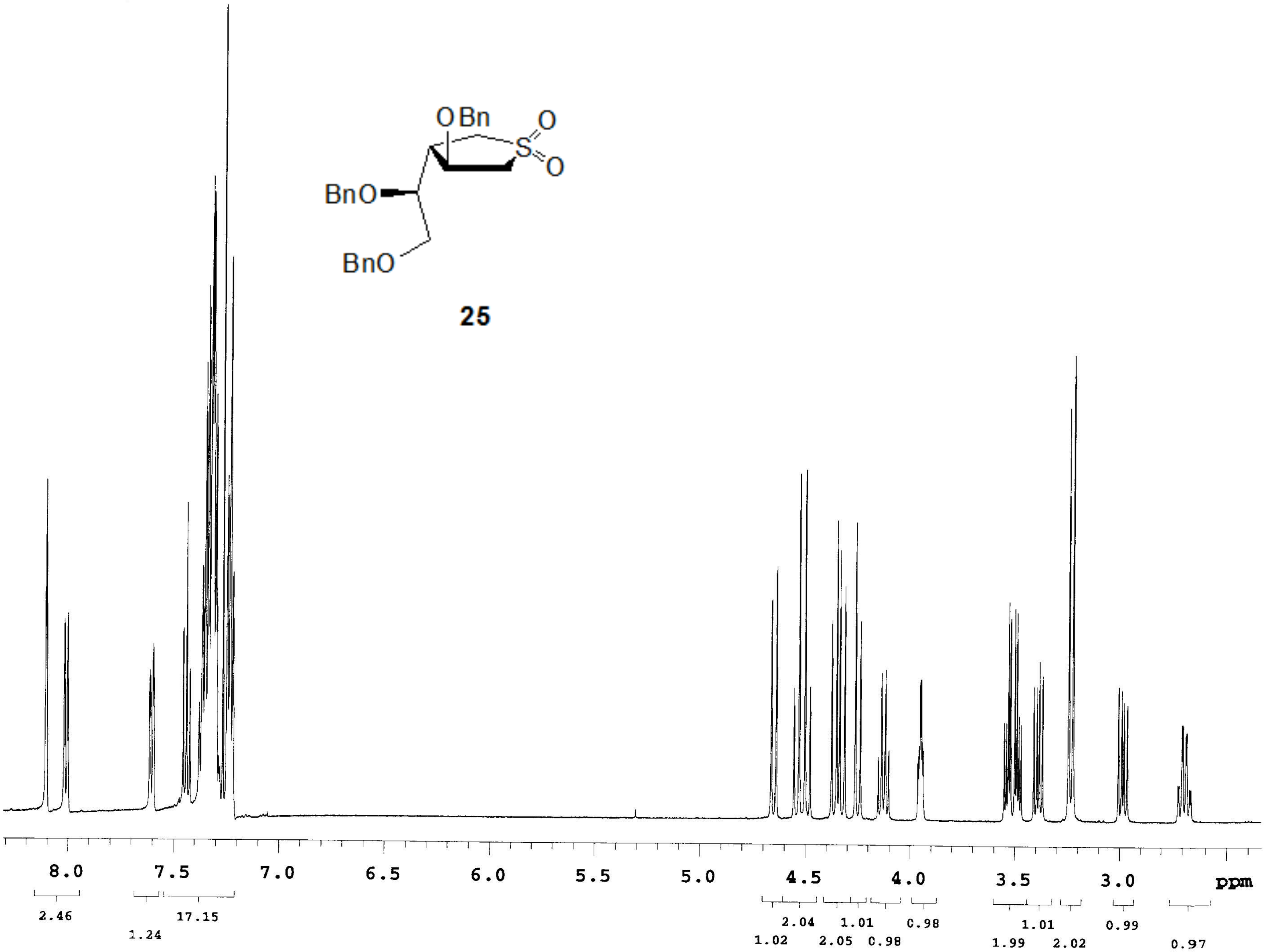
Pulse Sequence: apt



22

500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, sw500u probe

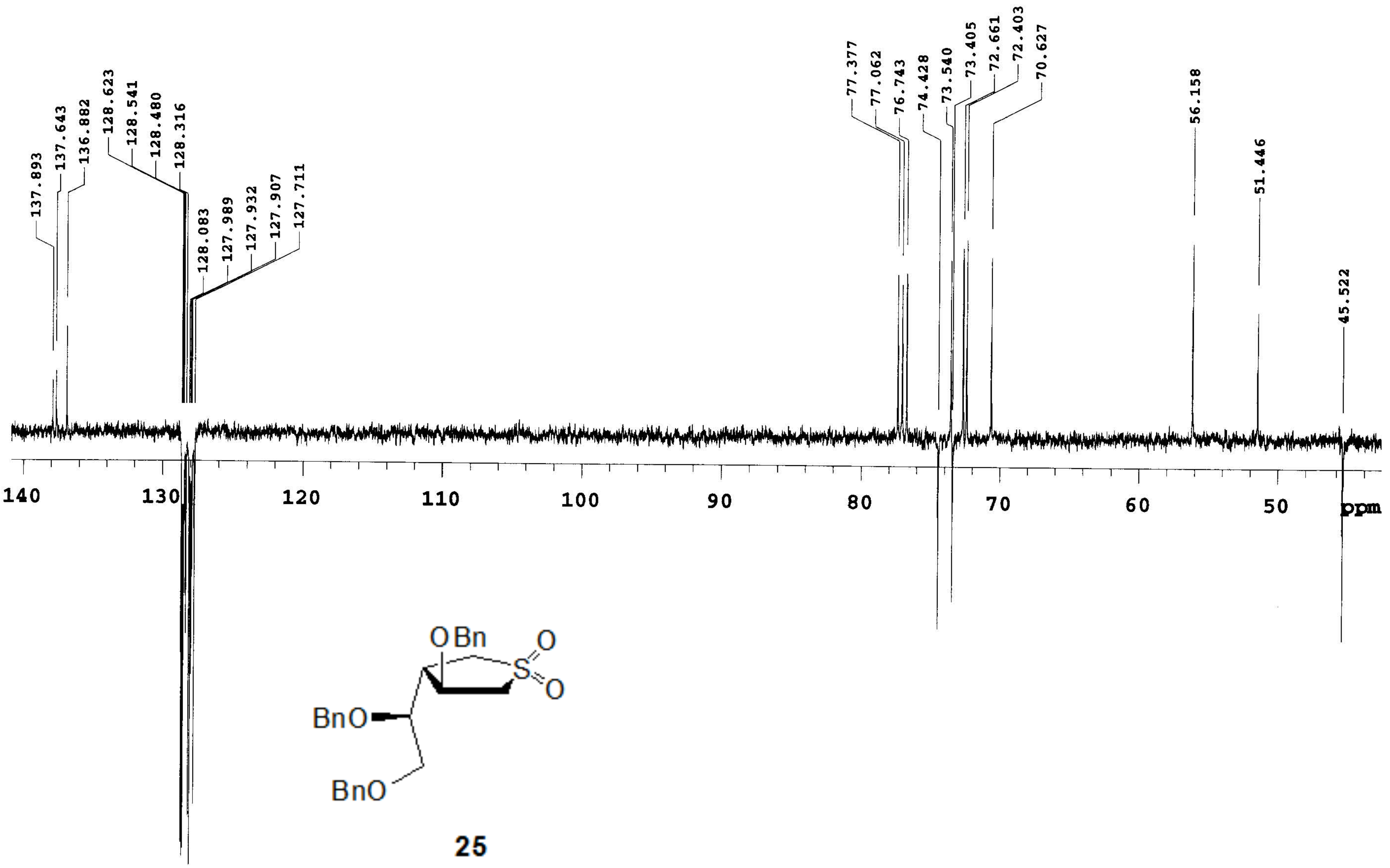
Pulse Sequence: s2pul



25

100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

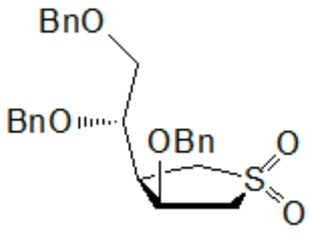
Pulse Sequence: apt



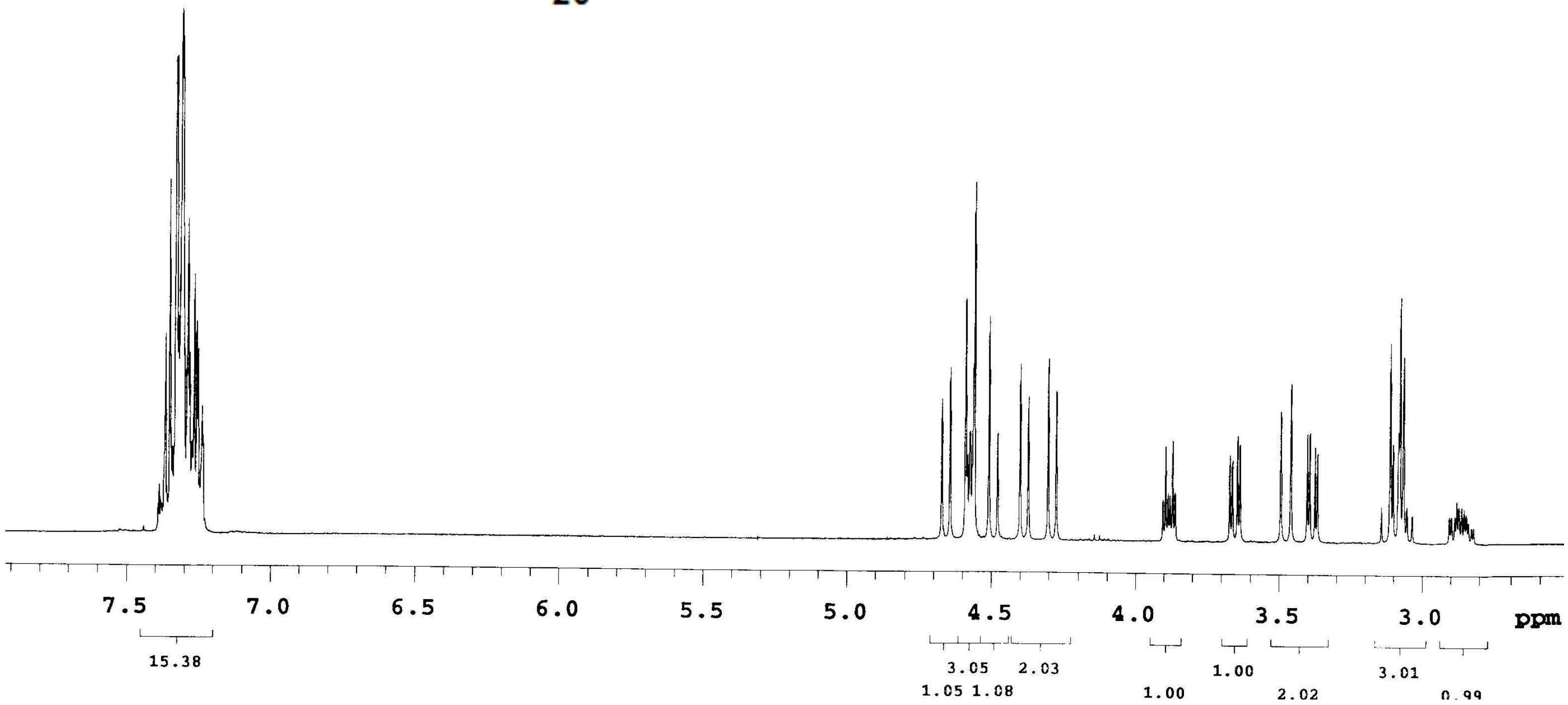
25

400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

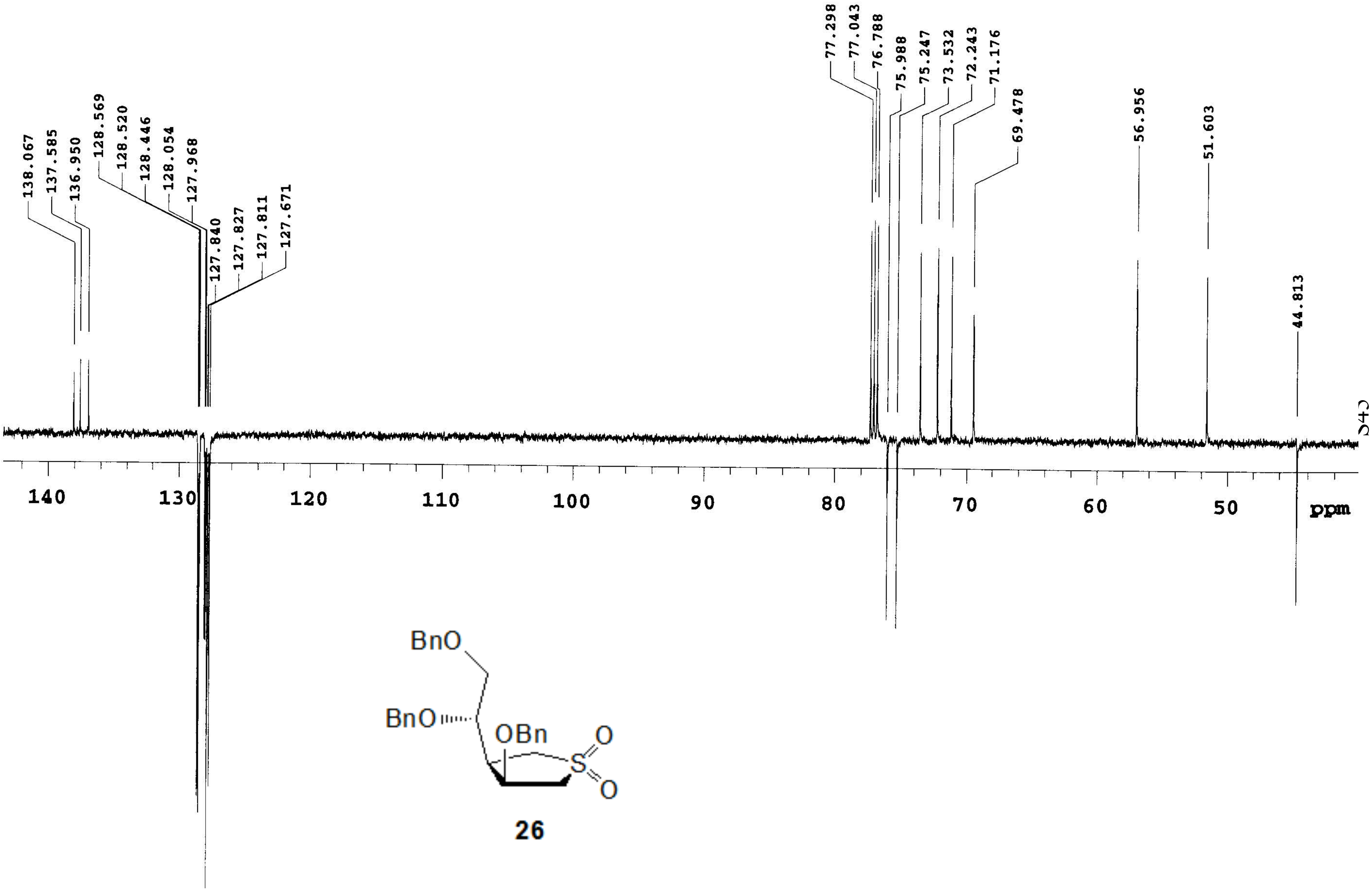


26



125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal

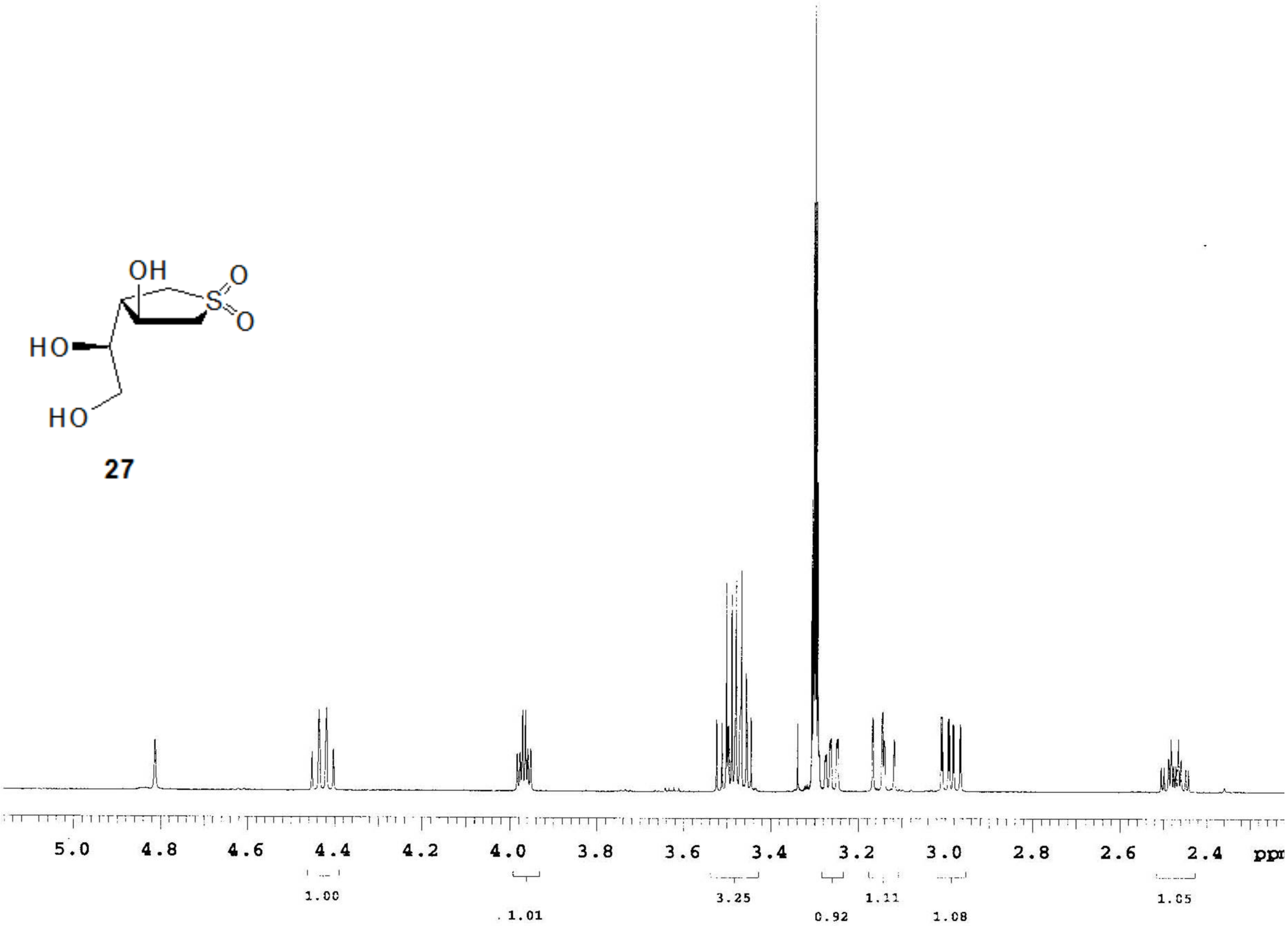
Pulse Sequence: apt



26

498.124 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe

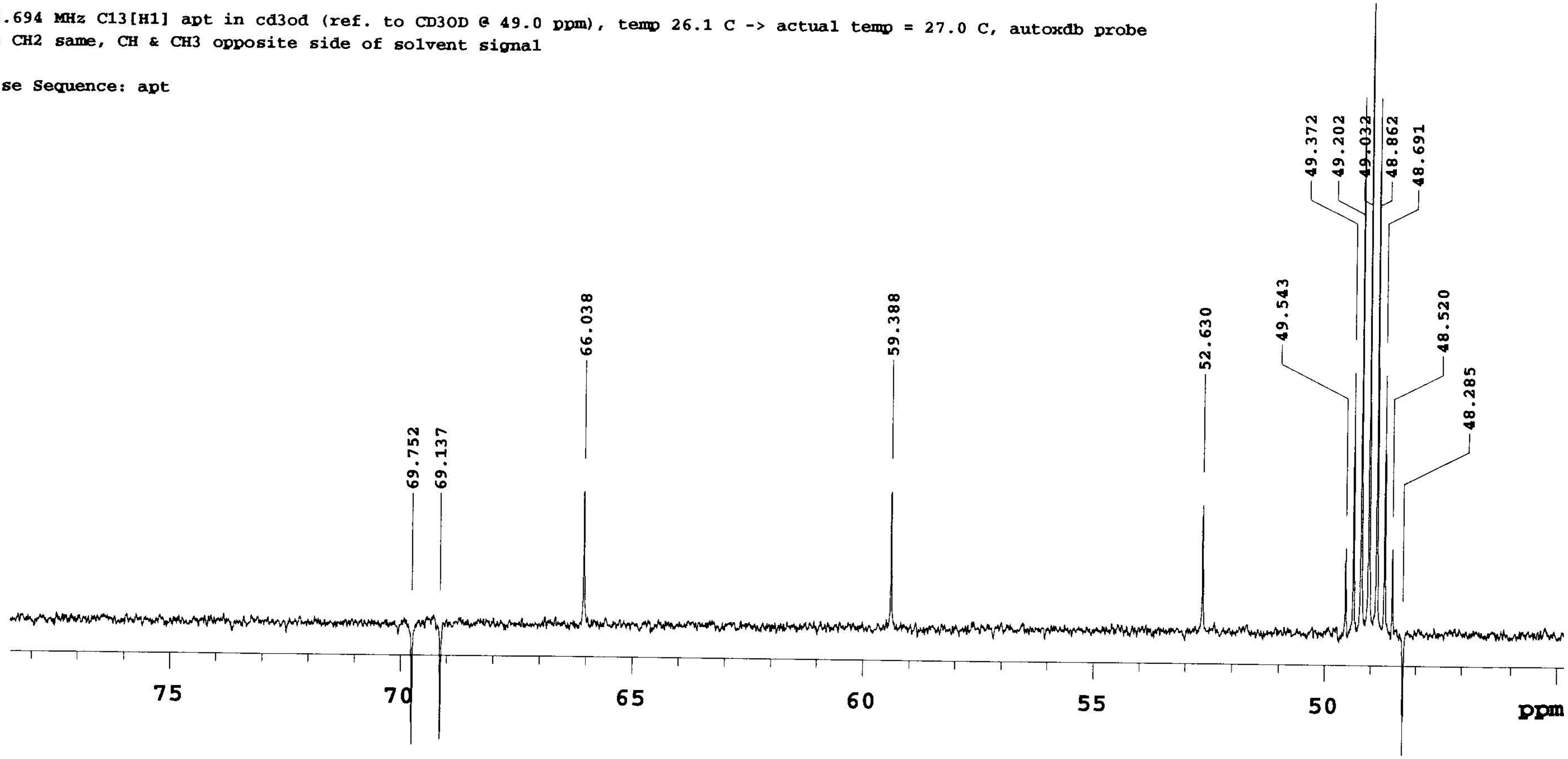
Pulse Sequence: s2pul

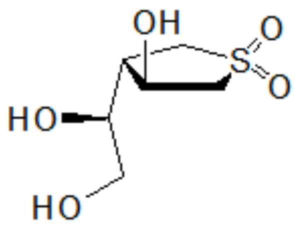


27

125.694 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

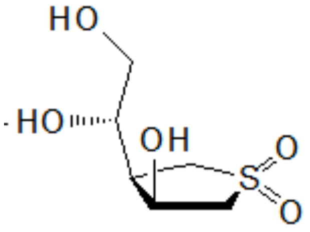




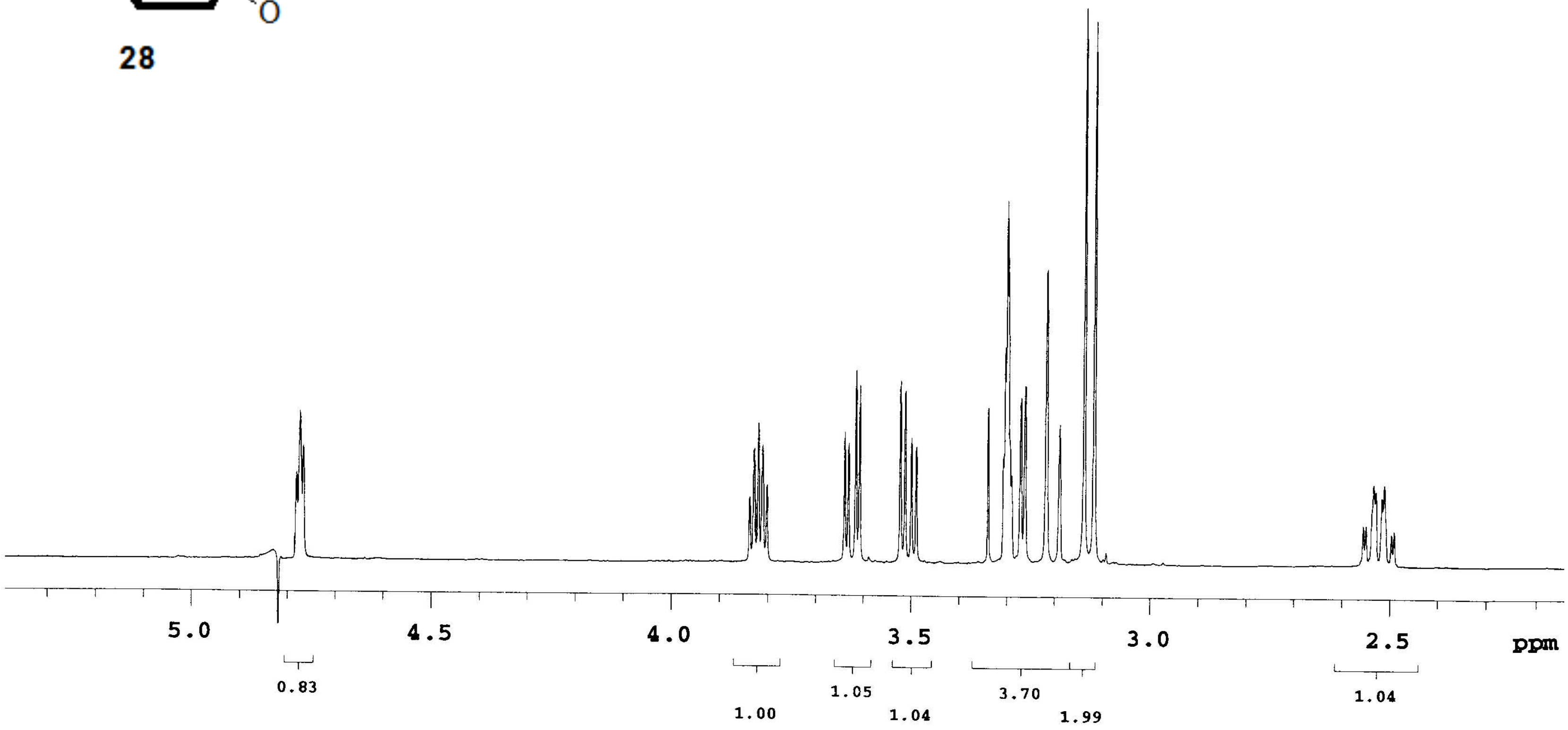
27

500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

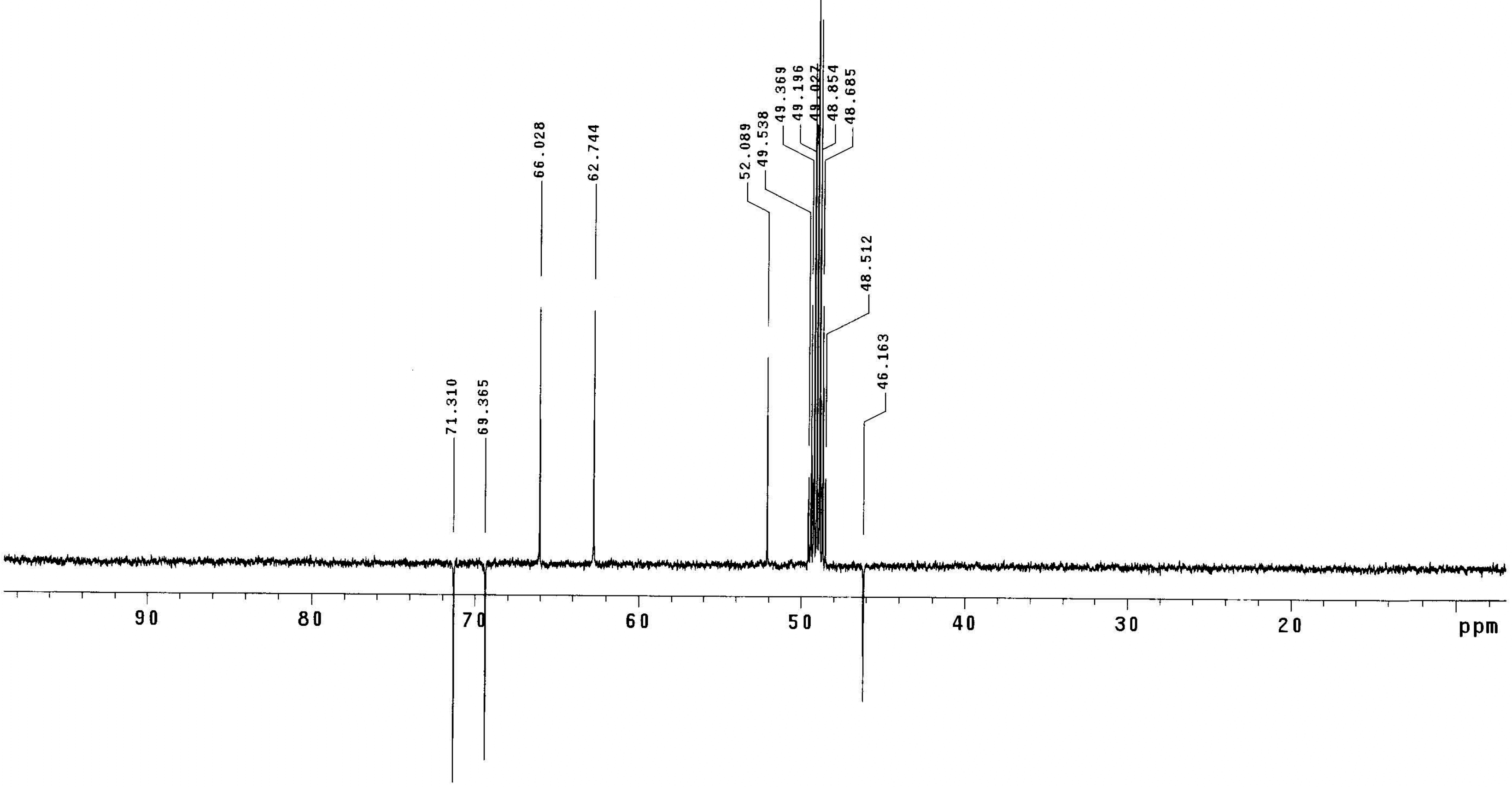
Pulse Sequence: s2pul

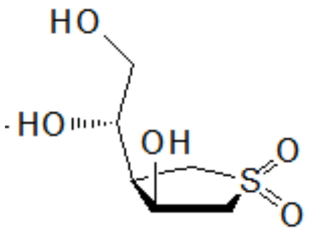


28



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

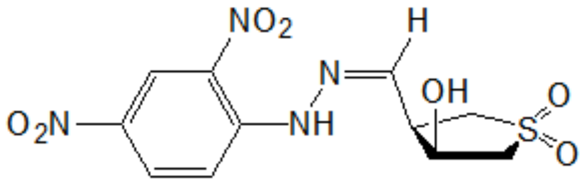




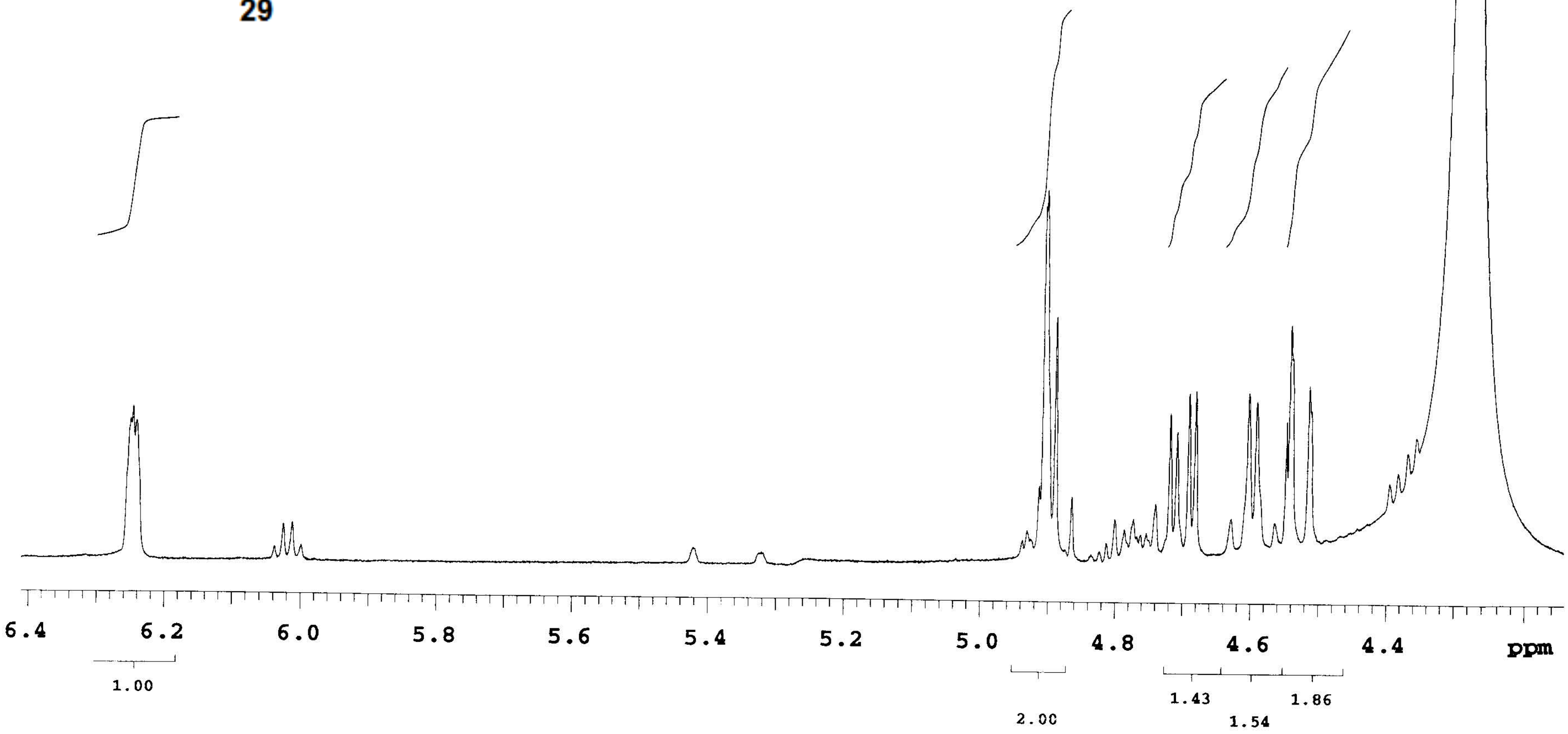
28

500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: presat

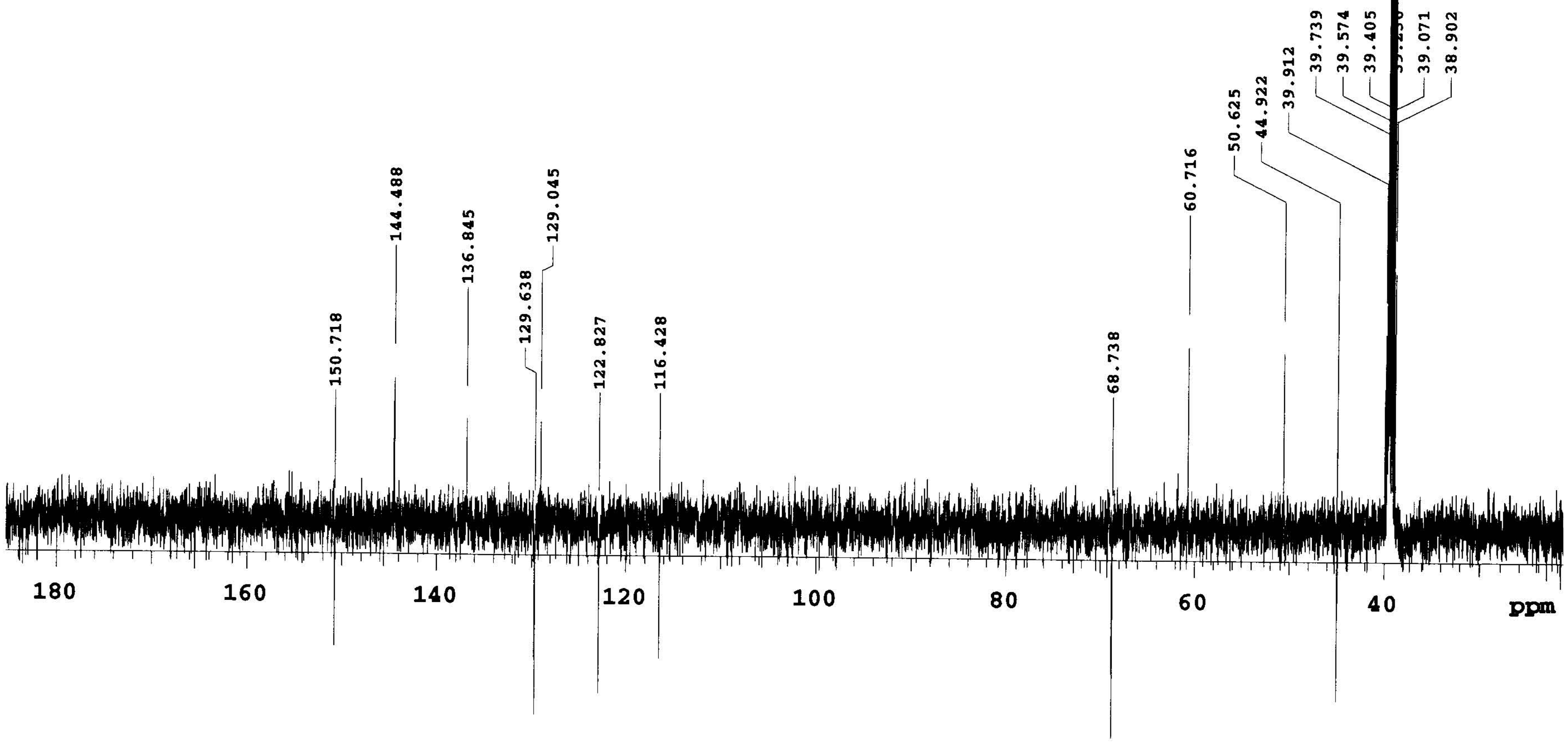


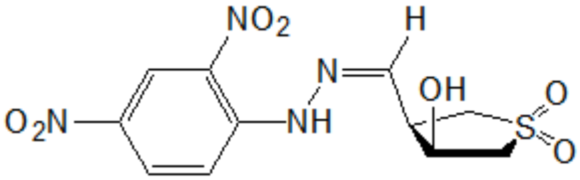
29



125.267 MHz C13[H1] apt in dmso (ref. to DMSO @ 39.5 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

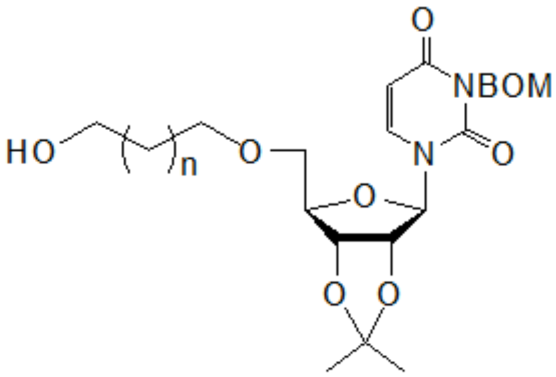




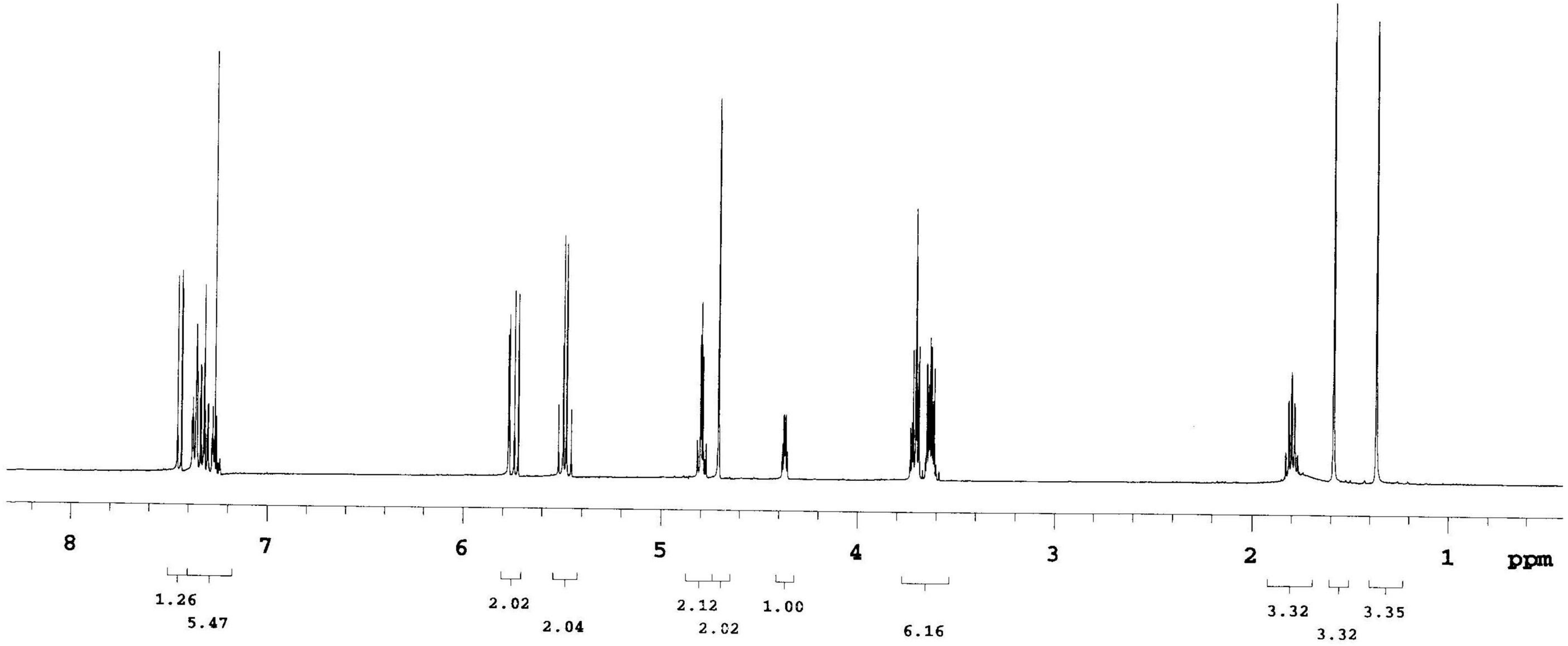
29

399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

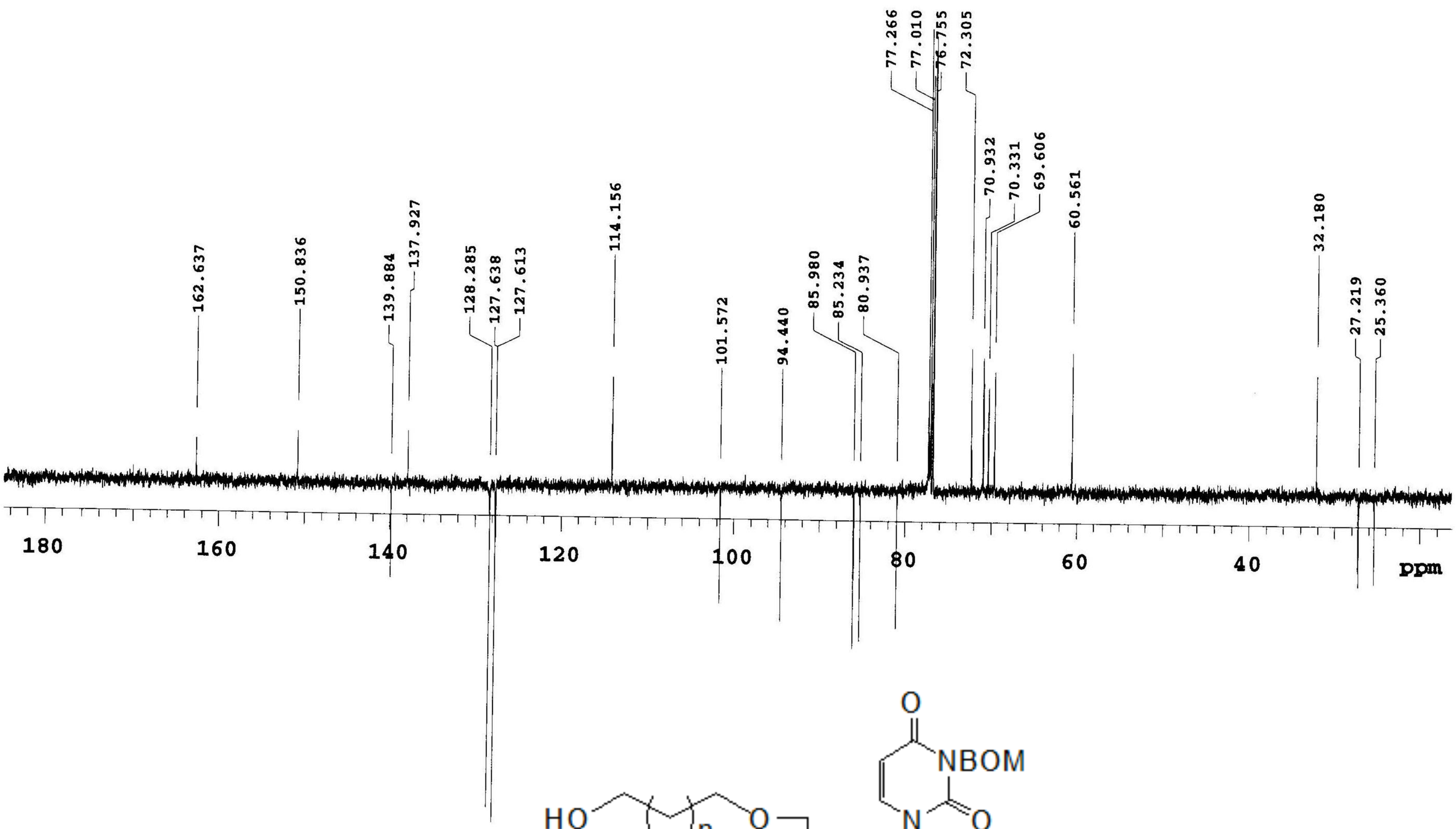


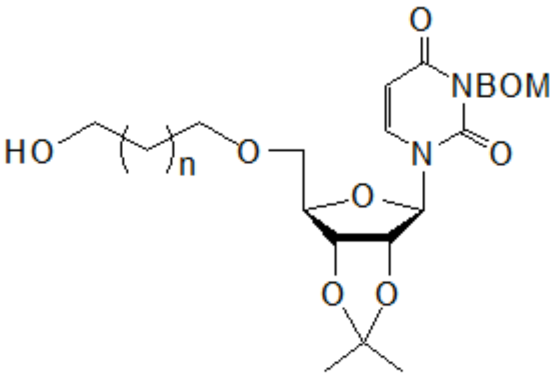
S6 n = 1



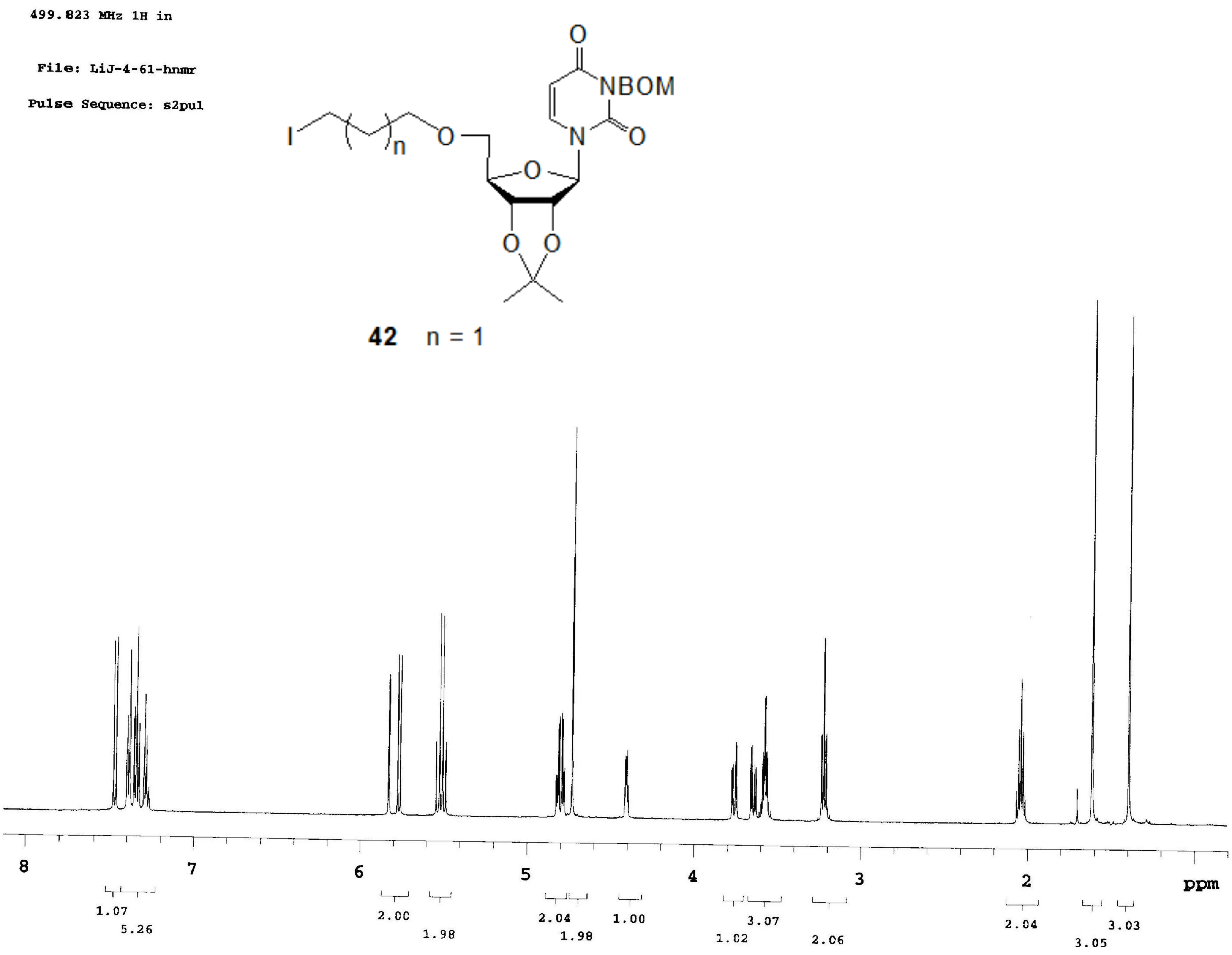
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt





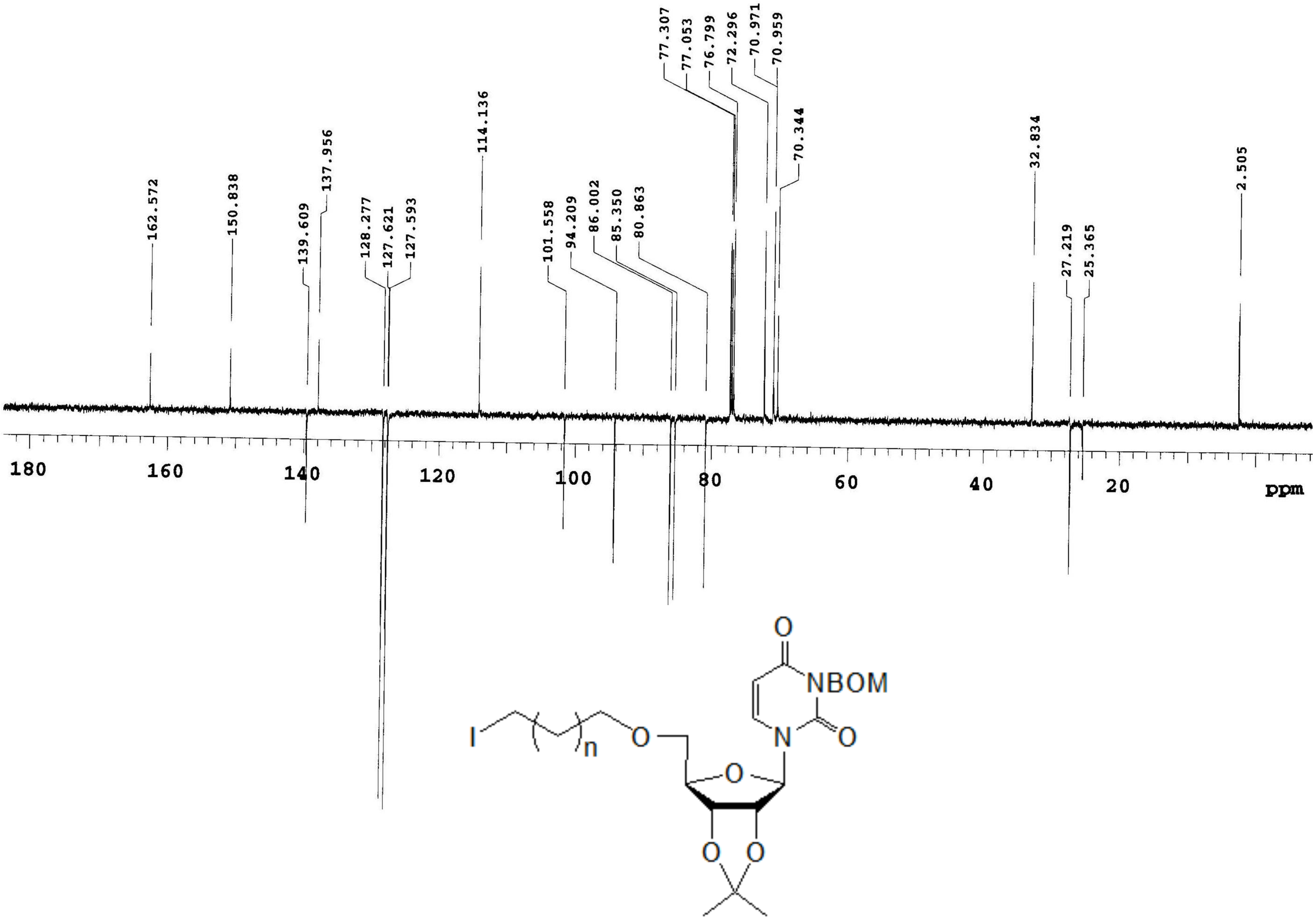
S6 n = 1


499.823 MHz 1H in
File: LiJ-4-61-hnmr
Pulse Sequence: s2pul
I
n
O
O
O
O
N
NBOM
O
O
8
7
6
5
4
3
2
ppm
1.07
5.26
2.00
1.98
2.04
1.98
1.00
1.02
3.07
2.06
2.04
3.05
3.03

42 n = 1

125.693 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

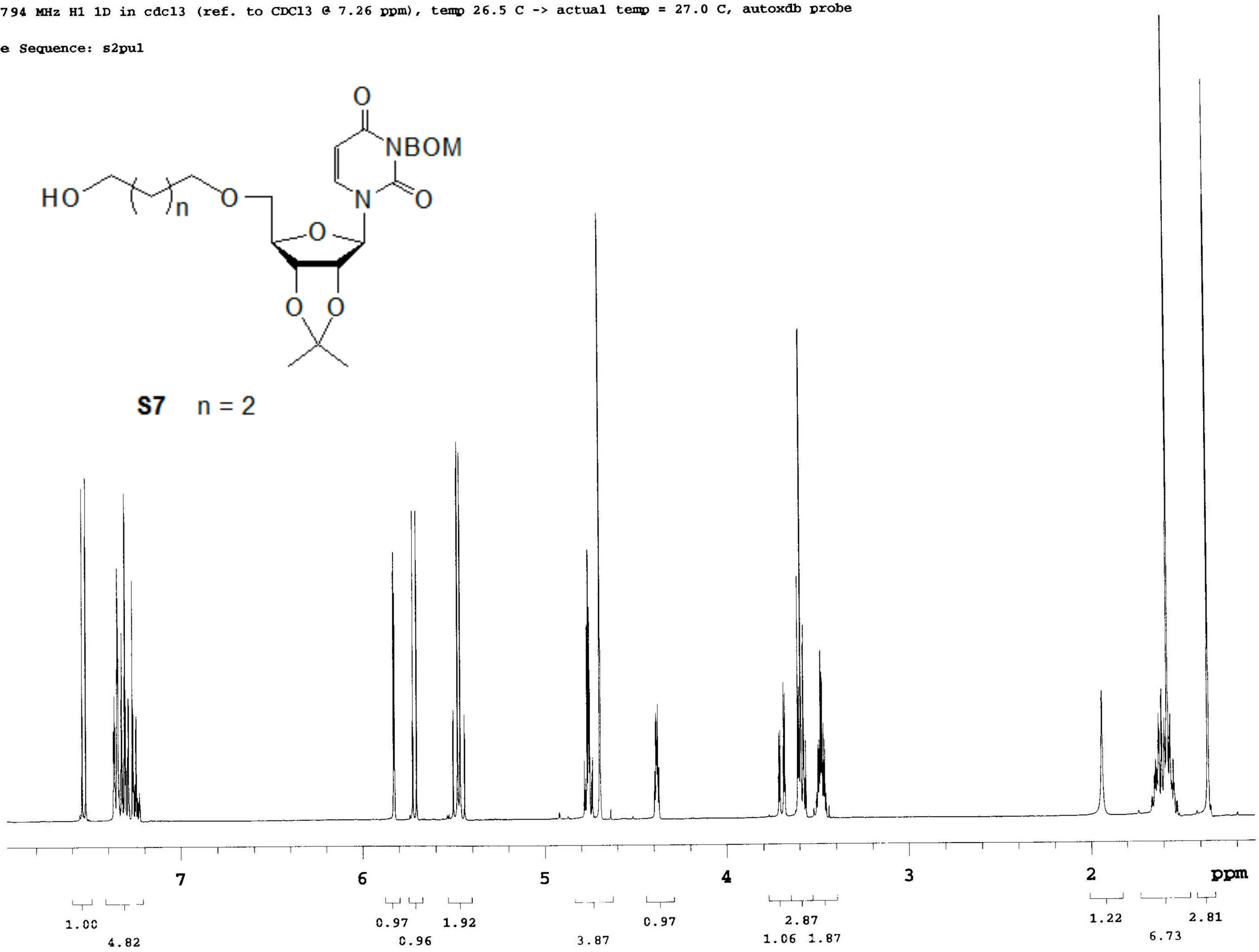
Pulse Sequence: apt



42 n = 1

399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

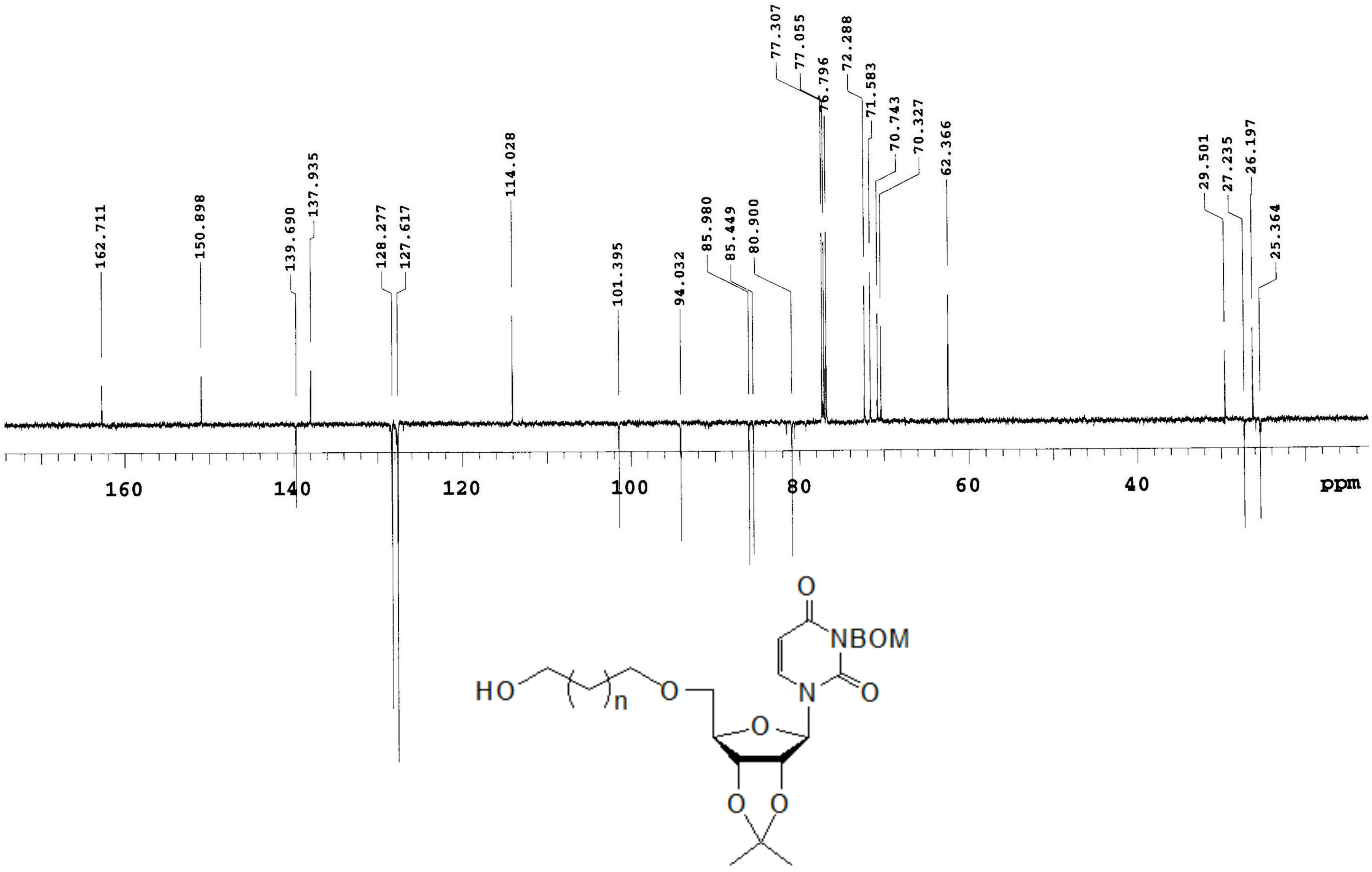
Pulse Sequence: s2pul



S7 n = 2

125.266 MHz C13[H1] apt in cdcl3 (ref. to CDC13 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

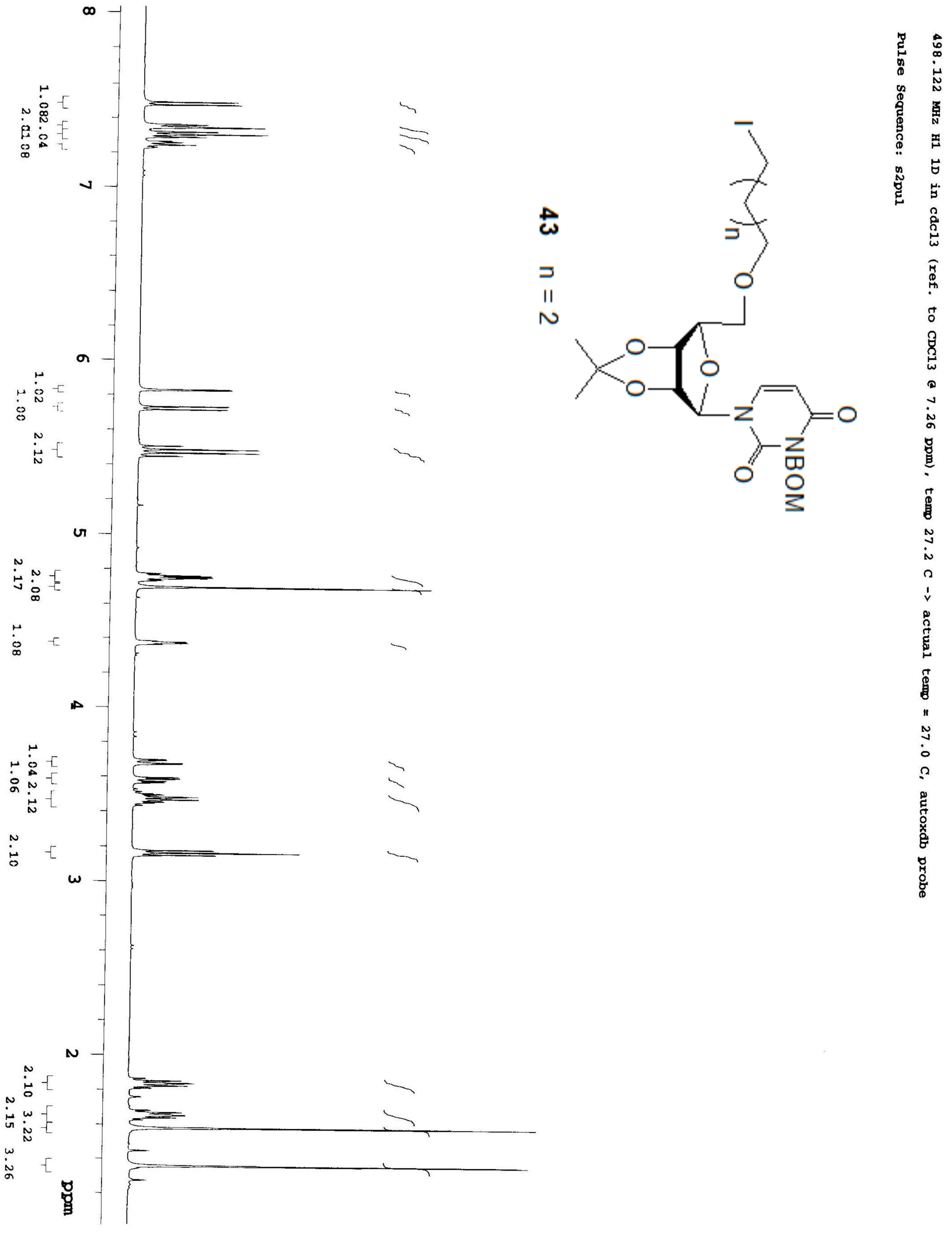
Pulse Sequence: apt



S7 n = 2

498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

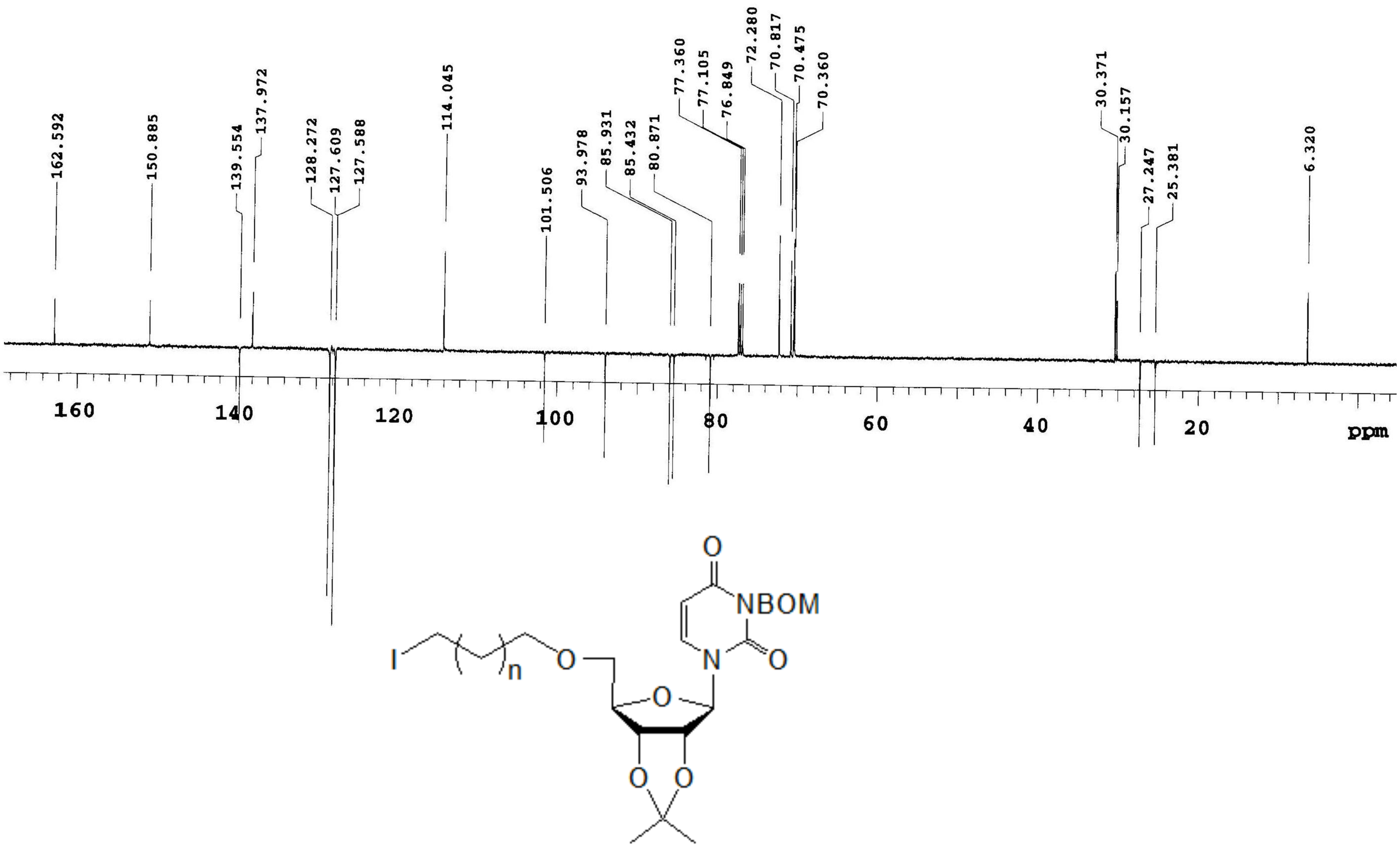
Pulse Sequence: s2pul



43 n = 2

125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

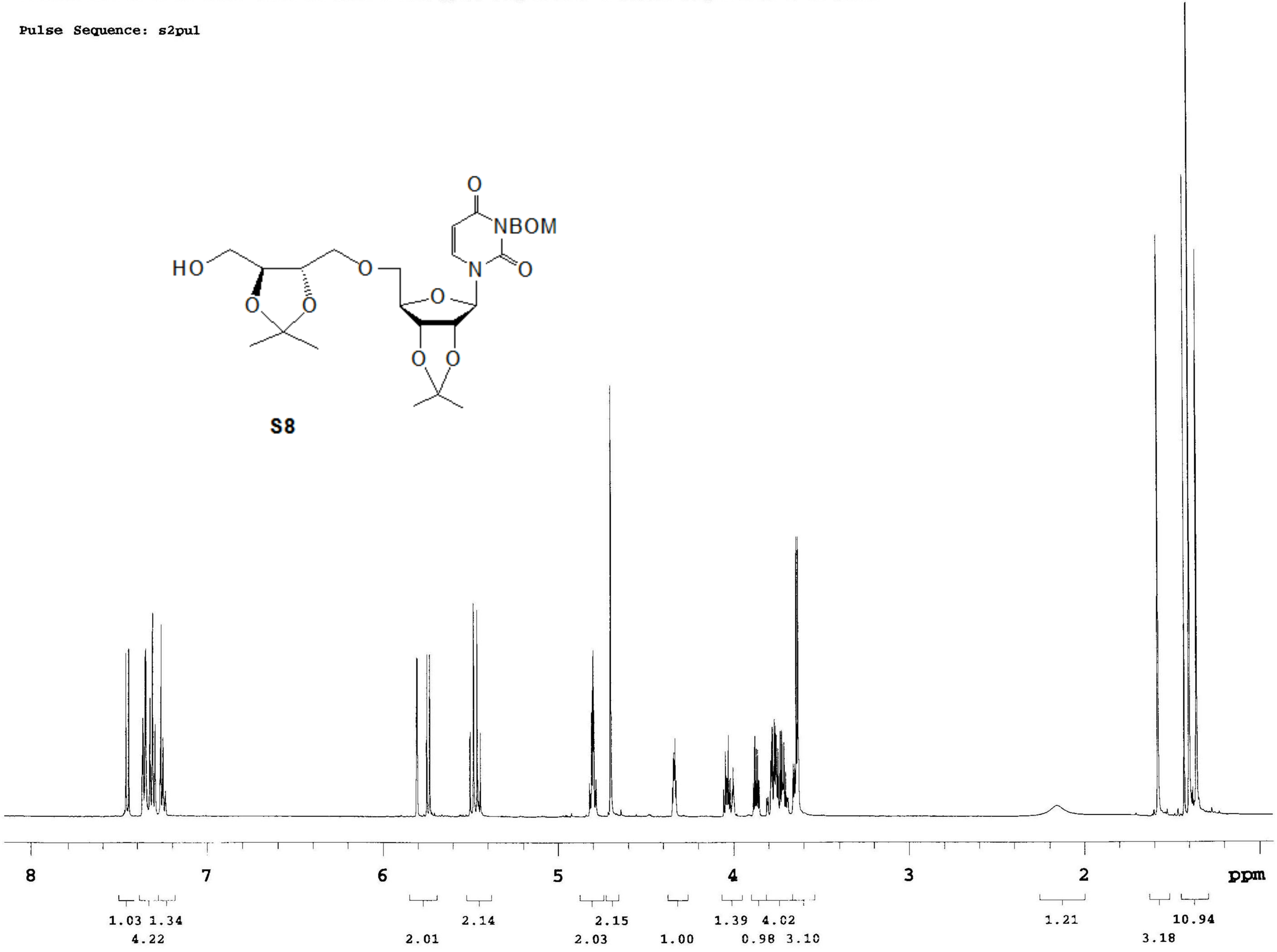
Pulse Sequence: apt



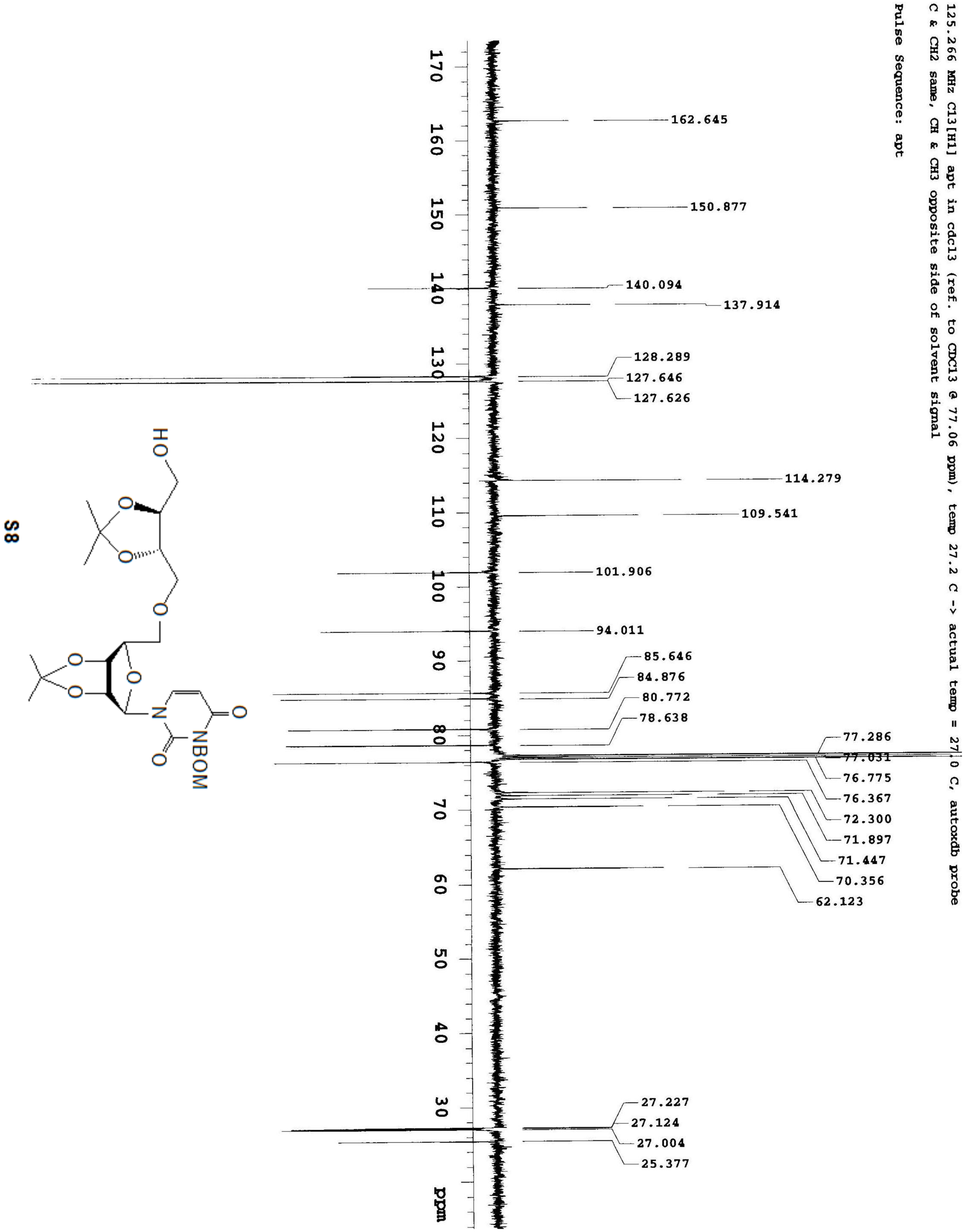
43 n = 2

498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe

Pulse Sequence: s2pul



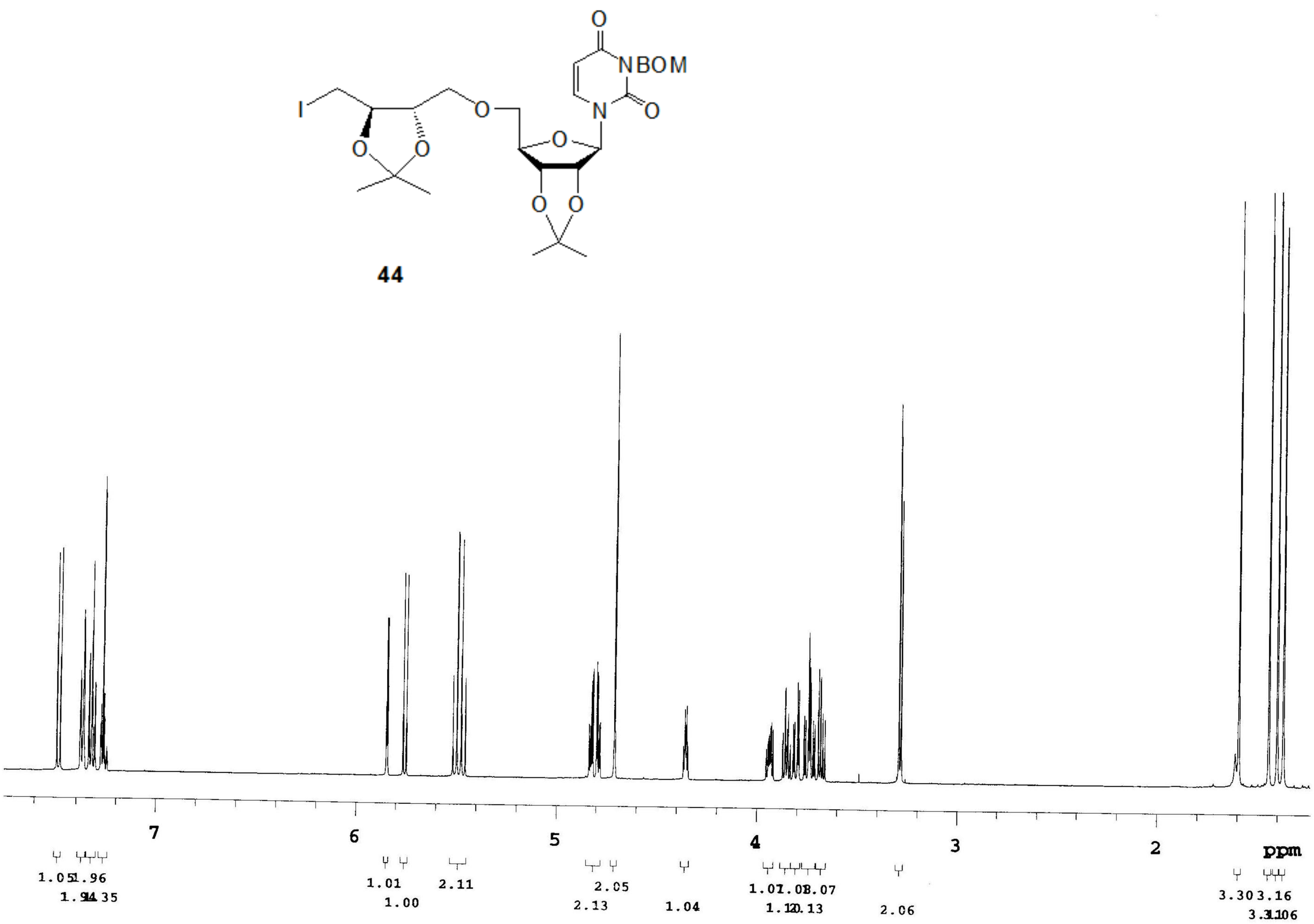
S8


125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
162.645
150.877
140.094
137.914
128.289
127.646
127.626
114.279
109.541
101.906
94.011
85.646
84.876
80.772
78.638
77.286
77.031
76.775
76.367
72.300
71.897
71.447
70.356
62.123
27.227
27.124
27.004
25.377
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
HO
O
O
O
O
O
O
N
NBOM
O
O

S8

499.821 MHz H1 1D in cdcl3 (ref. to CDC13 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

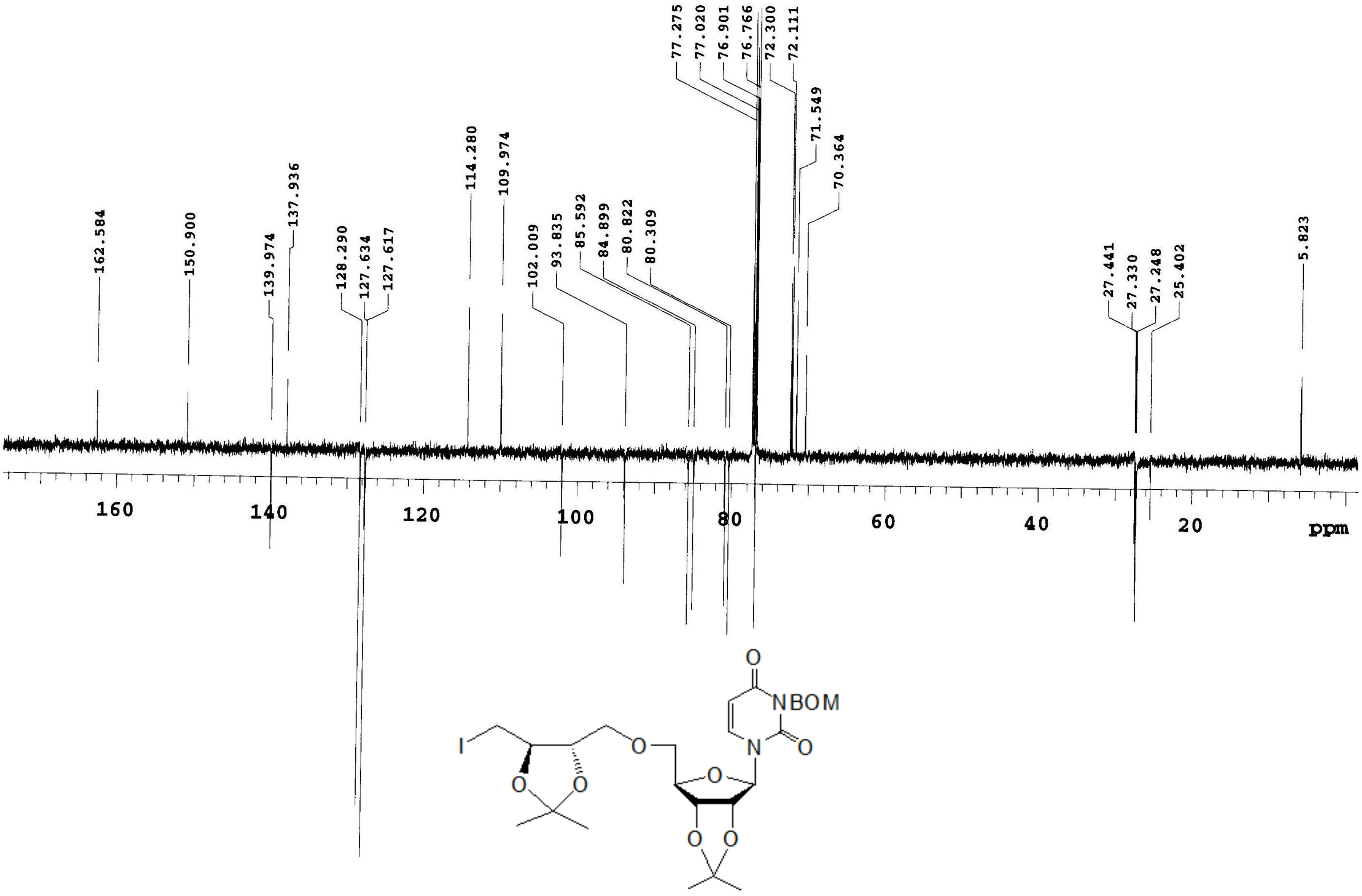
Pulse Sequence: s2pul



44

125.693 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

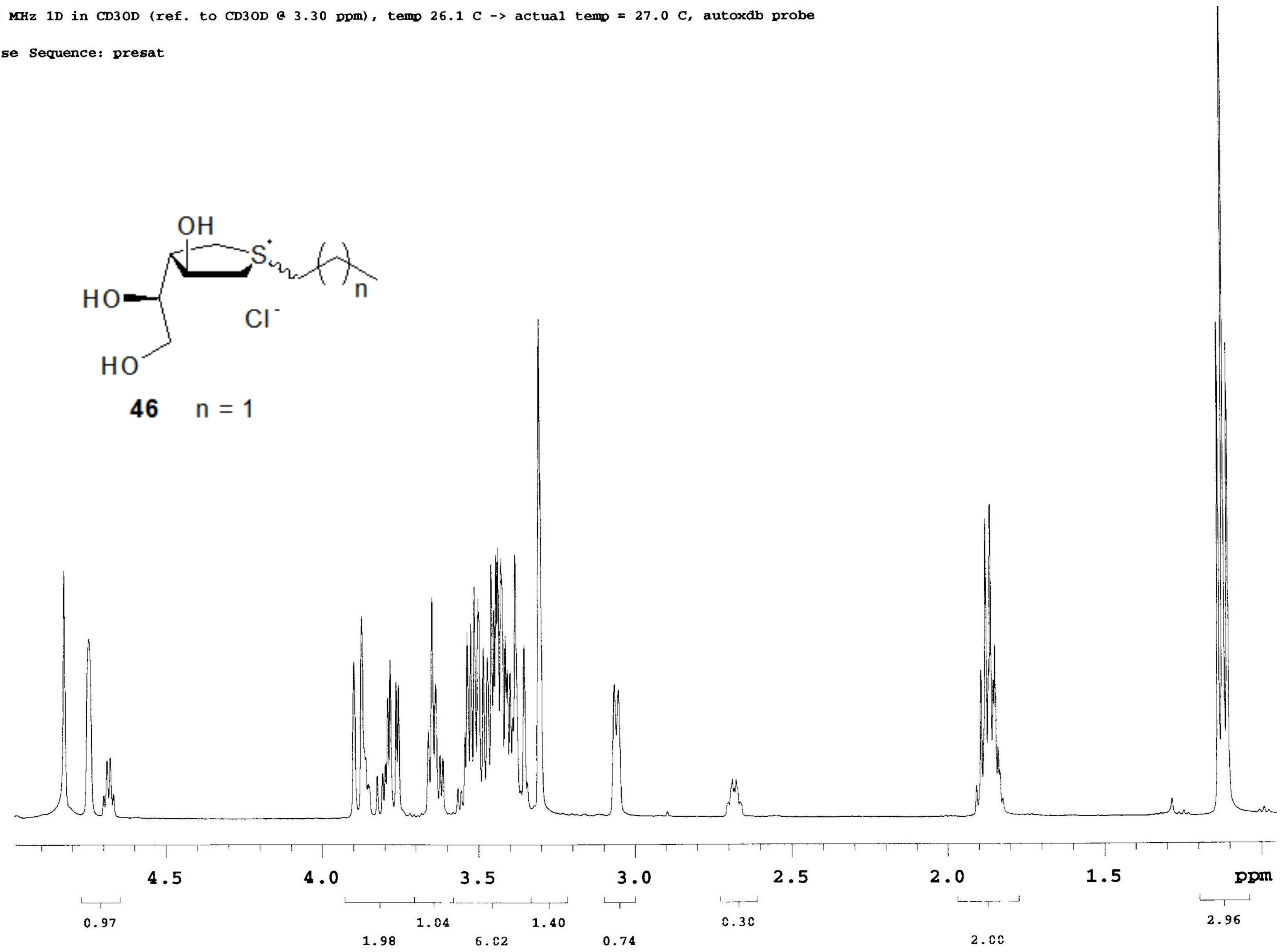
Pulse Sequence: apt

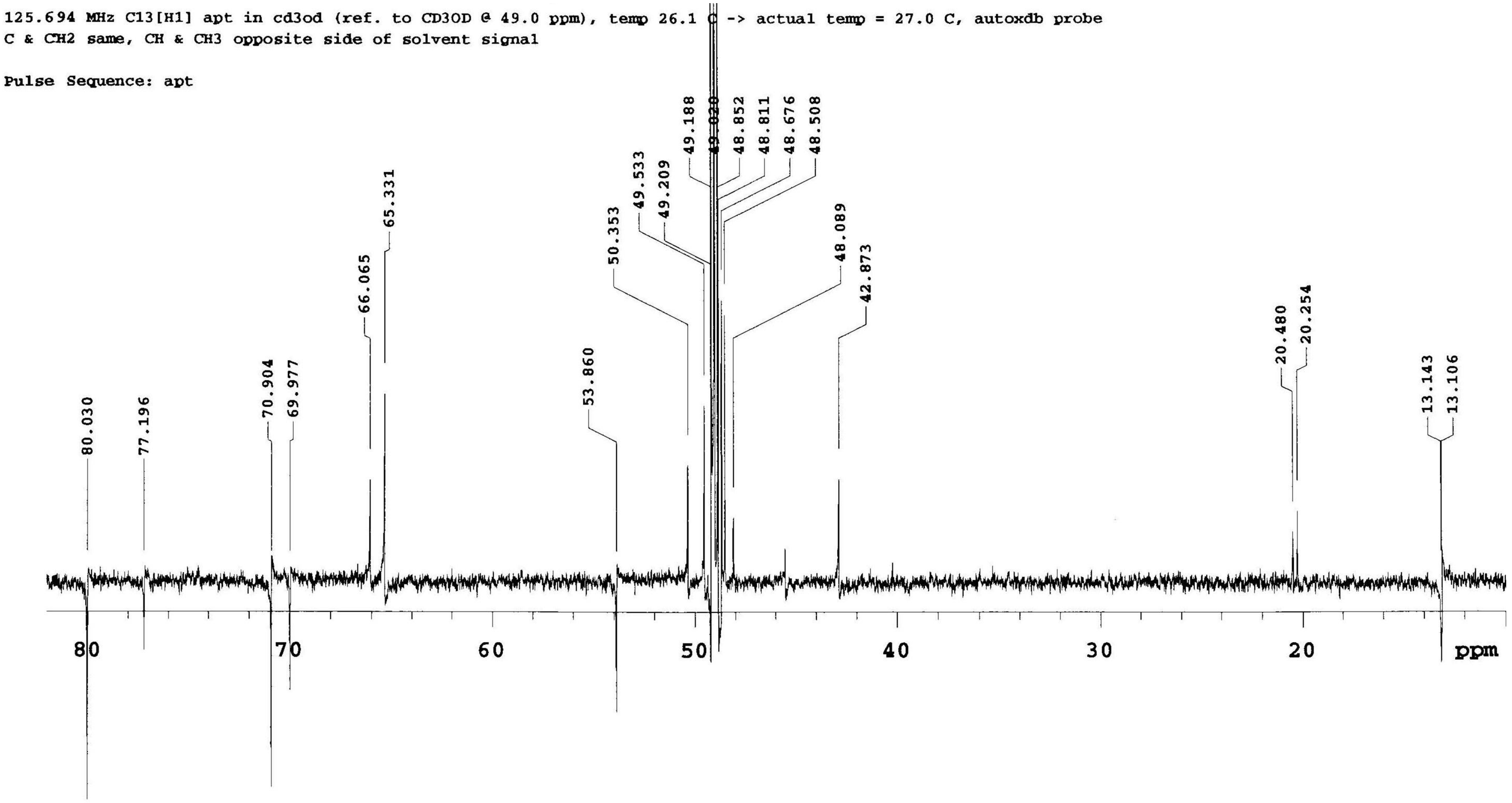


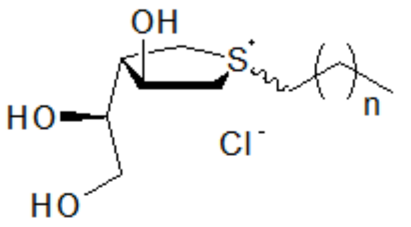
44

500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: presat


46 n = 1

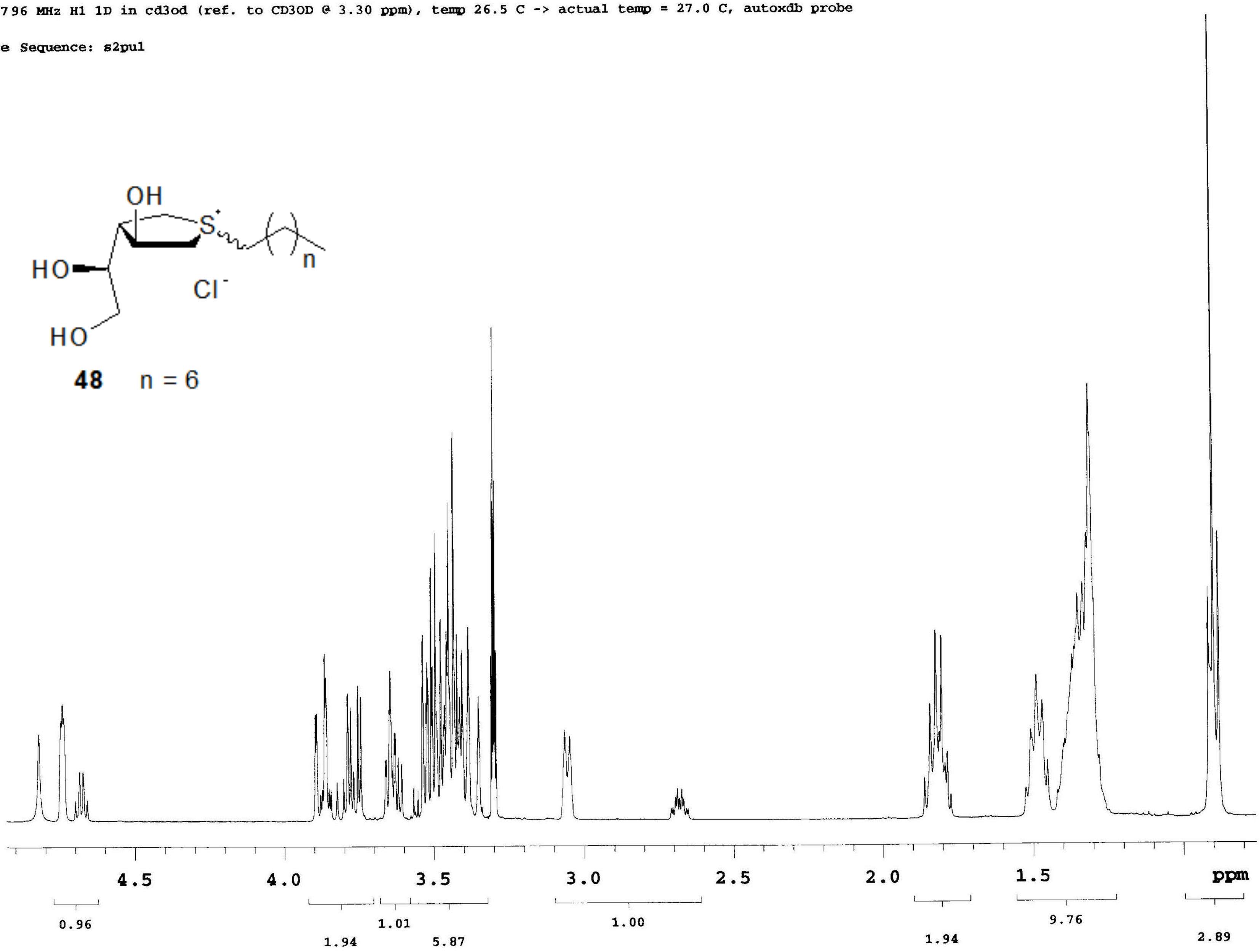

125.694 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
80.030
77.196
70.904
69.977
66.065
65.331
53.860
50.353
49.533
49.209
49.188
49.020
48.852
48.811
48.676
48.508
48.089
42.873
20.480
20.254
13.143
13.106
80
70
60
50
40
30
20
ppm


OH
S
+
n
HO
Cl
-
HO

46 n = 1

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

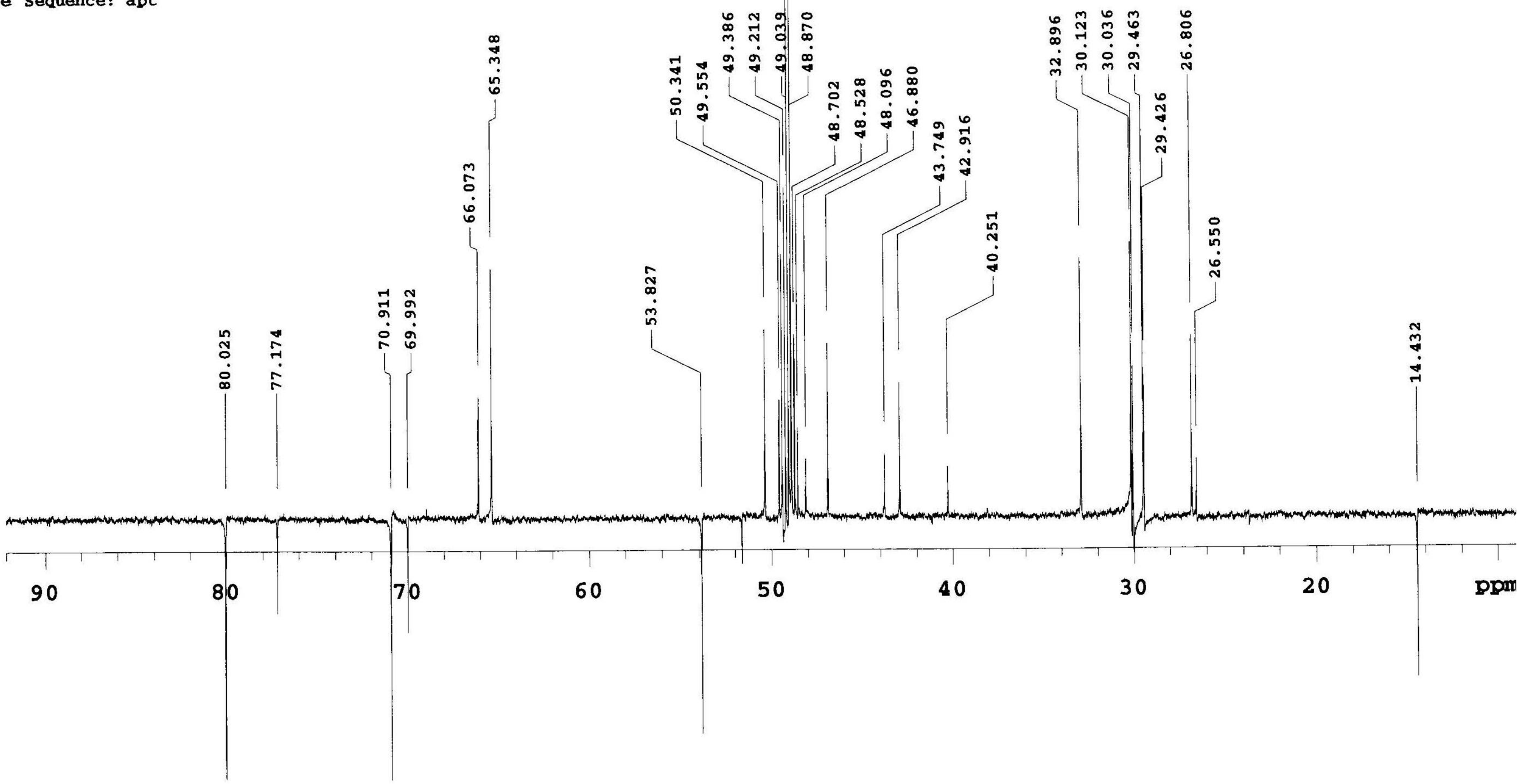
Pulse Sequence: s2pul

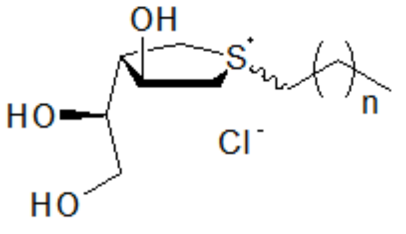


48 n = 6

125.267 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

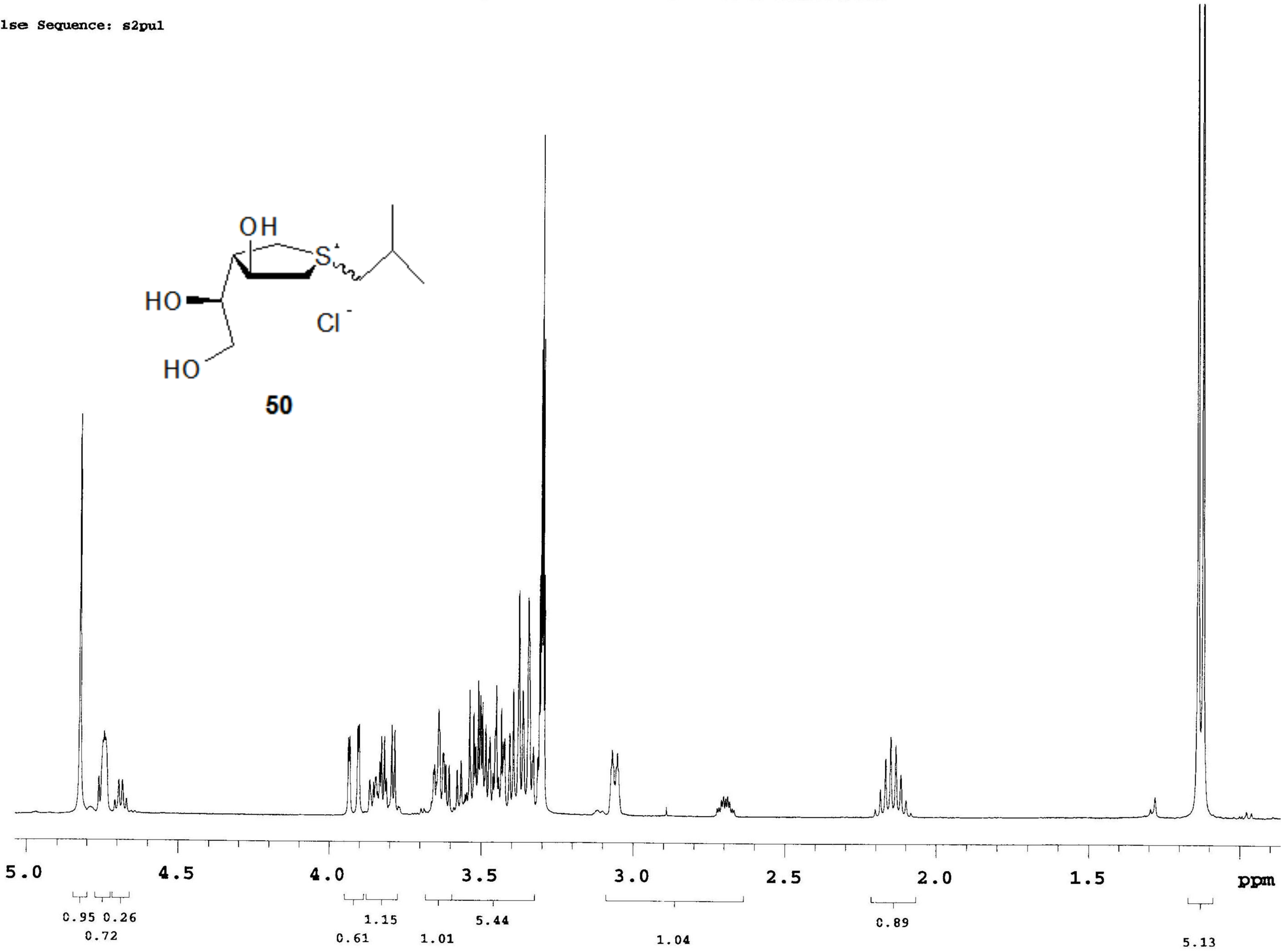




48 n = 6

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

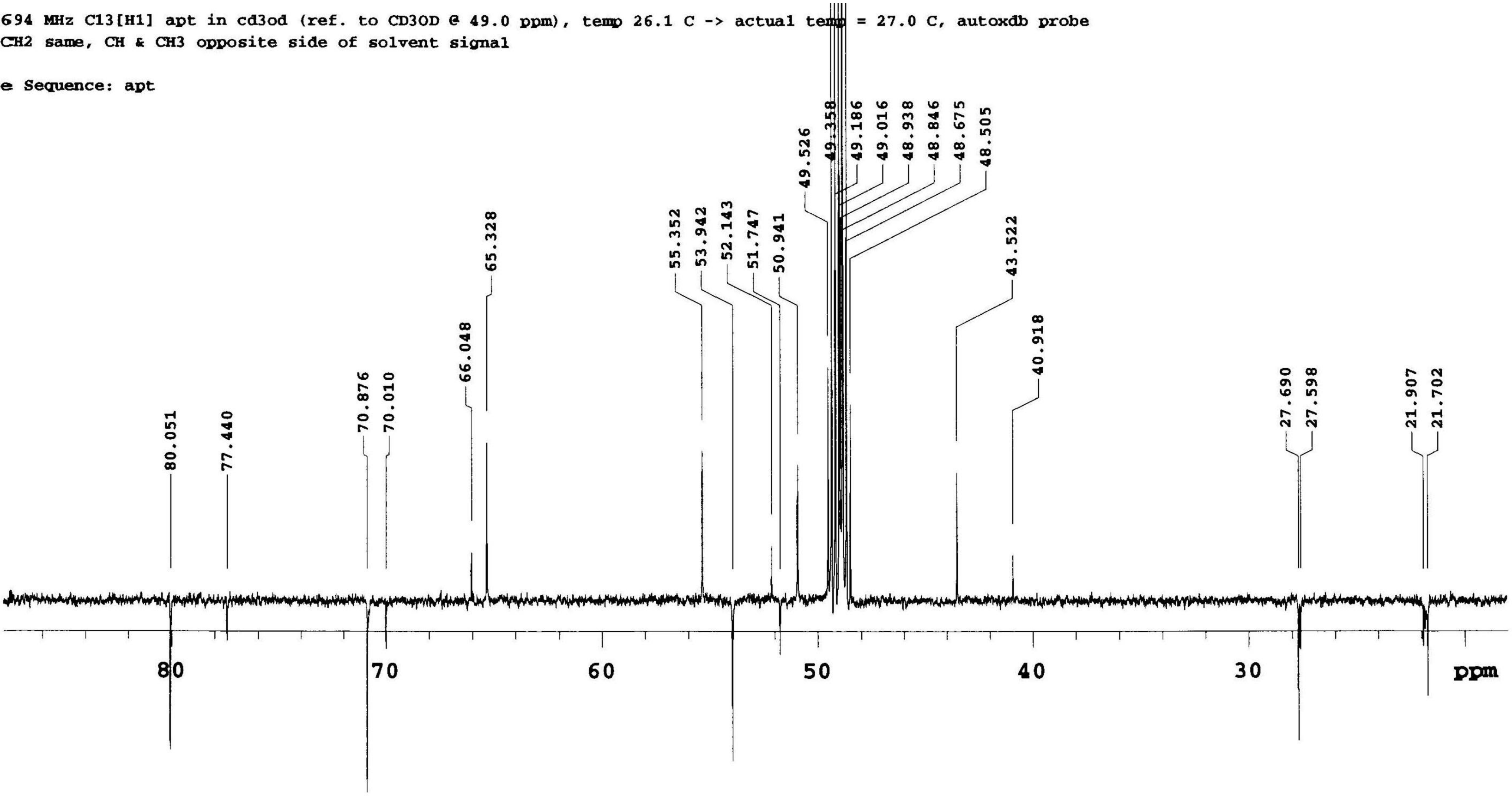
Pulse Sequence: s2pul

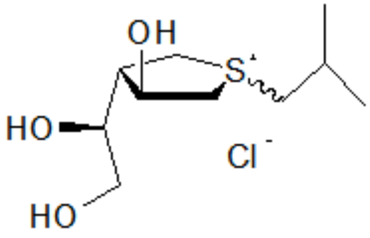


50

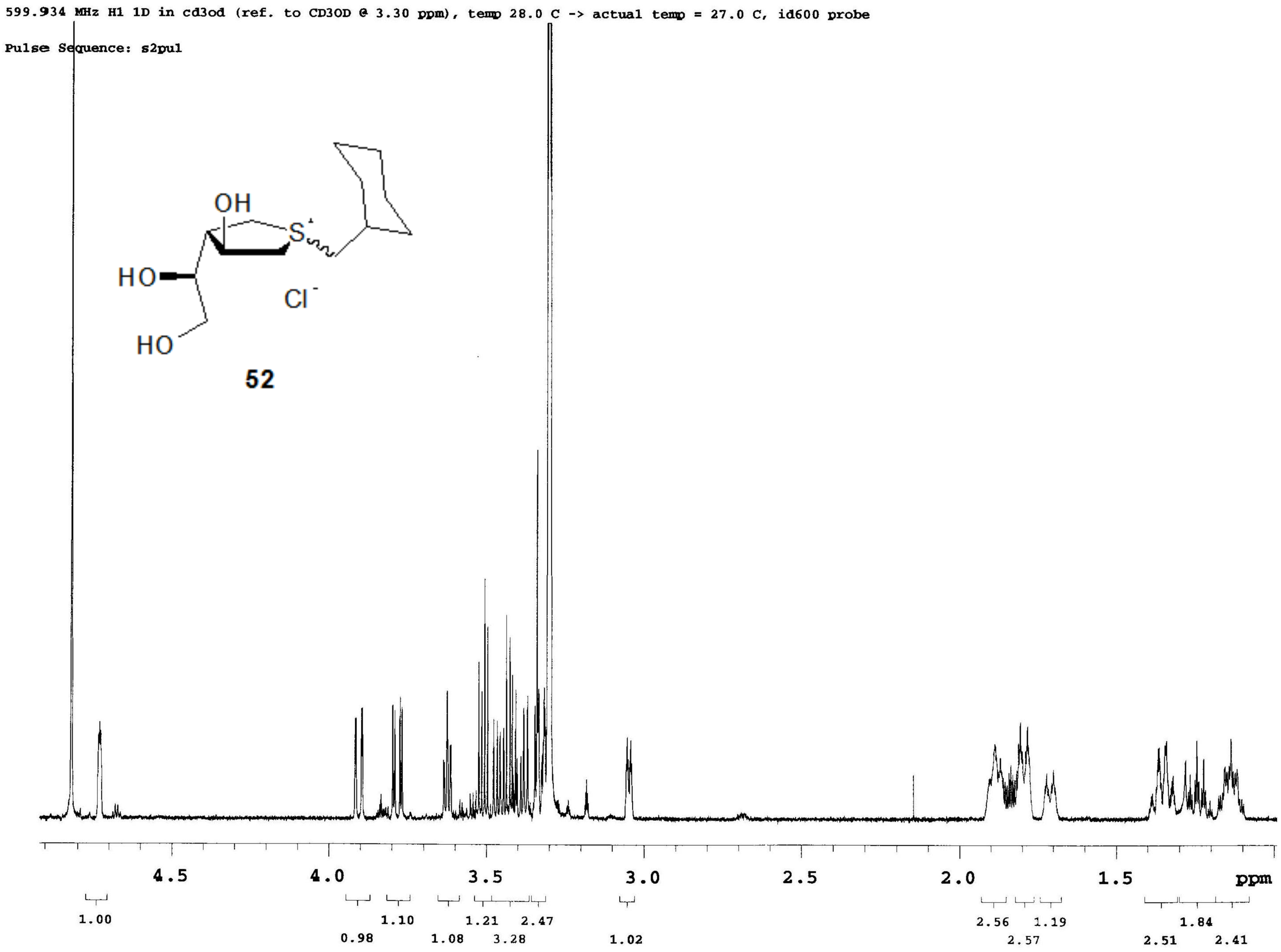
125.694 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt



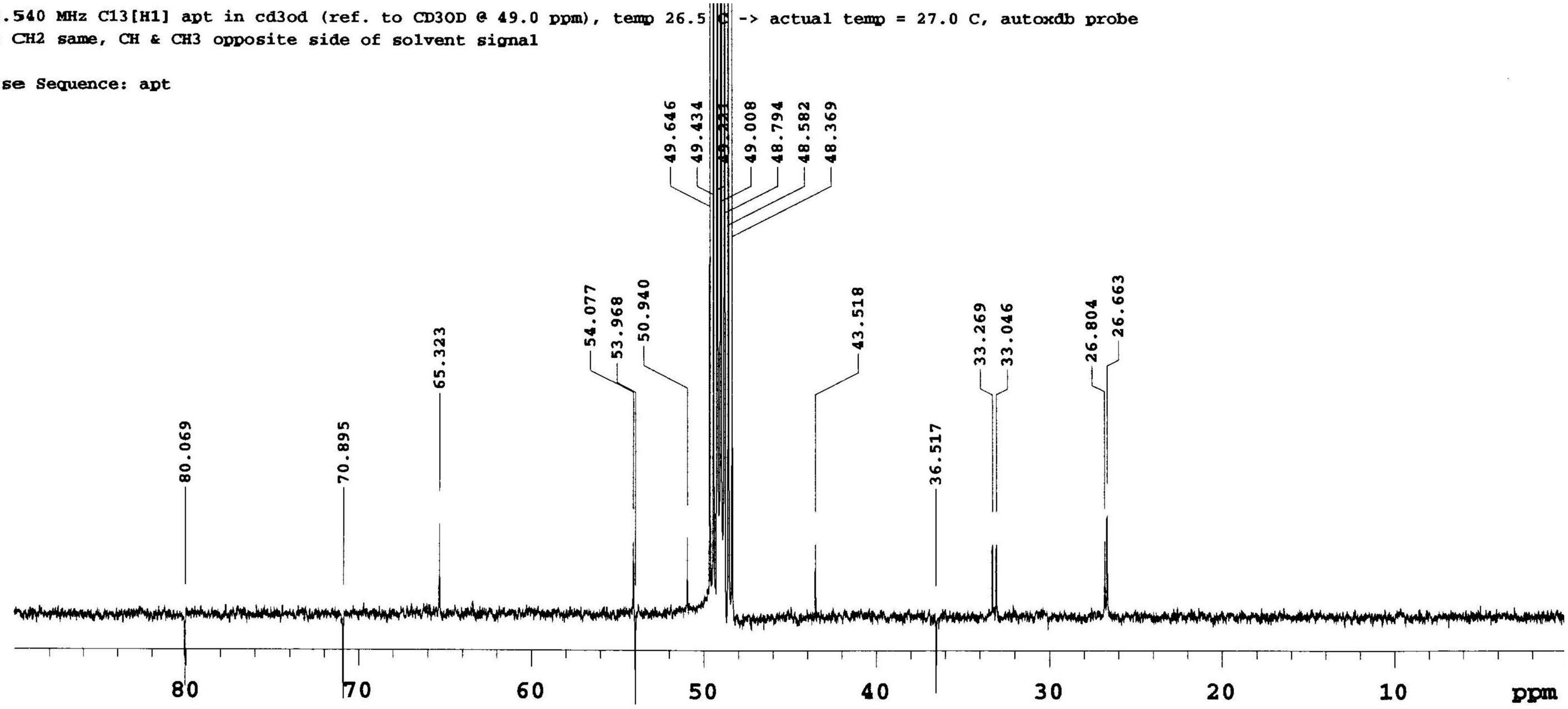


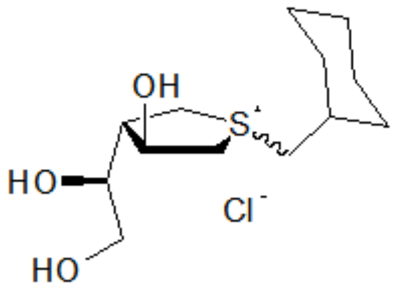
50


599.934 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 28.0 C -> actual temp = 27.0 C, id600 probe
Pulse Sequence: s2pul
OH
HO
HO
S+
Cl-
52
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
0.98
1.10
1.08
1.21
3.28
2.47
1.02
2.56
2.57
1.19
2.51
1.84
2.41

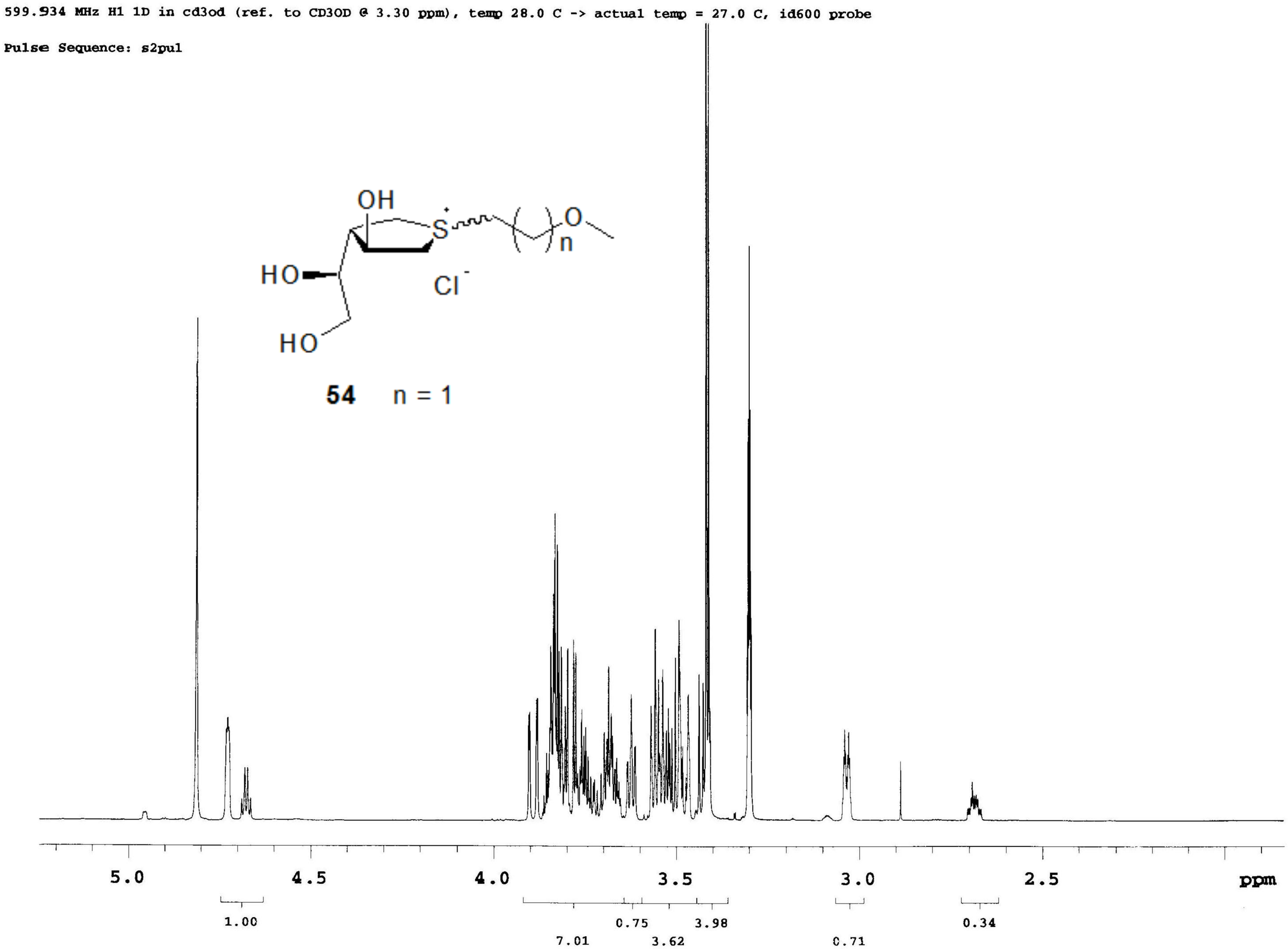
100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt





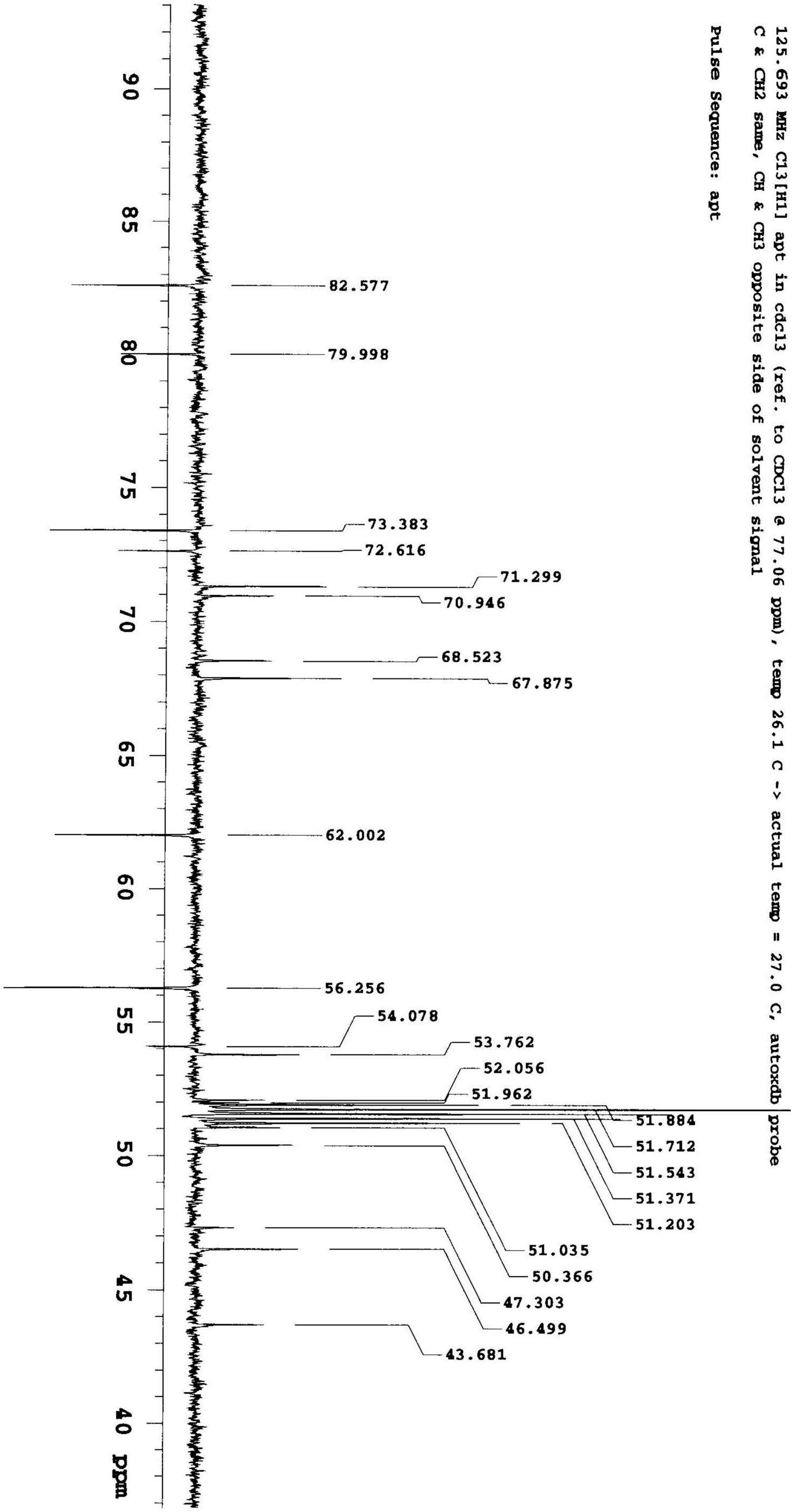
52

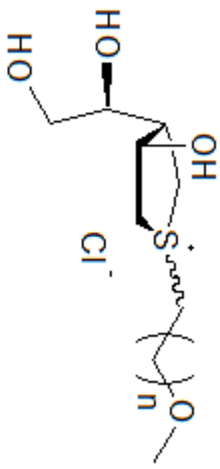


599.934 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 28.0 C -> actual temp = 27.0 C, id600 probe

Pulse Sequence: s2pul

54 n = 1

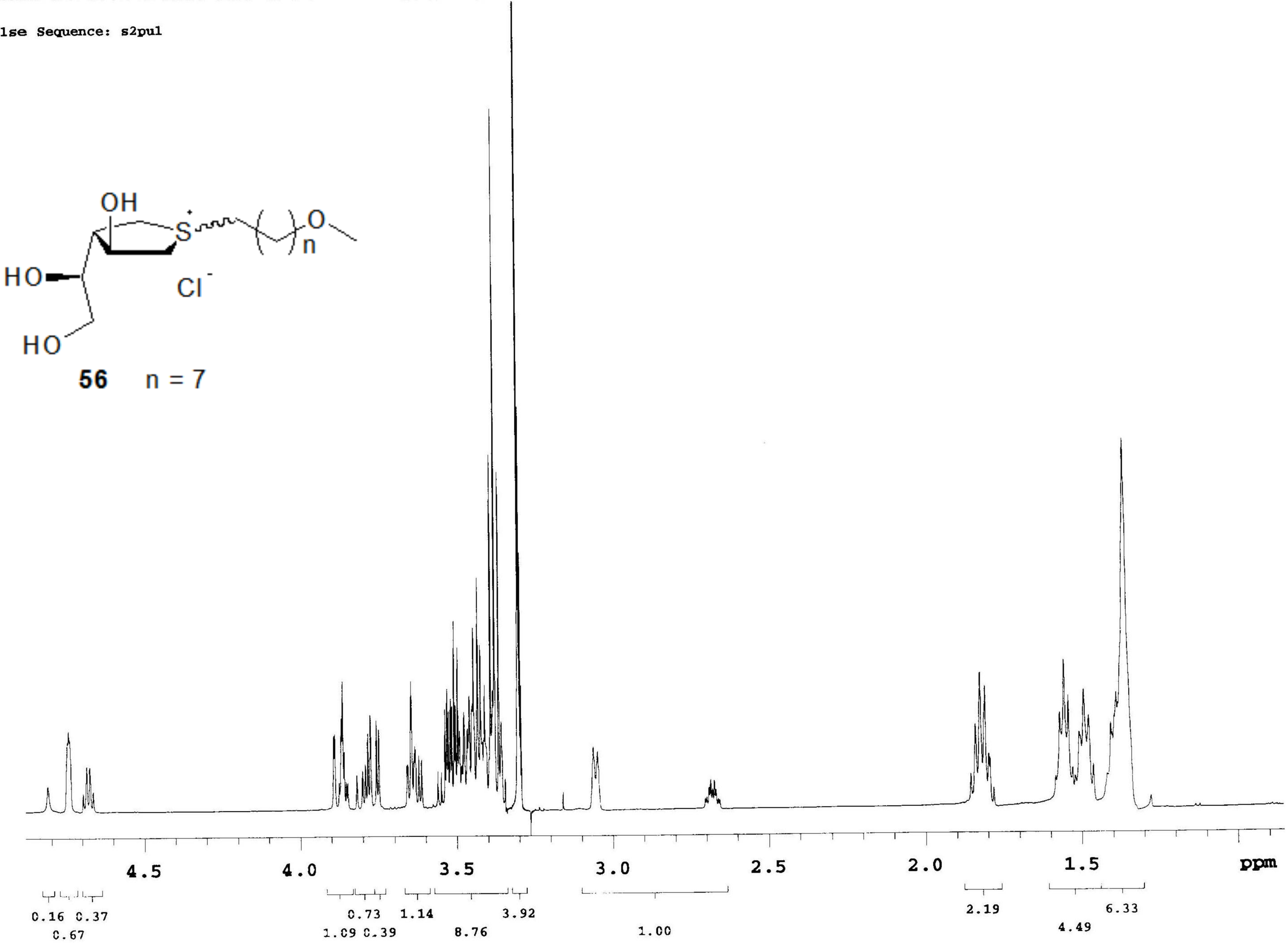

125.693 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
82.577
79.998
73.383
72.616
71.299
70.946
68.523
67.875
62.002
56.256
54.078
53.762
52.056
51.962
51.884
51.712
51.543
51.371
51.203
51.035
50.366
47.303
46.499
43.681
90
85
80
75
70
65
60
55
50
45
40 ppm


OH
HO
HO
S
+
Cl
-
O
n

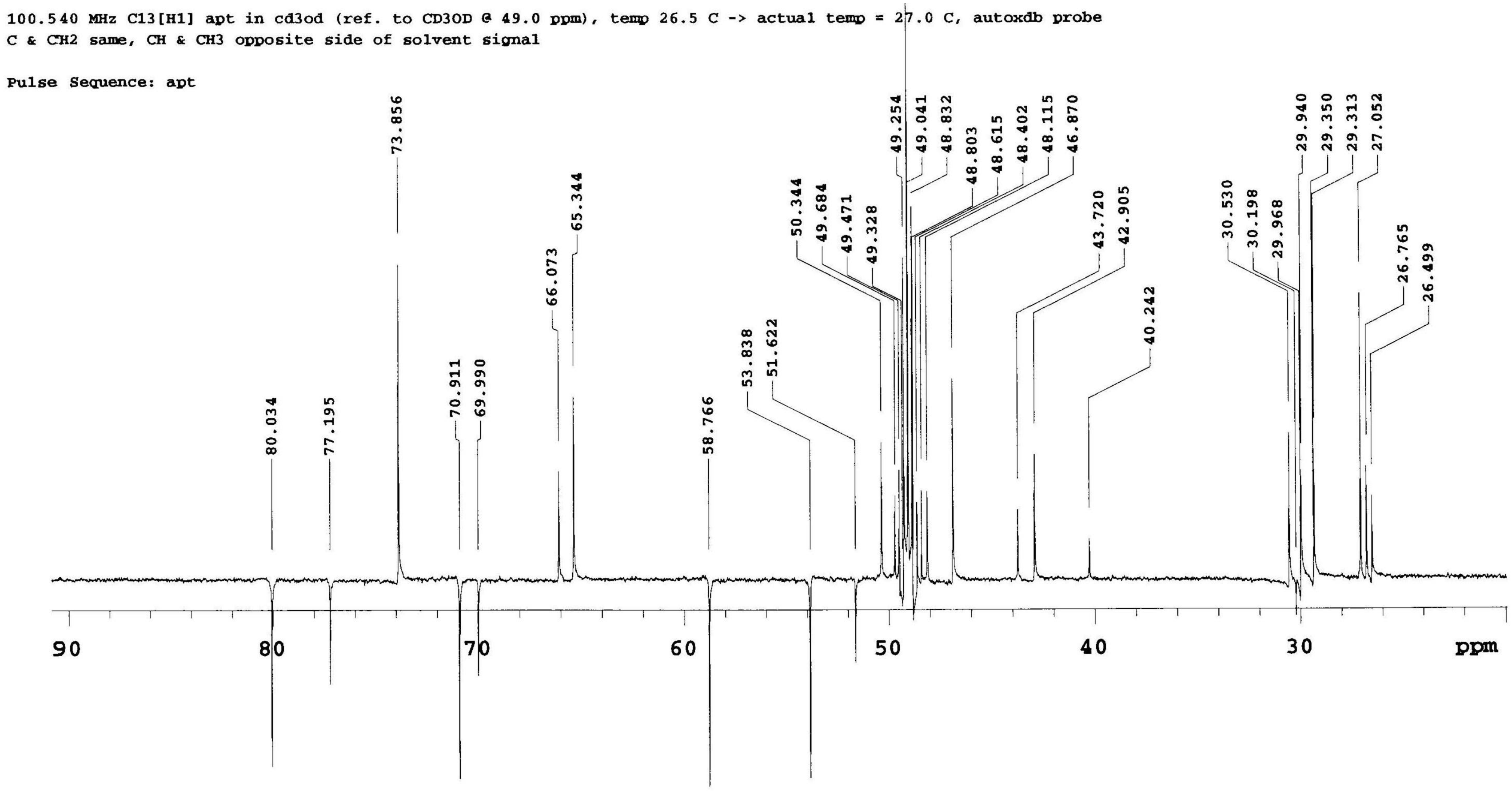
54 n = 1

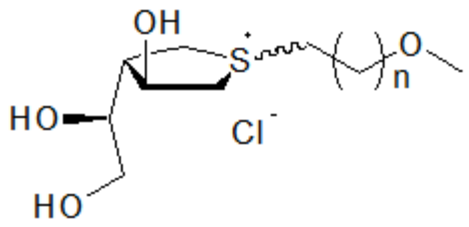
498.124 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul



56 n = 7

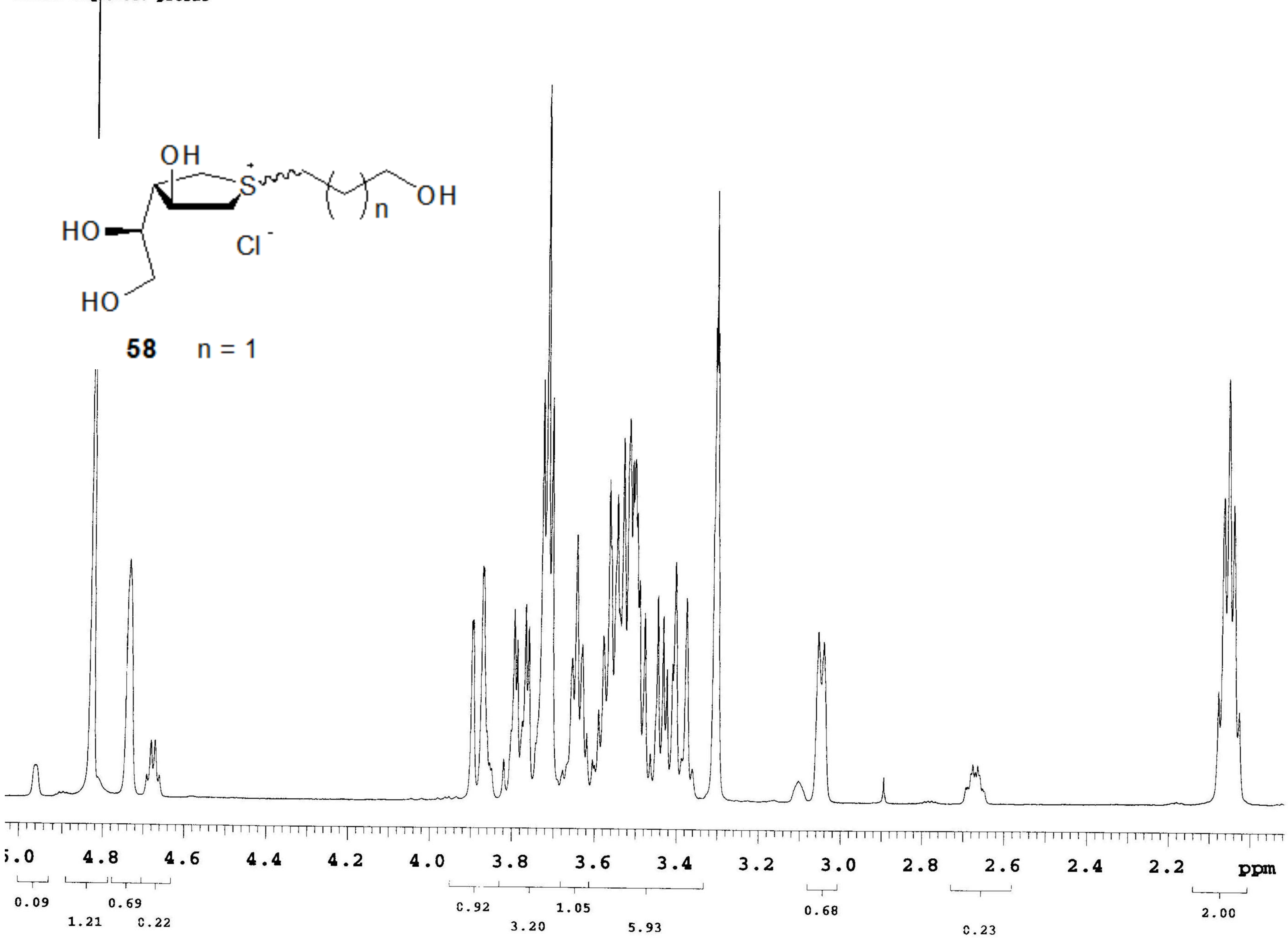

100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
80.034
77.195
73.856
70.911
69.990
66.073
65.344
58.766
53.838
51.622
50.344
49.684
49.471
49.328
49.254
49.041
48.832
48.803
48.615
48.402
48.115
46.870
43.720
42.905
40.242
30.530
30.198
29.968
29.940
29.350
29.313
27.052
26.765
26.499
90
80
70
60
50
40
30
ppm


OH
S
+
n
O
HO
Cl
-
HO

56 n = 7

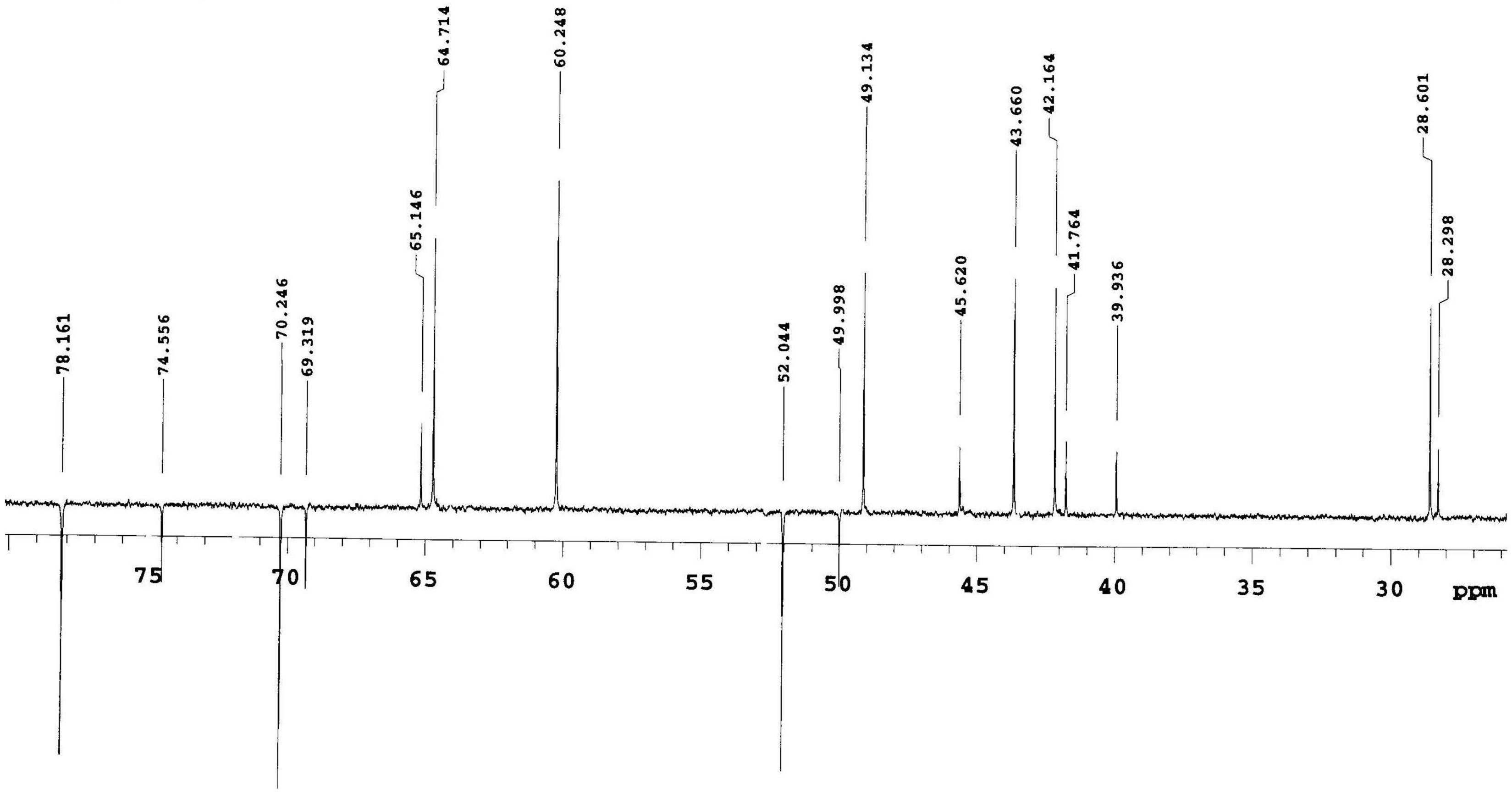
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe

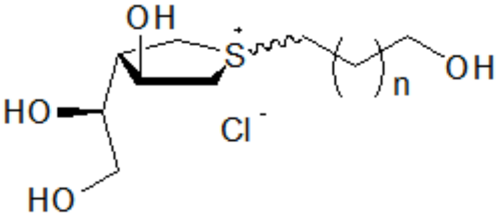
Pulse Sequence: presat


58 n = 1

125.266 MHz C13[H1] apt in d2o (ref. to external acetone @ 31.07 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

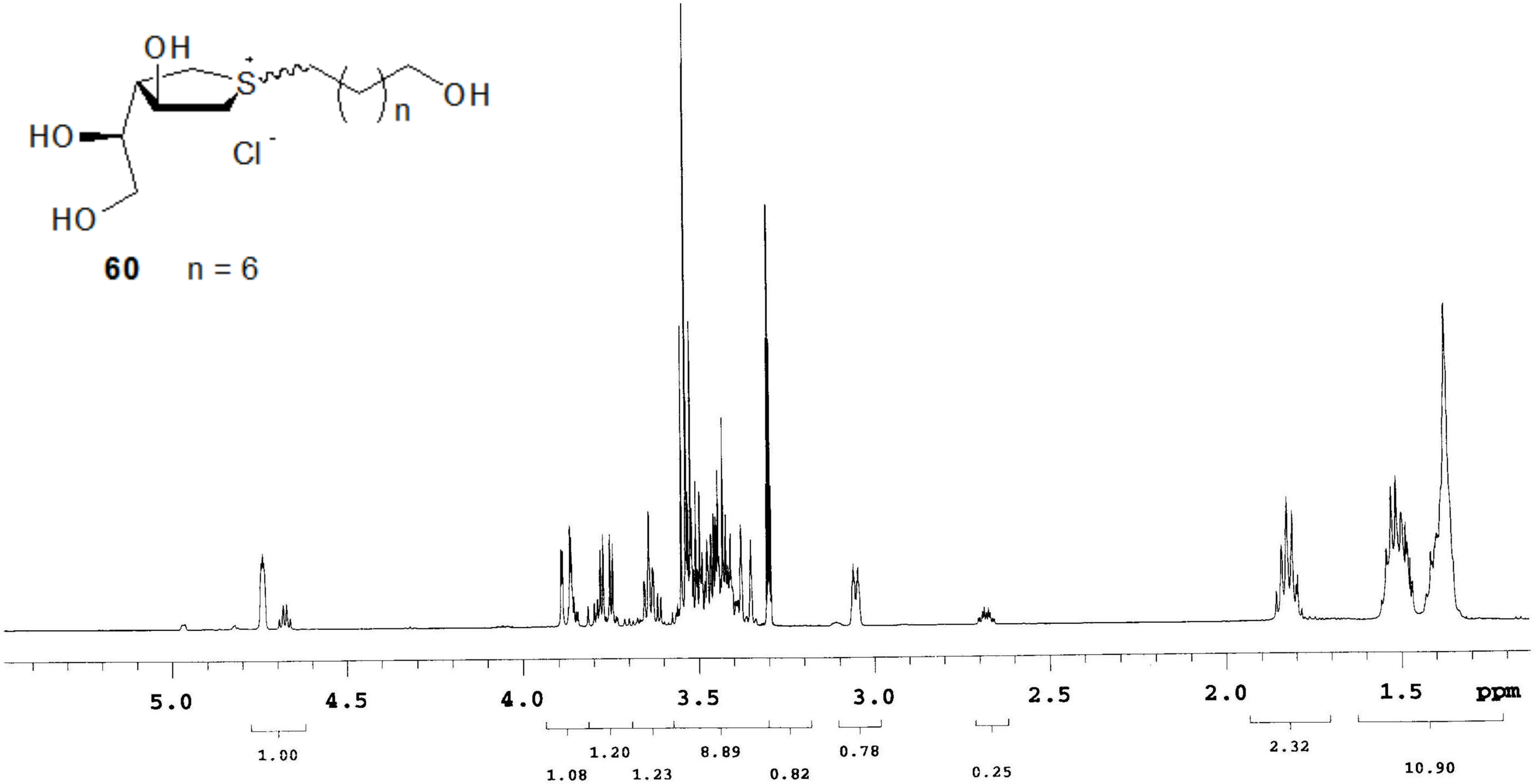




58 n = 1

498.124 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

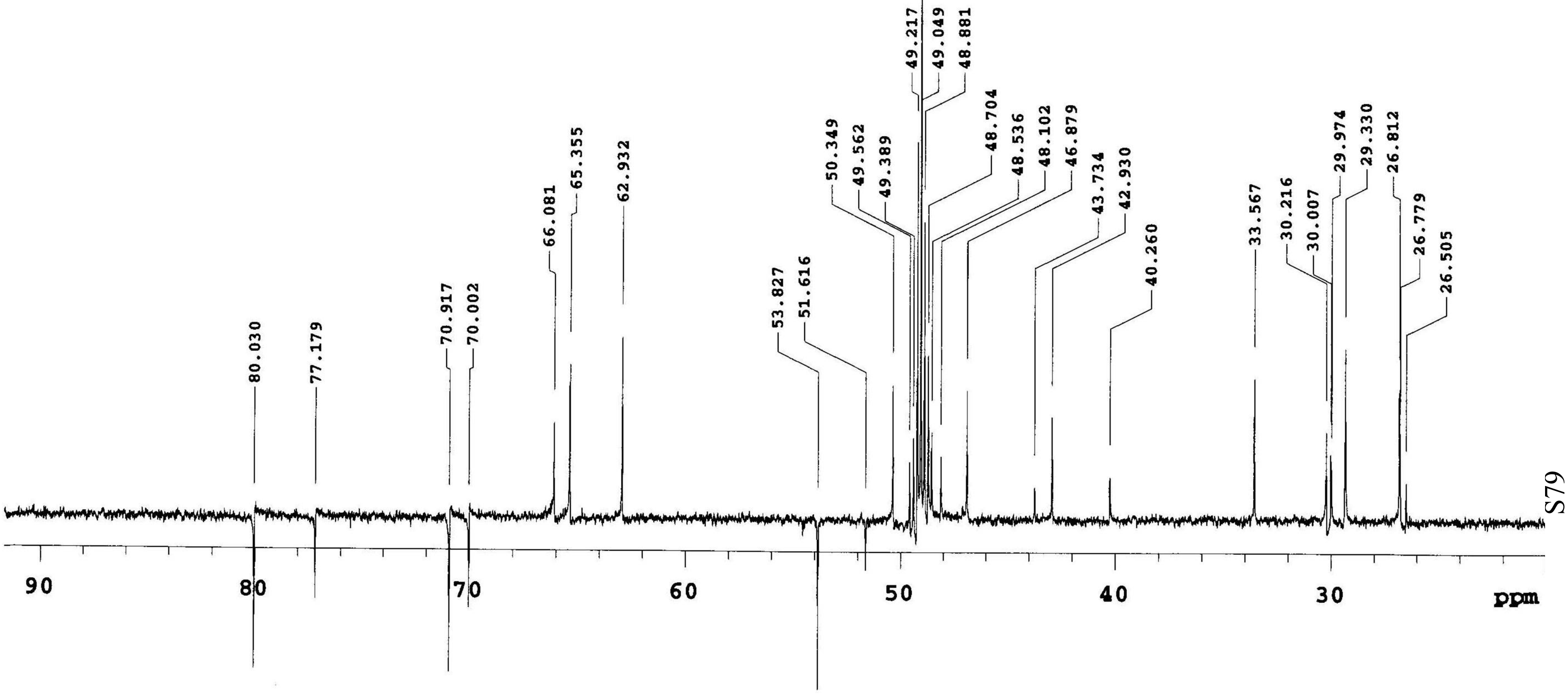
Pulse Sequence: s2pul

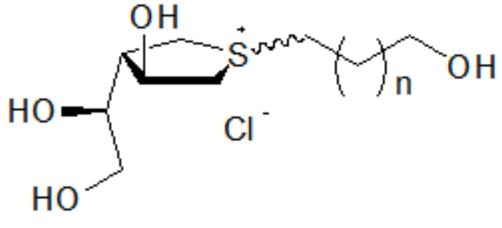


60 n = 6

125.694 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

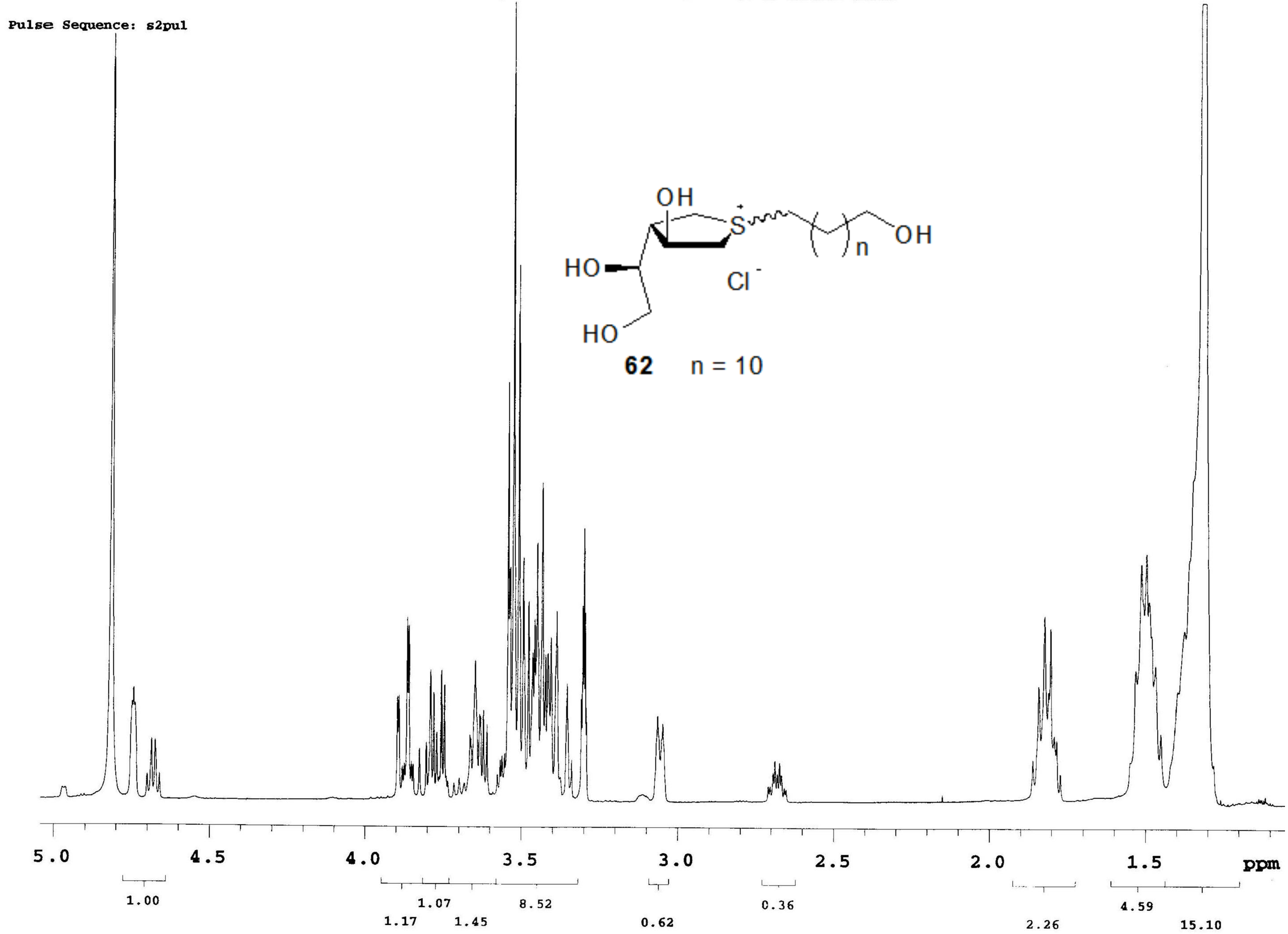




60 n = 6

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

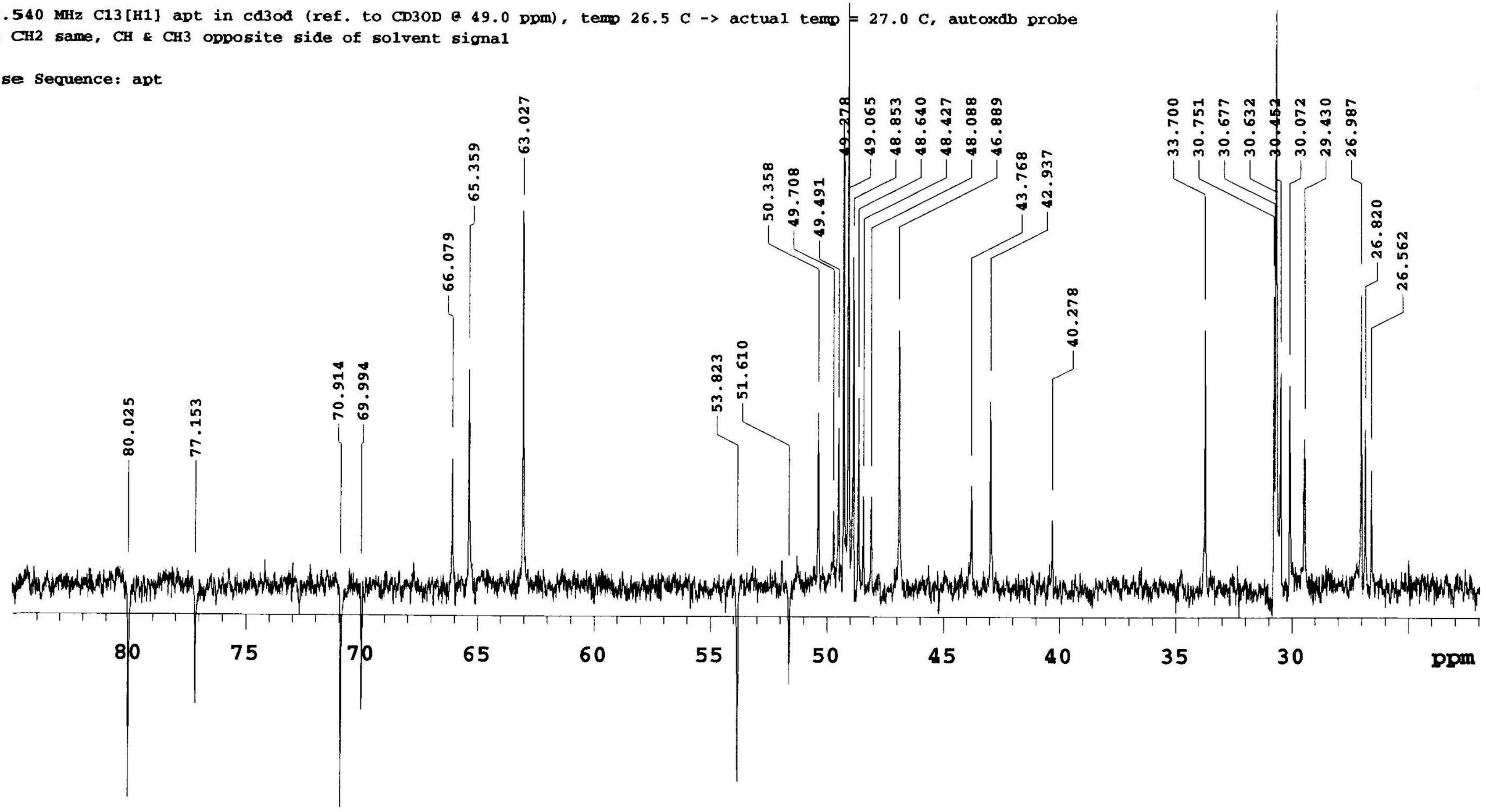
Pulse Sequence: s2pul

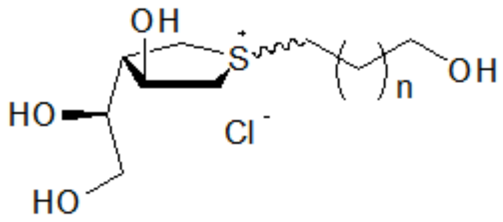


62 n = 10

100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

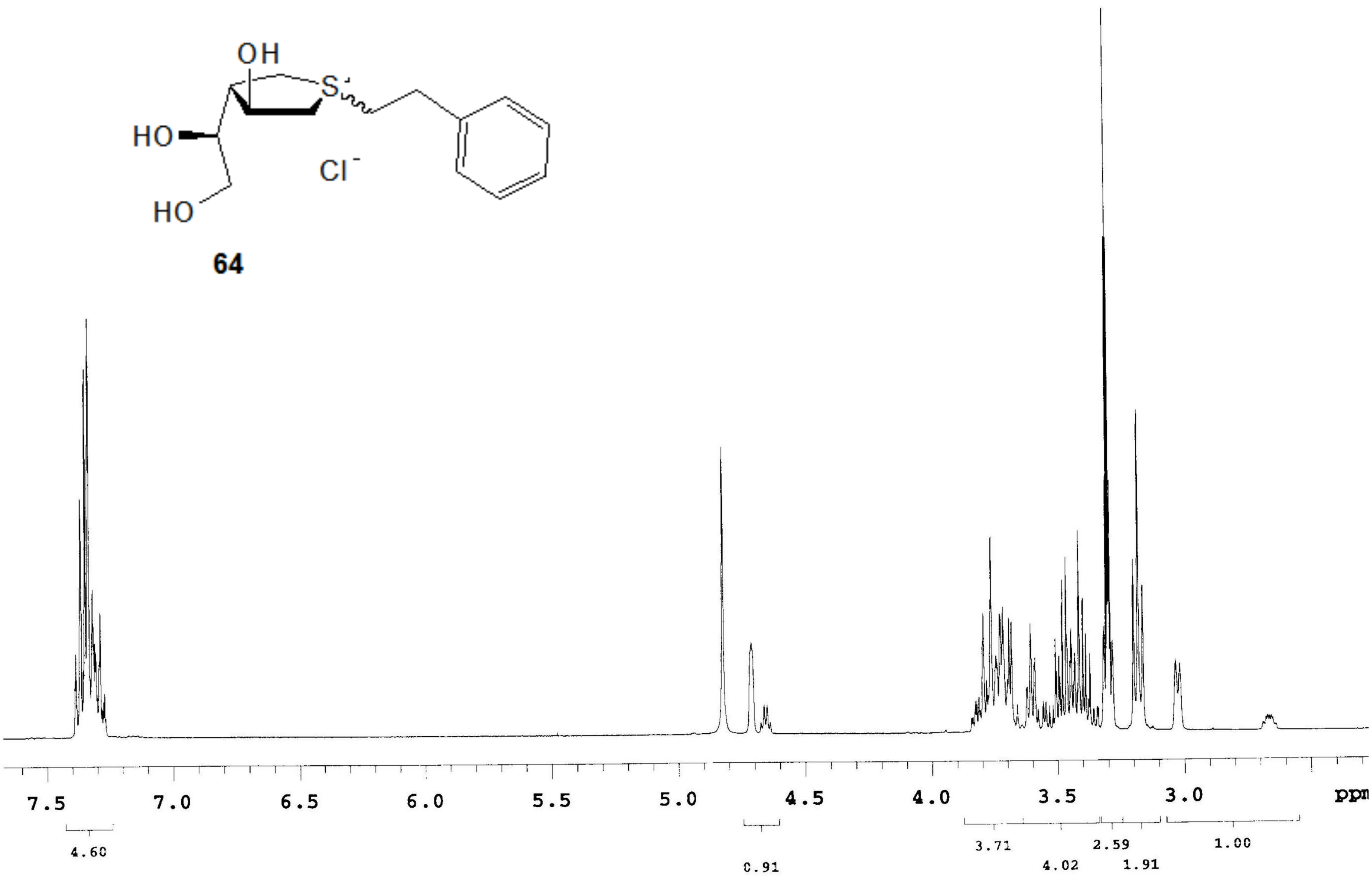




62 n = 10

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

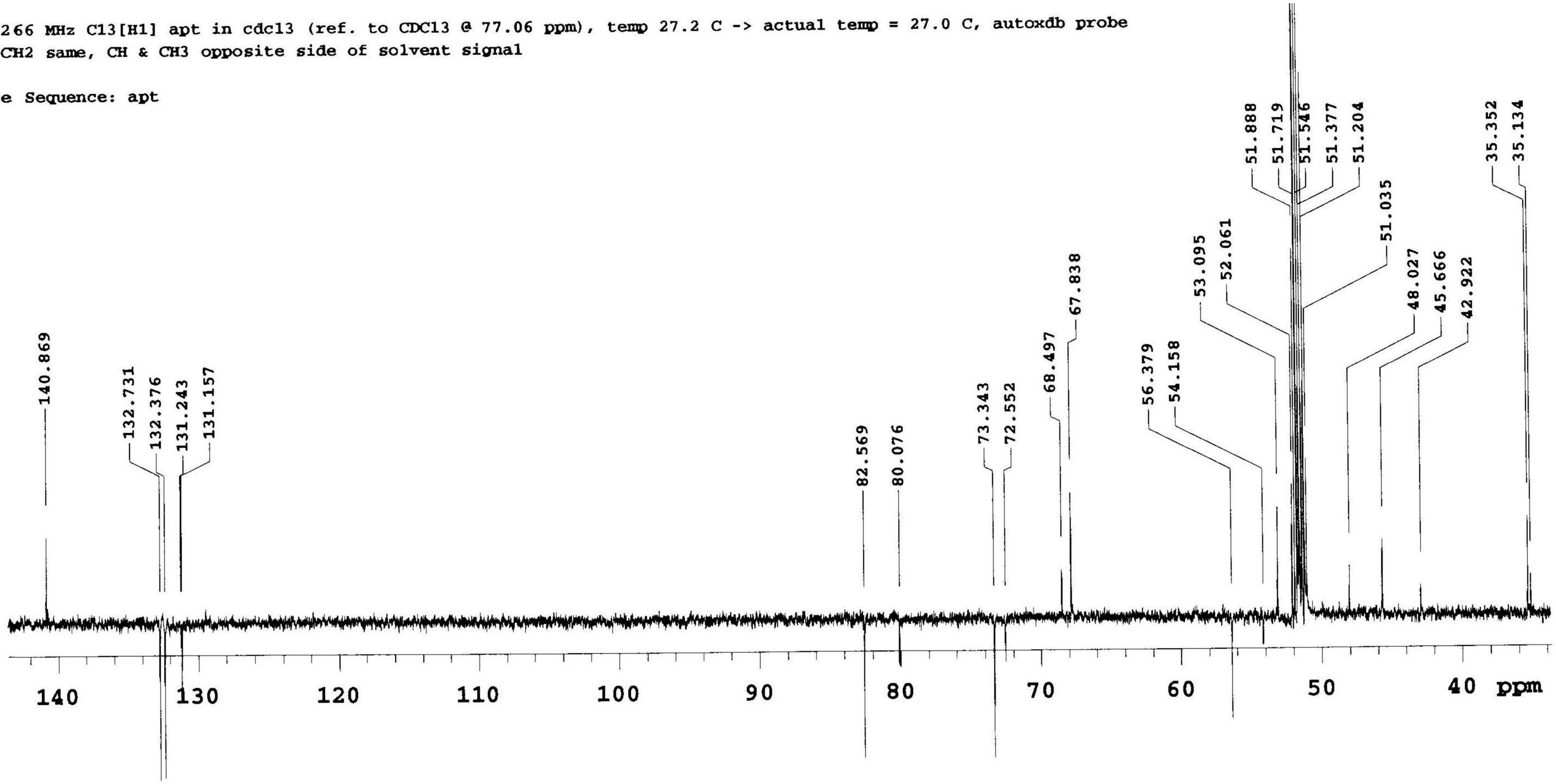
Pulse Sequence: s2pul

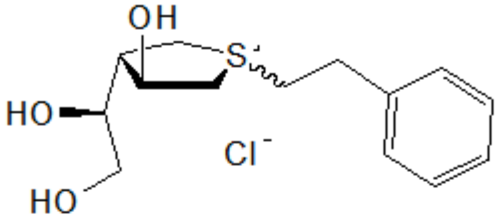


64

125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

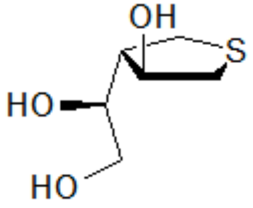




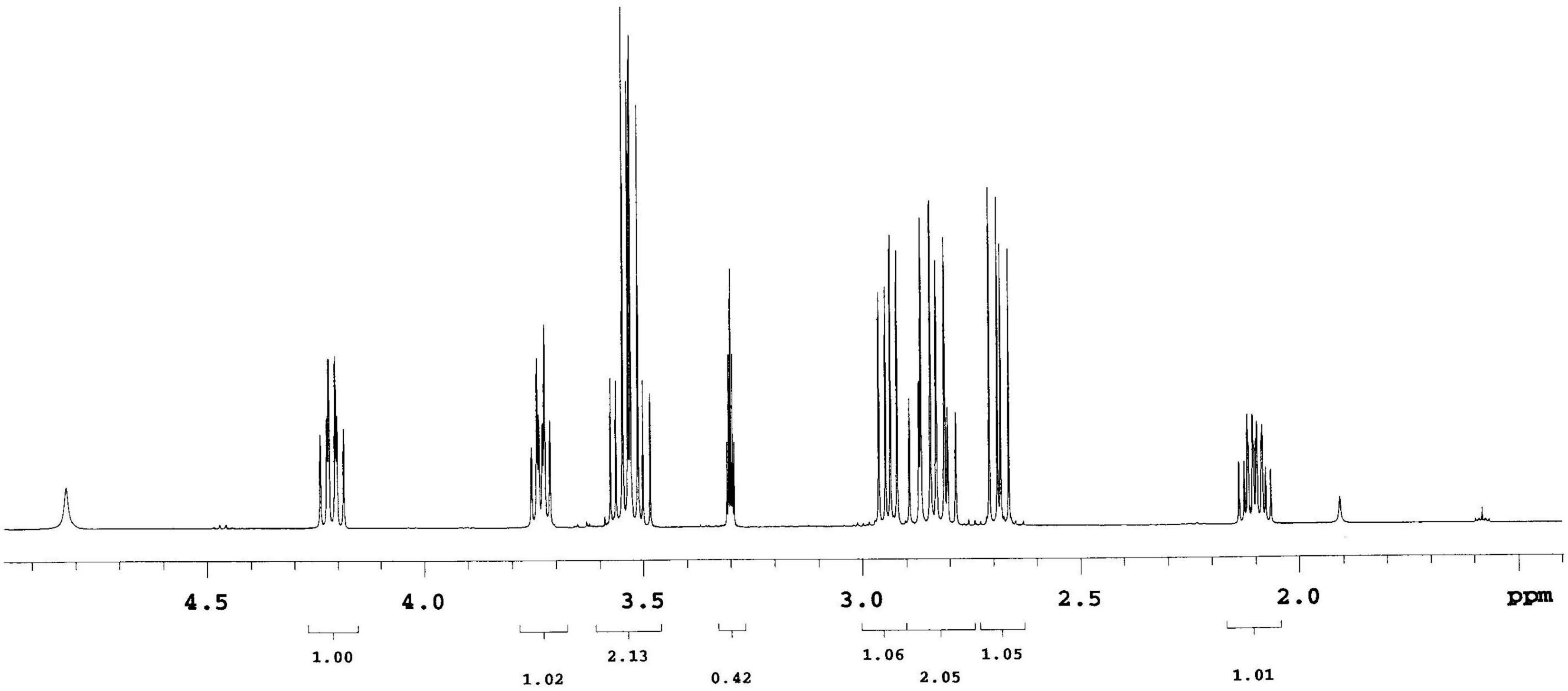
64

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

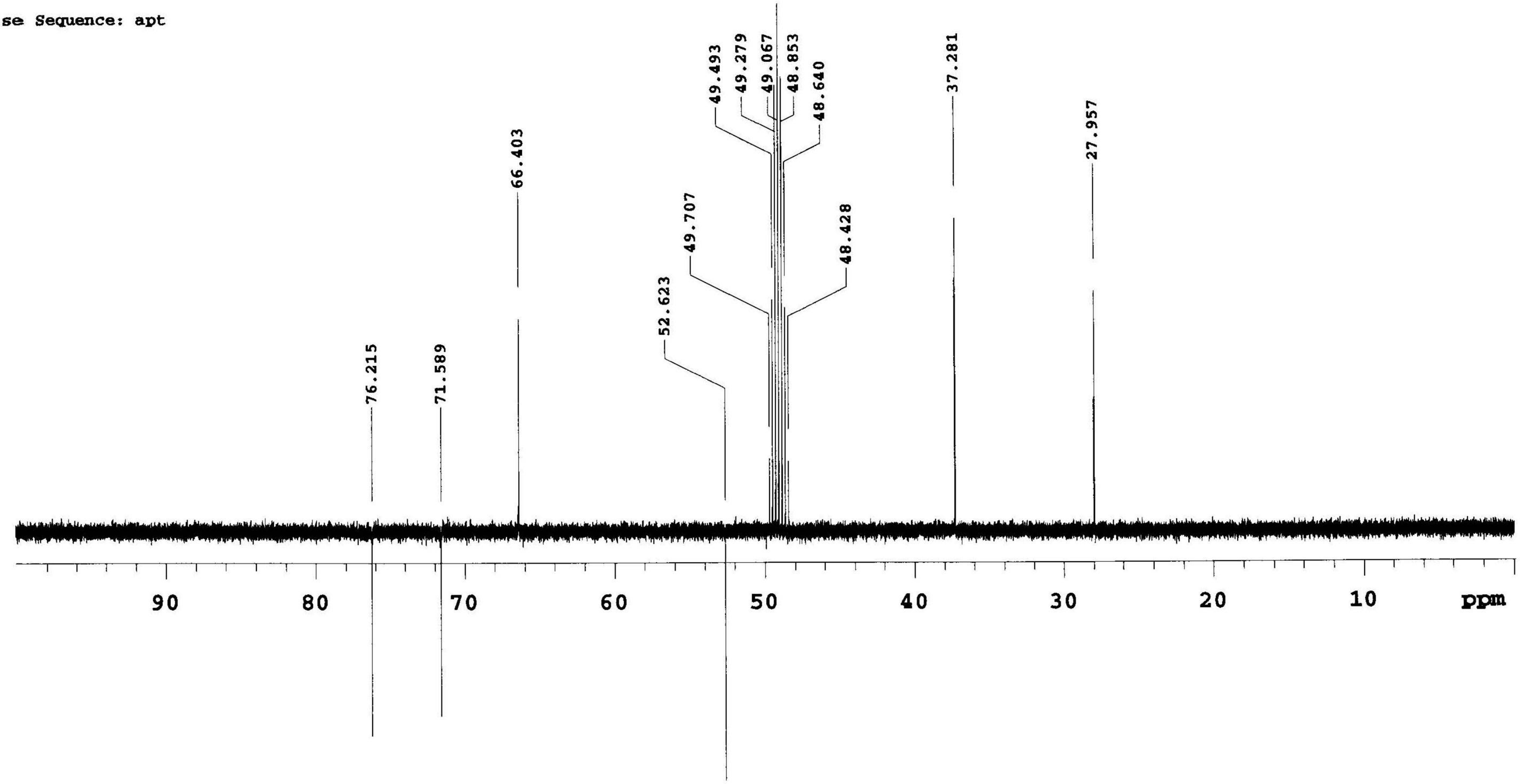


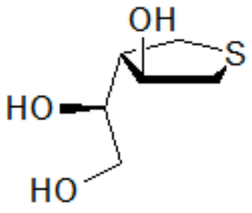
65



100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

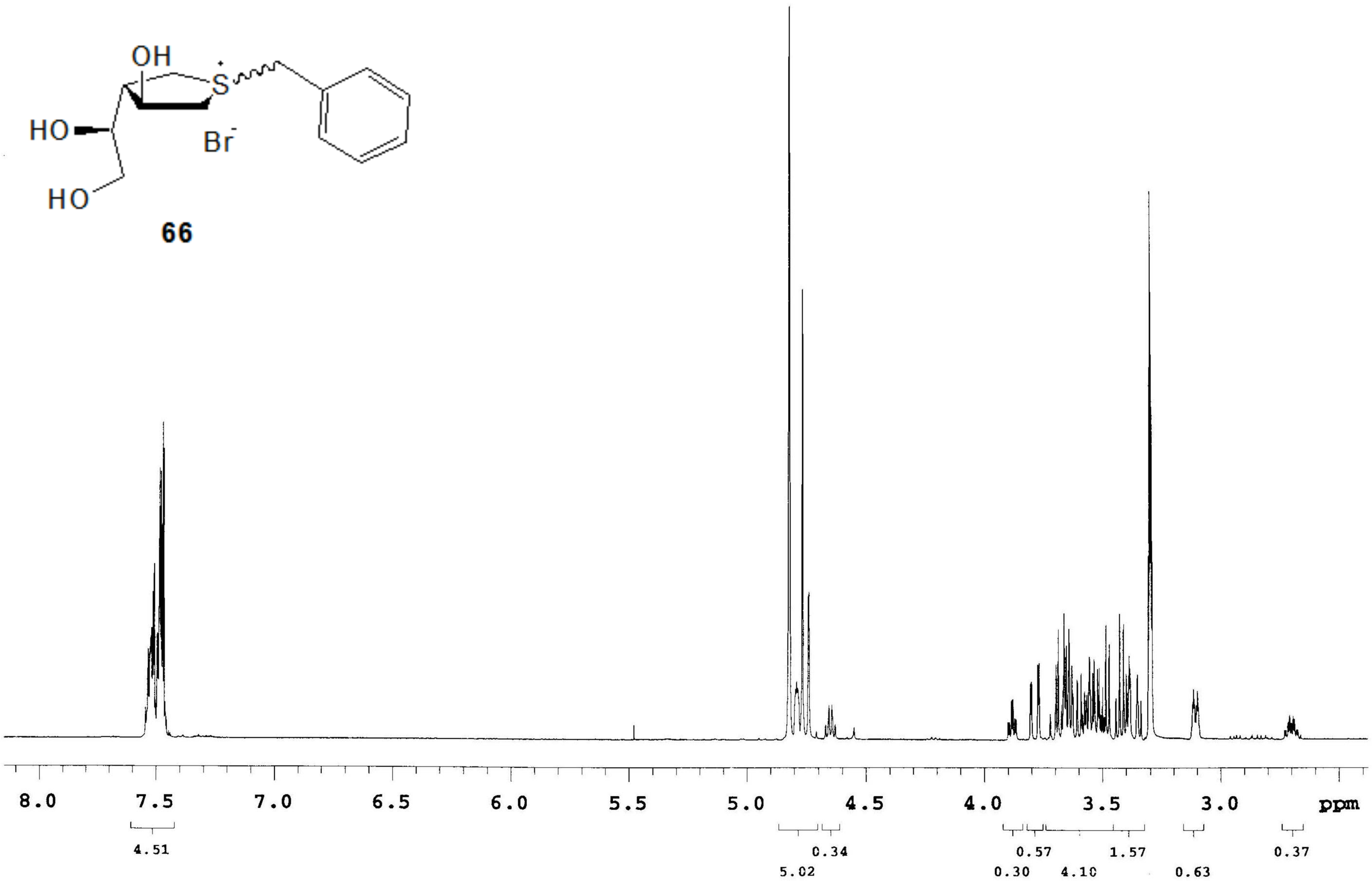




65

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

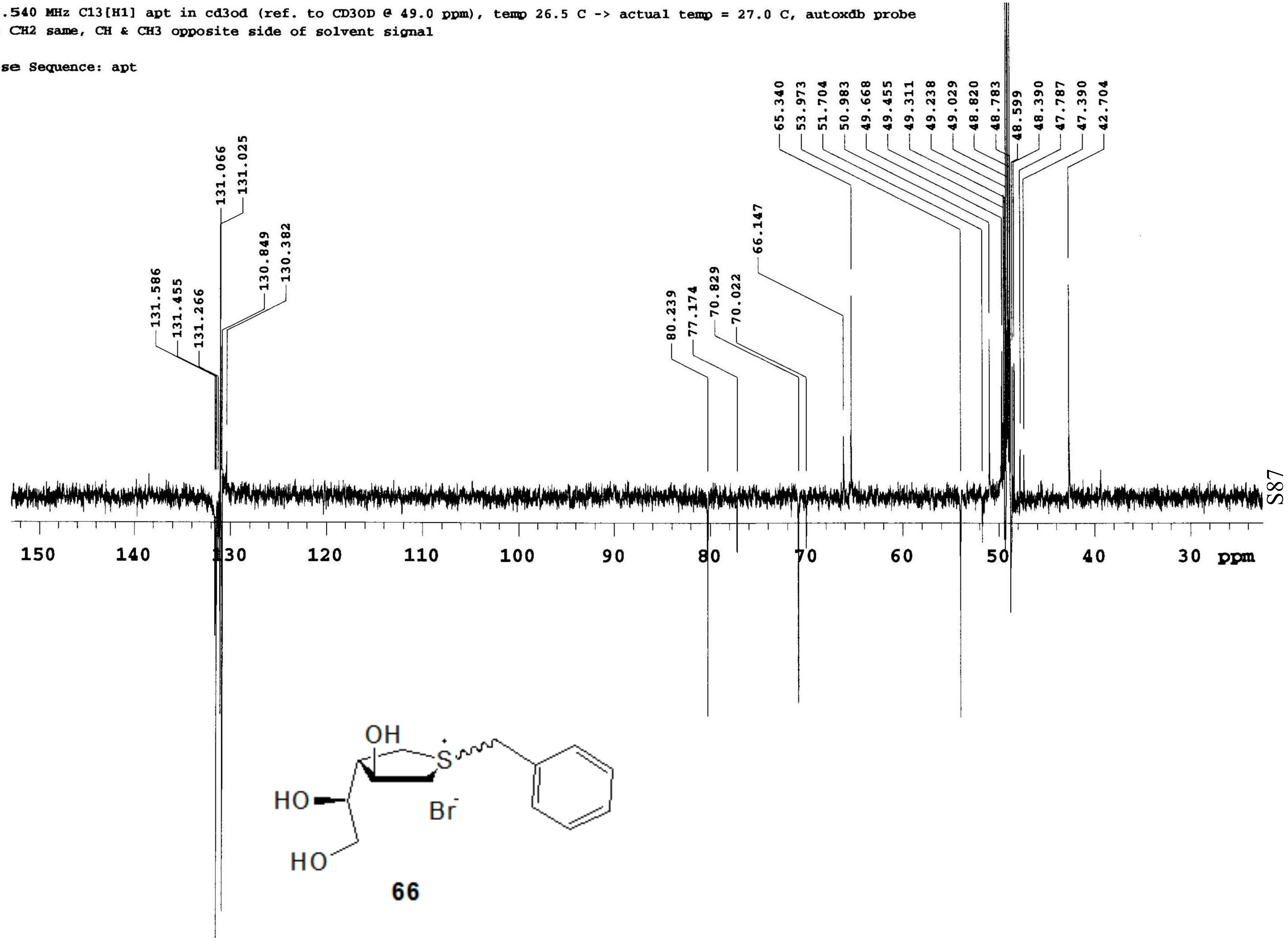
Pulse Sequence: s2pul



66

100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

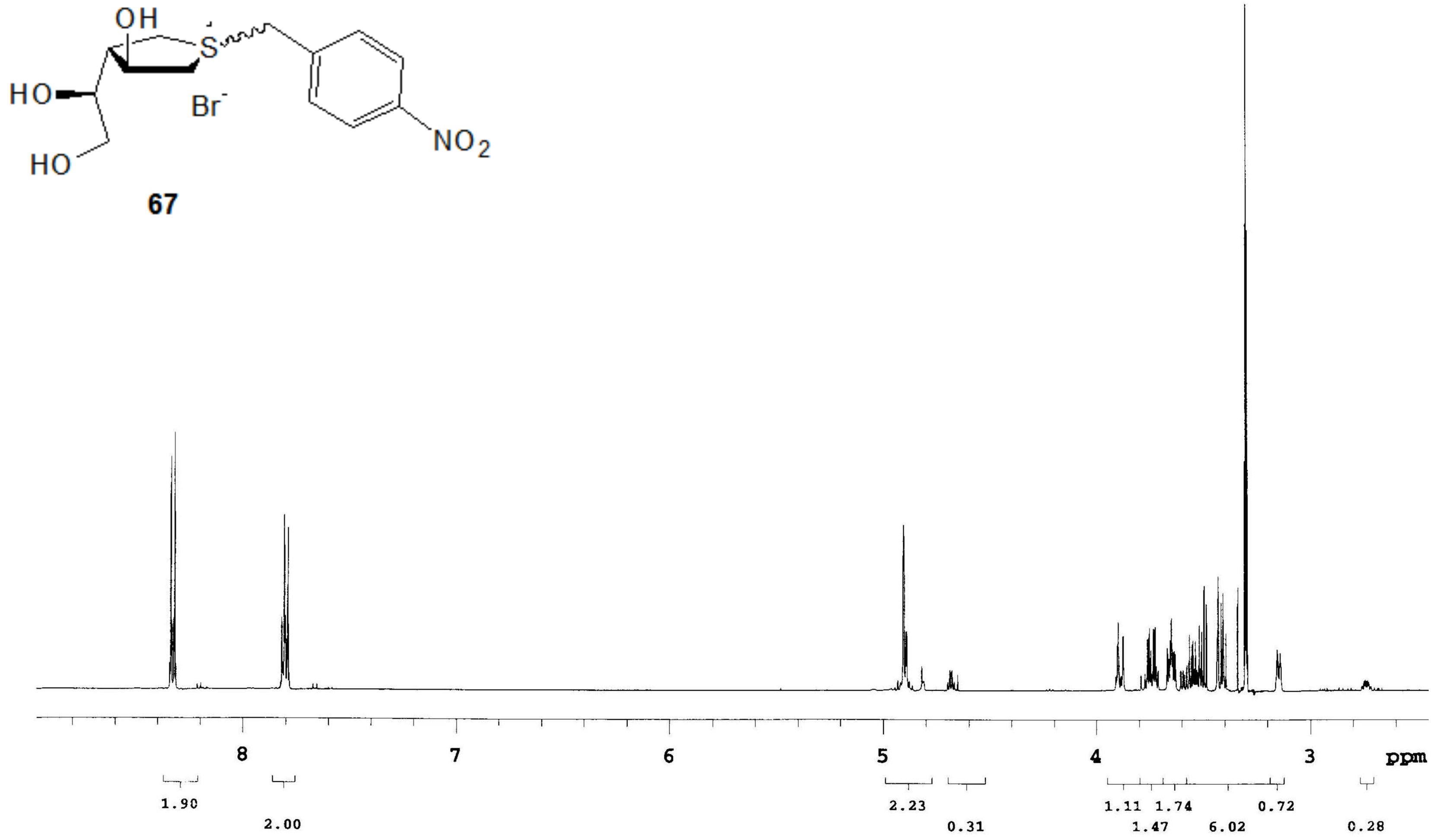
Pulse Sequence: apt



66

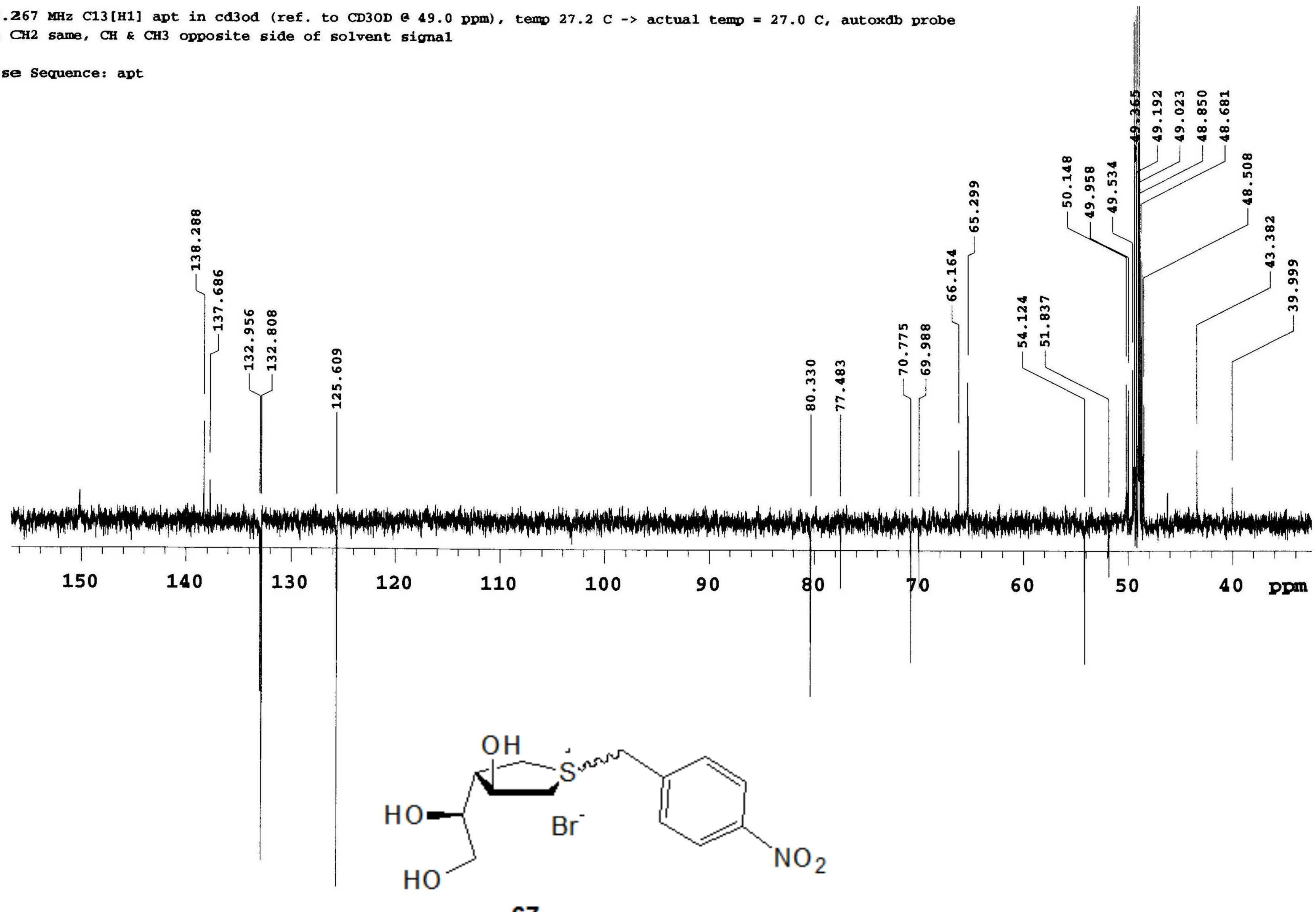
498.124 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul


67

125.267 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

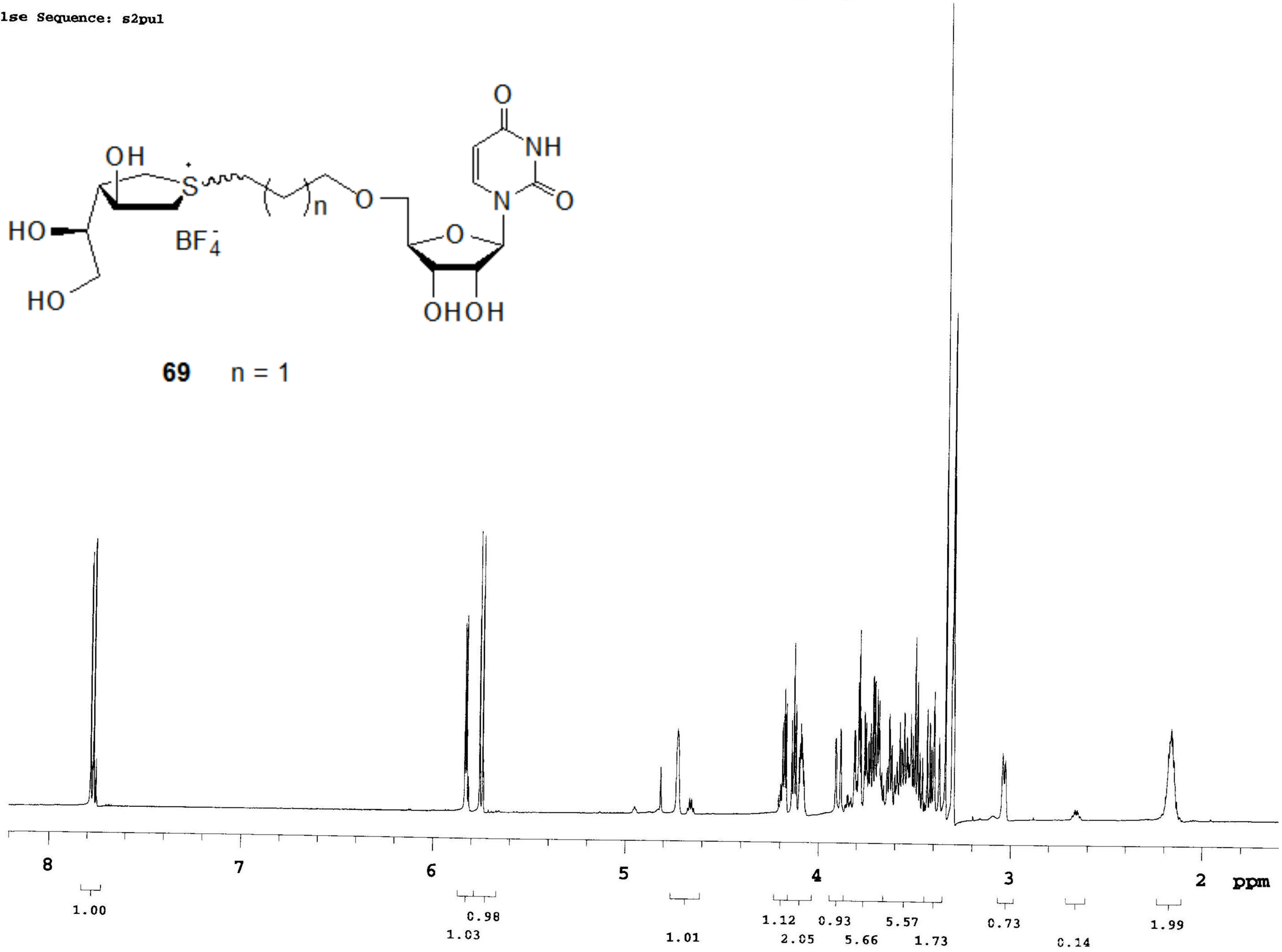


67

498.124 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

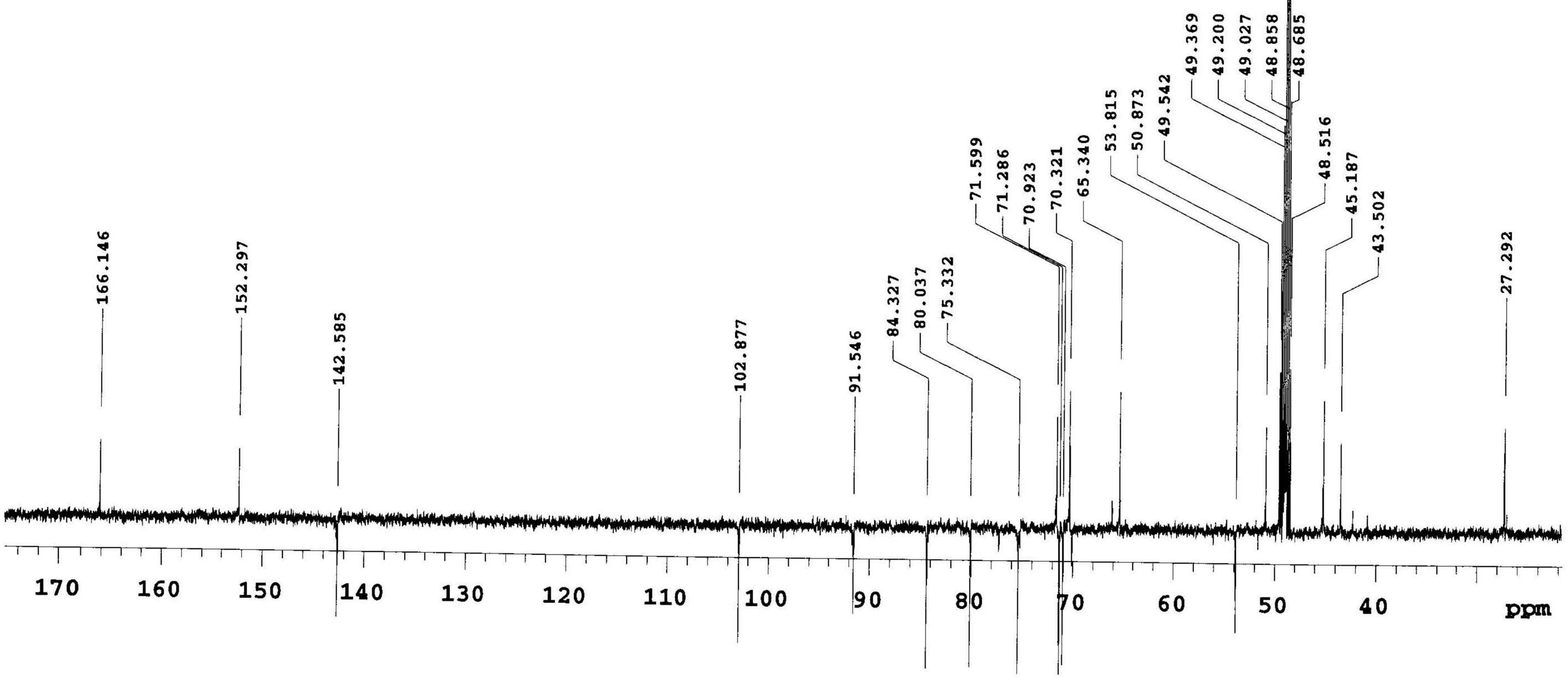
Pulse Sequence: s2pul

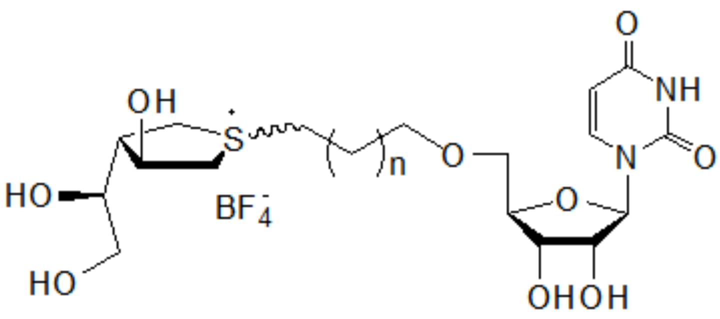
69 n = 1



125.267 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

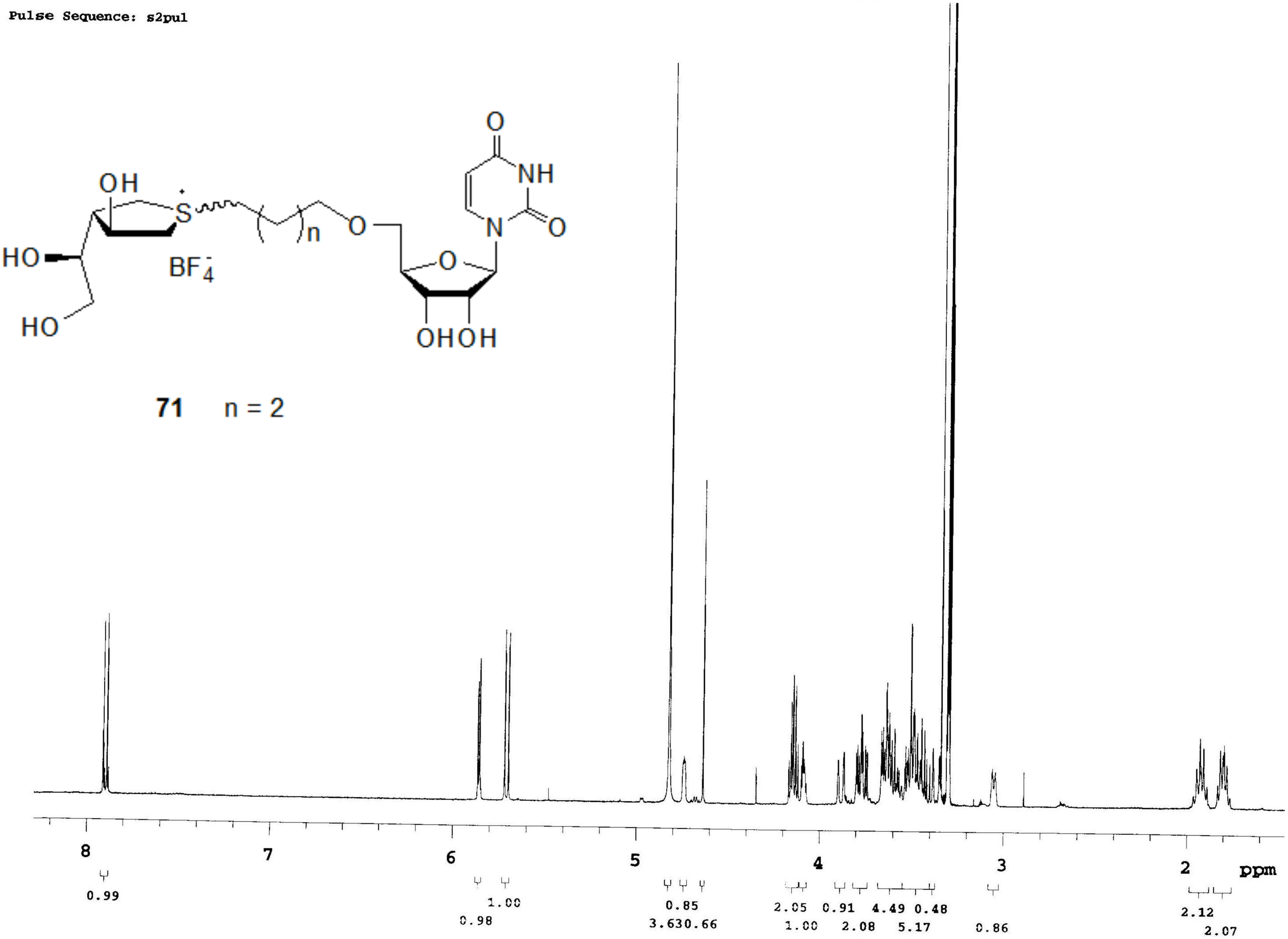




69 n = 1

399.796 MHz H1 1D in cd3od (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe

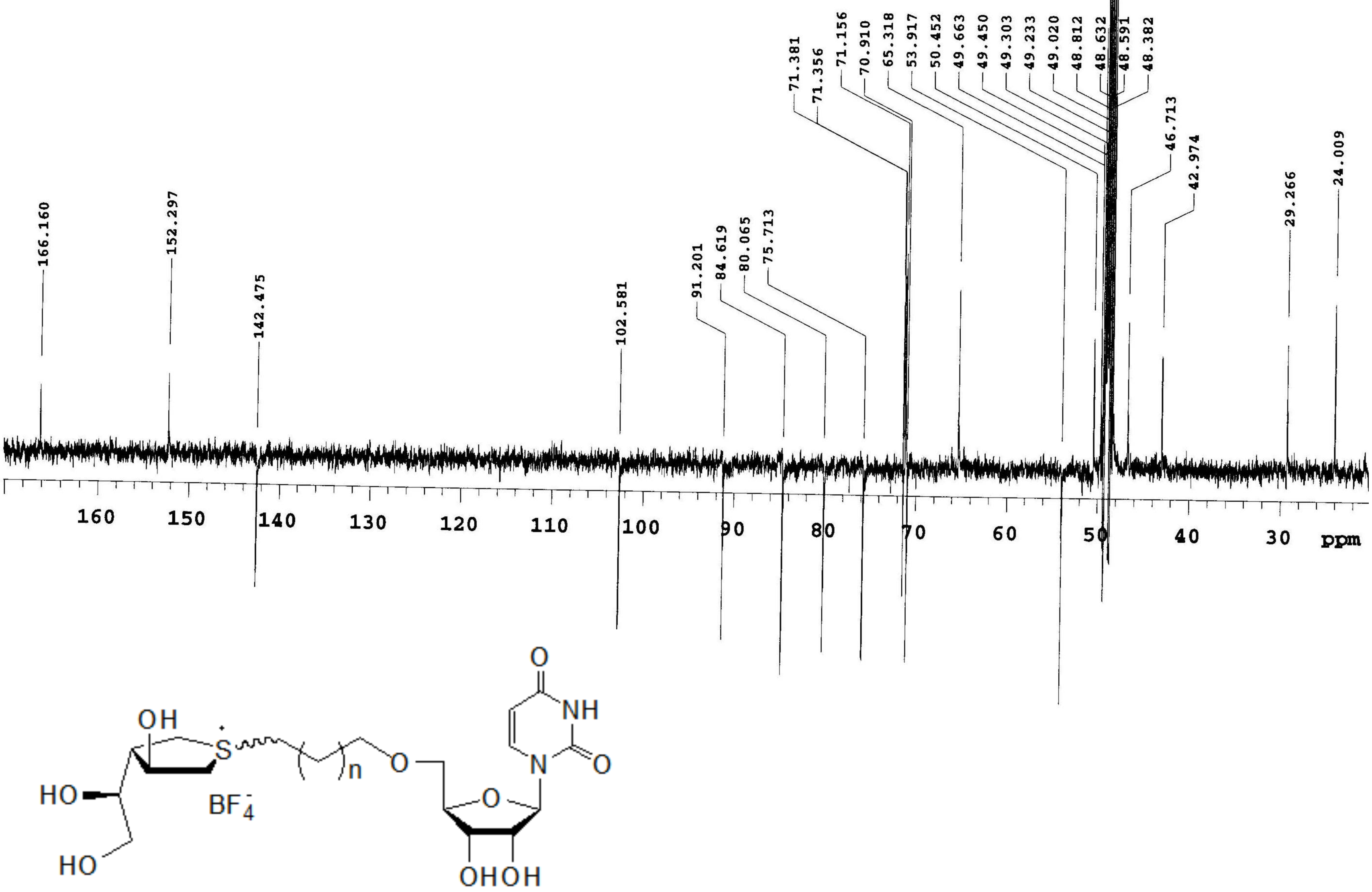
Pulse Sequence: s2pul



71 n = 2

100.540 MHz C13[H1] apt in cd3od (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt



71 n = 2