Supplementary Material

A Concise Route to Branched Erythrono-γ-Lactones. Synthesis of the Leaf-Closing Substance Potassium (±)-(2*R*,3*R*)-2,3,4-trihydroxy-2-methylbutanoate

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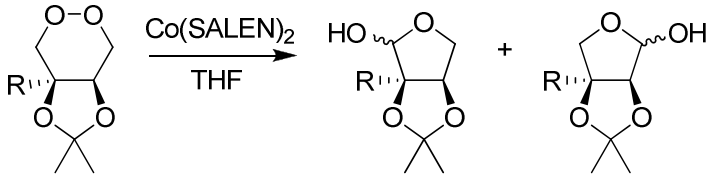
NMR Spectra

^{13}C NMR

^{1}H NMR

Table S1. Ring-opening of 1,2-dioxane 3

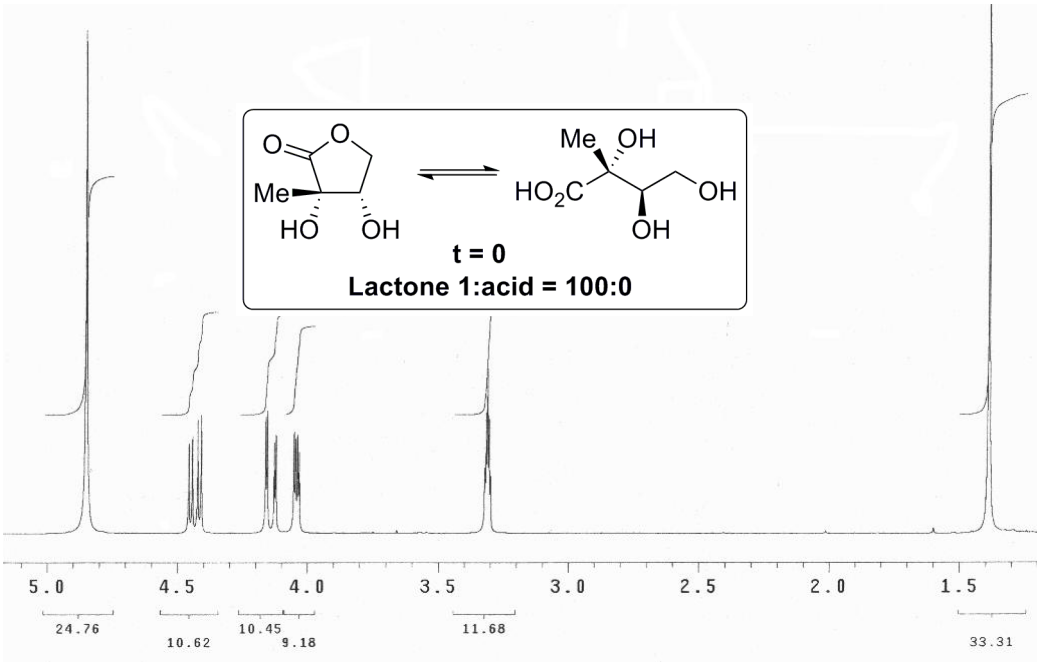


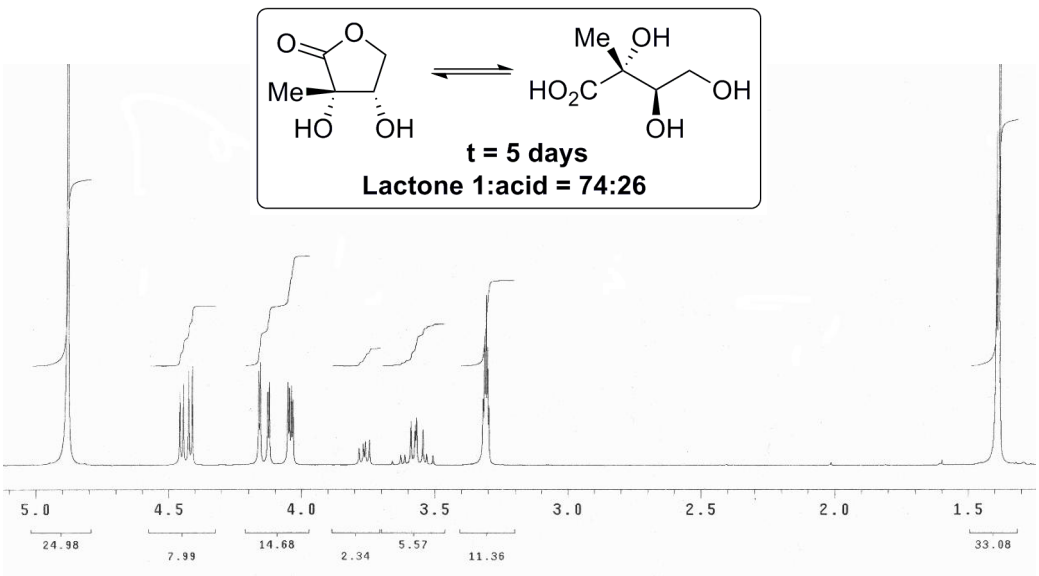
3 **4** **5**

R	Reagent[a]	**4:5**[b]	Solvent	Yield[e]
Ph	*R,R*-Jacobsen (5 mol %)	60:40	THF	high[f]
Ph	$CoSO_4.7H_2O$ (1.5 eq)	-	THF/H_2O	-
Ph	$(DHQ)_2PHAL$ (10 mol %)	50:50	THF	24 %
Ph	Rh(II) acetate dimer (10 mol %)	-	THF	-
Ph	$MnSO_4.2H_2O$ (1.6 eq)	-	THF/H_2O	-
Ph	Co(II)TPP (5 mol %)	53:47	THF	high[f]
Ph	Ferrocene (1 eq)	-	THF	-
Ph	$Cu(OAc)_2$ (10 mol %)	-	THF	-
Ph	$NiCl_2(PPh_3)_2$ (10 mol %)	-	THF	-
Ph	$FeSO_4.7H_2O$ (1.6 eq)	73:27	THF/H_2O[c]	high[f]
Ph	*R,R*-Jacobsen (5 mol %)	60:40	THF[c]	high[f]
Ph	*R,R*-Jacobsen (5 mol %)	60:40	THF[d]	high[f]
Ph	$FeCl_2(PPh_3)_2$ (20 mol %)	65:35	THF	high[f]

[a] Reactions performed with 25 mg of 1,2-dioxane and stirred at RT until completion was observed by TLC. [b] Ratio determined by ^{1}H NMR ($CDCl_3$) after 1 hr at RT. [c] 0 ^{o}C. [d] –20 ^{o}C. [e] Combined yield. [f] Products were not purified. ^{1}H NMR showed complete conversion and minimal by-products.

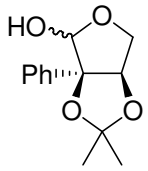
Figure S1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) showing the formation of open-chain acid (±)-2-*C*-Methyl-erythronic acid from lactone **1** in CD_3OD after 5 days.



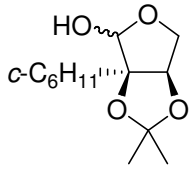


General Experimental

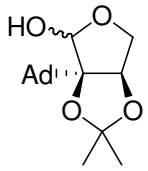
Reagents/solvents for anhydrous reactions were dried as follows: THF was distilled from sodium wire with benzophenone as indicator. Ether, dichloromethane, hexane, toluene, pyridine, *N*,*N*-dimethylformamide, triethylamine, dimethylsulfoxide and diisopropylamine were dried and stored over 4 Å molecular sieves. Methanol was dried and stored over 3 Å molecular sieves. Thin layer chromatography (TLC) was carried out on commercially available pre-coated aluminium plates ($60F_{254}$) and visualized under 254 nm light, or developed with Hanessian stain (2.5 g ammonium molybdate, 1 g cerium ammonium sulfate, 10 ml concentrated sulfuric acid, 90 ml water). Flash column chromatography was carried out using silica gel 60 (230-400 mesh). Dry Column Vacuum Chromatography (DCVC) was performed according to the published procedure.[1] ^{1}H, ^{13}C, DEPT, HMQC, COSY, and ROESY NMR spectra were recorded on 200, 300 or 600 Fourier transform spectrometers using an internal deuterium lock. $CDCl_3$, CD_3OD, DMSO-d_6 or tetramethyl silane were used as internal NMR standards. When D_2O was employed 3-(trimethylsilyl)proprionic-2,2,3,3-d_4 acid sodium salt (TSP-d_4) was used as an external NMR zero. Melting points were measured on a microscope hot stage melting point apparatus and are uncorrected. All yields reported refer to isolated material judged to be homogeneous by TLC and NMR spectroscopy.



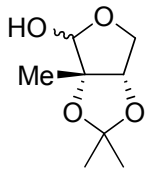
(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrofuranose (4a). Colourless oil (298 mg, 59.5%, 99% total); R_f 0.23 (2:3 ether/hexane); IR (neat): 3436, 1495, 1448, 1383, 1260, 1211, 1097, 1063 cm^{-1}; Major anomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.66 (s, 3H), 3.92 (dd, *J* = 3.3, 11.1 Hz, 1H), 3.97 (d, *J* = 11.7 Hz, 1H), 4.15 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 3.3 Hz, 1H), 4.90 (d, *J* = 11.7 Hz, 1H), 7.29-7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.6, 68.6, 86.9, 89.7, 104.2, 113.8, 124.6, 127.8, 128.6, 140.6; MS *m/z* (EI): 236 (M^+, 3), 219 (47), 178 (16), 161 (27), 132 (42), 105 (100); HRMS calcd. for M + Na) $C_{13}H_{16}O_4Na$: 259.0946; Found: 259.0943.
Minor anomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 3H), 1.59 (s, 3H), 2.22 (br s, 1H), 4.11 (d, *J* = 10.4 Hz, 1H), 4.39 (dd, *J* = 3.6, 10.4 Hz, 1H), 4.96 (d, *J* = 3.6 Hz, 1H), 5.34 (s, 1H), 7.30-7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.6, 27.0, 72.9, 86.3, 94.8, 103.3, 112.9, 126.2, 127.9, 128.0, 139.0.



(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrofuranose (4b). Colourless solid (337 mg, 42%, 97% total); mp 118-121 ^oC; R_f 0.41 (3:37 ether/CH_2Cl_2); IR (nujol): 3384, 1244, 1216, 1094, 1056, 979 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.02-1.32 (m, 5H), 1.45 (s, 3H), 1.56 (s, 3H), 1.58-1.86 (m, 6H), 3.50 (dd, *J* = 3.6, 11.1 Hz, 1H), 3.93 (d, *J* = 3.3 Hz, 1H), 3.97 (d, *J* = 3.6 Hz, 1H), 4.52 (d, *J* = 3.3 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 26.2, 26.2, 27.3, 27.4, 27.5, 27.7, 42.6, 68.1, 83.0, 91.7, 98.2, 113.2; MS *m/z* (EI): 242 (M^+, 5), 227 (27), 184 (32), 138 (58), 96 (54), 83 (100), 55 (95); Anal. calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; Found: C, 64.58; H, 9.05.

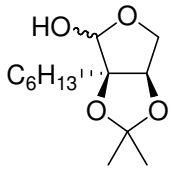


(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrofuranose (4c). Colourless solid (322 mg, 45%, 98% total); mp 164-166 ^{o}C; R_f 0.41 (1:19 ether/CH_2Cl_2); IR (nujol): 3480, 1423, 1368, 1238, 1222, 1107, 1088, 1057 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 3H), 1.58 (s, 3H), 1.62-1.78 (m, 12H), 2.03 (br s, 3H), 3.42 (dd, *J* = 3.3, 11.1 Hz, 1H), 3.92 (d, *J* = 11.1 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 3.3 Hz, 1H), 5.16 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.6, 27.9, 28.0, 35.3, 36.8, 37.2, 69.0, 81.0, 94.6, 96.2, 113.7; MS *m/z* (EI): 294 (M^+, 3), 236 (12), 190 (14), 162 (19), 135 (100); Anal. Calcd. for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90; Found: C, 69.62; H, 8.90.



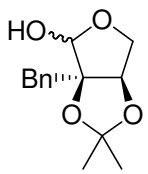
(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrofuranose 4d.[2] Colourless oil (200 mg, 46%, 86% total); R_f 0.31 (3:17 ether/CH_2Cl_2); IR (neat): 3430, 1456, 1379, 1247, 1212, 1095, 1016 cm^{-1}; Major anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 3H), 1.47 (s, 3H), 1.54 (s, 3H), 3.57 (dd, *J* = 3.3, 11.1 Hz, 1H), 3.82 (d, *J* = 11.4 Hz, 1H), 3.96 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 3.3 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 26.7, 27.0, 67.2, 85.0, 86.1, 101.5, 113.0; MS *m/z* (EI): 174 (M^+, 1), 159 (57), 116 (33), 99 (23), 71 (55), 55 (85), 43 (100).

Minor anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.45 (s, 3H), 1.50 (s, 3H), 2.54 (br s, 1H), 3.93 (d, *J* = 10.5 Hz, 1H), 4.10 (dd, *J* = 3.6, 10.5 Hz, 1H), 4.42 (d, *J* = 3.6 Hz, 1H), 5.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 27.5, 27.7, 71.8, 86.2, 91.5, 103.4, 112.5.



(±)-2,3-*O*-Isopropylidene-2-*C*-hexyl-erythrofuranose (4e). Colourless gum (0.35 g, 46%, 99% total); R_f 0.45 (2:23 acetone/CH_2Cl_2); IR (neat): 3435, 2932, 1459, 1379, 1244, 1108, 1055 cm^{-1}; Major anomer: ^1H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7 Hz, 3H), 1.25-1.35 (m, 6H), 1.39-1.49 (m, 2H), 1.43 (d, *J* = 0.5 Hz, 3H), 1.54 (d, *J* = 0.5 Hz, 3H), 1.64-1.76 (m, 2H), 3.54 (dd, *J* = 3.5, 11 Hz, 1H), 3.85 (d, *J* = 11.5, 1H), 3.94 (d, *J* = 11 Hz, 1H), 4.39 (d, *J* = 3.5 Hz, 1H), 4.74 (dd, *J* = 0.5, 11.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 23.6, 27.1, 27.3, 29.6, 31.6, 35.4, 67.6, 84.4, 89.1, 100.3, 113.2; MS *m/z* (+EI): 244 (M^+, 9), 229 (100), 169 (41), 151 (6), 140 (9), 133 (11), 113 (9), 109 (12); HRMS calcd. for M + Na) $C_{13}H_{24}O_4Na$: 267.1572; Found: 267.1576; Anal. calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90; Found: C, 63.93; H, 10.00.

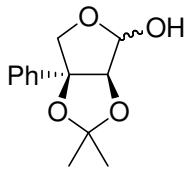
Minor anomer: ^1H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7 Hz, 3H), 1.25-1.35 (m, 6H), 1.39-1.49 (m, 2H), 1.40 (d, *J* = 0.5 Hz, 3H), 1.46 (d, *J* = 0.5 Hz, 3H), 1.88 (ddd, *J* = 6, 10.5, 14, 2H), 2.54 (d, *J* = 2.5 Hz, 1H), 3.88 (dd, *J* = 0.5, 10.5 Hz, 1H), 4.08 (ddd, *J* = 0.5, 4, 10.5 Hz, 1H), 4.42 (d, *J* = 4 Hz, 1H), 5.28 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.1, 22.6, 24.4, 27.7, 28.3, 29.8, 31.7, 33.1, 72.1, 85.4, 94.5, 102.7, 112.7.



(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrofuranose (4f). Colourless oil (434 mg, 45%, 98% total); R_f 0.42 (1:9 ether/CH_2Cl_2); IR (neat): 3434, 1498, 1455, 1381, 1218, 1058, 703 cm^{-1}; Major anomer: ^1H NMR (600 MHz, $CDCl_3$): δ 1.12 (s, 3H), 1.51 (s, 3H), 2.99 (d, *J* = 14.4 Hz, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 3.48 (dd, *J* = 3.0, 10.8 Hz, 1H), 3.77 (d, *J* = 5.4 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 1H), 4.57 (d, *J* = 3.0 Hz, 1H), 4.85 (d, *J* = 5.4 Hz, 1H), 7.22-7.33 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 27.3,

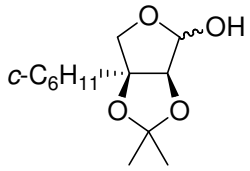
40.5, 67.6, 83.1, 89.2, 100.0, 113.7, 127.1, 128.4, 130.6, 135.2; MS *m/z* (EI): 250 (M^+, 5), 235 (15), 192 (21), 146 (100), 118 (33), 91 (90), 55 (88); Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; Found: C, 66.92; H, 7.24; HRMS calcd. for M + Na) $C_{14}H_{18}O_4Na$: 273.1103; Found: 273.1104.

Minor anomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.20 (s, 3H), 1.44 (s, 3H), 2.58 (br s, 1H), 3.06 (d, *J* = 14.4 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 4.18 (dd, *J* = 4.2, 10.2 Hz, 1H), 4.59 (d, *J* = 4.2 Hz, 1H), 5.22 (d, *J* = 3.0 Hz, 1H), 7.23-7.37 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 27.8, 28.2, 38.4, 72.2, 84.9, 94.4, 102.6, 113.4, 126.4, 127.9, 130.8, 137.2.



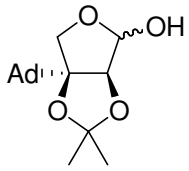
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrofuranose (5a). Colourless solid (198 mg, 39.5%, 99% total); mp 151-152 ^{o}C; R_f 0.36 (2:3 ether/hexane); IR (nujol): 3365, 1493, 1335, 1263, 1068, 912 cm^{-1}; Major anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 3H), 1.59 (s, 3H), 2.71 (d, *J* = 2.1 Hz, 1H), 4.09 (d, *J* = 10.2 Hz, 1H), 4.18 (d, *J* = 10.2 Hz, 1H), 4.62 (s, 1H), 5.57 (d, *J* = 2.1 Hz, 1H), 7.25-7.40 (m, 3H), 7.56-7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 27.0, 80.6, 92.1, 92.9, 102.7, 112.8, 125.4, 127.4, 128.2, 141.2; MS *m/z* (EI): 236 (M^+, 7), 221 (89), 161 (97), 147 (95), 132 (53), 105 (86), 43 (100); Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83; Found: C, 66.30; H, 6.81.

Minor anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (s, 3H), 1.65 (s, 3H), 2.84 (br s, 1H), 3.52 (d, *J* = 10.8 Hz, 1H), 4.08 (d, *J* = 10.8 Hz, 1H), 4.56 (d, *J* = 3.3 Hz, 1H), 5.28 (d, *J* = 3.3 Hz, 1H), 7.25-7.40 (m, 5H).



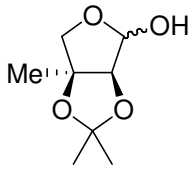
(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrofuranose (5b). Colourless solid (442 mg, 55%, 97% total); mp 74.5-75.5 °C; R_f 0.24 (3:37 ether/CH_2Cl_2); IR (nujol): 3387, 1333, 1246, 1208, 1100, 1082, 1064 cm^{-1}; Major anomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.10-1.31 (m, 5H), 1.40 (s, 3H), 1.46 (s, 3H), 1.56-1.86 (m, 6H), 2.59 (br s, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 4.09 (d, *J* = 9.9 Hz, 1H), 4.32 (s, 1H), 5.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.3, 26.4, 27.9, 28.0, 28.2, 28.3, 43.6, 75.5, 87.6, 95.0, 102.6, 112.9; MS *m/z* (EI): 242 (M^+, 2), 227 (100), 209 (13), 167 (15), 149 (20), 71 (26); Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; Found: C, 64.47; H, 9.07.

Minor anomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.10-1.31 (m, 5H), 1.44 (s, 3H), 1.54 (s, 3H), 1.56-1.86 (m, 6H), 3.60 (d, *J* = 10.5 Hz, 1H), 3.86 (d, *J* = 10.5 Hz, 1H), 3.89 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 3.0 Hz, 1H), 4.93 (d, *J* = 3.0, 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 26.3, 26.4, 27.8, 27.9, 28.1, 28.2, 43.5, 71.5, 81.9, 94.1, 97.8, 113.9.



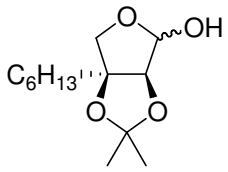
(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrofuranose (5c). Colourless solid (385 mg, 53%, 98% total); mp 163-165 °C; R_f 0.20 (1:19 ether/CH_2Cl_2); IR (nujol): 3415, 1370, 1244, 1105, 1088, 1064, 1052, 858 cm^{-1}; Major anomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.49 (s, 3H), 1.60-1.78 (m, 12H), 2.02 (br s, 3H), 2.36 (d, *J* = 2.7 Hz, 1H), 3.89 (d, *J* = 9.9 Hz, 1H), 4.33 (d, *J* = 9.9 Hz, 1H), 4.39 (s, 1H), 5.38 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 28.0, 28.1, 35.9, 36.9, 37.8, 73.1, 85.4, 98.1, 103.0, 112.9; MS *m/z* (EI): 294 (M^+, 1), 279 (84), 219 (8), 194 (10), 135 (100); Anal. Calcd. for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90; Found: C, 69.52; H, 8.86.

Minor anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, 3H), 1.57 (s, 3H), 1.60-1.78 (m, 12H), 2.02 (br s, 3H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.83 (d, *J* = 12.0 Hz, 1H), 3.92 (d, *J* = 10.8 Hz, 1H), 4.26 (d, *J* = 2.7 Hz, 1H), 4.86 (dd, *J* = 2.7, 12.0 Hz, 1H).



(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrofuranose (5d).[3] Colourless oil (177 mg, 40%, 86% total); R_f 0.24 (3:17 ether/CH_2Cl_2); IR (neat): 3419, 1456, 1379, 1208, 1136, 1070, 991 cm^{-1}; Major anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s. 3H), 1.46 (s, 3H), 1.56 (s, 3H), 2.62 (br s, 1H), 3.90 (d, *J* = 9.6 Hz, 1H), 4.00 (d, *J* = 9.6 Hz, 1H), 4.23 (s, 1H), 5.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1, 27.3, 27.5, 77.7, 88.6, 90.0, 102.4, 112.4; MS *m/z* (EI): 174 (M^+, 2), 159 (100), 99 (26), 85 (17), 71 (46), 59 (73), 43 (62).

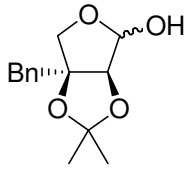
Minor anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, 3H), 1.50 (s, 3H), 1.53 (s, 3H), 3.33 (d, *J* = 10.5 Hz, 1H), 3.90 (d, *J* = 10.5 Hz, 1H), 3.95 (d, *J* = 12.0 Hz, 1H), 4.15 (d, *J* = 3.3 Hz, 1H), 5.04 (dd, *J* = 3.3, 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.7, 27.4, 27.7, 73.7, 84.2, 88.2, 97.8, 113.8.



(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrofuranose (5e). Colourless gum (0.41 g, 53%, 99% total); R_f 0.35 (2:23 acetone/CH_2Cl_2); IR (neat): 3427, 2934, 1459, 1371, 1246, 1215, 1071, 992 cm^{-1}; Major anomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7 Hz, 3H), 1.25-1.37 (m, 6H), 1.39 (d, *J* = 0.5 Hz, 3H), 1.39 (m, *J* = 0.5 Hz, 3H), 1.46-1.51 (m, 2H), 1.75-1.83 (m, 2H), 2.56 (d, *J* = 2.5 Hz, 1H), 3.95-3.99 (m, 2H), 4.16 (s, 1H), 5.33 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.6, 24.6, 27.7, 27.8, 29.6, 31.7, 36.9, 76.7, 89.1, 92.0, 102.4, 112.6; MS *m/z* (+EI): 229 (75), 169 (100), 151 (8), 133 (25), 123 (12), 109 (37), 81 (6); HRMS calcd. for M +

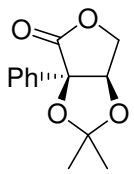
Na) $C_{13}H_{24}O_4Na$: 267.1572; Found: 267.1575; Anal. calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90; Found: C, 63.89; H, 9.75.

Minor anomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.82 (t, *J* = 7 Hz, 3H), 1.25-1.37 (m, 6H), 1.38 (d, *J* = 0.5 Hz, 3H), 1.47 (d, *J* = 0.5 Hz, 3H), 1.46-1.51 (m, 2H), 1.60-1.65 (m, 2H), 3.36 (d, *J* = 10.5 Hz, 1H), 3.82 (d, *J* = 10.5 Hz, 1H), 3.84 (d, *J* = 12 Hz, 1H), 4.07 (d, *J* = 3 Hz, 1H), 4.92 (ddd, *J* = 0.5, 3, 12, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 24.2, 27.6, 28.0, 29.6, 31.6, 36.6, 72.8, 83.4, 91.4, 97.7, 113.8.

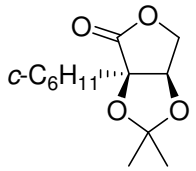


(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrofuranose (5f). Colourless oil (506 mg, 53%, 98% total); R_f 0.31 (1:9 ether/CH_2Cl_2); IR (neat): 3418, 1497, 1456, 1372, 1213, 1151, 1065, 703 cm^{-1}; Major anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (s, 3H), 1.44 (s, 3H), 2.55 (d, *J* = 2.7 Hz, 1H), 3.08 (d, *J* = 14.1 Hz, 1H), 3.17 (d, *J* = 14.1 Hz, 1H), 3.86 (d, *J* = 9.9 Hz, 1H), 4.06 (d, *J* = 9.9 Hz, 1H), 4.35 (s, 1H), 5.42 (d, *J* = 2.7 Hz, 1H), 7.21-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.5, 27.8, 42.7, 76.8, 88.5, 91.7, 102.3, 113.1, 126.7, 128.2, 130.3, 136.7; MS *m/z* (EI): 250 (M^+, 3), 235 (100), 157 (13), 145 (18), 129 (17), 91 (37); HRMS calcd. for M + Na) $C_{14}H_{18}O_4Na$: 273.1103; Found: 273.1104.

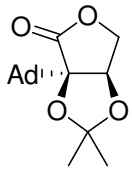
Minor anomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 3H), 1.53 (s, 3H), 3.00 (d, *J* = 14.1 Hz, 1H), 3.10 (d, *J* = 14.1 Hz, 1H), 3.53 (d, *J* = 10.5 Hz, 1H), 3.78 (d, *J* = 10.5 Hz, 1H), 3.92 (d, *J* = 11.7 Hz, 1H), 4.29 (d, *J* = 3.3 Hz, 1H), 5.00 (dd, *J* = 3.3, 11.7 Hz, 1H), 7.21-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 27.8, 42.1, 72.5, 82.8, 91.2, 97.6, 114.4, 127.0, 128.4, 130.2, 135.8.



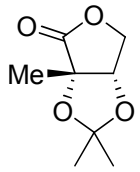
(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrono-1,4-lactone (8a). Colourless solid (223 mg, 90%); mp 85-86 °C; R_f 0.33 (2:3 ether/hexane); IR (nujol): 1770, 1499, 1479, 1271, 1238, 1195, 1055, 996 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 3H), 1.60 (s, 3H), 4.48 (dd, *J* = 3.3, 11.1 Hz, 1H), 4.55 (d, *J* = 11.1 Hz, 1H), 4.70 (d, *J* = 3.3 Hz, 1H), 7.41 (br s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 27.0, 69.0, 82.1, 86.0, 113.9, 125.1, 129.1, 129.2, 134.3, 175.5; MS *m/z* (EI): 234 (M^+, 19), 219 (7), 176 (24), 161 (36), 132 (60), 105 (100), 77 (23); Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02; Found: C, 66.53; H, 6.06.



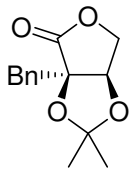
(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrono-1,4-lactone (8b). Colourless needles (242 mg, 89%); mp 86-88 °C; R_f 0.41 (CH_2Cl_2); IR (nujol): 1769, 1247, 1221, 1171, 1086, 1018 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98-1.34 (m, 5H), 1.40 (s, 3H), 1.44 (s, 3H), 1.64-2.05 (m, 6H), 4.25 (dd, *J* = 3.6, 10.8 Hz, 1H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 25.8, 26.1, 26.7, 26.7, 27.0, 27.2, 40.0, 70.8, 77.3, 87.3, 112.7, 177.0; MS *m/z* (EI): 240 (M^+, 6), 225 (100), 182 (27), 167 (39), 138 (25), 83 (33); Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; Found: C, 65.23; H, 8.47.



(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrono-1,4-lactone (8c). Colourless needles (234 mg, 83%); mp 167.5-168.5 °C; R_f 0.39 (CH_2Cl_2); IR (nujol): 1763, 1349, 1243, 1229, 1204, 1178, 1077 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 3H), 1.44 (s, 3H), 1.61-1.78 (m, 9H), 1.82-1.91 (m, 3H), 2.04 (br s, 3H), 4.25 (dd, *J* = 3.6, 10.8 Hz, 1H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.67 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.8, 27.4, 27.8, 35.6, 36.3, 36.6, 70.7, 76.5, 89.5, 112.7, 175.9; MS *m/z* (EI): 292 (M^+, 7), 277 (46), 234 (9), 219 (12), 162 (15), 135 (100); Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27; Found: C, 69.70; H, 8.19.

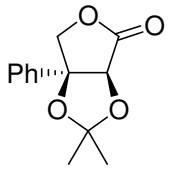


(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrono-1,4-lactone 8d.[4] Colourless oil (115 mg, 86%); R_f 0.20 (CH_2Cl_2); IR (neat): 1790, 1466, 1377, 1219, 1171, 1106, 1004, 851 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.46 (s, 3H), 1.57 (s, 3H), 4.32 (dd, *J*= 3.6, 10.8 Hz, 1H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.49 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.4, 26.6, 26.9, 68.9, 80.3, 81.4, 113.0, 176.7.

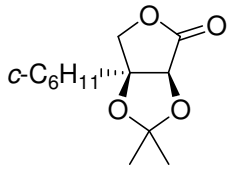


(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrono-1,4-lactone (8f). Colourless needles (345 mg, 89%); mp 122-123 °C; R_f 0.41 (4:1 CH_2Cl_2/hexane); IR (nujol): 1774, 1496, 1267, 1222, 1167, 1102 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (s,

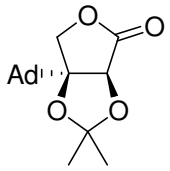
3H), 1.45 (s, 3H), 3.15 (d, *J* = 13.5 Hz, 1H), 3.27 (d, *J* = 13.5 Hz, 1H), 3.53 (dd, *J* = 3.6, 10.8 Hz, 1H), 4.20 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 3.6 Hz, 1H), 7.21-7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 27.0, 38.7, 69.3, 78.3, 84.7, 113.0, 127.8, 128.8, 130.1, 132.9, 176.6; MS *m/z* (EI): 248 (M^+, 7), 233 (100), 190 (11), 175 (19), 118 (22), 91 (45); Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50; Found: C, 67.97; H, 6.41.



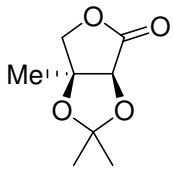
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrono-1,4-lactone (9a). Colourless oil (115 mg, 80%); R_f 0.49 (1:1 ether/hexane); IR (neat): 1789, 1498, 1449, 1374, 1233, 1083, 1026 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 3H), 1.55 (s, 3H), 4.33 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 5.02 (s, 1H), 7.35-7.47 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 27.8, 76.5, 74.9, 87.6, 114.8, 125.1, 128.7, 128.9, 138.1, 174.0; MS *m/z* (EI): 234 (M^+, 7), 219 (100), 177 (55), 176 (42), 161 (25), 105 (60); HRMS calcd. for M + Na) $C_{13}H_{14}O_4Na$: 257.0789; Found: 257.0793.



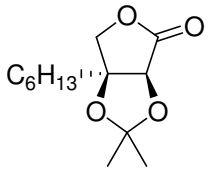
(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrono-1,4-lactone (9b). Colourless oil (310 mg, 86%); R_f 0.26 (CH_2Cl_2); IR (neat): 1789, 1452, 1374, 1246, 1210, 1143, 1091 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00-1.35 (m, 5H), 1.41 (s, 3H), 1.49 (s, 3H), 1.56-1.88 (m, 6H), 4.39 (s, 2H), 4.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 26.0, 26.1, 26.9, 27.4, 27.5, 27.5, 43.5, 74.9, 76.8, 88.6, 113.6, 175.0; MS *m/z* (EI): 240 (M^+, 3), 225 (100), 183 (16), 165 (42), 137 (25), 119 (27); HRMS calcd. for M + Na) $C_{13}H_{20}O_4Na$: 263.1259; Found: 263.1260.



(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrono-1,4-lactone (9c). Colourless solid (303 mg, 88%); mp 176-177 ^{o}C; R_f 0.39 (CH_2Cl_2); IR (nujol): 1790, 1270, 1248, 1217, 1189, 1091, 1003 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.49 (s, 3H), 1.52-1.79 (m, 12H), 2.05 (br s, 3H), 4.29 (d, *J* = 10.8 Hz, 1H), 4.50 (s, 1H), 4.69 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.6, 27.2, 27.7, 36.4, 36.5, 36.6, 74.0, 74.5, 90.9, 113.6, 174.9; MS *m/z* (EI): 292 (M^+, 5), 277 (100), 235 (39), 217 (12), 135 (77); Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27; Found: C, 70.03; H, 8.15.

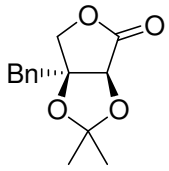


(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrono-1,4-lactone (9d).[4] Colourless oil (96 mg, 72%); R_f 0.29 (CH_2Cl_2); IR (neat): 1791, 1459, 1380, 1216, 1165, 1138, 1084, 1022 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.50 (s, 3H), 1.54 (s, 3H), 4.15 (d, *J*= 10.5 Hz, 1H), 4.46 (s, 1H), 4.46 (d, *J* = 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 27.7, 28.5, 75.6, 79.4, 83.5, 114.0, 174.7.



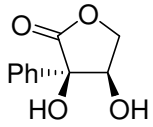
(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrono-1,4-lactone (9e).

(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrofuranose (**3e**) (0.204 g, 0.84 mmol) was dissolved in anhydrous dichloromethane (2.0 ml). 4 Å molecular sieves (0.20 g) and *N*-methylmorpholine-*N*-oxide (0.20 g, 1.67 mmol) was added followed by tetrapropylammonium perruthenate (15 mg, 42 μmol). After stirring at ambient temperature under nitrogen overnight the reaction mixtre was filtered through a pad of celite and the solid residue was washed with dichloromethane. The combined organic phases were concentrated *in vacuo* to give a black gum. Purification by DCVC [id. 4cm; 20 ml fractions; 4 × hexanes; 5-75% EtOAc in hexanes (v/v) – 5% increments] gave lactone **5e** (0.18 g, 90%) as a clear colourless oil. R_f 0.3 (1:5 ethyl acetate/hexane); IR (neat): 2931, 1794, 1458, 1373, 1250, 1214, 1140, 1079, 1022 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7 Hz, 3H), 1.28-1.49 (m, 6H), 1.40 (d, *J* = 0.5 Hz, 3H), 1.47 (d, *J* = 0.5 Hz, 3H), 1.74 (ddd, *J* = 4.5, 11.5, 14, 1H), 1.81 (ddd, *J* = 4.5, 11, 14, 1H), 4.21 (d, *J* = 10.5, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 4.43 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 23.6, 27.6, 28.2, 29.3, 31.5, 35.9, 75.4, 78.6, 86.2, 113.8, 174.7; MS *m/z* (+EI): 242 (M^+, 1), 227 (100), 184 (2), 167 (25), 139 (4), 121 (6), 84 (9), 69 (9), 59 (11); HRMS calcd. for M + Na) $C_{13}H_{22}NaO_4$: 265.1416; Found: 265.1412; Anal. calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15; Found: C, 64.92; H, 9.49.

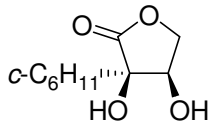


(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrono-1,4-lactone (9f). Colourless solid (328 mg, 76%); mp 60-62 ^oC; R_f 0.31 (CH_2Cl_2); IR (neat): 1790, 1497, 1455, 1374, 1222, 1141, 1019 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 3H), 1.46 (s, 3H), 3.02

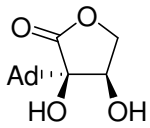
(d, J = 14.1 Hz, 1H), 3.16 (d, J = 14.1 Hz, 1H), 4.27 (d, J = 10.8 Hz, 1H), 4.31 (d, J = 10.8 Hz, 1H), 4.60 (s, 1H), 7.22-7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 28.3, 41.7, 74.3, 78.1, 86.3, 114.4, 127.4, 128.7, 130.0, 134.6, 174.4; MS *m/z* (EI): 248 (M^+, 3), 233 (100), 145 (30), 117 (34), 91 (31); Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50; Found: C, 67.83; H, 6.65.



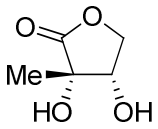
(±)-2-*C*-Phenyl-erythrono-1,4-lactone (6a). Colourless solid (115 mg, 87%); mp 108-109 °C; R_f 0.34 (1:1 ethyl acetate/hexane); IR (nujol): 3446, 1753, 1495, 1305, 1219, 1185, 1145 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (br s, 1H), 3.50 (br s, 1H), 4.24 (dd, J = 3.0, 10.2 Hz, 1H), 4.37 (d, J = 10.2 Hz, 1H), 4.41 (d, J = 3.0 Hz, 1H), 7.42 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$ + 1 drop d_6-DMSO): δ 71.3, 74.6, 78.8, 126.0, 128.9, 129.0, 137.4, 176.7; MS *m/z* (EI): 194 (M^+, 5), 150 (21), 136 (11), 131 (13), 105 (100), 77 (35); Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19; Found: C, 62.08; H, 5.26.



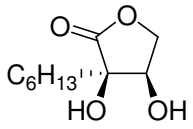
(±)-2-*C*-Cyclohexyl-erythrono-1,4-lactone (6b). Colourless flakes (149 mg, 89%); mp 110-112 °C; R_f 0.39 (1:1 ethyl acetate/hexane); IR (nujol): 3460, 3340, 1744, 1226, 1193, 1146, 987 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10-1.34 (m, 5H), 1.54-1.90 (m, 6H), 2.99 (br s, 2H), 4.28 (d, J = 9.9 Hz, 1H), 4.31-4.33 (m, 1H), 4.39 (ddd, J = 1.2, 3.3, 9.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 25.9, 26.1, 26.3, 26.8, 41.8, 69.6, 72.7, 78.4, 177.6; MS *m/z* (EI): 200 (M^+, 2), 142 (11), 118 (85), 100 (30), 83 (61), 55 (100); Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; Found: C, 60.25; H, 8.20.



(±)-2-*C*-(1-Adamantyl)-erythrono-1,4-lactone (6c). Colourless rhombic clusters (113 mg, 65%); mp 233-235 ^{o}C; R_f 0.46 (1:1 ethyl acetate/hexane); IR (nujol): 3423, 3384, 1733, 1447, 1310, 1220, 1178, 1147, 988 cm^{-1}; ^{1}H NMR (600 MHz, d_6-DMSO): δ 1.55-1.80 (m, 12 H), 1.95 (br s, 3H), 3.94 (dd, *J* = 2.4, 9.6 Hz, 1H), 4.30 (dd, *J* = 2.4, 6.0 Hz, 1H), 4.33 (dd, *J* = 6.0, 9.6 Hz, 1H), 4.92 (br s, 1H), 5.68 (br s, 1H); ^{13}C NMR (75 MHz, d_6-DMSO): δ 27.5, 35.1, 36.4, 37.2, 66.5, 72.5, 78.2, 175.9; MS *m/z* (EI): 252 (M^+, 3), 136 (13), 135 (100), 107 (9), 93 (15), 79 (16); Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99; Found: C, 66.73; H, 7.70.

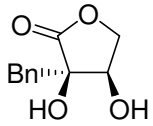


(±)-2-*C*-D-Methyl-erythrono-1,4-lactone 1.[3] Colourless solid (60 mg, 76%); mp 62-64 ^{o}C; R_f 0.42 (ethyl acetate); IR (nujol): 3447, 3324, 1770, 1204, 1108, 1081, 1030 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD): δ 1.39 (s, 3H), 4.04 (dd, *J* = 1.8, 4.2 Hz, 1H), 4.14 (dd, *J* = 1.8, 10.2 Hz, 1H), 4.43 (dd, *J* = 4.2, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 21.6, 73.3, 74.4, 74.5, 180.4; ^{1}H NMR (300 MHz, $CDCl_3$ + 2 drops d_6-DMSO): δ 1.45 (s, 3H), 4.06 (ddd, *J* = 1.5, 3.3, 3.6 Hz, 1H), 4.26 (dd, *J* = 1.5, 10.5 Hz, 1H), 4.35 (dd, *J* = 3.6, 10.5 Hz, 1H), 4.36 (br d, *J* = 3.3 Hz, 1H), 5.00 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + 2 drops d_6-DMSO): δ 21.2, 71.6, 72.9, 73.1, 178.0.

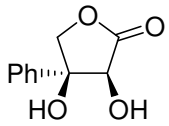


(±)-2-*C*-Hexyl-erythrono-1,4-lactone (6e). Colourless gum (121 mg, 88%); R_f 0.4 (1:1 ethyl acetate/hexane); IR (neat): 3436, 2930, 1770, 1469, 1166, 1121, 970 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7 Hz, 3H), 1.26-1.34 (m, 6H), 1.41-1.52

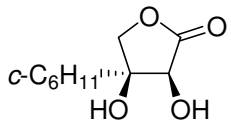
(m, 2H), 1.63-1.72 (m, 2H), 3.07 (br s, 1H), 3.23 (br s, 1H), 4.19 (br d, *J* = 3.5 Hz, 1H), 4.31 (dd, *J* = 1, 10.5, 1H), 4.38 (dd, *J* = 3.5, 10.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 22.7, 29.3, 31.5, 34.6, 71.9, 72.3, 76.2, 177.8; MS *m/z* (+EI): 184 (M^+ – 18, 1), 144 (12), 138 (6), 131 (12), 118 (84), 113 (69), 101 (28), 95 (16), 88 (50), 73 (100), 55 (54); HRMS calcd. for M + Na) $C_{10}H_{18}NaO_4$: 225.1103; Found: 225.1098.



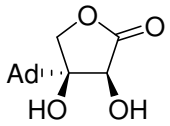
(±)-2-*C*-Benzyl-erythrono-1,4-lactone (6f). Colourless solid (211 mg, 84%); mp 92-93 °C; R_f 0.35 (1:1 ethyl acetate/hexane); IR (nujol): 3477, 3343, 1760, 1496, 1455, 1179, 1019 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.91 (br s, 1H), 3.01 (d, *J* = 14.4 Hz, 1H), 3.07 (d, *J* = 14.4 Hz, 1H), 3.33 (br s, 1H), 4.02 (dd, *J* = 3.6, 10.5 Hz, 1H), 4.21 (dd, *J* = 1.2, 10.5 Hz, 1H), 4.24 (dd, *J* = 1.2, 3.6 Hz, 1H), 7.21-7.23 (m, 2H), 7.30-7.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.3, 71.2, 72.1, 76.2, 127.8, 128.7, 130.1, 133.1, 177.2; MS *m/z* (EI): 208 (M^+, 9), 190 (8), 92 (16), 91 (100); Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; Found: C, 63.74; H, 5.86.



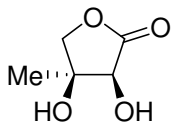
(±)-3-*C*-Phenyl-erythrono-1,4-lactone (7a). Colourless solid (53 mg, 75%); mp 147-148 °C; R_f 0.40 (1:1 ethyl acetate/hexane); IR (nujol): 3503, 3430, 1789, 1494, 1354, 1164, 1115 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.03 (br s, 1H), 3.16 (br s, 1H), 4.38 (d, *J* = 10.2 Hz, 1H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.84 (s, 1H), 7.36-7.54 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$ + 2 drop d_6-DMSO): δ 73.6, 75.3, 77.9, 125.5, 128.3, 128.7, 138.9, 175.2; MS *m/z* (EI): 194 (M^+, 13), 137 (79), 120 (81), 105 (50), 91 (100), 77 (57); Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19; Found: C, 61.98; H, 5.37.



(±)-3-*C*-Cyclohexyl-erythrono-1,4-lactone (7b). Colourless flakes (186 mg, 80%); mp 137-138 ^{o}C; R_f 0.32 (2:3 ethyl acetate/hexane); IR (nujol): 3515, 3399, 1771, 1299, 1204, 1145, 1108, 1031 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05-1.38 (m, 5H), 1.52-1.96 (m, 6H), 2.74 (d, *J* = 1.8 Hz, 1H), 3.14 (d, *J* = 3.0 Hz, 1H), 4.15 (dd, *J* = 1.8, 10.2 Hz, 1H), 4.30 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 26.5, 26.6, 44.4, 72.2, 74.4, 78.6, 176.8; MS *m/z* (EI): 200 (M^+, 2), 142 (11), 118 (85), 100 (30), 83 (61), 55 (100); Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; Found: C, 60.02; H, 7.91.

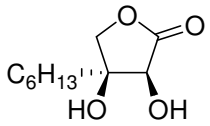


(±)-3-*C*-(1-Adamantyl)-erythrono-1,4-lactone (7c). Colourless flakes (174 mg, 76%); mp 188-190 ^{o}C; R_f 0.41 (2:3 ethyl acetate/hexane); IR (nujol): 3495, 3390, 1798, 1344, 1280, 1146, 1111, 1096, 1008 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55-1.83 (m, 12 H), 2.06 (br s, 3H), 2.83 (br s, 1H), 2.89 (br s, 1H), 4.18 (d, *J* = 9.9 Hz, 1H), 4.36 (d, *J* = 9.9 Hz, 1H), 4.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 36.5, 36.6, 37.1, 68.7, 71.5, 81.0, 177.1; MS *m/z* (EI): 252 (M^+, 6), 195 (64), 178 (11), 135 (100), 93 (18); Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99; Found: C, 66.75; H, 8.01.

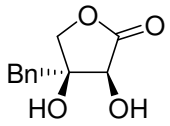


(±)-3-*C*-Methyl-erythrono-1,4-lactone (7d).[4] Colourless oil (54 mg, 94%); R_f 0.49 (1:19 MeOH/ethyl acetate); IR (neat): 3418, 1770, 1464, 1385, 1294, 1111, 1008 cm^{-}

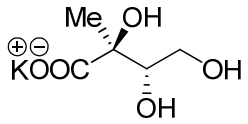
[1]; ^{1}H NMR (300 MHz, D_2O): δ 1.46 (s, 3H), 4.33 (s, 2H), 4.50 (s, 1H); ^{13}C NMR (75 MHz, D_2O): δ 19.9, 73.6, 75.4, 76.3, 178.9.



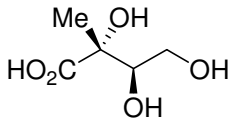
(±)-3-*C*-Hexyl-erythrono-1,4-lactone (7e). Colourless gum (66 mg, 79%); R_f 0.35 (1:1 ethyl acetate/hexane); IR (neat): 3401, 2929, 1774, 1638, 1466, 1116, 1010 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86-0.91 (m, 3H), 1.25-1.42 (m, 6H), 1.47-1.84 (m, 4H), 2.94 (br s, 1H), 3.70 (br s, 1H), 4.12 (d, *J* = 10 Hz, 1H), 4.24 (br s, 1H), 4.31 (d, *J* = 10 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.7, 23.5, 29.7, 31.8, 36.5, 73.3, 75.0, 77.0, 176.9; MS *m/z* (+EI): 185 (M^+ – 17, 1), 145 (100), 127 (9), 109 (18), 83 (4), 67 (10), 55 (10); HRMS calcd. for M + Na) $C_{10}H_{18}NaO_4$: 225.1103; Found: 225.1094.



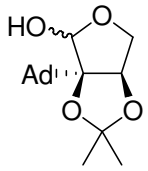
(±)-3-*C*-Benzyl-erythrono-1,4-lactone (7f). Colourless gum (194 mg, 93%); R_f 0.46 (3:2 ethyl acetate/hexane); IR (neat): 3412, 1777, 1496, 1455, 1152, 1008, 704 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.95 (br s, 1H), 2.99 (d, *J* = 14.4 Hz, 1H), 3.06 (d, *J* = 14.4 Hz, 1H), 3.39 (br s, 1H), 4.18 (d, *J* = 10.2 Hz, 1H), 4.21 (d, *J* = 10.2 Hz, 1H), 4.32 (s, 1H), 7.21-7.24 (m, 2H), 7.28-7.36 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.0, 71.9, 73.6, 76.9, 127.5, 128.8, 129.9, 134.6, 175.8; MS *m/z* (EI): 208 (M^+, 17), 151 (29), 133 (78), 91 (100); HRMS calcd. for M + Na) $C_{11}H_{12}O_4Na$: 231.0633; Found: 231.0636.



(±)-Potassium 2,3,4-trihydroxy-2-methylbutanoate 2.[4] Methyl-erythrono-1,4-lactone **6d** (10 mg, 0.075 mmol) was dissolved in H_2O (1 mL) and stirred with KOH (4.2 mg, 0.075 mmol) for 20 minutes. The water was removed *in vacuo* and the residue dried under high vacuum, and then taken up in D_2O for characterization. ^{1}H NMR (300 MHz, D_2O): δ 1.34 (s, 3H), 3.57 (d, *J* = 6.3 Hz, 1H), 3.58 (d, *J* = 4.8 Hz, 1H), 3.79 (dd, *J* = 4.8, 6.3 Hz, 1H); ^{13}C NMR (75 MHz, D_2O): δ 22.8, 62.6, 76.3, 77.3, 181.2.

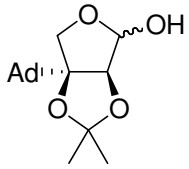


(±)-2-*C*-Methyl-erythronic acid.[5] ^{1}H NMR (300 MHz, CD_3OD): δ 1.40 (s, 3H), 3.54 (dd, *J* = 7.2, 11.4 Hz, 1H), 3.60 (dd, *J* = 4.8, 11.4 Hz, 1H), 3.76 (dd, *J* = 4.8, 7.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 22.7, 63.6, 77.0, 77.2, 176.9.



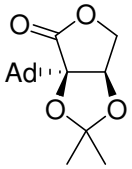
Details of crystal structure determination of $C_{17}H_{26}O_4$ (4c).

Crystal data for $C_{17}H_{26}O_4$: M = 294.38, T = 153(2) K, orthorhombic, *Pbca*, a = 12.370(3), b = 11.328(2), c = 21.465(4) Å, V = 3007.8(11) Å^3, Z = 8, D_x = 1.300 g cm^{-3}, $F(000)$ = 1280, μ = 0.091 mm^{-1}, no. of unique data (AFC12/SATURN724 using Mo Kα radiation so that θ_{max} = 26.5°) = 3061, no. of parameters = 193, R (2896 data with $I \geq 2\sigma(I)$) = 0.042, wR (all data) = 0.115. The structure was solved by direct-methods (SIR92) and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.060P^2 + 0.728P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL-97 on F^2. CCDC deposition number: 701947.



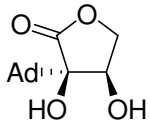
Details of crystal structure determination of $C_{17}H_{26}O_4$ (5c).

Crystal data for $C_{17}H_{26}O_4$: M = 294.38, T = 153(2) K, triclinic, P-1, a = 10.1757(14), b = 12.1846(15), c = 12.5108(17) Å, α = 90.253(7), β = 106.973(7), γ = 99.206(7)º, V = 1462.4(3) Å^3, Z = 4, D_x = 1.337 g cm^{-3}, $F(000)$ = 640, μ = 0.093 mm^{-1}, no. of unique data for a single twin component (AFC12/SATURN724 using Mo Kα radiation so that θ_{max} = 25.0°) = 4097, no. of parameters = 385, R (3476 data with $I \geq 2\sigma(I)$) = 0.093, wR (all data) = 0.239. The structure was solved by direct-methods (SIR92) and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.092P^2 + 2.723P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL-97 on F^2. The structure analysis was performed using a single component of a multiple, poorly diffracting crystal and the data completeness is low. CCDC deposition number: 701946.



Details of crystal structure determination of $C_{17}H_{24}O_4$ (8c).

Crystal data for $C_{17}H_{24}O_4$: M = 292.36, T = 153(2) K, orthorhombic, *Pbca*, a = 13.0782(19), b = 11.7364(17), c = 18.817(3) Å, V = 2888.3(7) Å^3, Z = 8, D_x = 1.345 g cm^{-3}, $F(000)$ = 1264, μ = 0.094 mm^{-1}, no. of unique data (AFC12/SATURN724 using Mo Kα radiation so that θ_{max} = 26.5°) = 2981, no. of parameters = 190, R (2919 data with $I \geq 2\sigma(I)$) = 0.044, wR (all data) = 0.107. The structure was solved by direct-methods (SIR92) and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.045P^2 + 1.237P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL-97 on F^2. CCDC deposition number: 701948.



Details of crystal structure determination of $C_{14}H_{20}O_4$ (6c).

Crystal data for $C_{14}H_{20}O_4$: M = 252.30, T = 153(2) K, triclinic, *P*-1, a = 6.374(3), b = 6.410(3), c = 16.590(4) Å, α = 91.781(4), β = 96.664(5), γ = 118.379(11)º, V = 589.4(4) Å^3, Z = 2, D_x = 1.422 g cm^{-3}, $F(000)$ = 272, μ = 0.103 mm^{-1}, no. of unique data (AFC12/SATURN724 using Mo Kα radiation so that θ_{max} = 25.0°) = 1978, no. of parameters = 169, R (1928 data with $I \geq 2\sigma(I)$) = 0.034, wR (all data) = 0.084. The structure was solved by direct-methods (SIR92) and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.034P^2 + 0.278P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL-97 on F^2. CCDC deposition number: 701949.

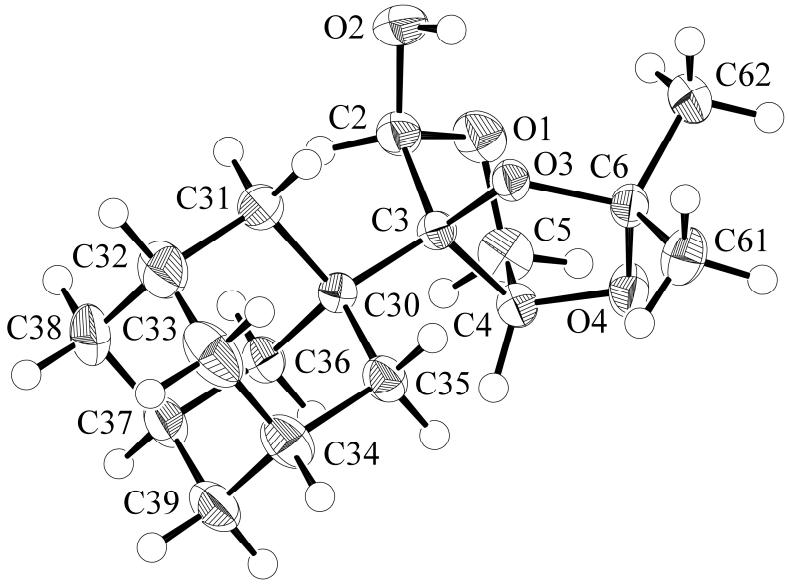


Figure S2. Molecular structure of (**4c**) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

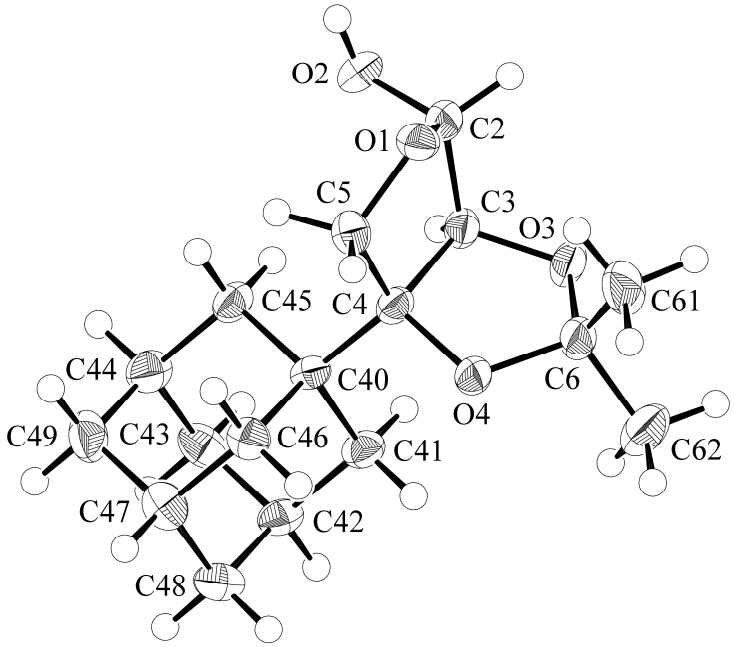


Figure S3. Molecular structure of (**5c**) showing atom labelling scheme; first independent molecule. Displacement ellipsoids are drawn at the 50% probability level.

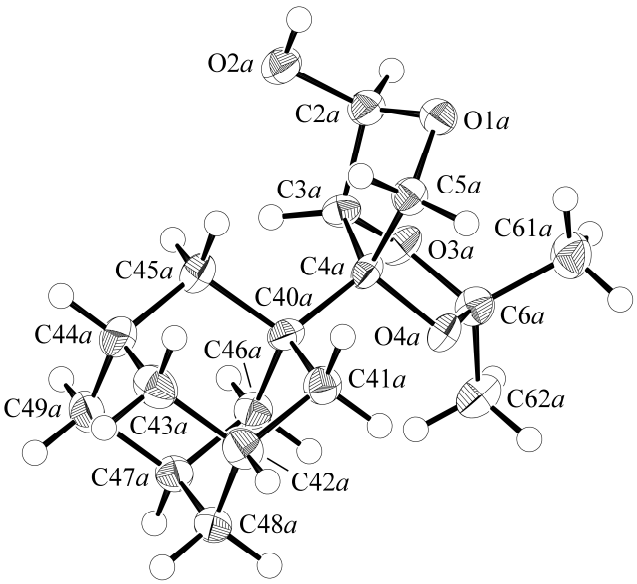


Figure S4. Molecular structure of (**5c**) showing atom labelling scheme; second independent molecule. Displacement ellipsoids are drawn at the 50% probability level.

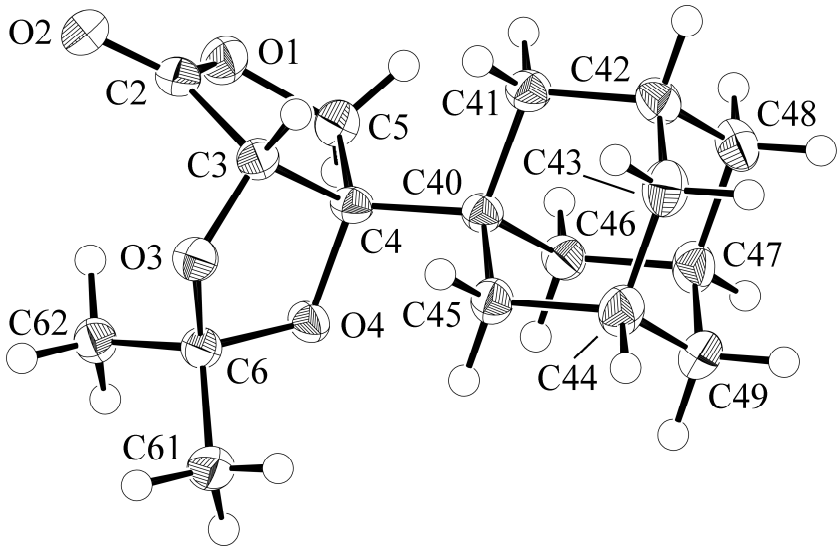


Figure S5. Molecular structure of (**8c**) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

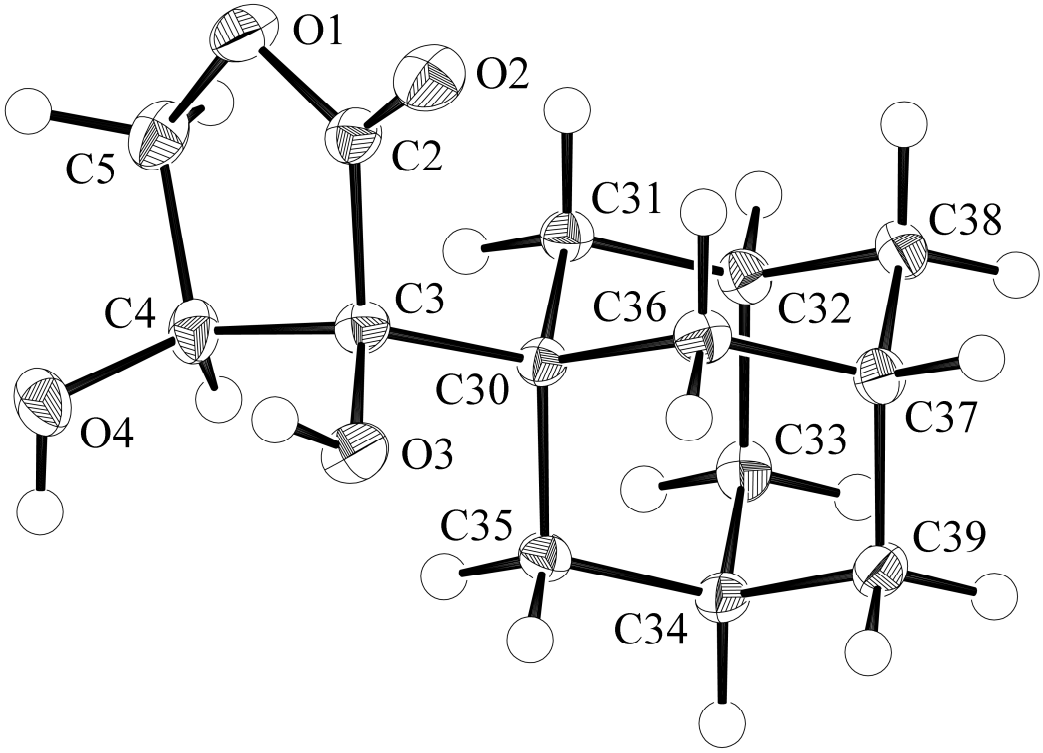
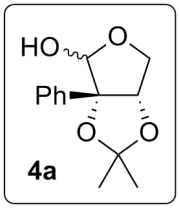
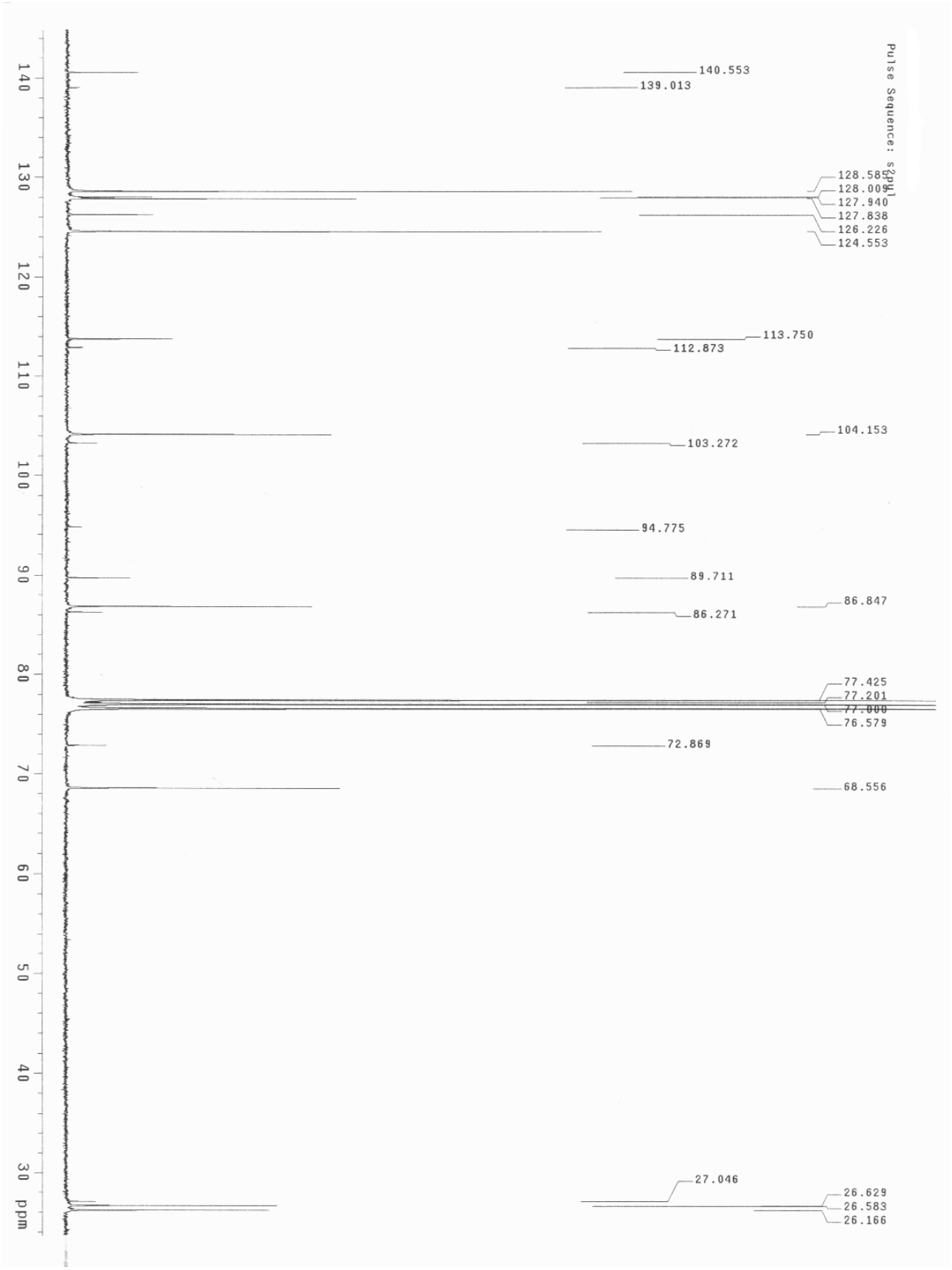


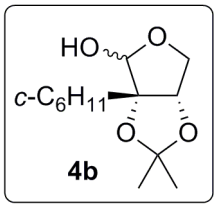
Figure S6. Molecular structure of (**6c**) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

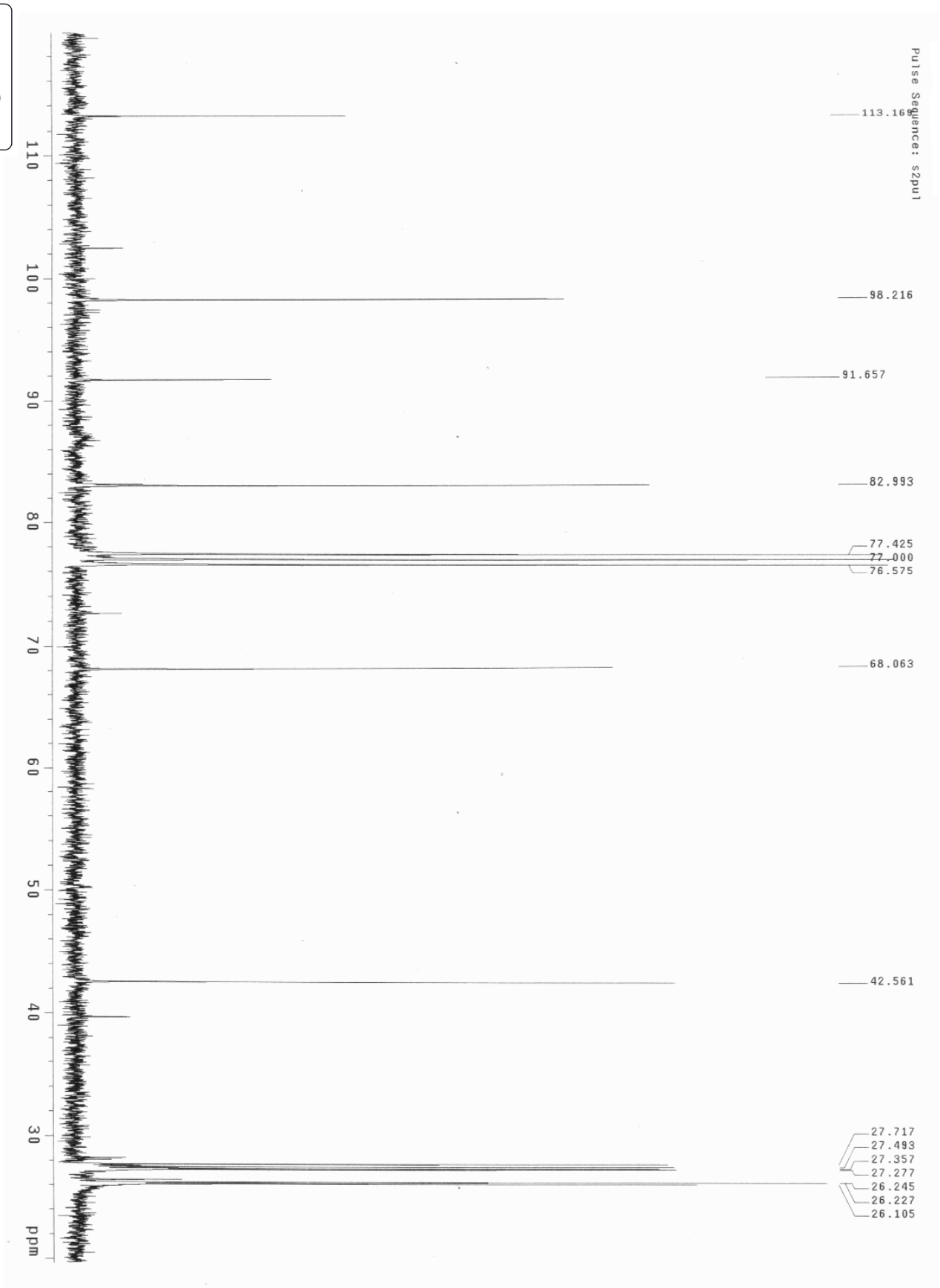
(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrofuranose (**4a**) [75 MHz, $CDCl_3$].



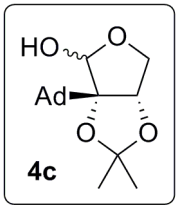


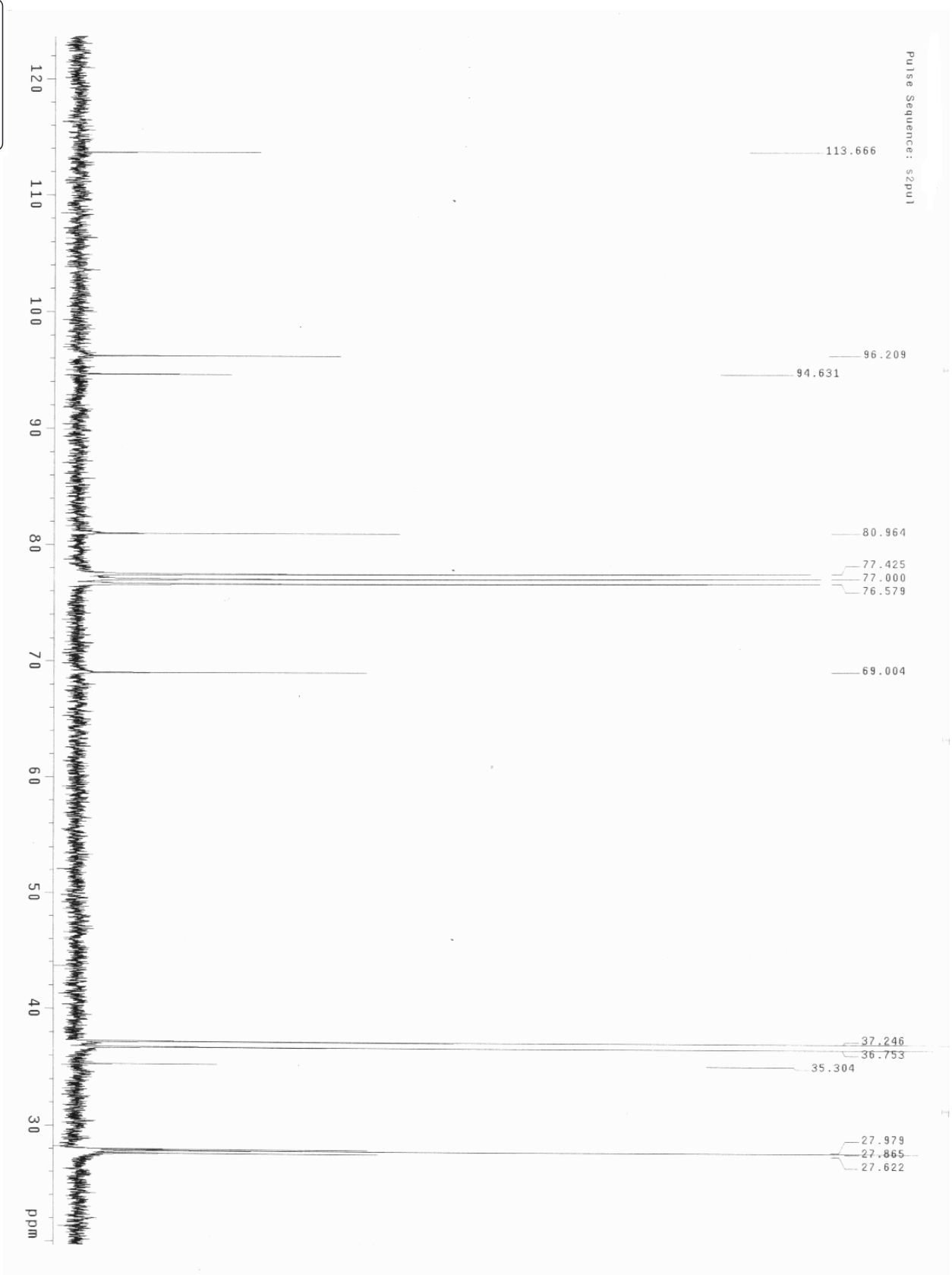
(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrofuranose (**4b**) [75 MHz, $CDCl_3$].



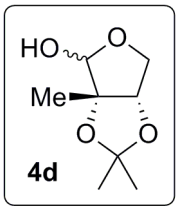


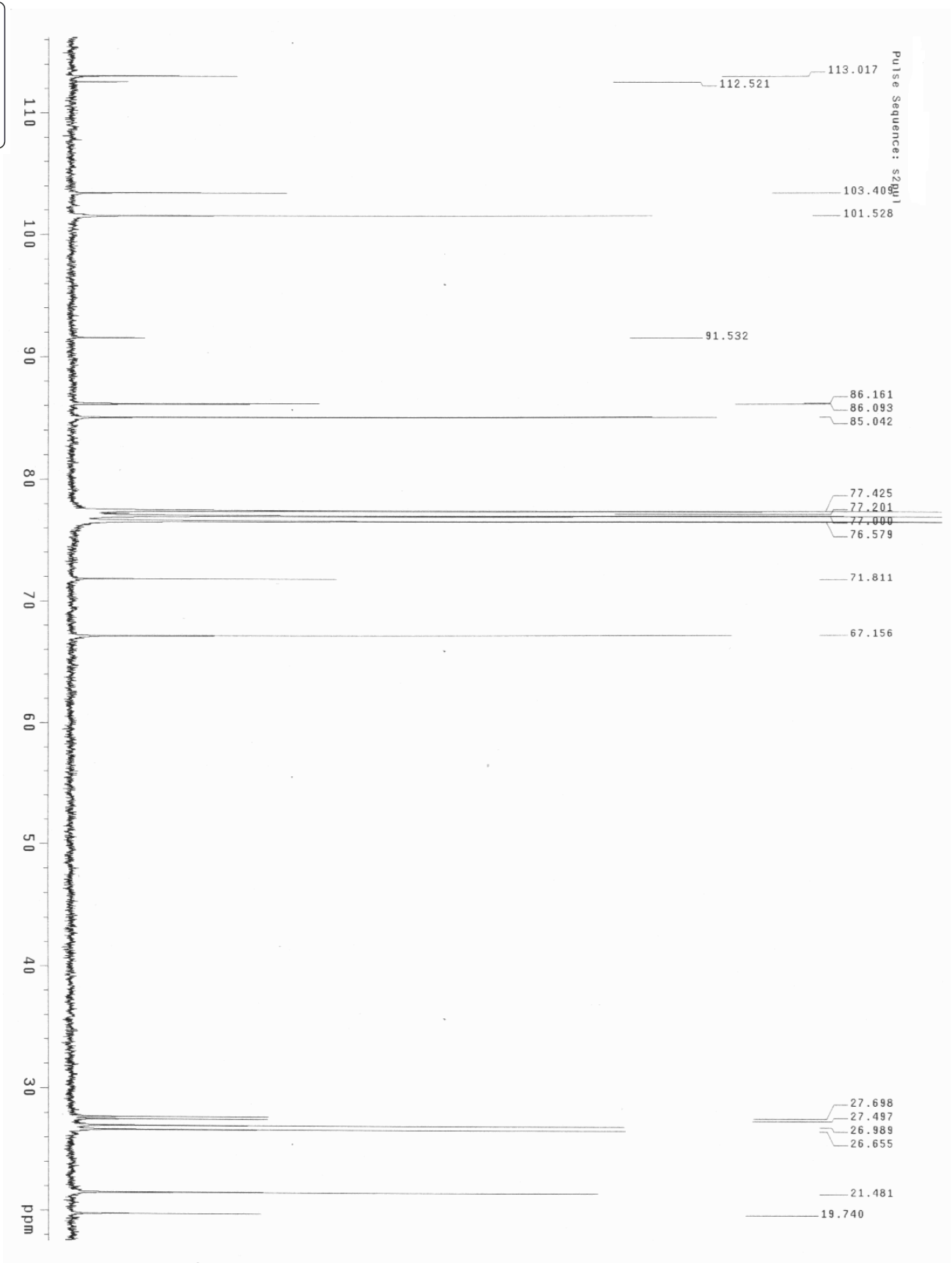
(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrofuranose (**4c**). [75 MHz, $CDCl_3$]



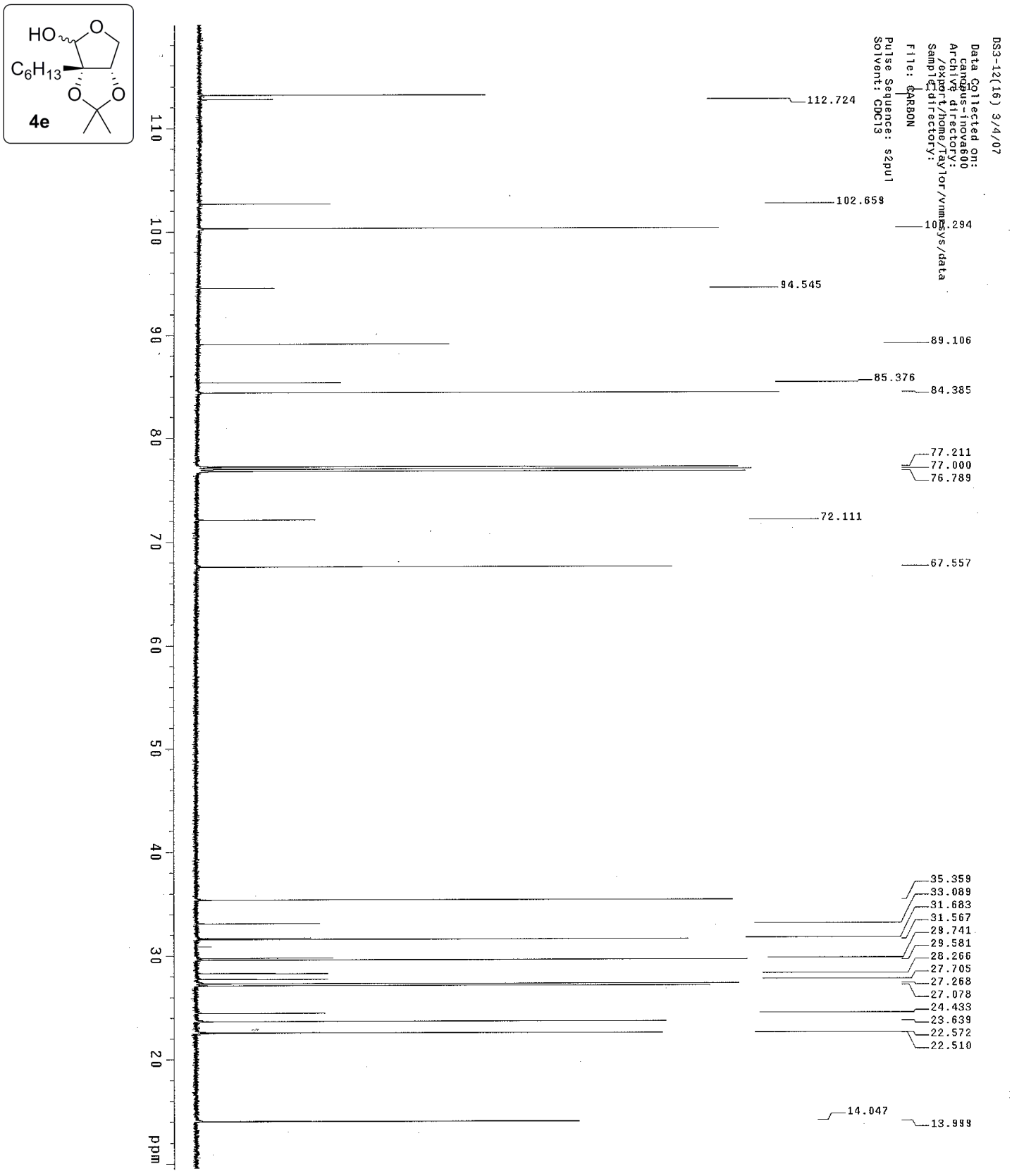


(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrofuranose (**4d**) [150 MHz, $CDCl_3$].

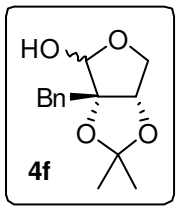


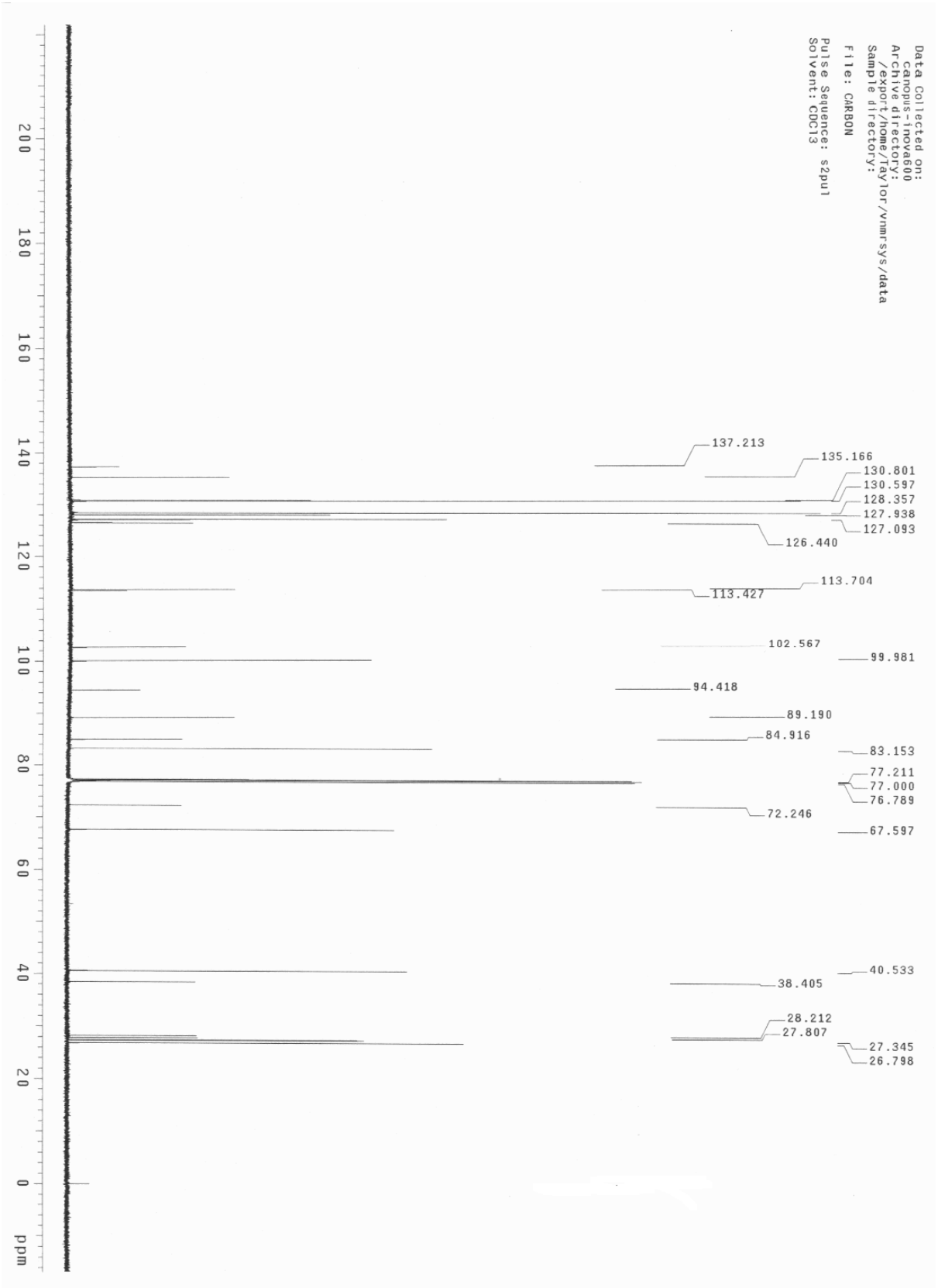


(±)-2,3-*O*-Isopropylidene-2-*C*-hexyl-erythrofuranose (**4e**) [150 MHz, $CDCl_3$].

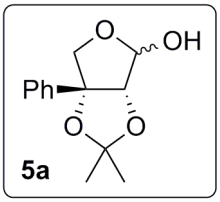


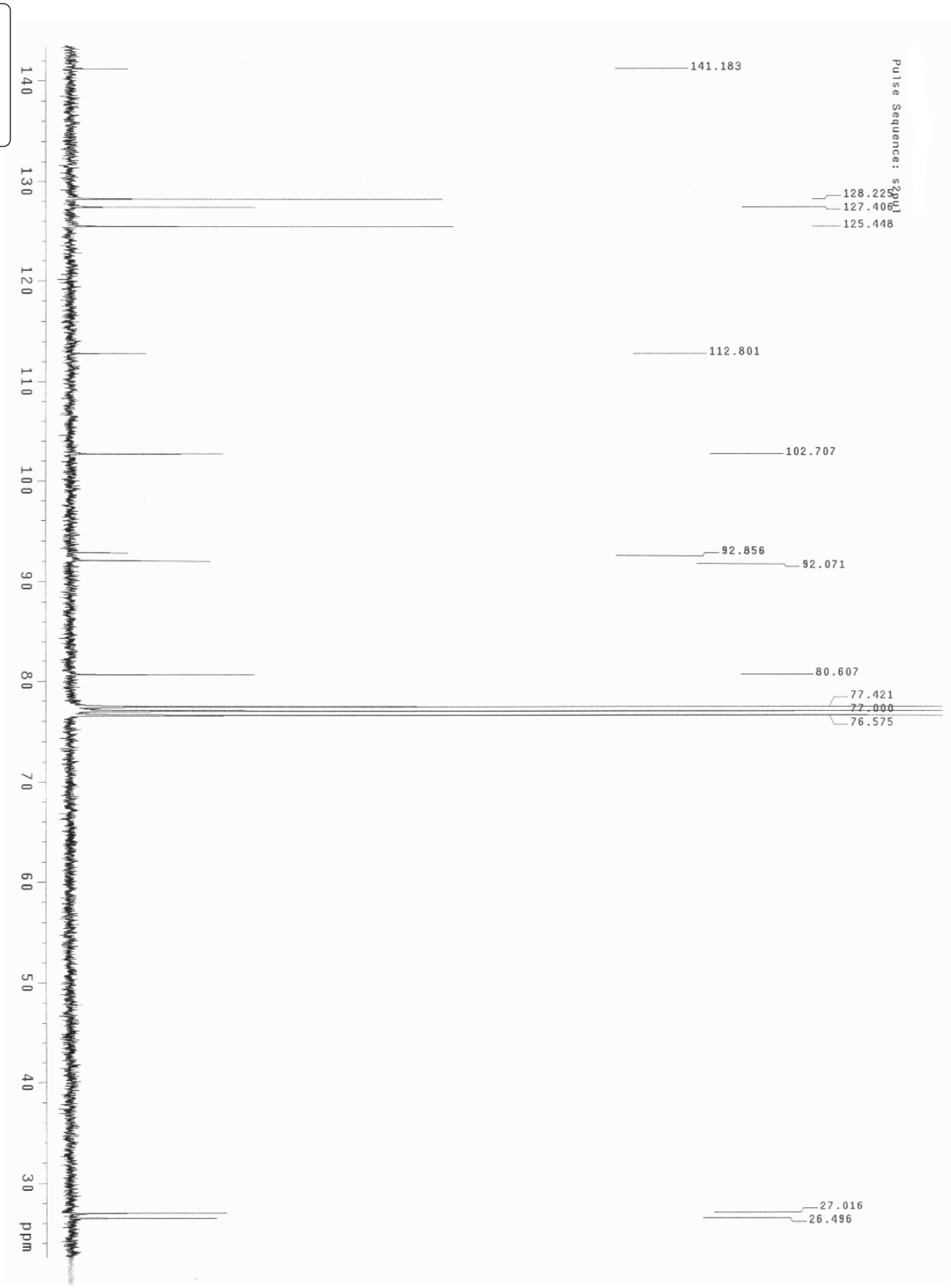
(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrofuranose (**4f**) [150 MHz, $CDCl_3$].



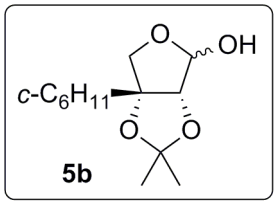


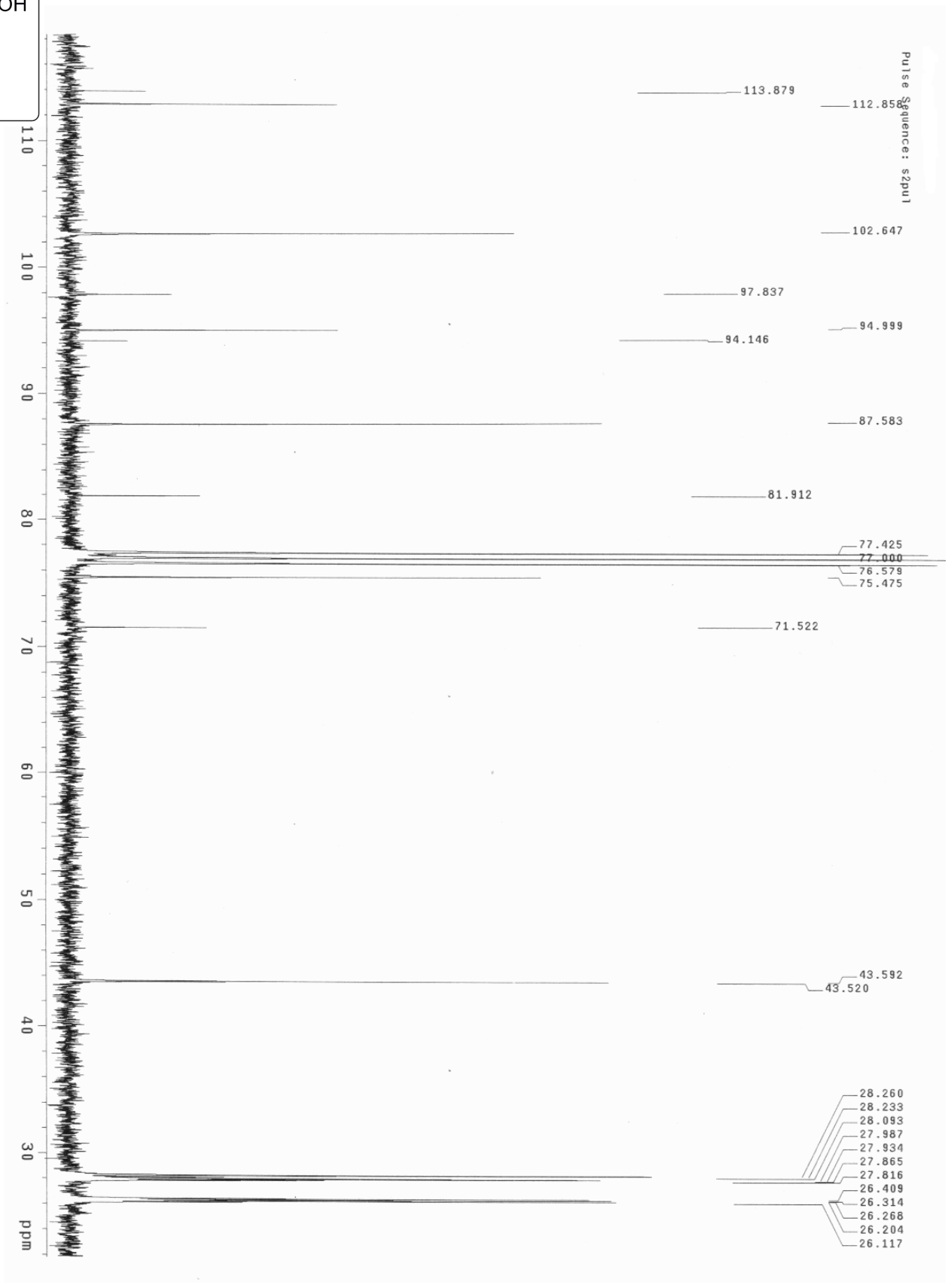
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrofuranose (**5a**) [75 MHz, $CDCl_3$].



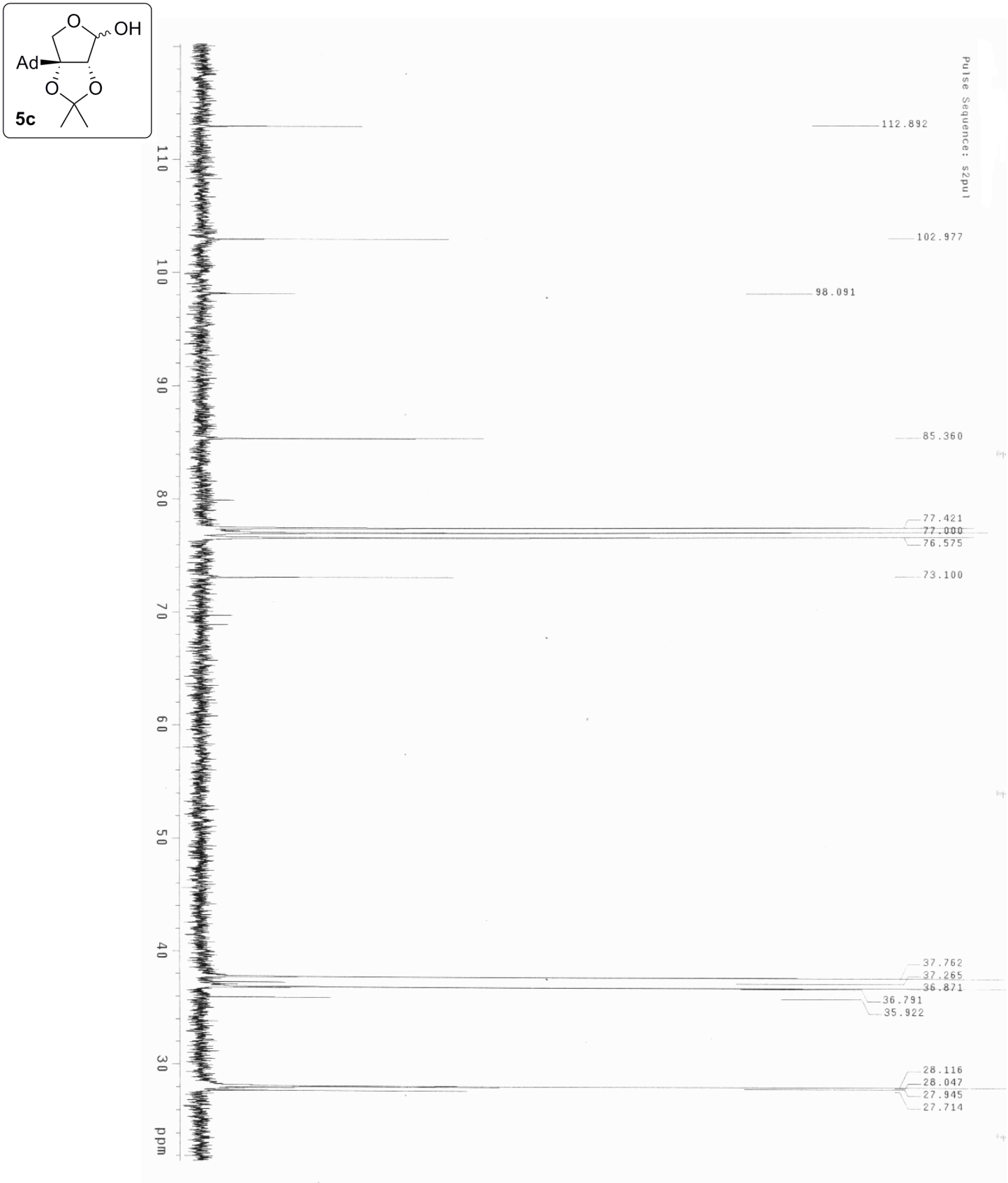


(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrofuranose (**5b**) [75 MHz, $CDCl_3$].

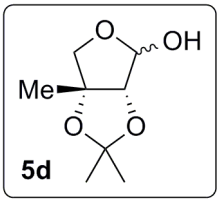


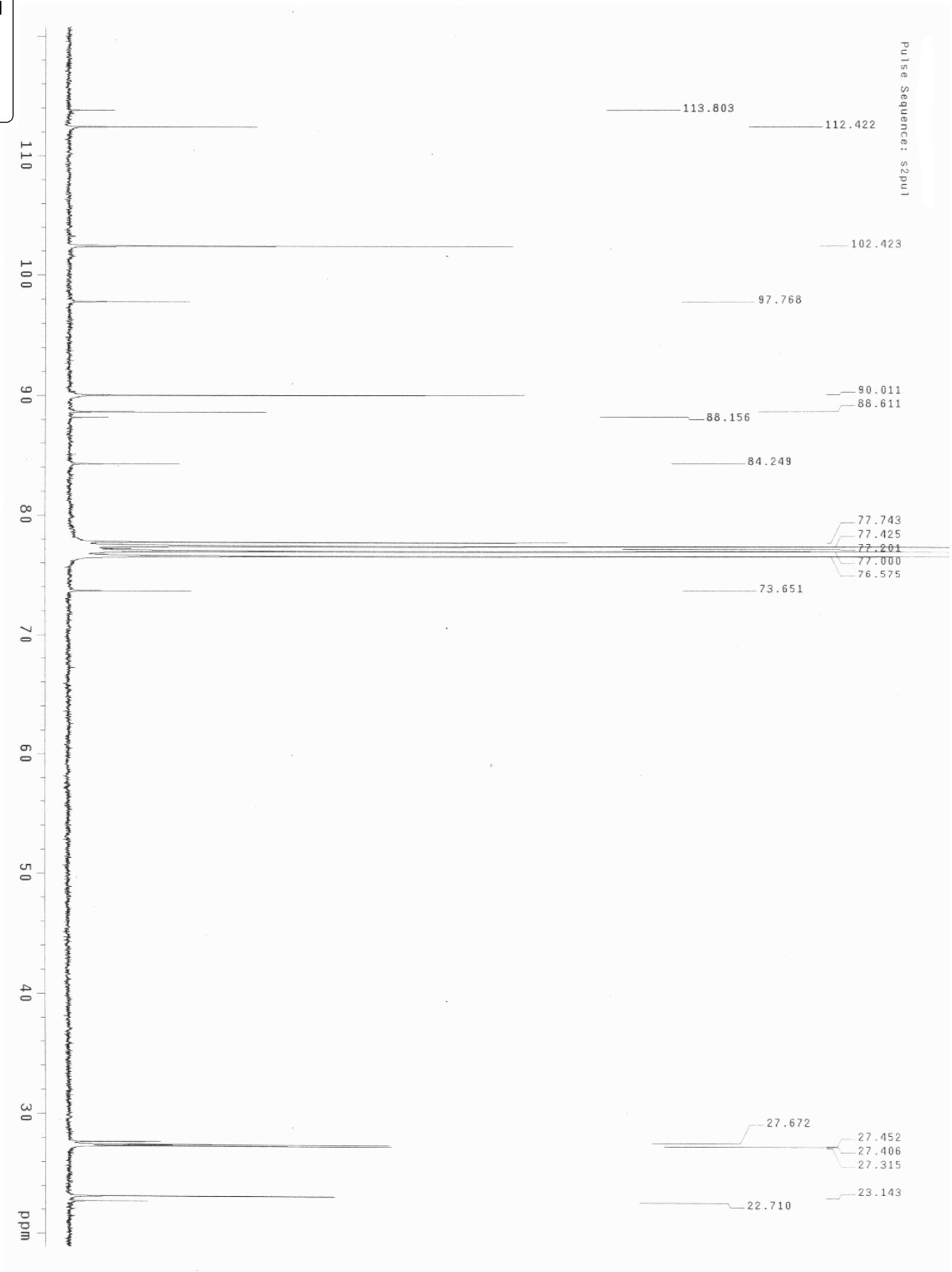


(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrofuranose (**5c**) [75 MHz, $CDCl_3$].

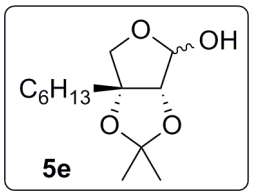


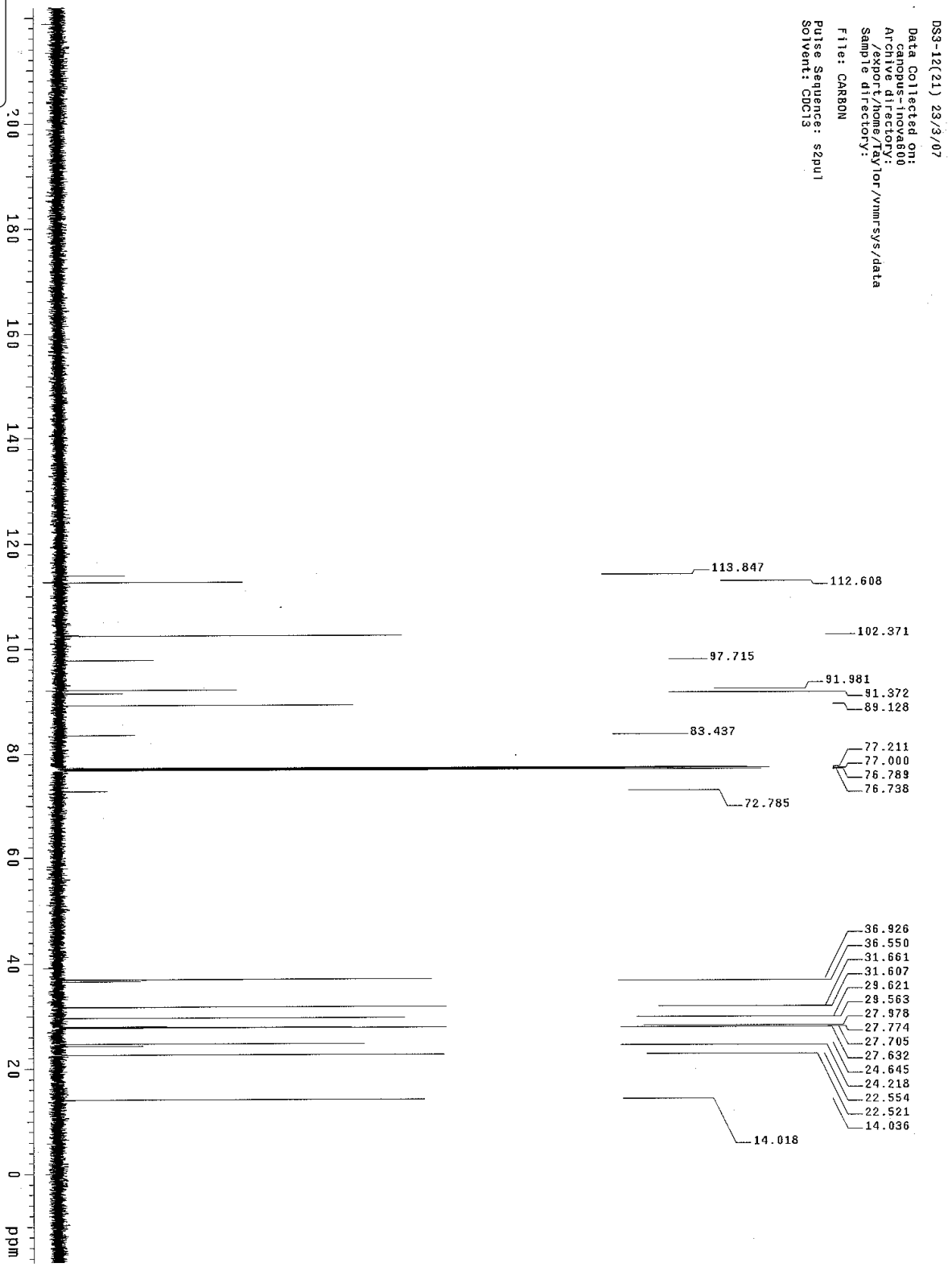
(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrofuranose (**5d**) [75 MHz, $CDCl_3$].



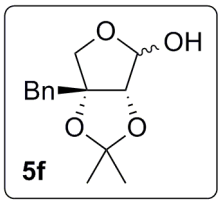


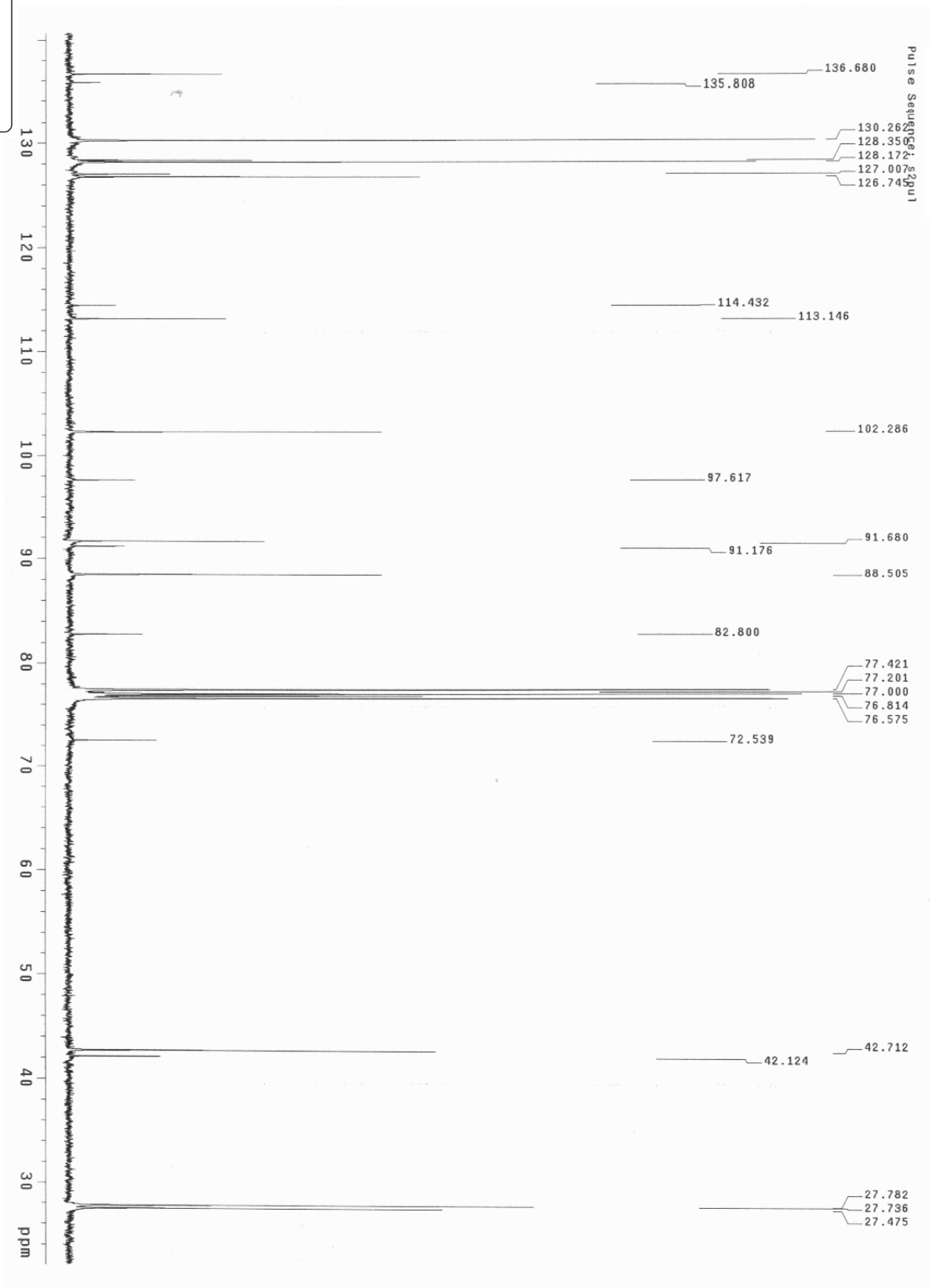
(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrofuranose (**5e**) [150 MHz, $CDCl_3$].



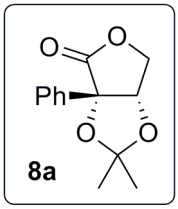


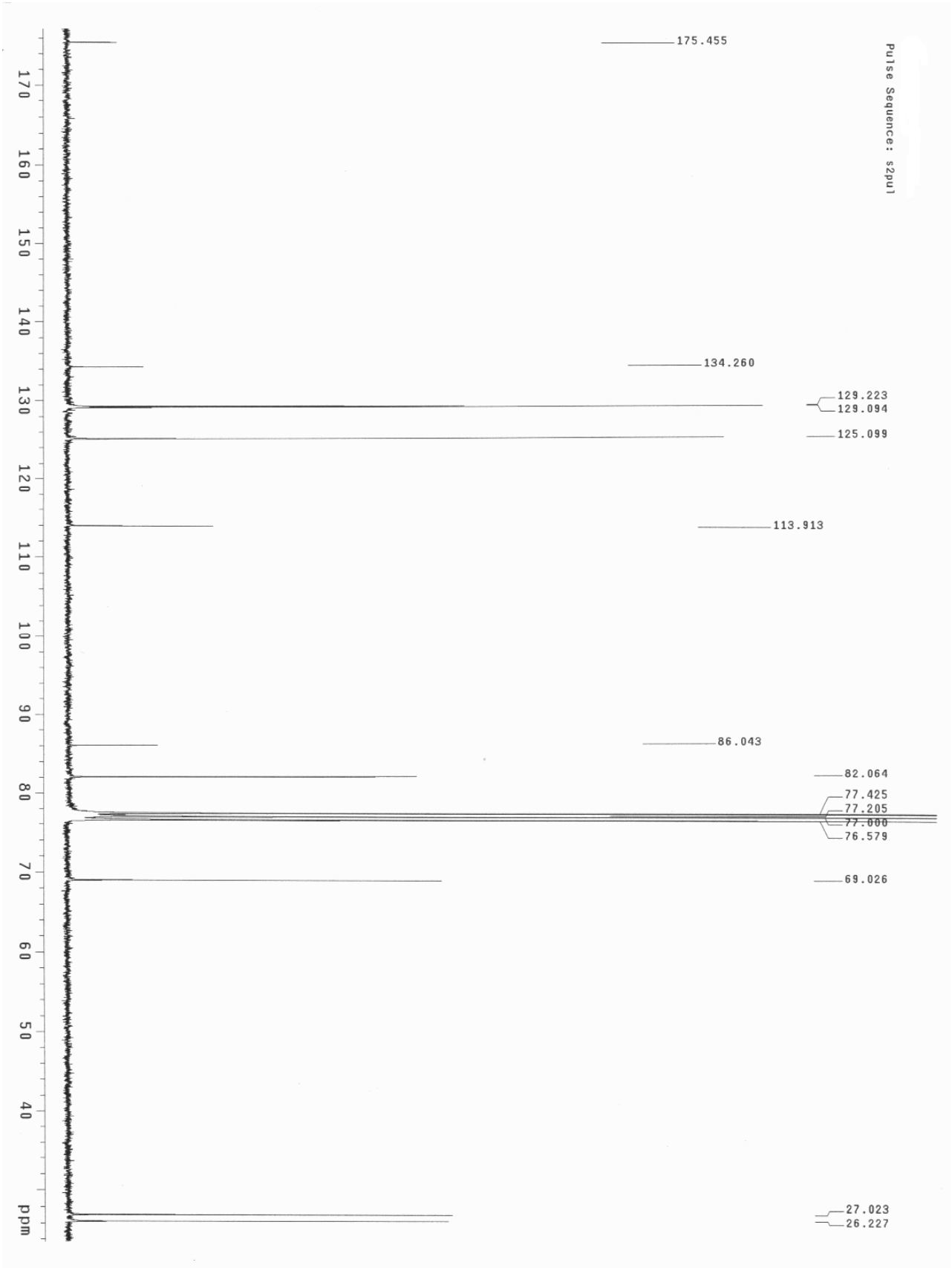
(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrofuranose (**5f**) [75 MHz, $CDCl_3$].



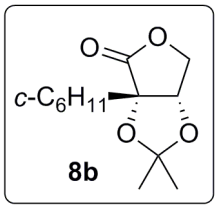


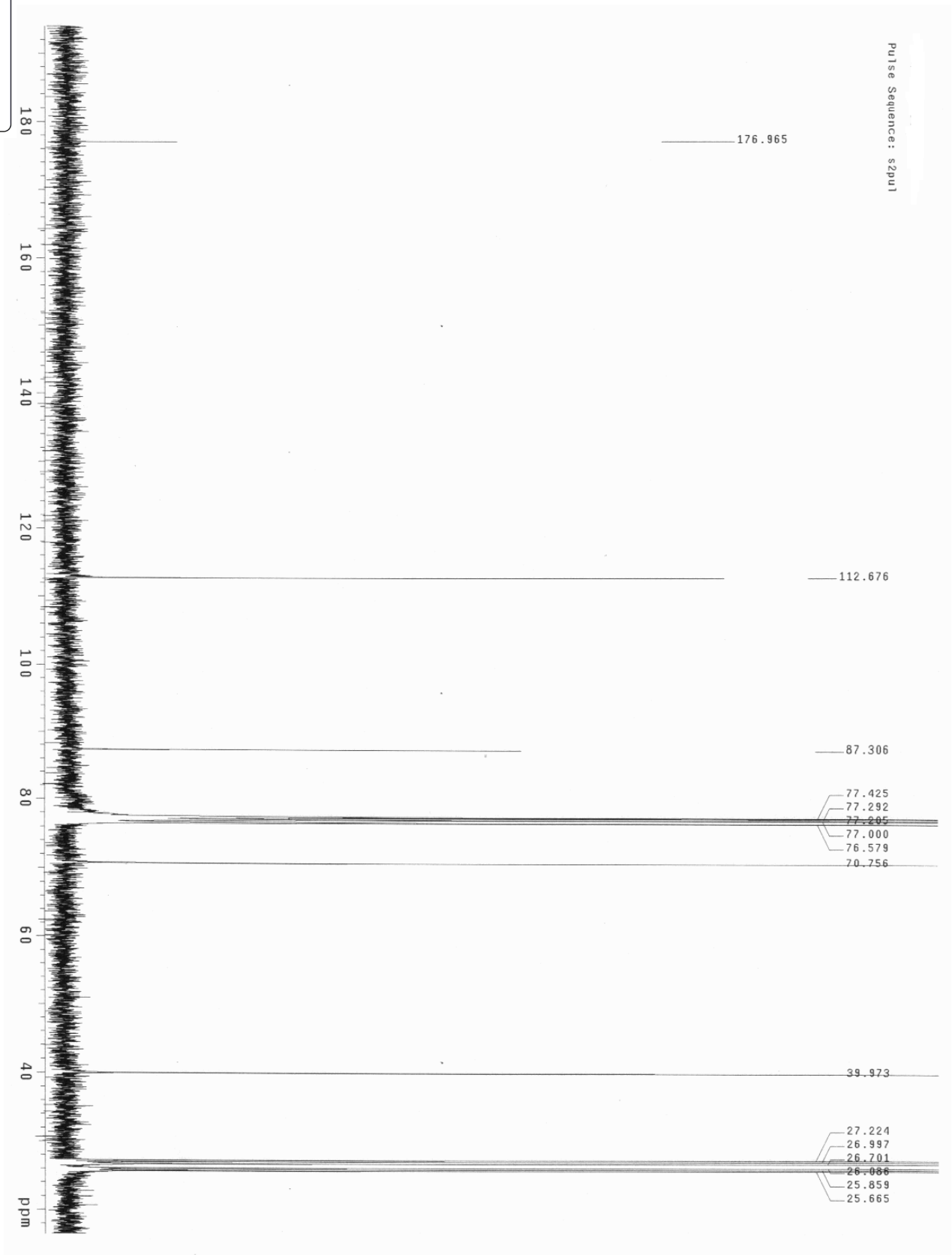
(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrono-1,4-lactone (**8a**) [75 MHz, $CDCl_3$].



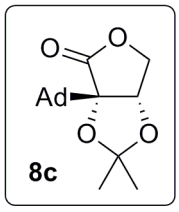


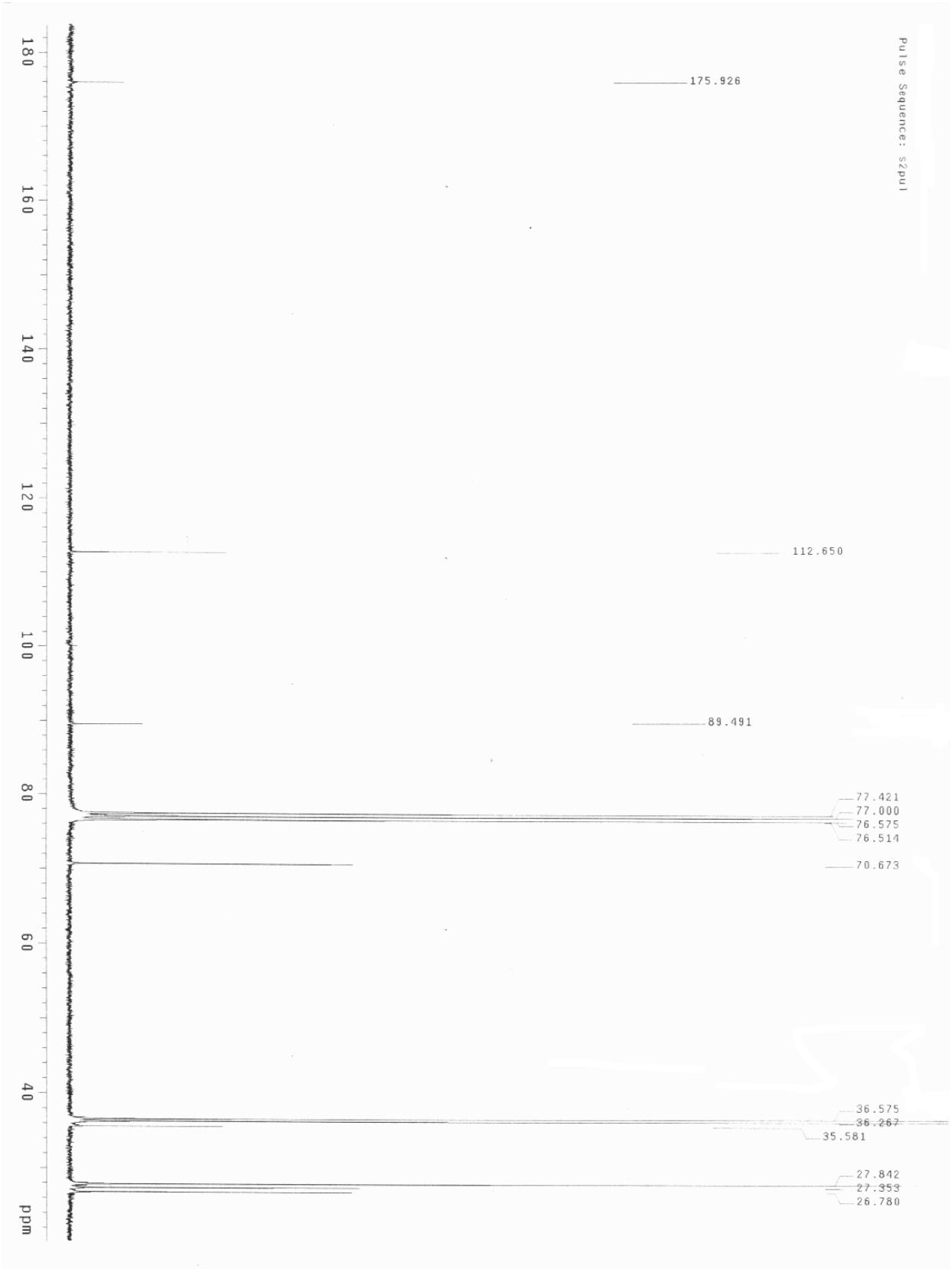
(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrono-1,4-lactone (**8b**) [75 MHz, $CDCl_3$].



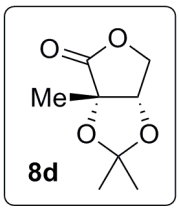


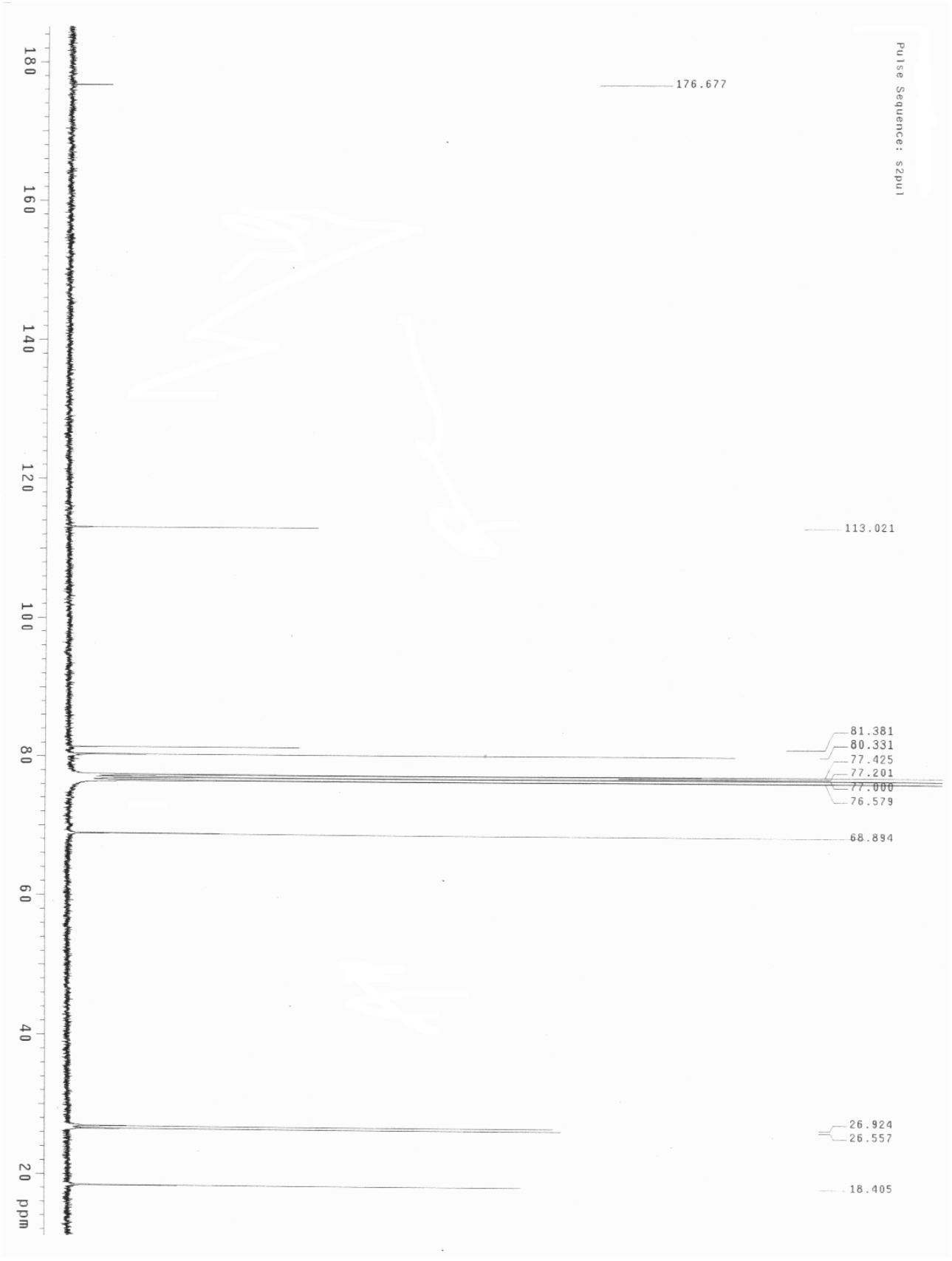
(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrono-1,4-lactone (**8c**) [75 MHz, $CDCl_3$].



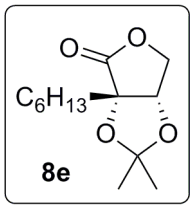


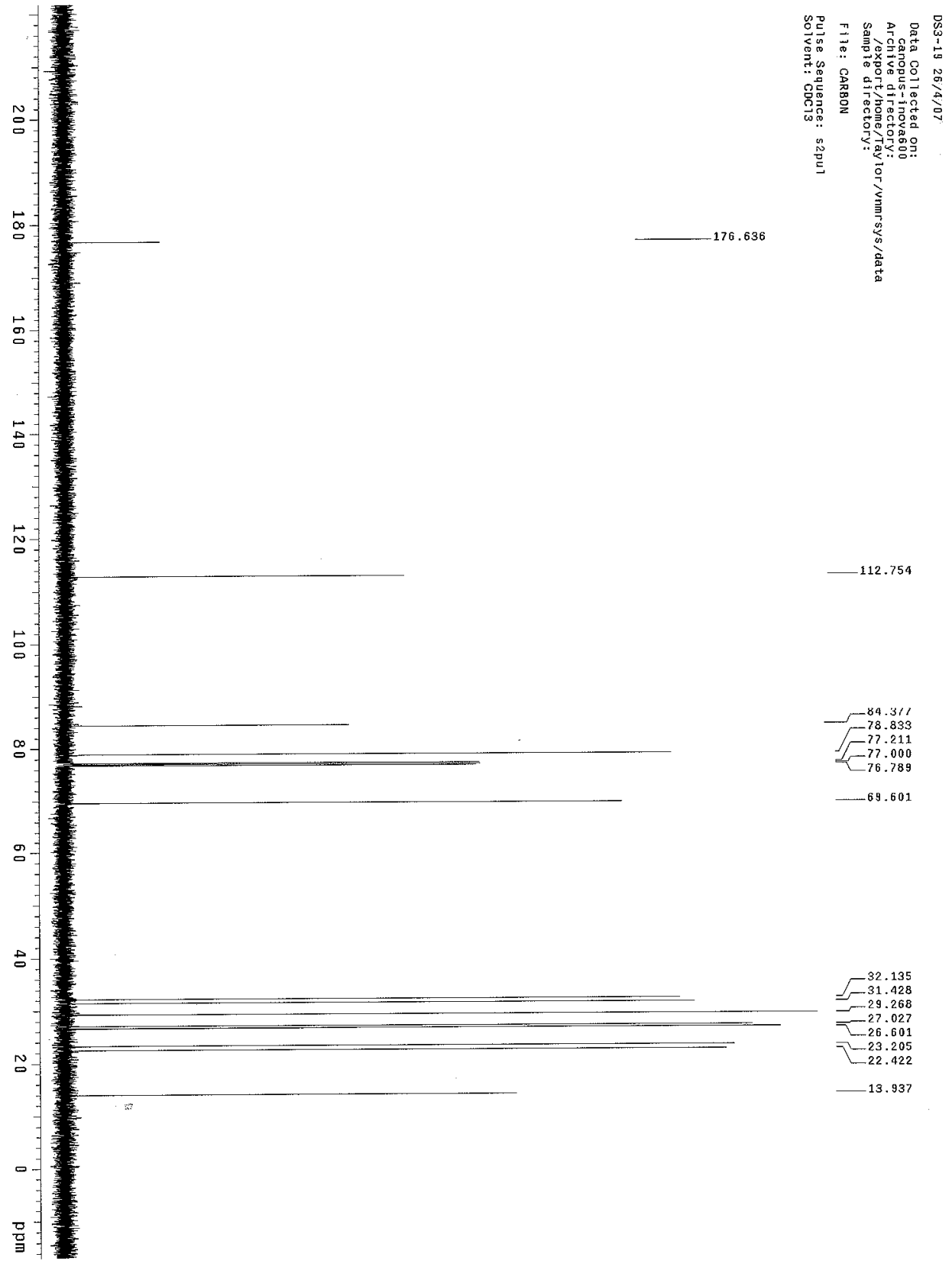
(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrono-1,4-lactone (**8d**) [75 MHz, $CDCl_3$].



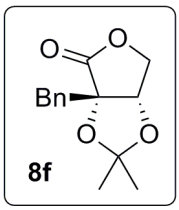


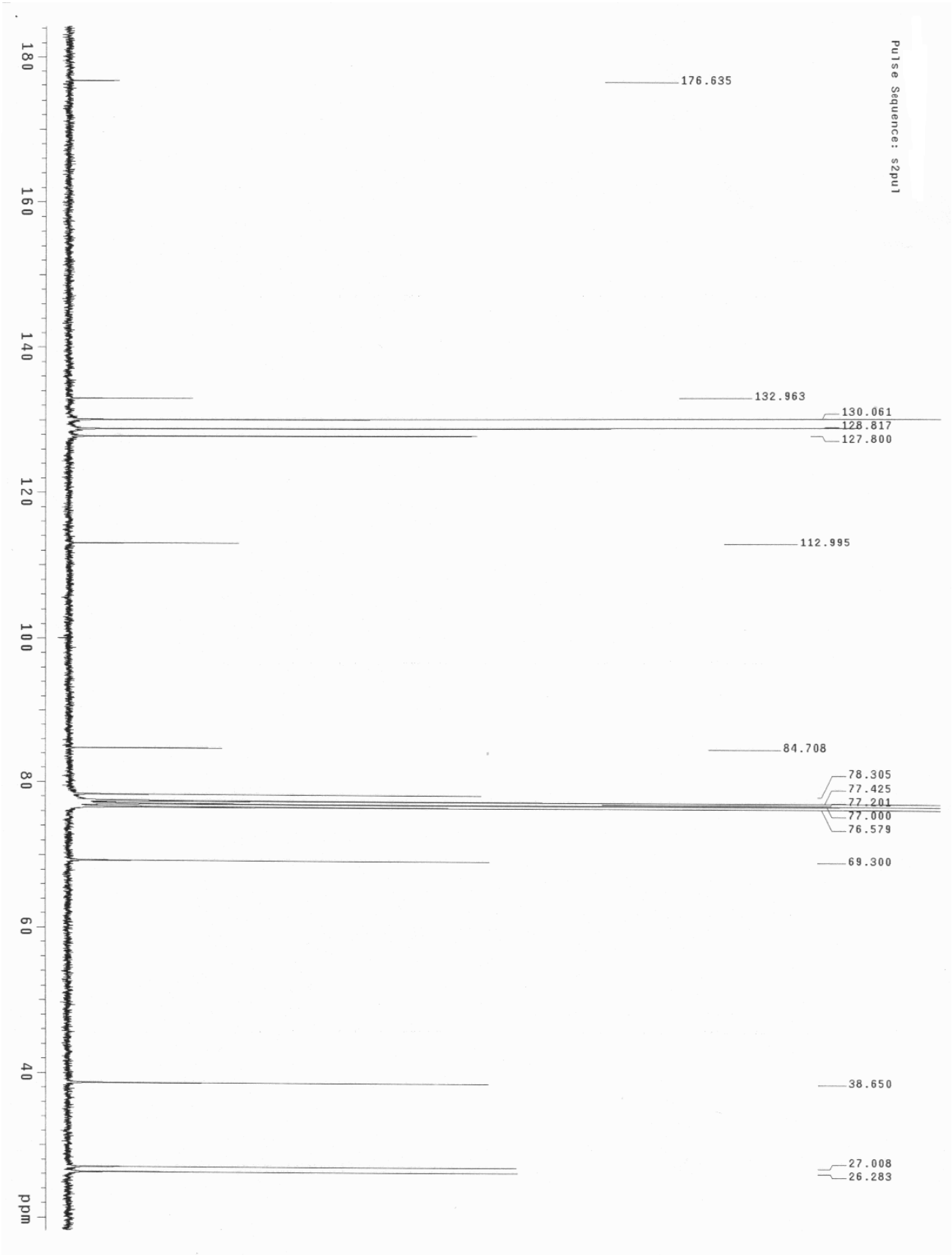
(±)-2,3-*O*-Isopropylidene-2-*C*-hexyl-erythrono-1,4-lactone (**8e**) [150 MHz, $CDCl_3$].



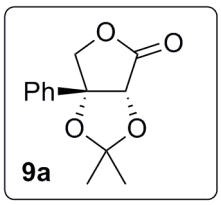


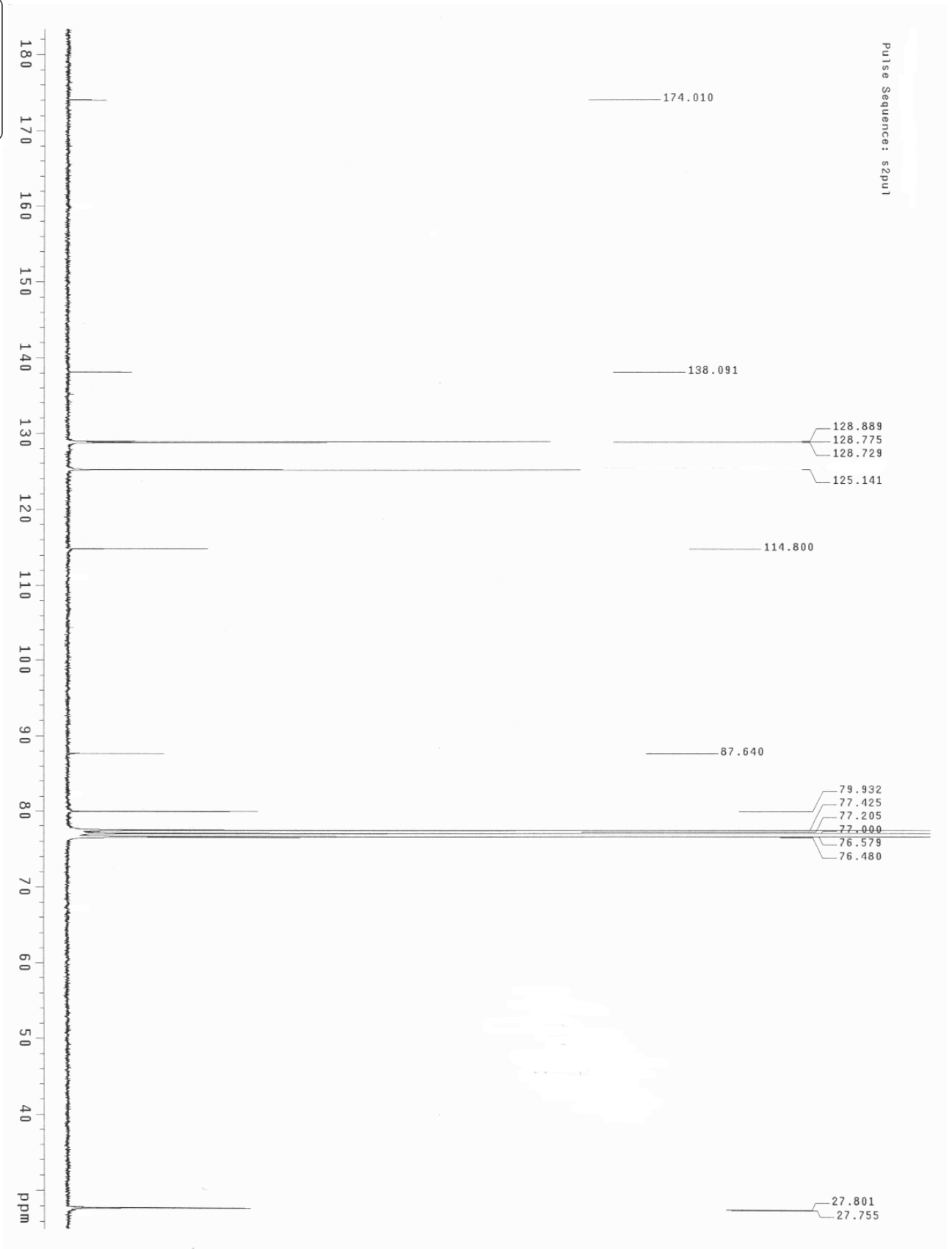
(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrono-1,4-lactone (**8f**) [75 MHz, $CDCl_3$].



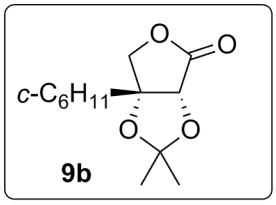


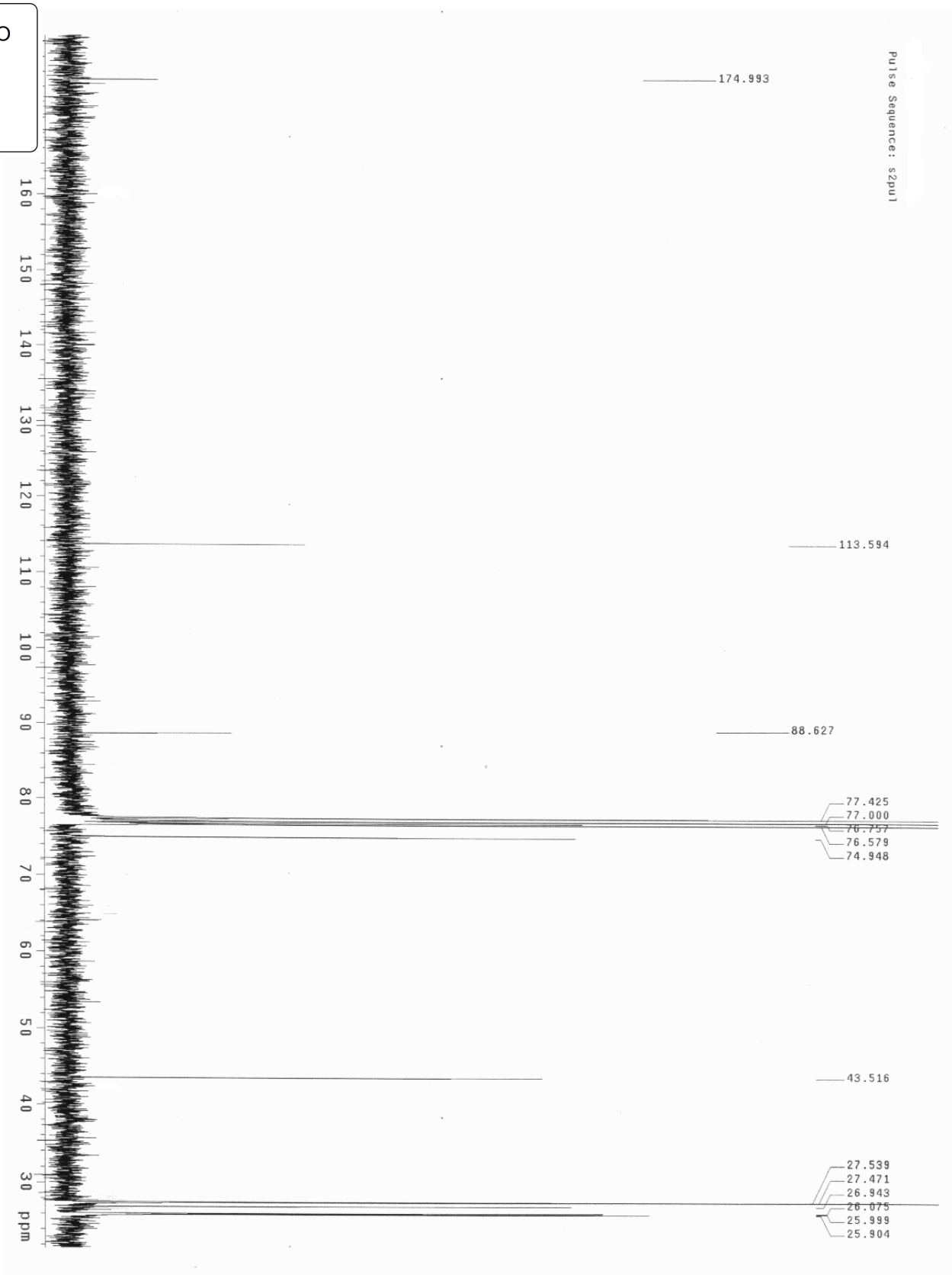
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrono-1,4-lactone (**9a**) [75 MHz, $CDCl_3$].



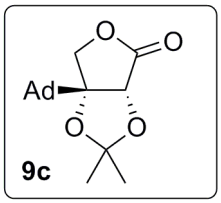


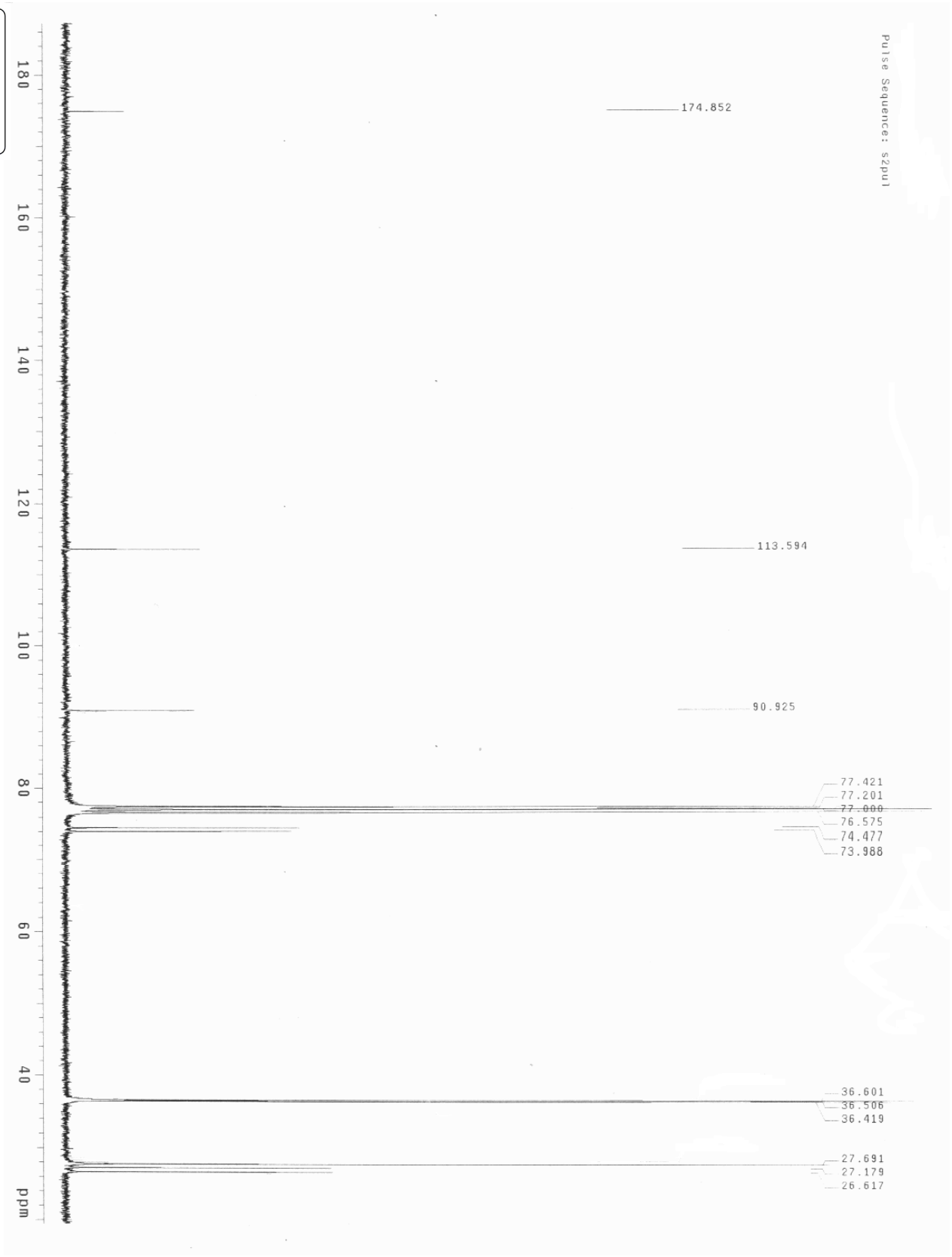
(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrono-1,4-lactone (**9b**) [75 MHz, $CDCl_3$].



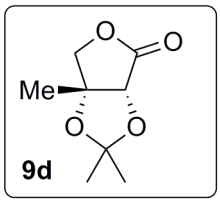


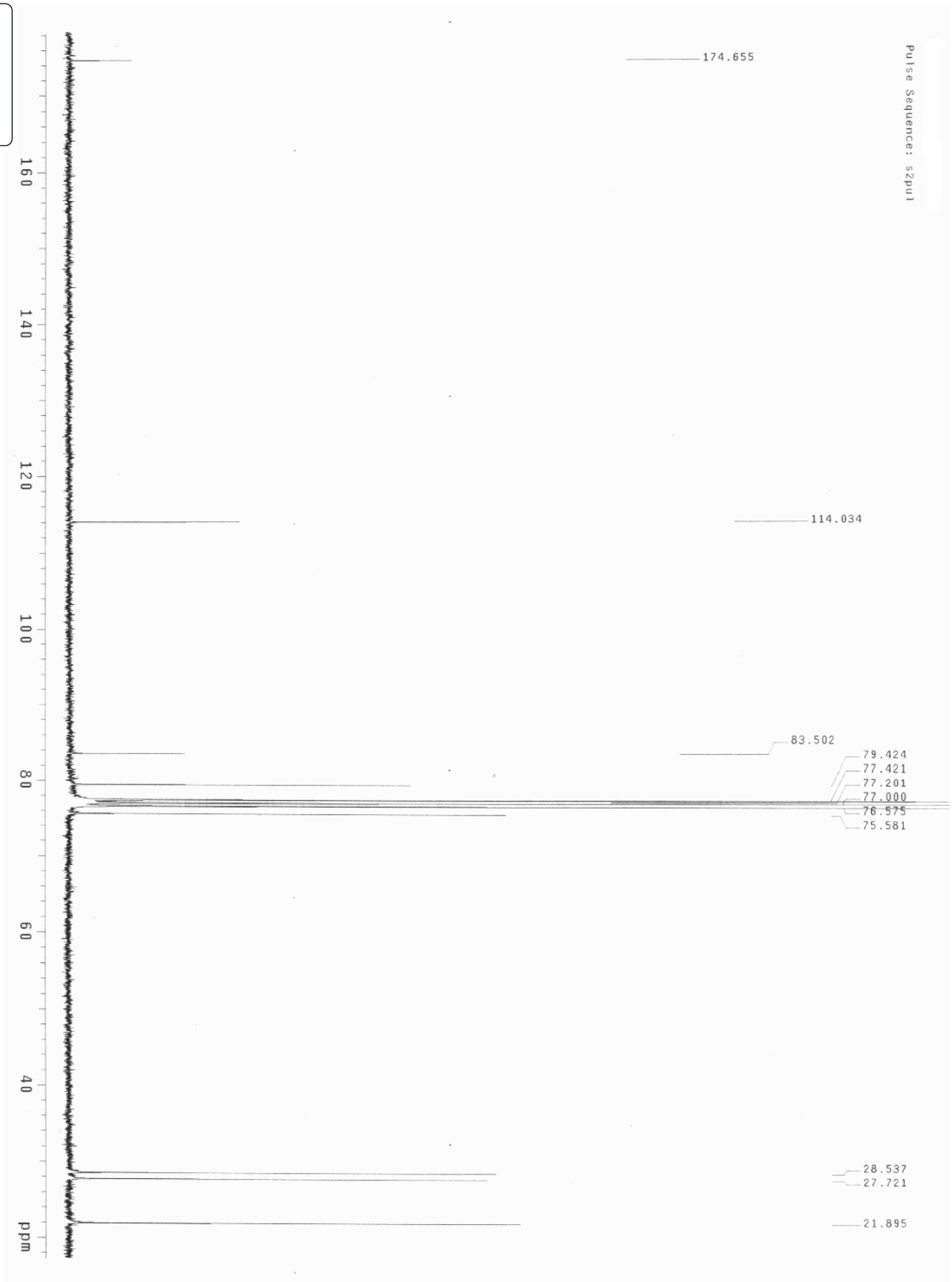
(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrono-1,4-lactone (**9c**) [75 MHz, $CDCl_3$].



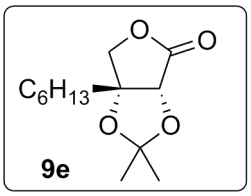


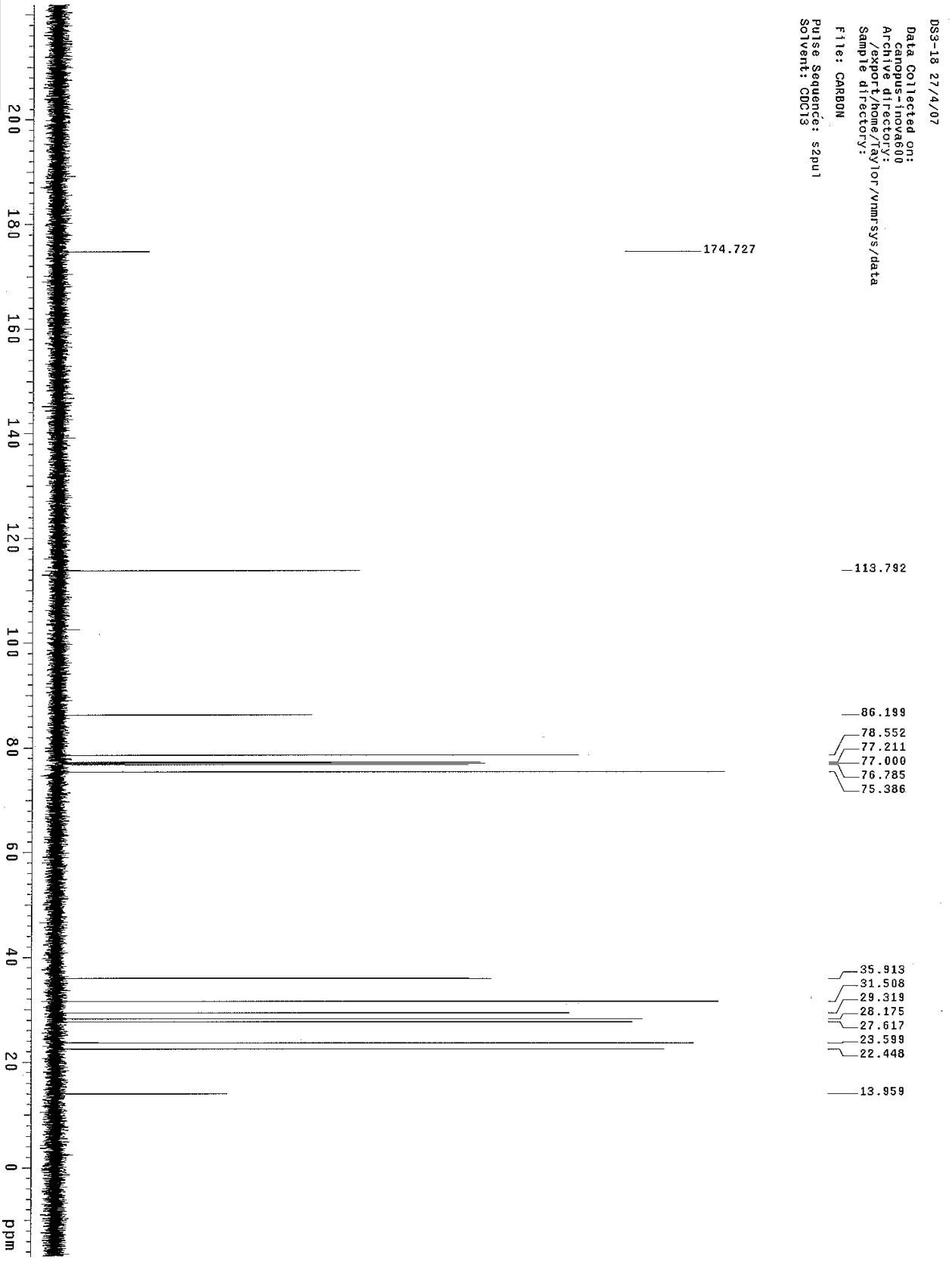
(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrono-1,4-lactone (**9d**) [75 MHz, $CDCl_3$].



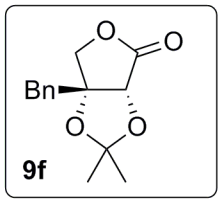


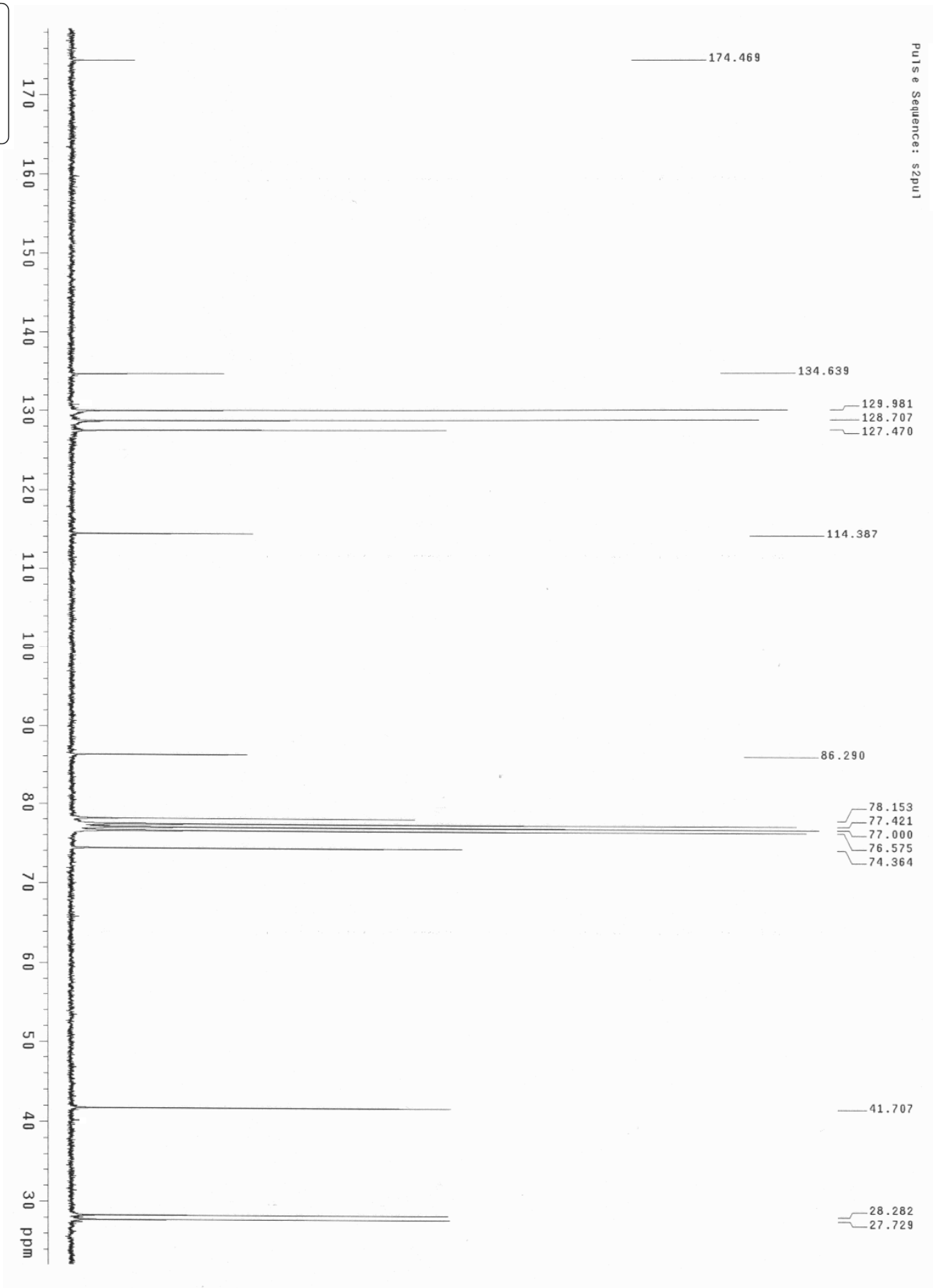
(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrono-1,4-lactone (**9e**) [150 MHz, $CDCl_3$].



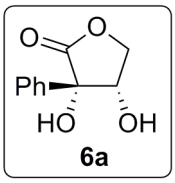


(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrono-1,4-lactone (**9f**) [75 MHz, $CDCl_3$].

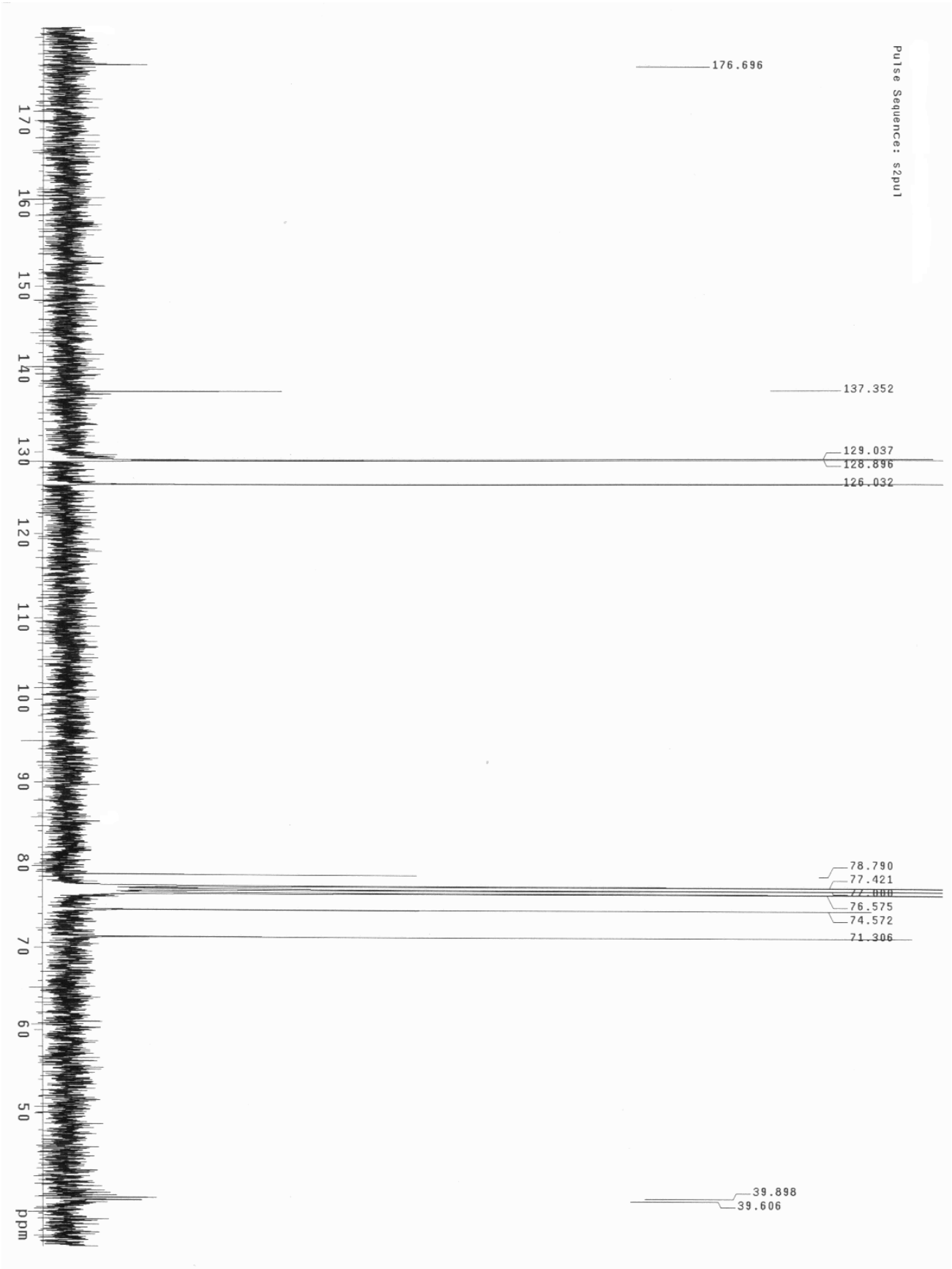




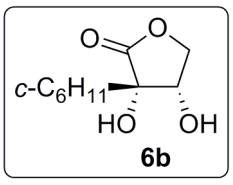
(±)-2-*C*-Phenyl-erythrono-1,4-lactone (**6a**) [75 MHz, $CDCl_3$].

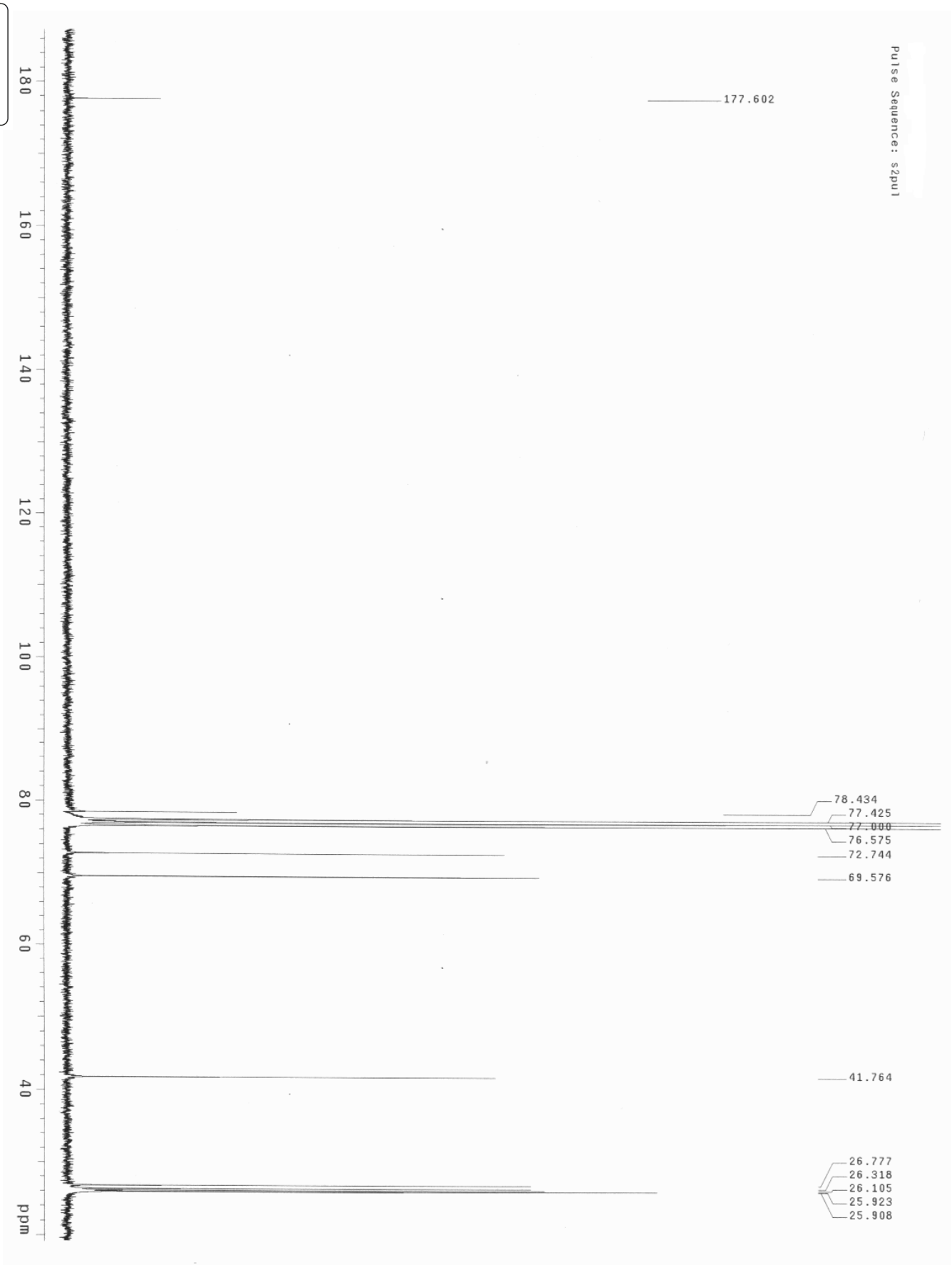


6a

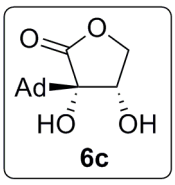


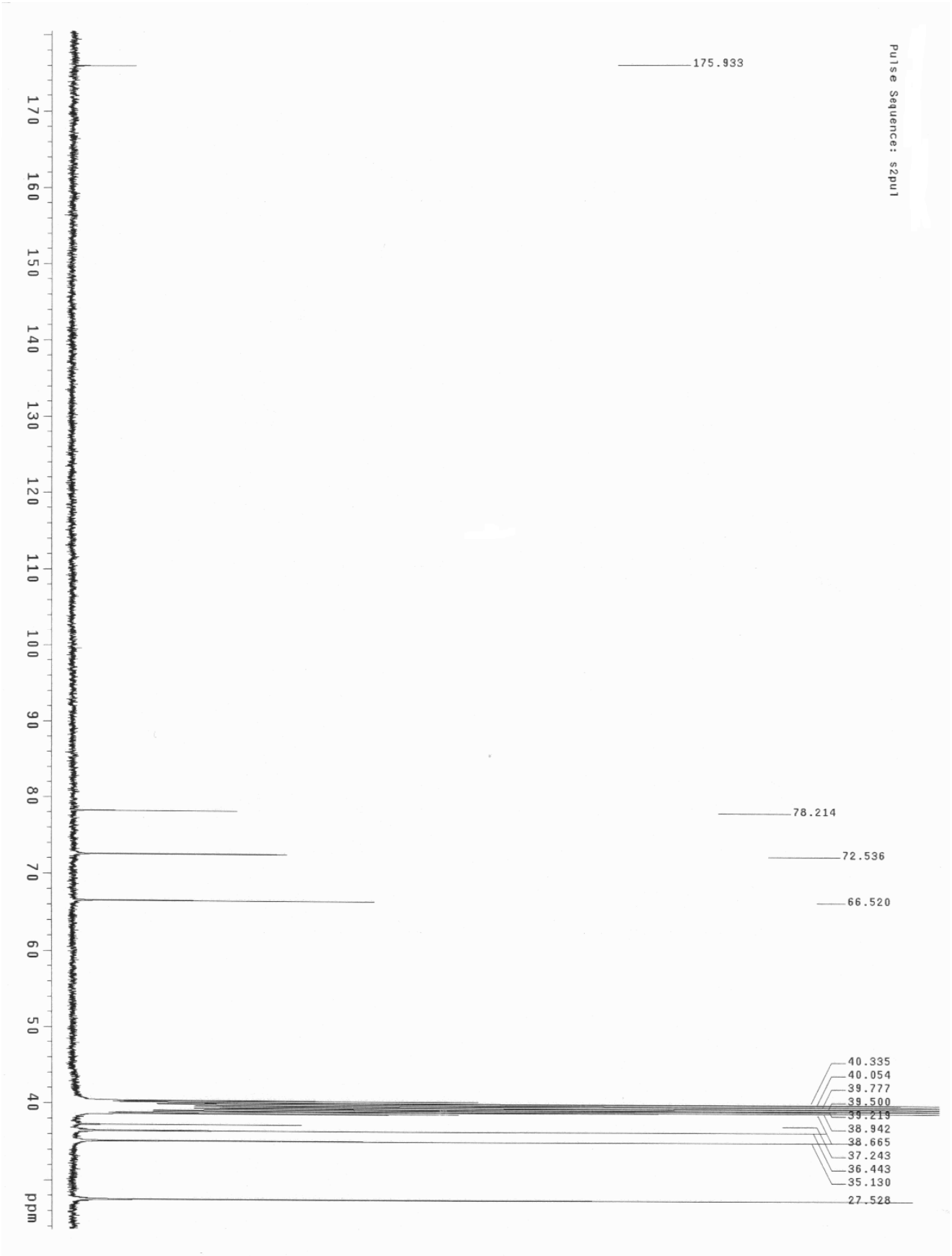
(±)-2-*C*-Cyclohexyl-erythrono-1,4-lactone (**6b**) [75 MHz, $CDCl_3$].



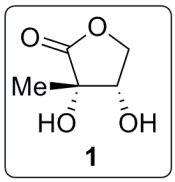


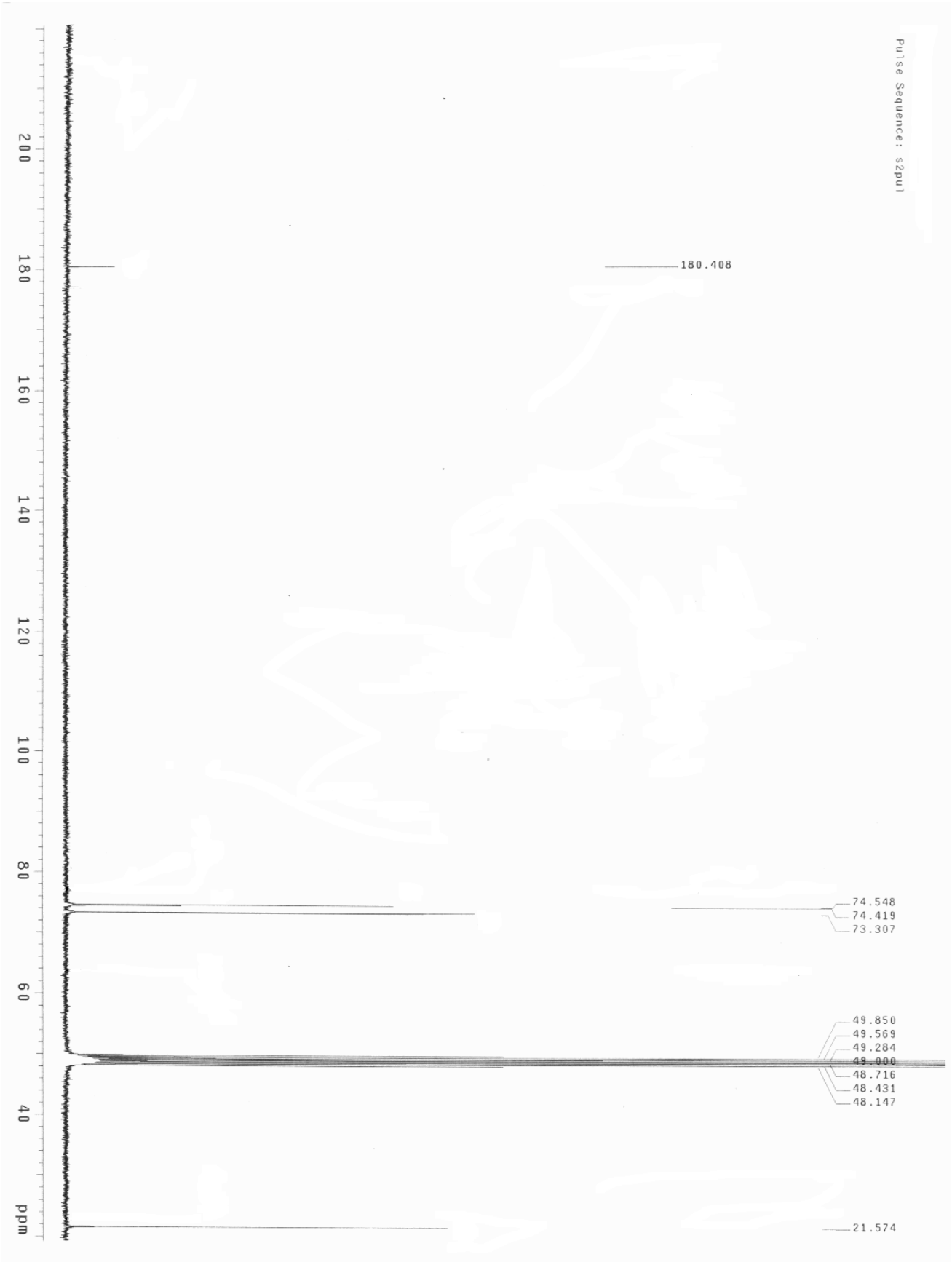
(±)-2-*C*-(1-Adamantyl)-erythrono-1,4-lactone (**6c**) [150 MHz, DMSO-d_6].



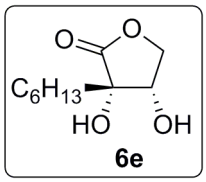


(±)-2-*C*-D-Methyl-erythrono-1,4-lactone (**1**) [75 MHz, CD_3OD].

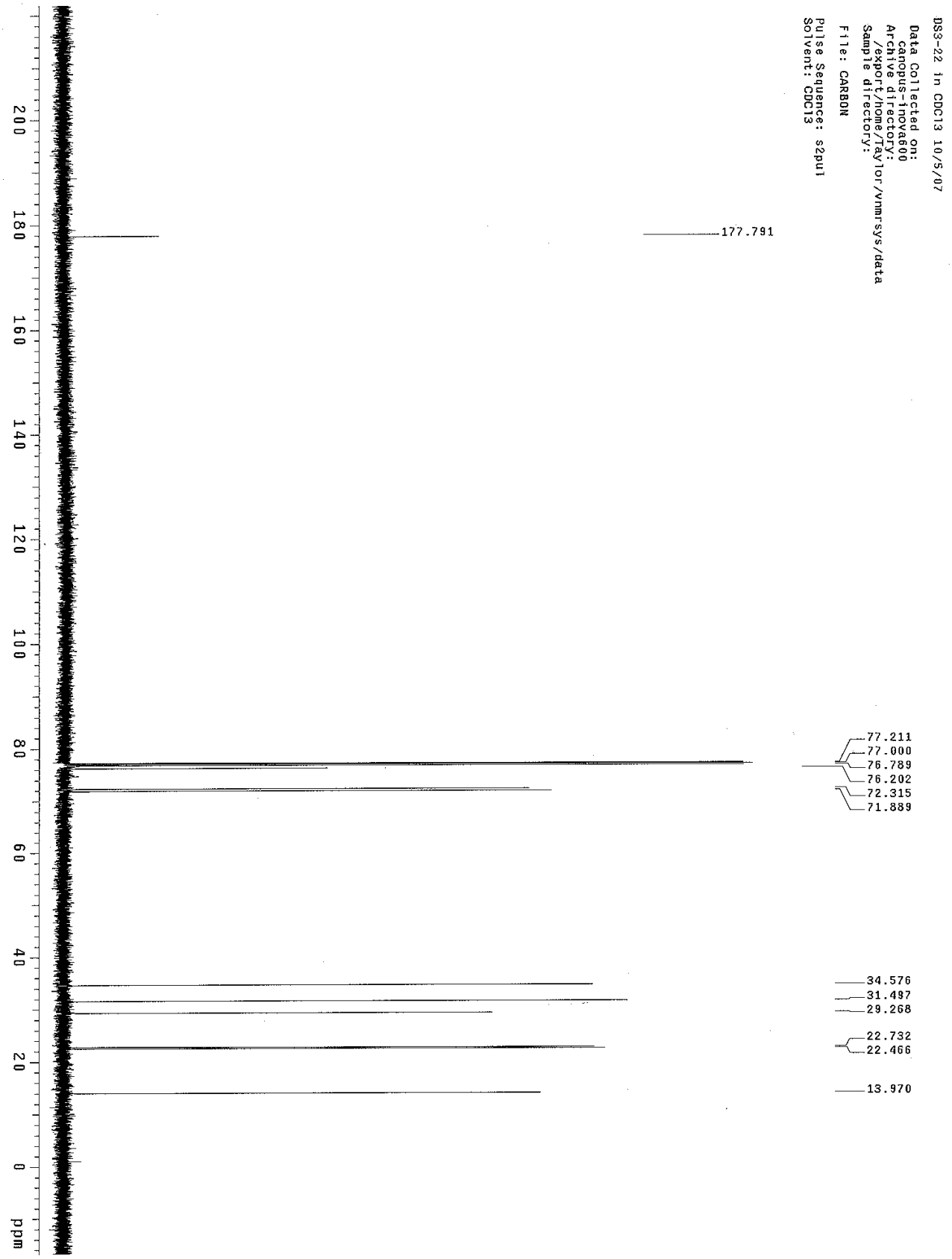




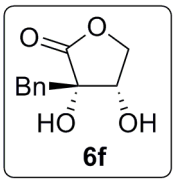
(±)-2-*C*-Hexyl-erythrono-1,4-lactone (**6e**) [150 MHz, $CDCl_3$].



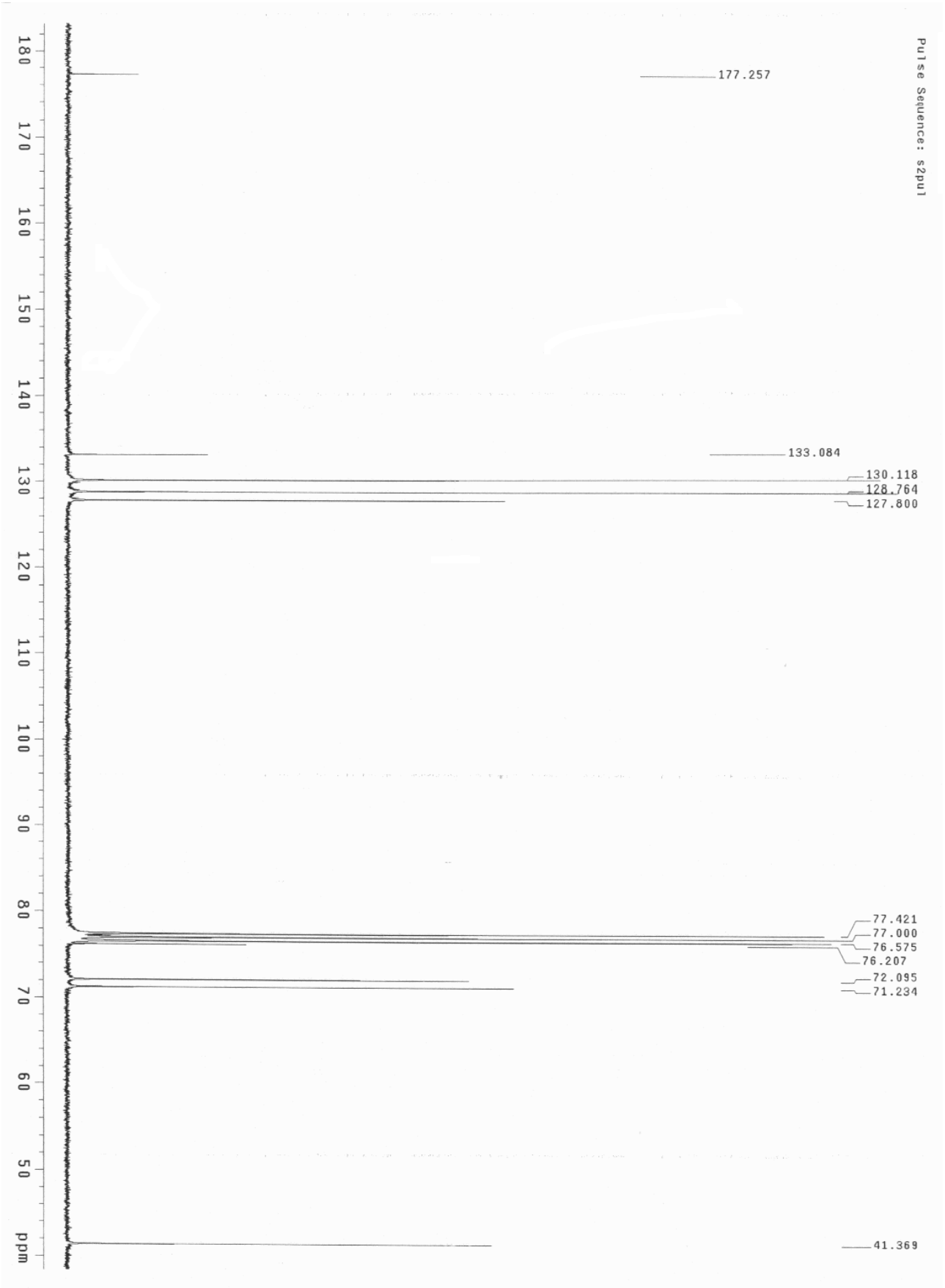
6e



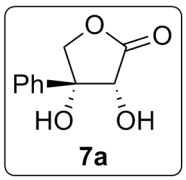
(±)-2-*C*-Benzyl-erythrono-1,4-lactone (**6f**) [150 MHz, $CDCl_3$].

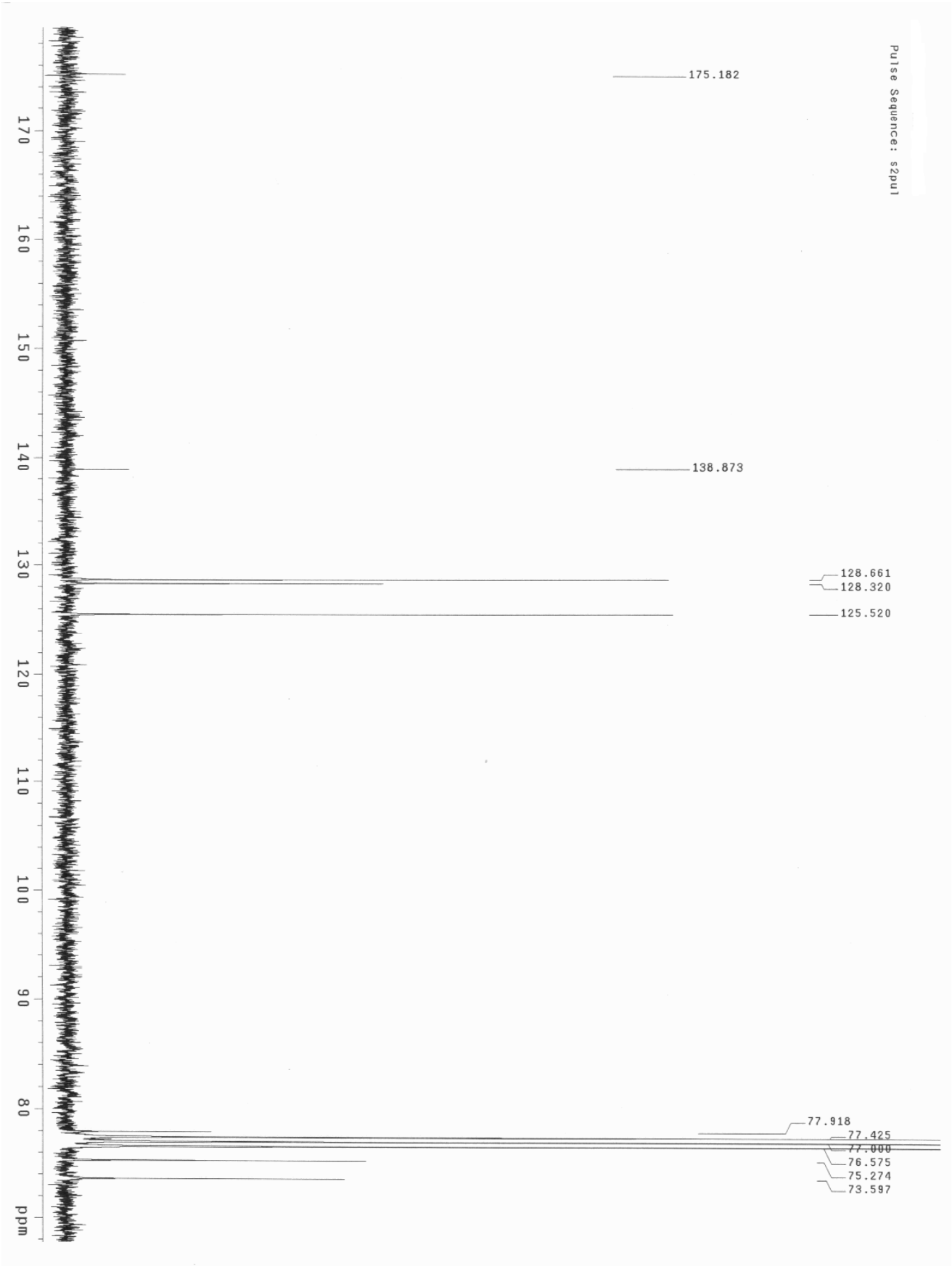


6f

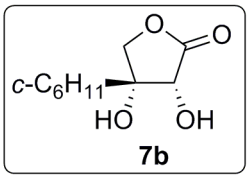


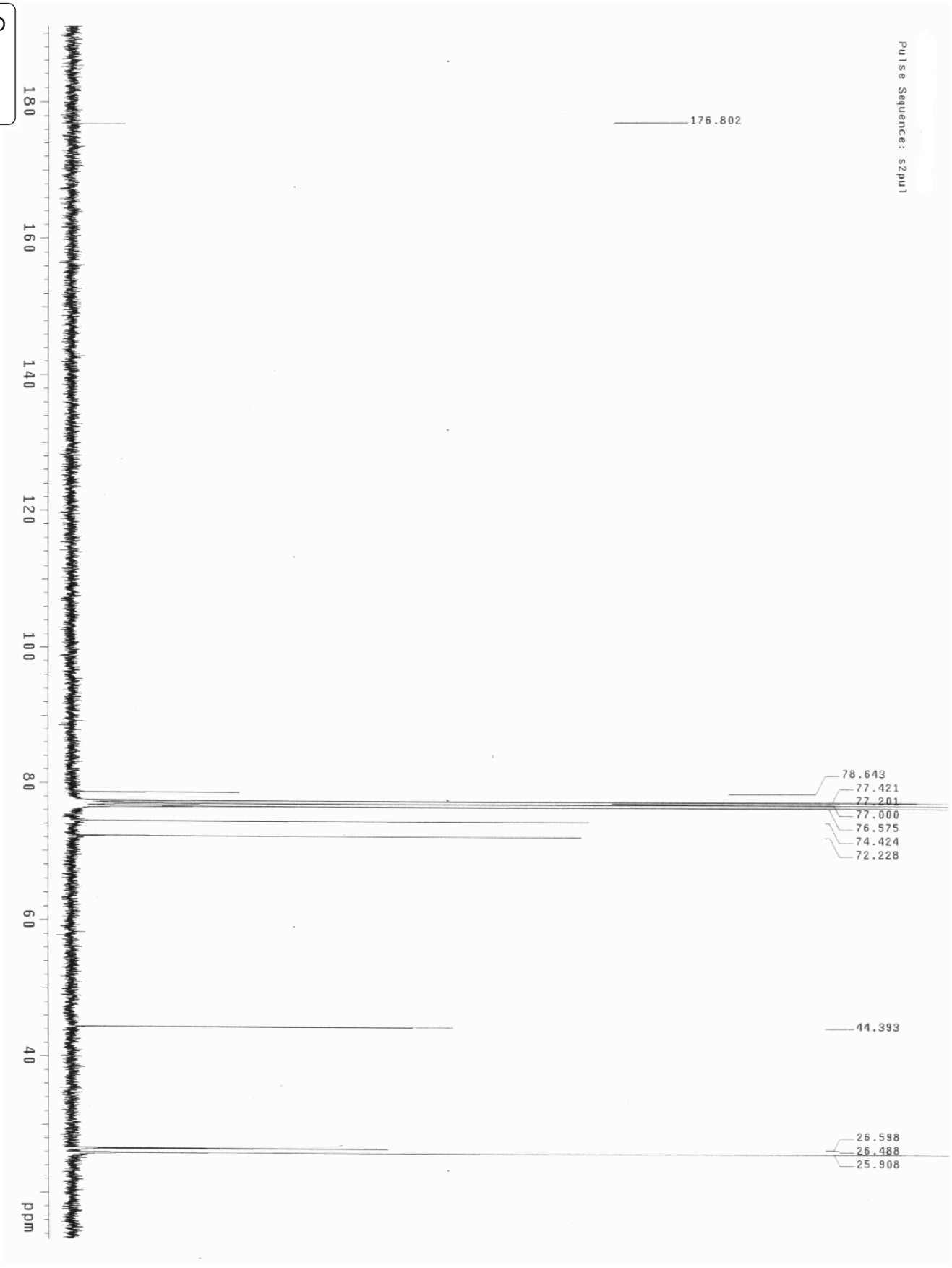
(±)-3-*C*-Phenyl-erythrono-1,4-lactone (**7a**) [75 MHz, $CDCl_3$ + 2 drop DMSO-d_6].



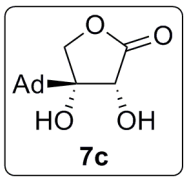


(±)-3-*C*-Cyclohexyl-erythrono-1,4-lactone (**7b**) [75 MHz, $CDCl_3$].

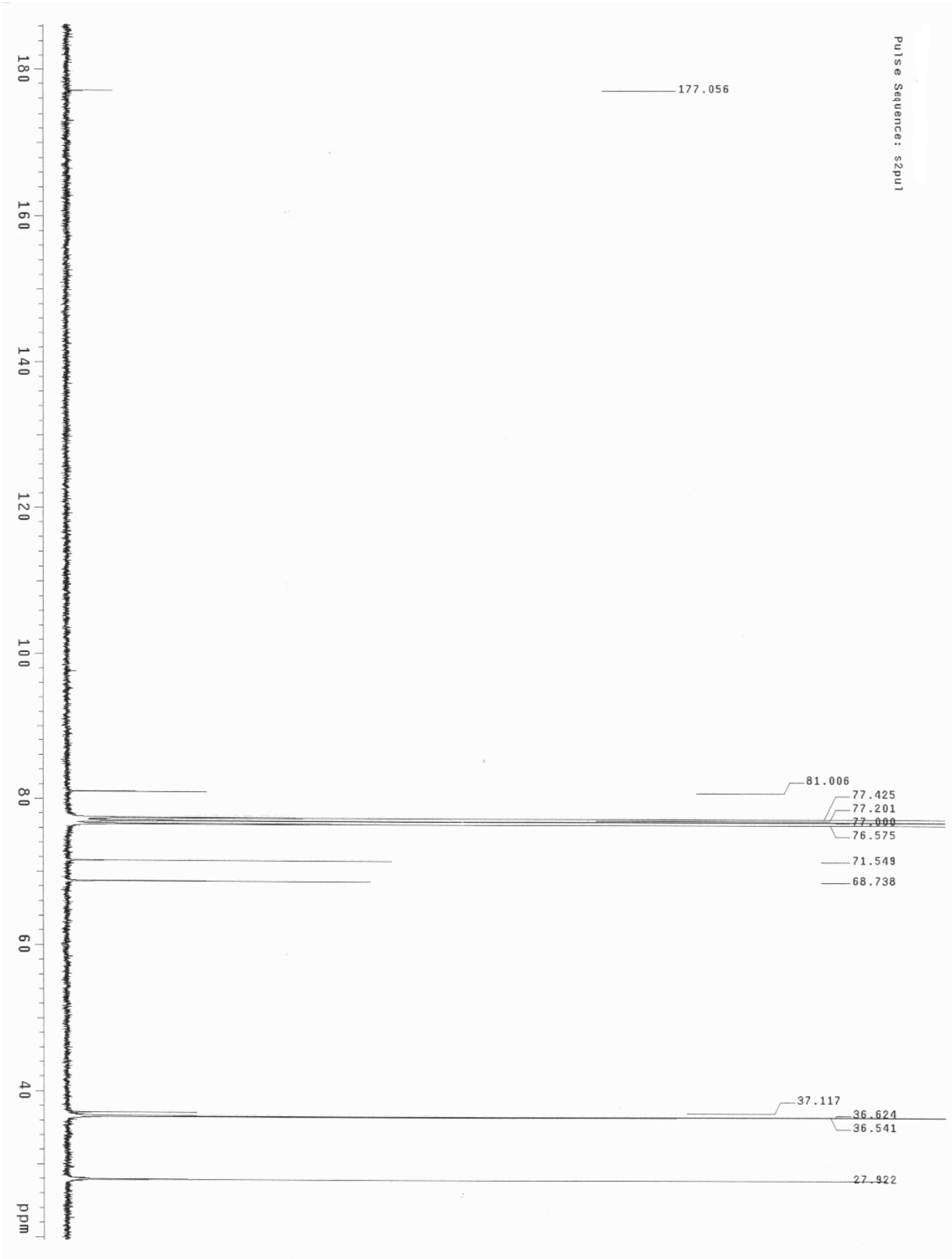




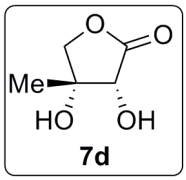
(±)-3-*C*-(1-Adamantyl)-erythrono-1,4-lactone (**7c**) [75 MHz, $CDCl_3$].

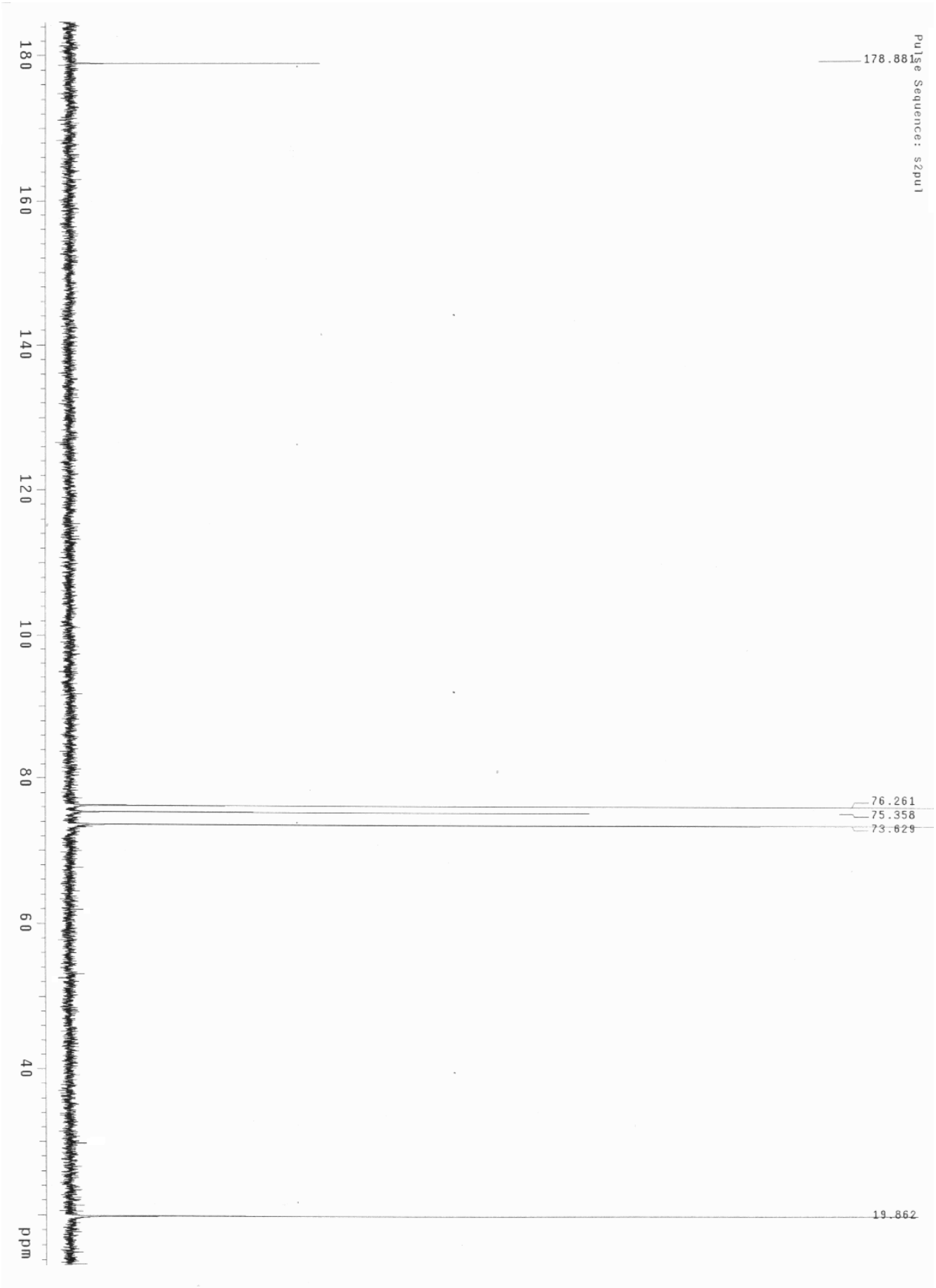


7c

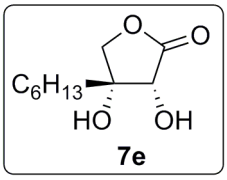


(±)-3-*C*-Methyl-erythrono-1,4-lactone (**7d**) [75 MHz, D_2O].

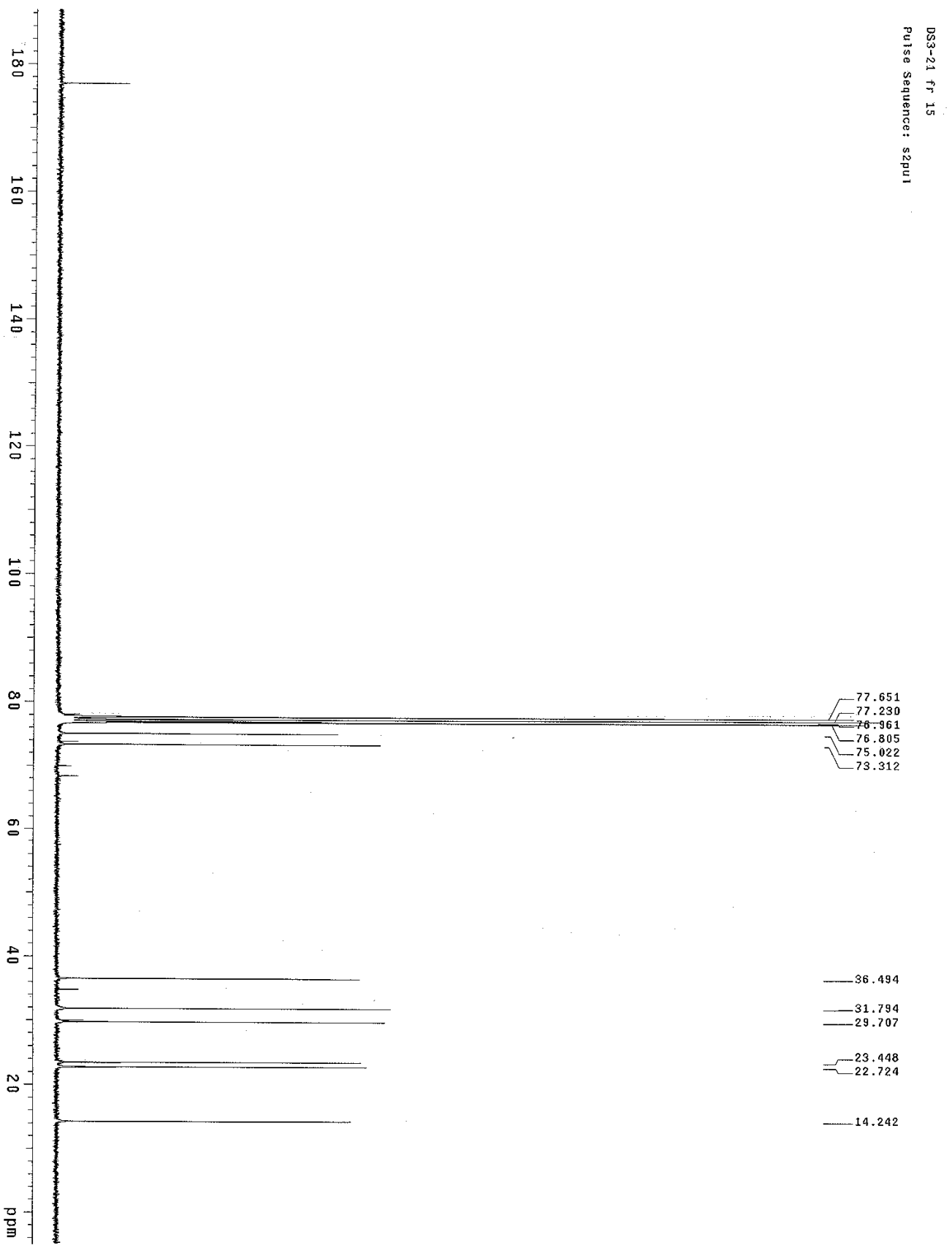




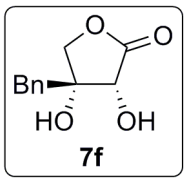
(±)-3-*C*-Hexyl-erythrono-1,4-lactone (**7e**) [75 MHz, $CDCl_3$].



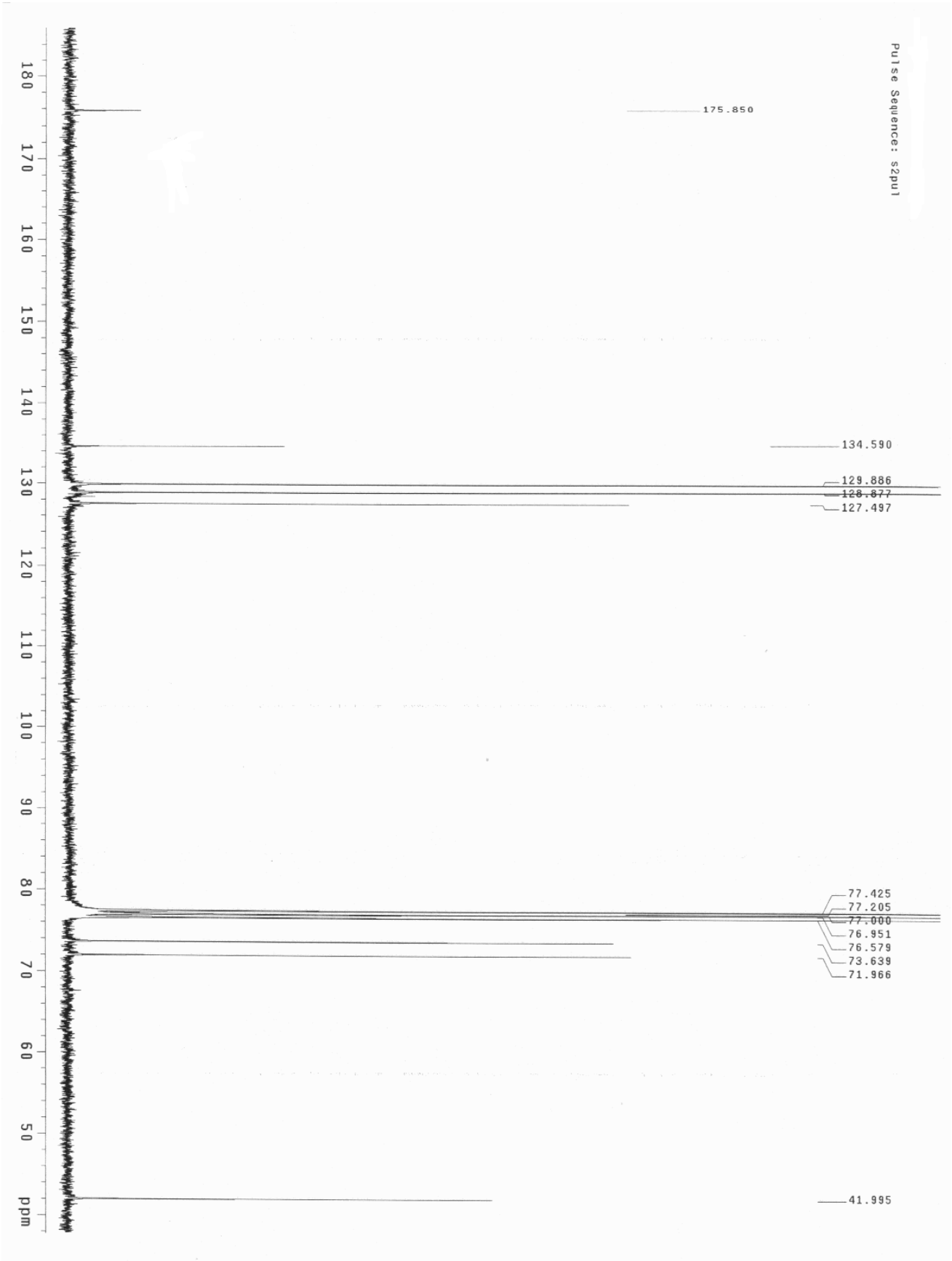
7e



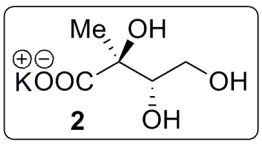
(±)-3-*C*-Benzyl-erythrono-1,4-lactone (**7f**) [75 MHz, $CDCl_3$].

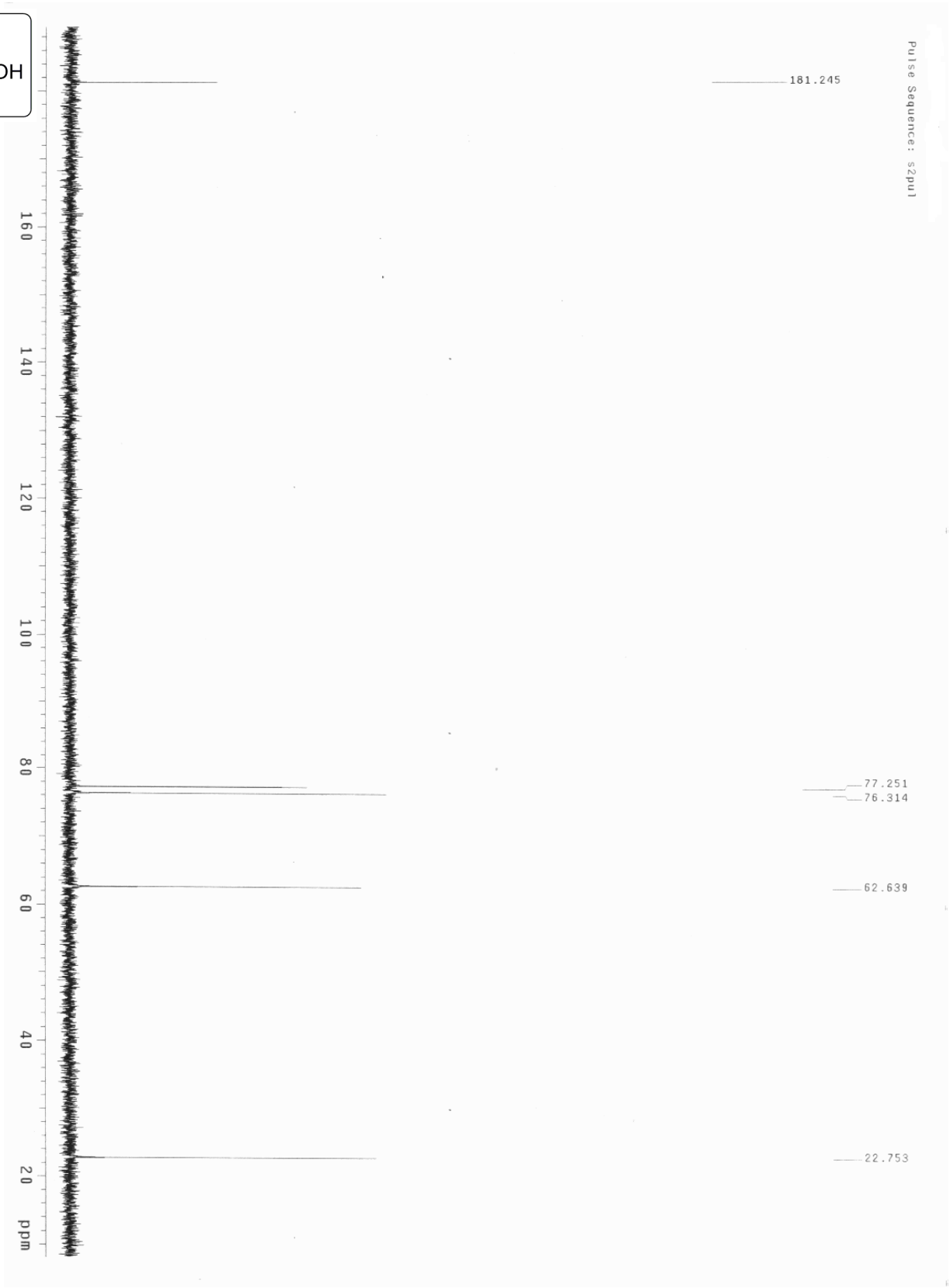


7f

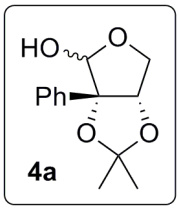


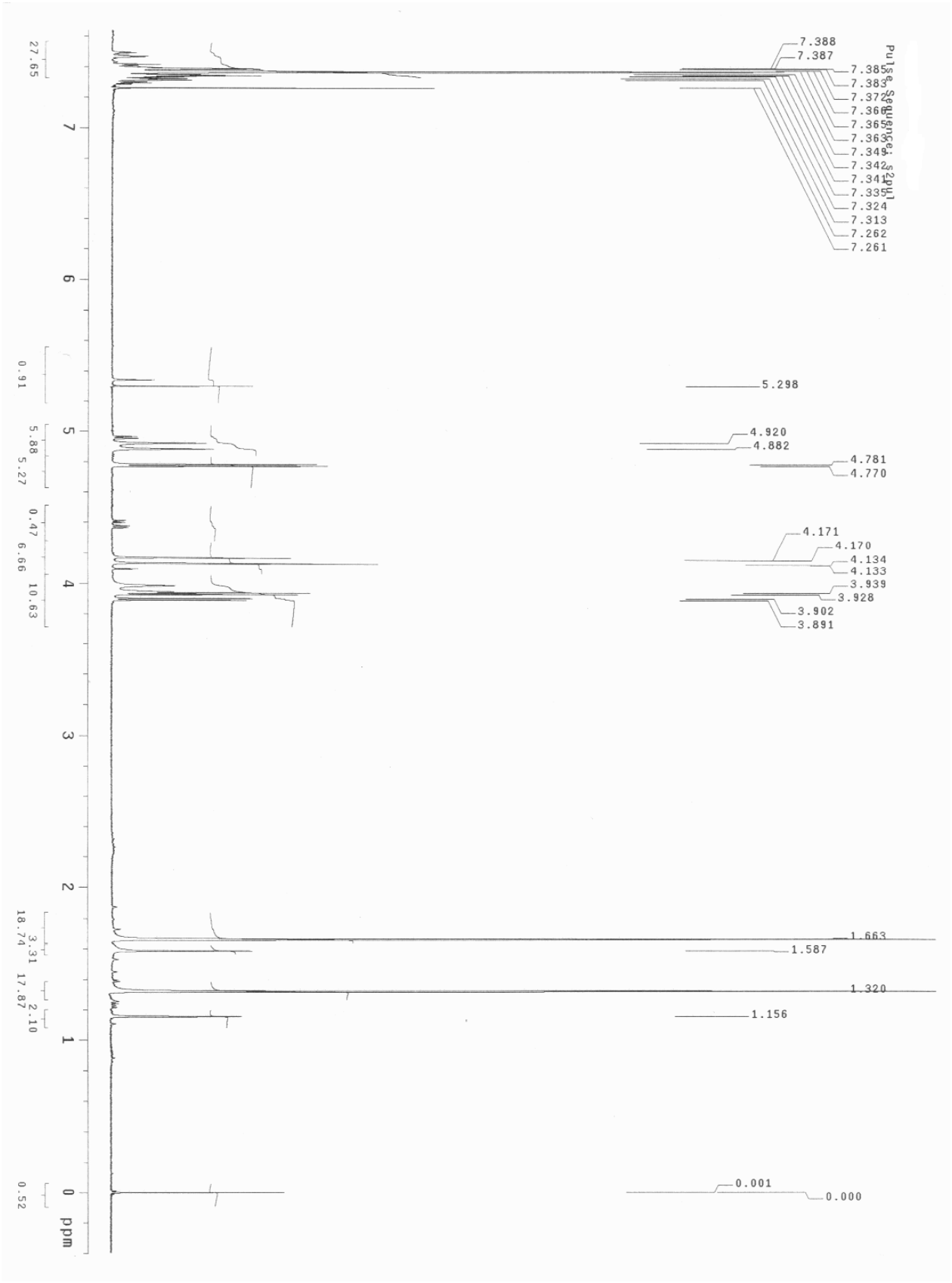
(±)-Potassium 2,3,4-trihydroxy-2-methylbutanoate (**2**) [75 MHz, D_2O].



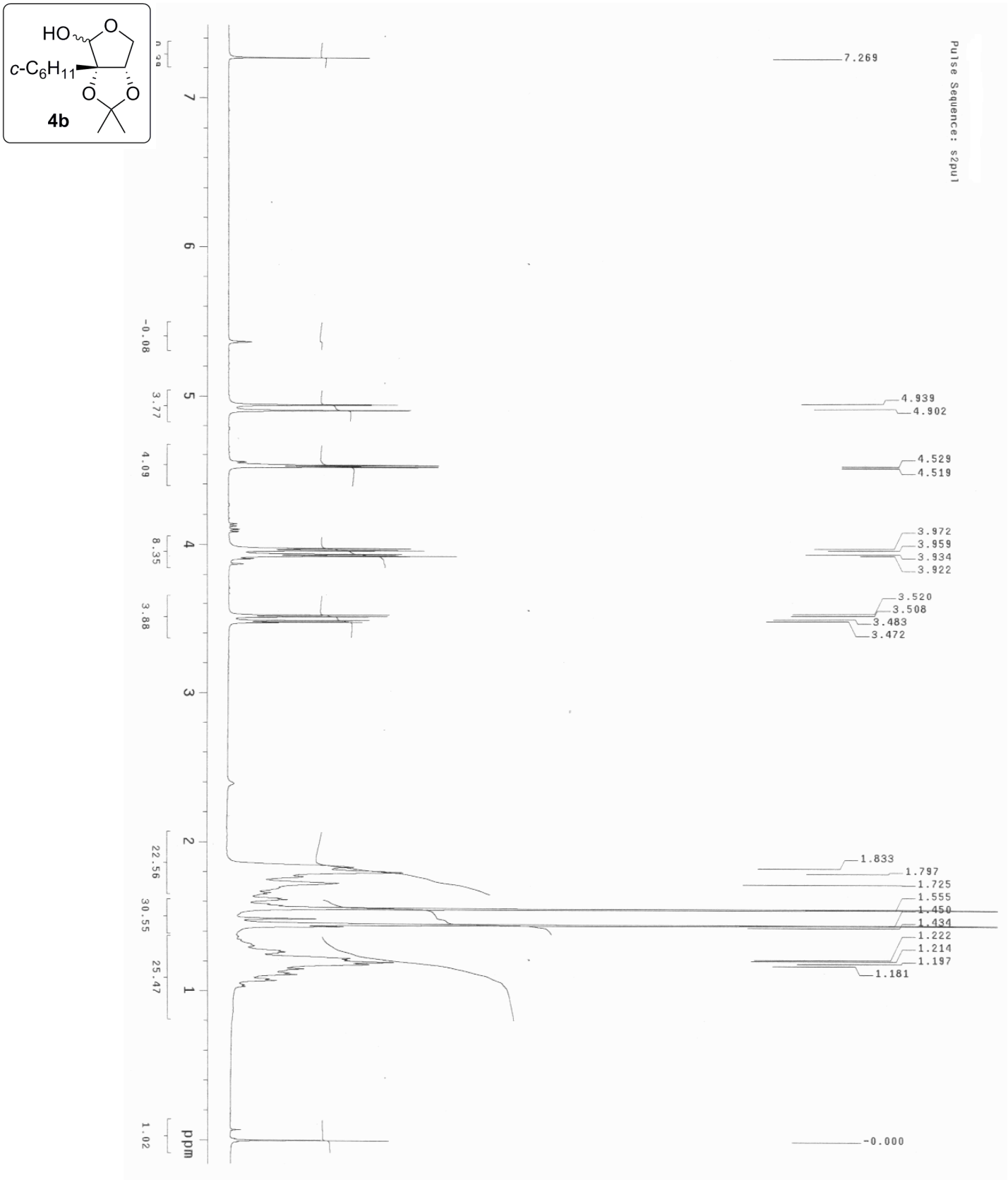


(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrofuranose (**4a**) [300 MHz, $CDCl_3$].

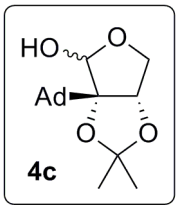


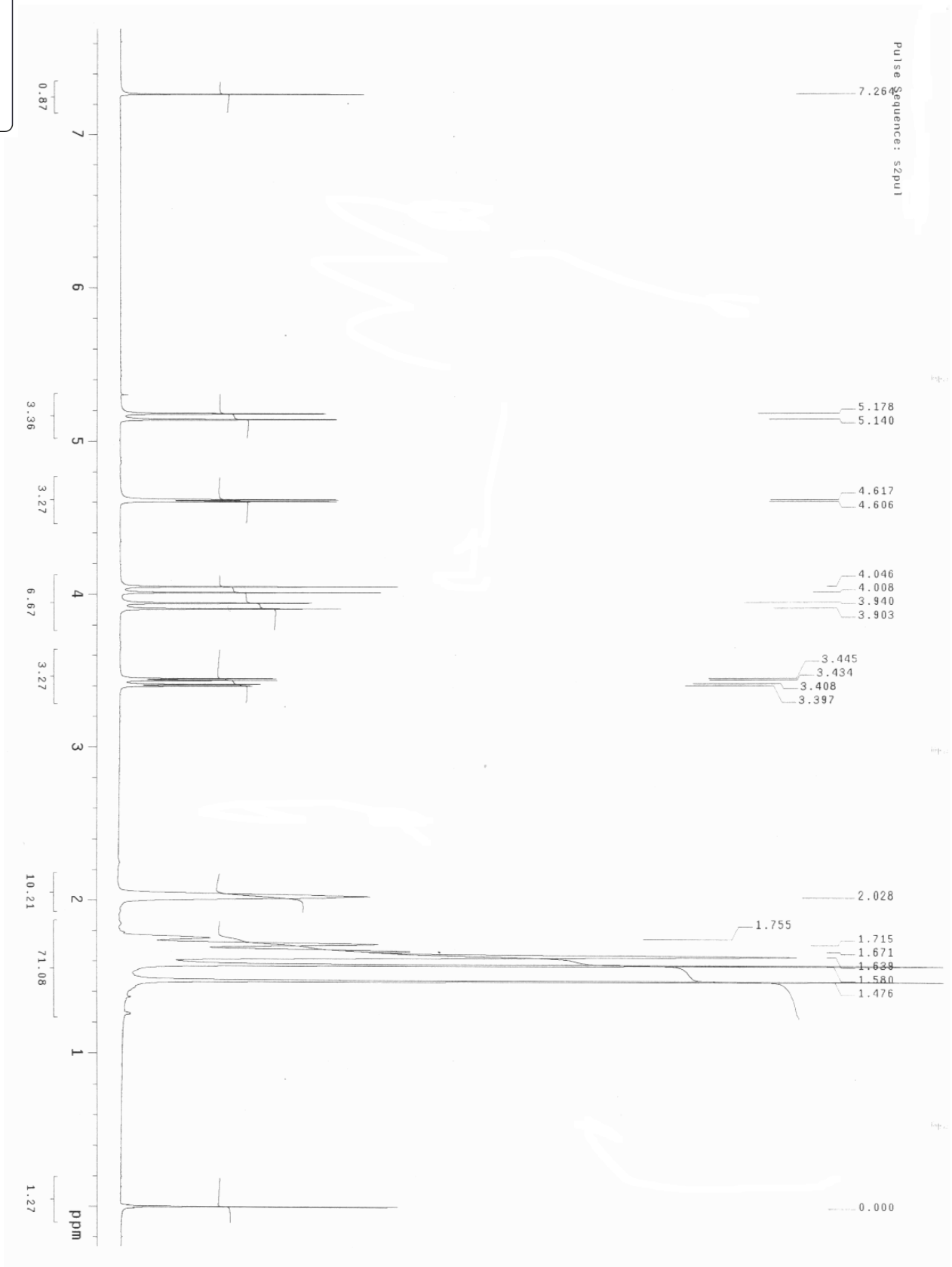


(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrofuranose (**4b**) [300 MHz, $CDCl_3$].

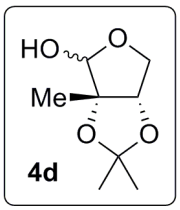


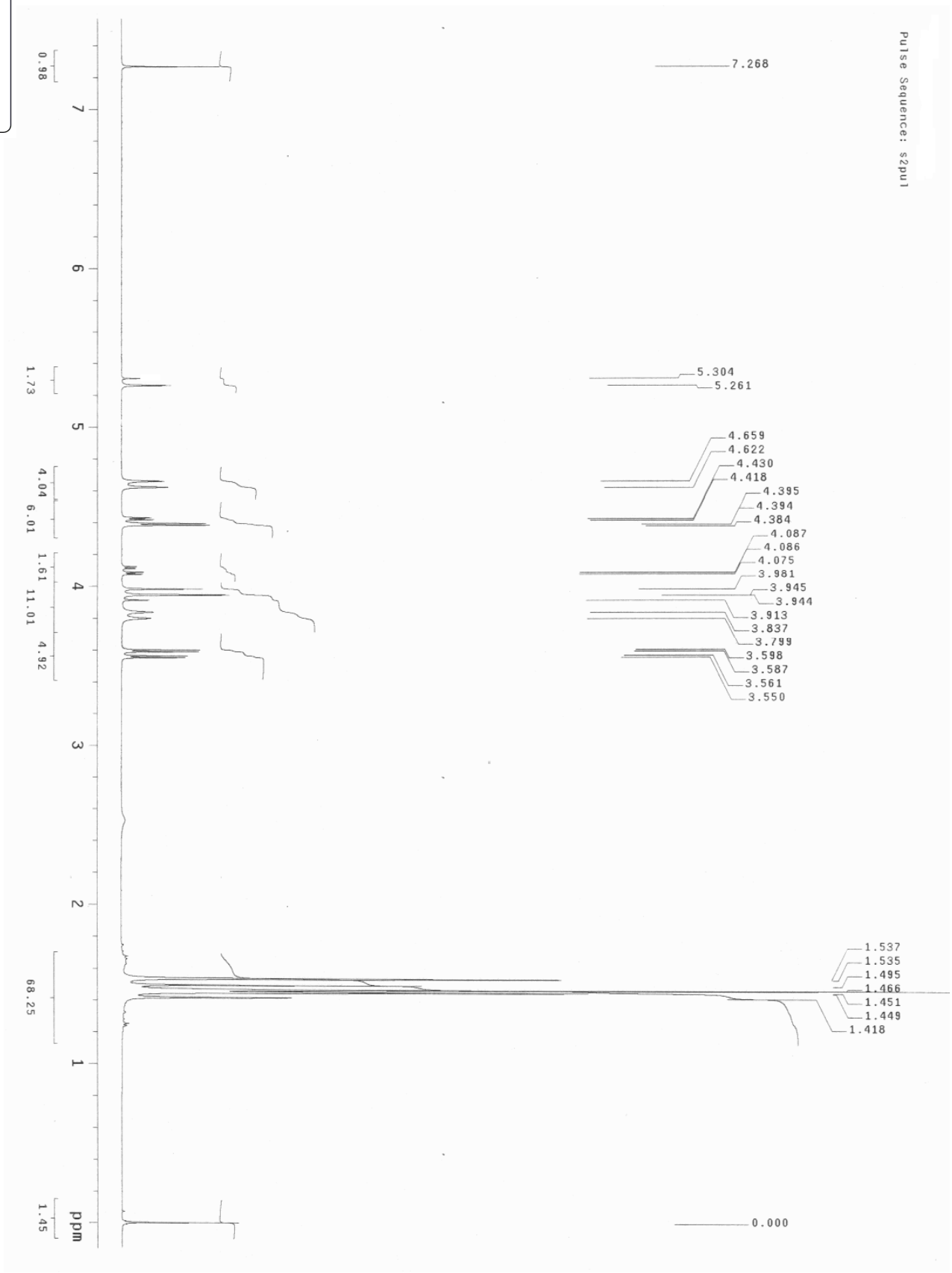
(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrofuranose (**4c**) [300 MHz, $CDCl_3$].



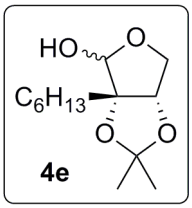


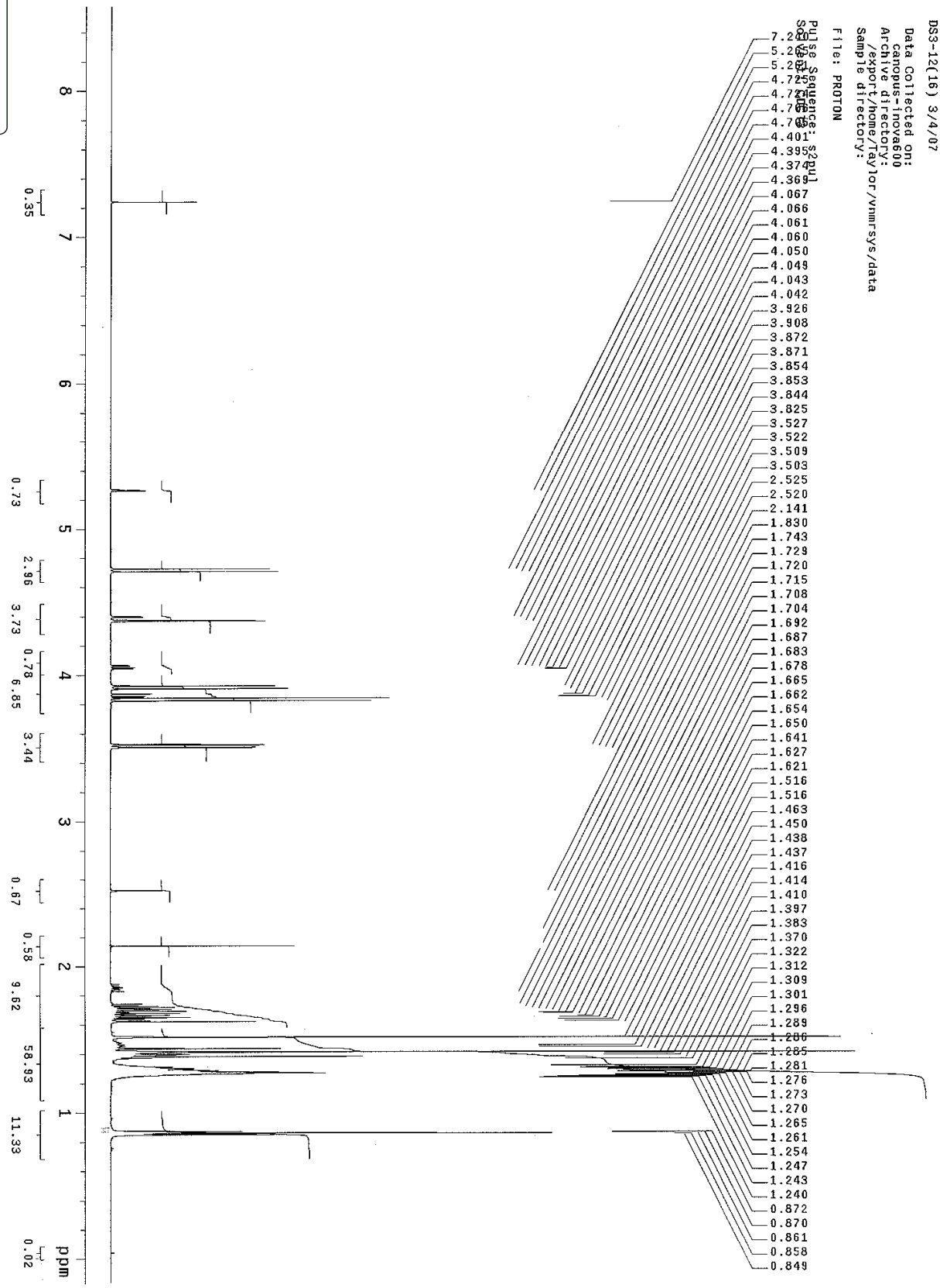
(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrofuranose (**4d**) [300 MHz, $CDCl_3$].



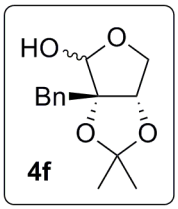


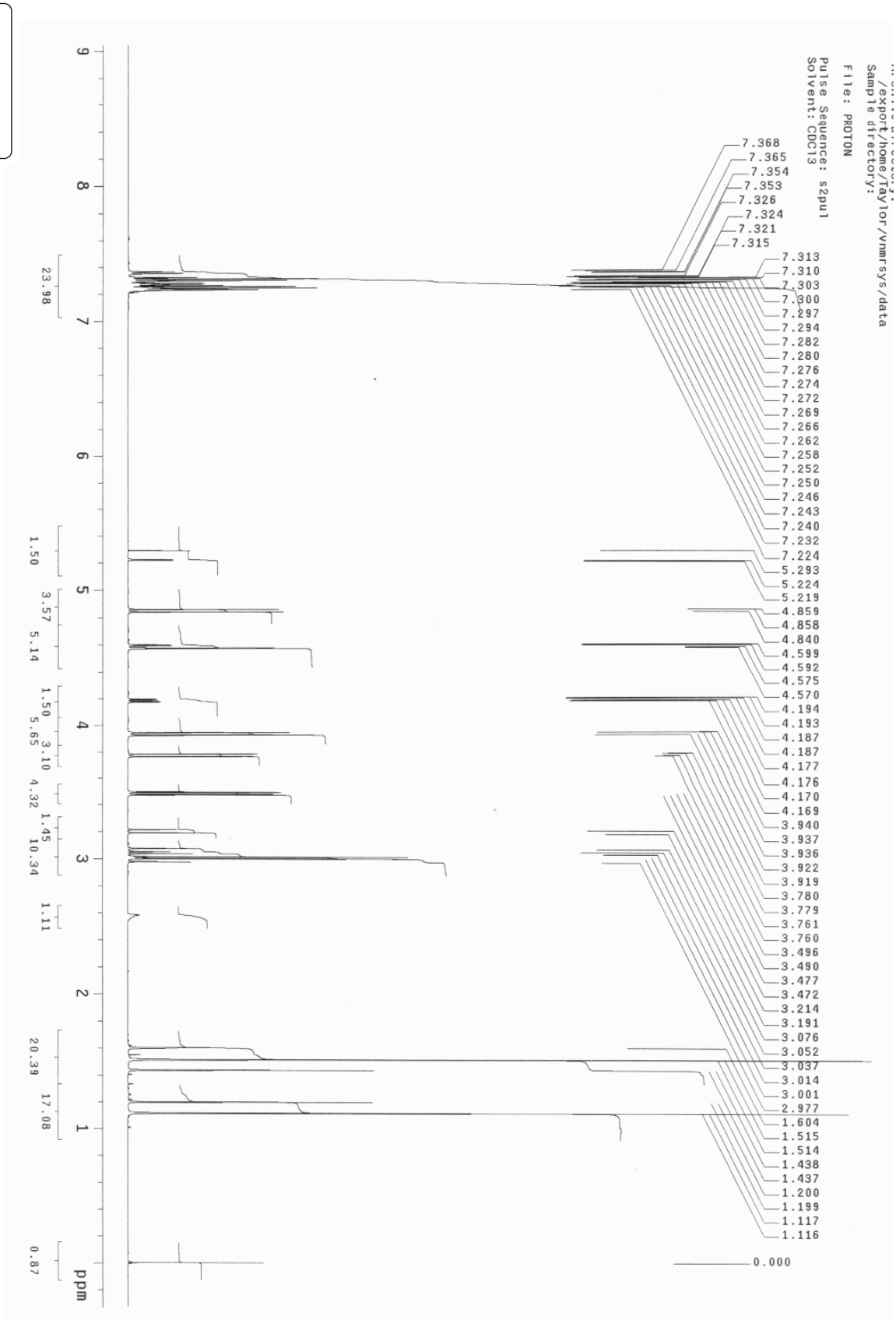
(±)-2,3-*O*-Isopropylidene-2-*C*-hexyl-erythrofuranose (**4e**) [600 MHz, $CDCl_3$].



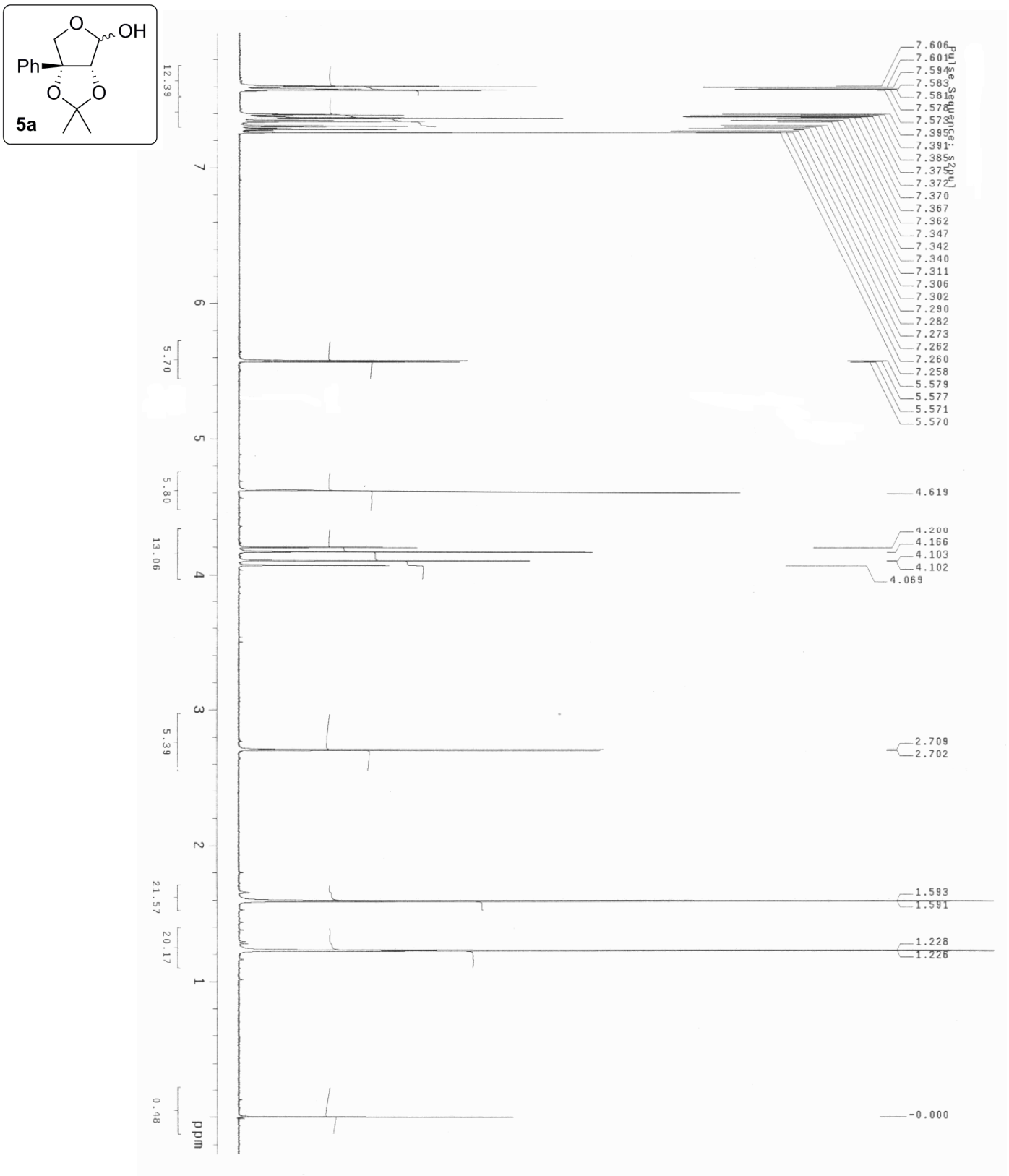


(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrofuranose (**4f**) [600 MHz, $CDCl_3$].

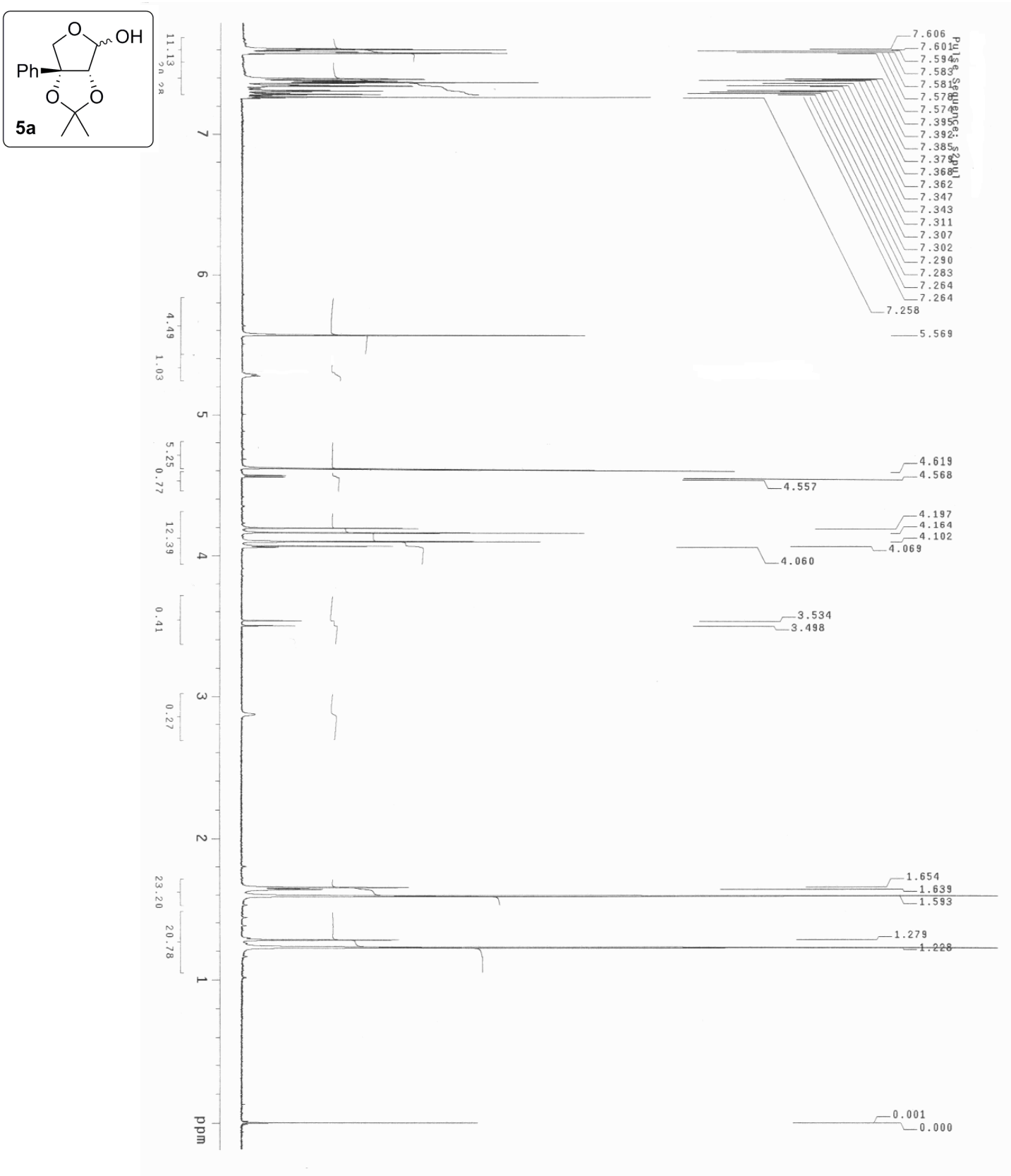




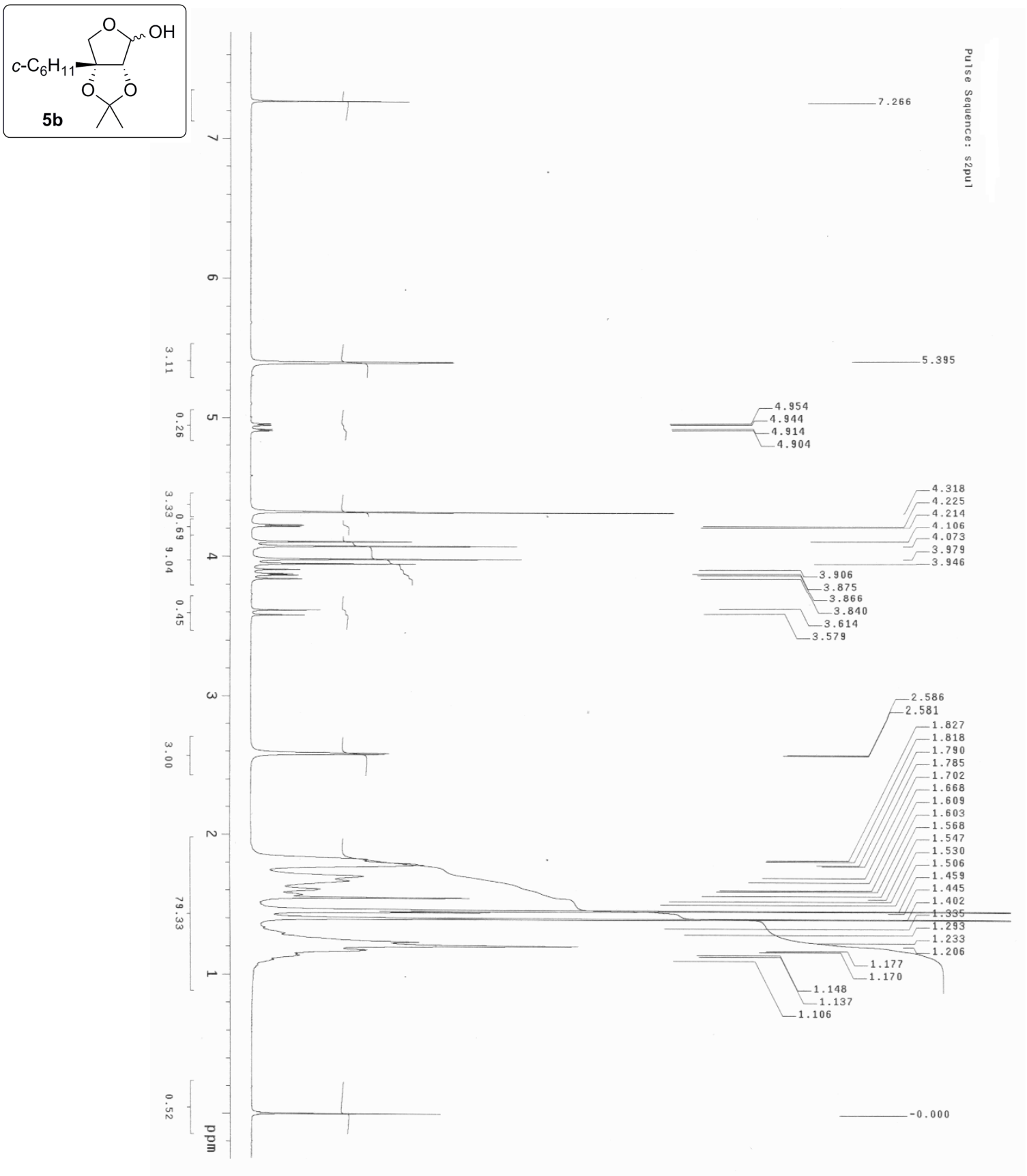
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrofuranose (**5a**) [300 MHz, $CDCl_3$]. Major anomer.



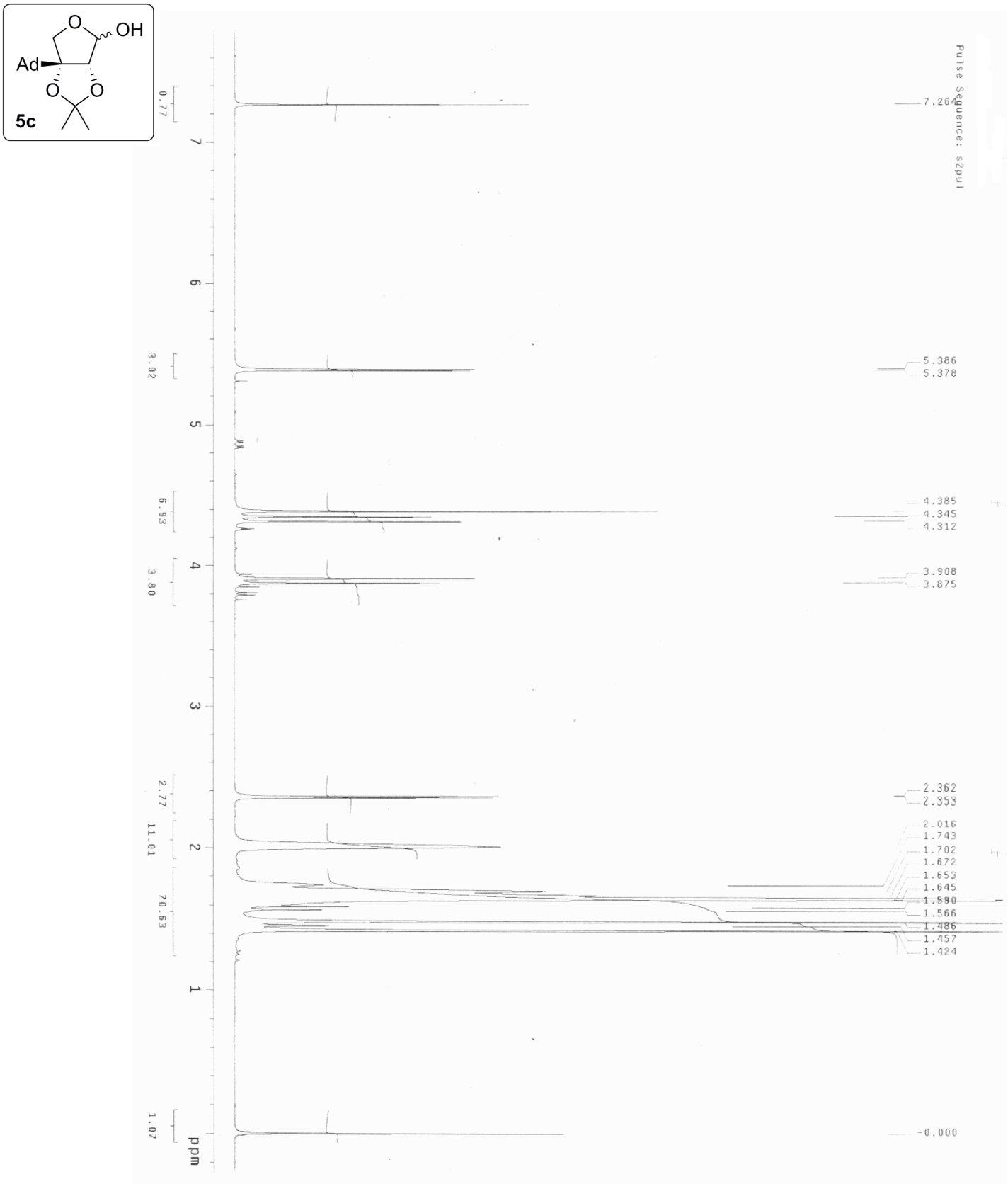
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrofuranose (**5a**) [300 MHz, $CDCl_3$].



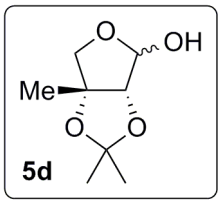
(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrofuranose (**5b**) [300 MHz, $CDCl_3$].

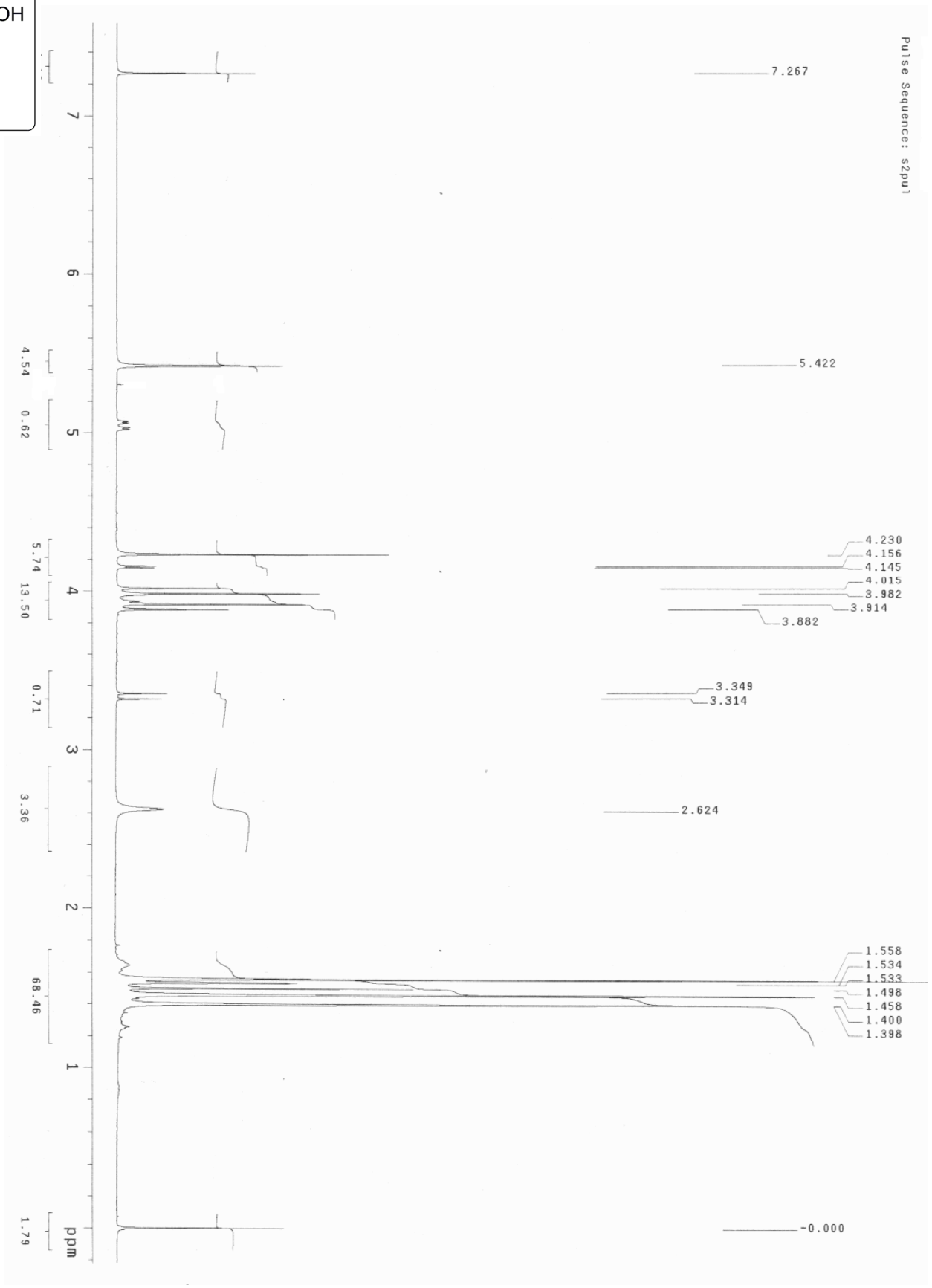


(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrofuranose (**5c**) [300 MHz, $CDCl_3$].

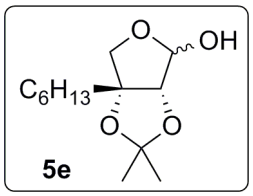


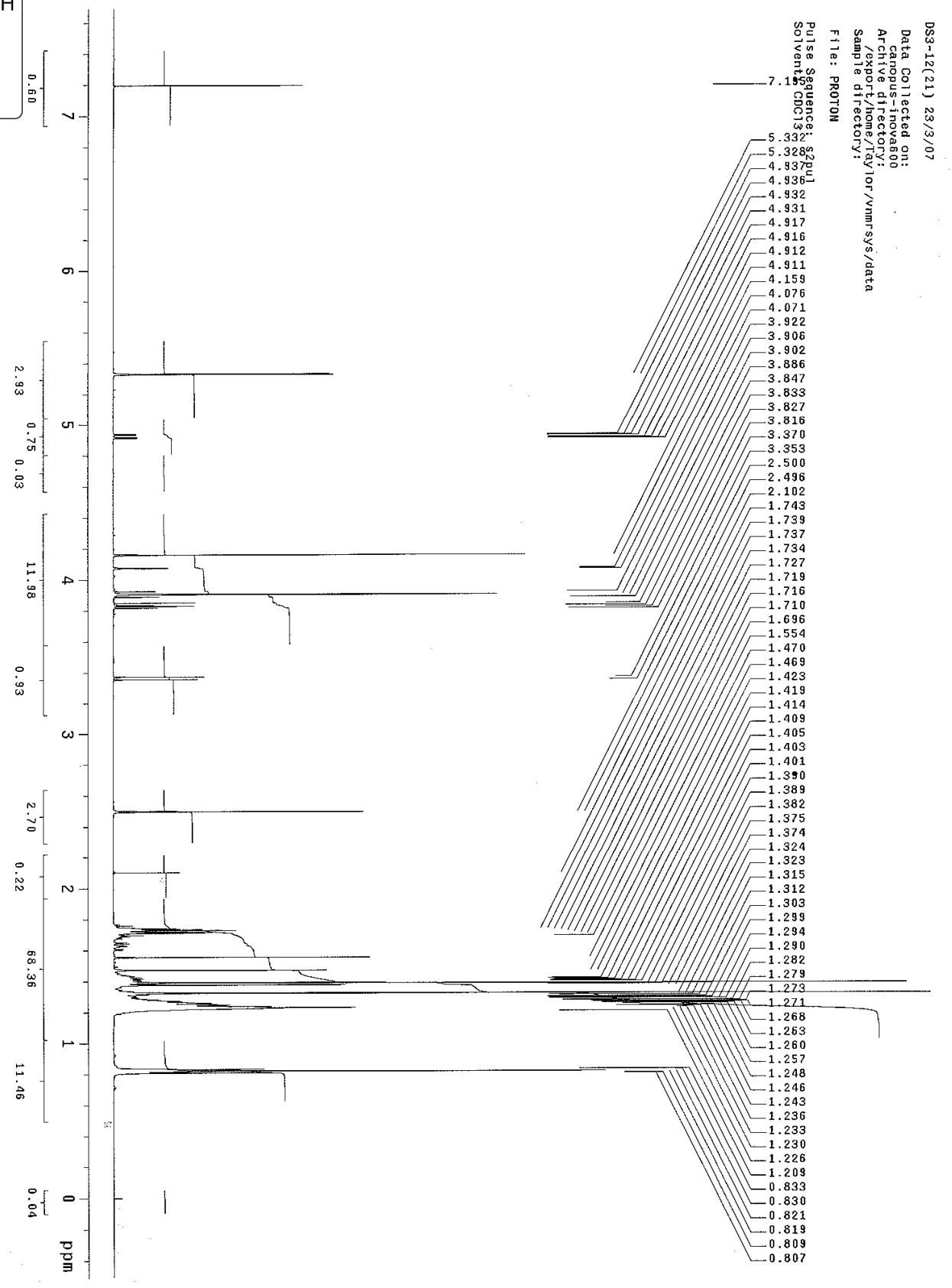
(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrofuranose (**5d**).



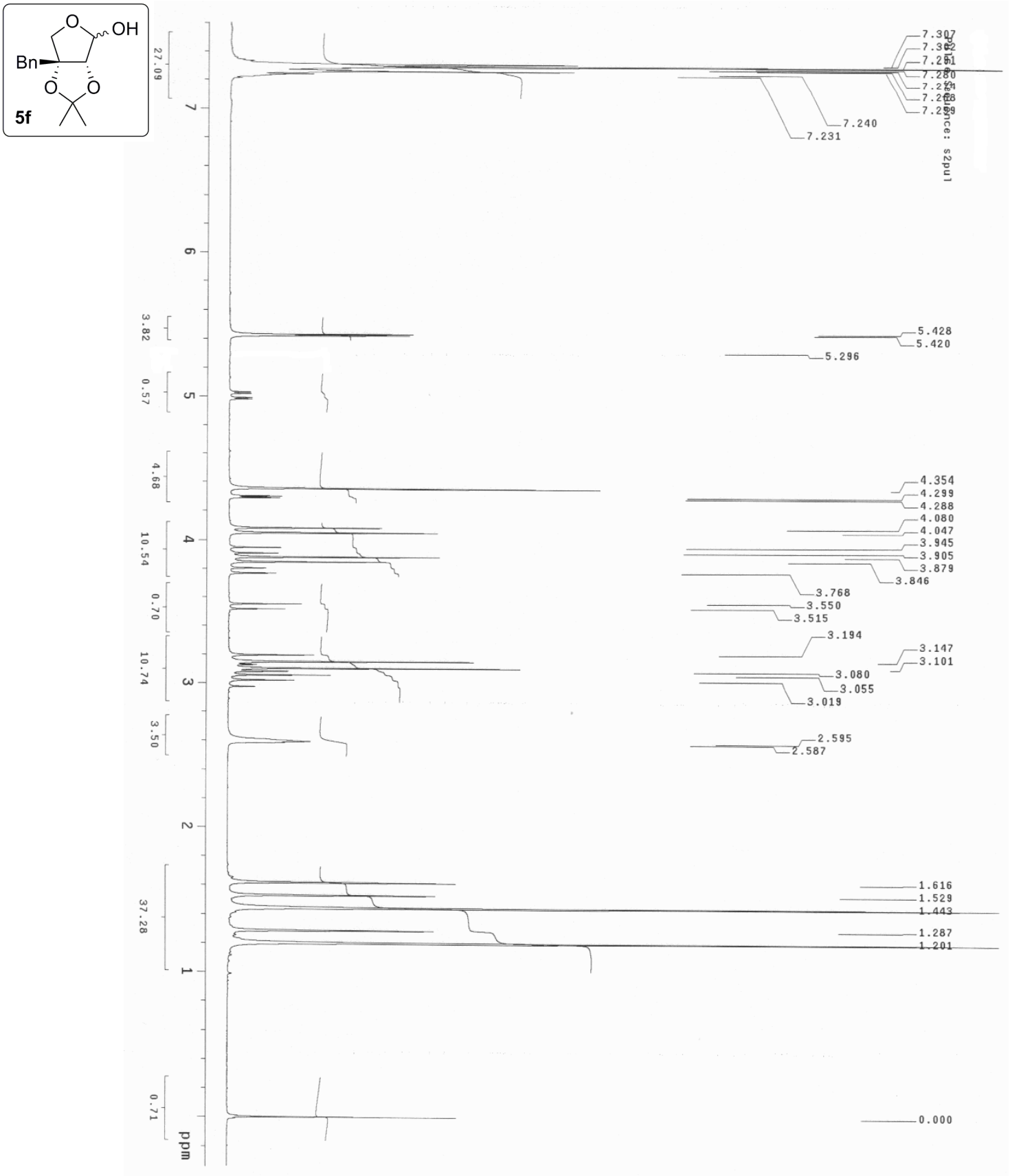


(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrofuranose (**5e**) [600 MHz, $CDCl_3$].

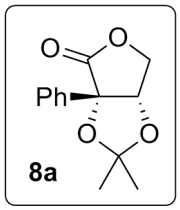


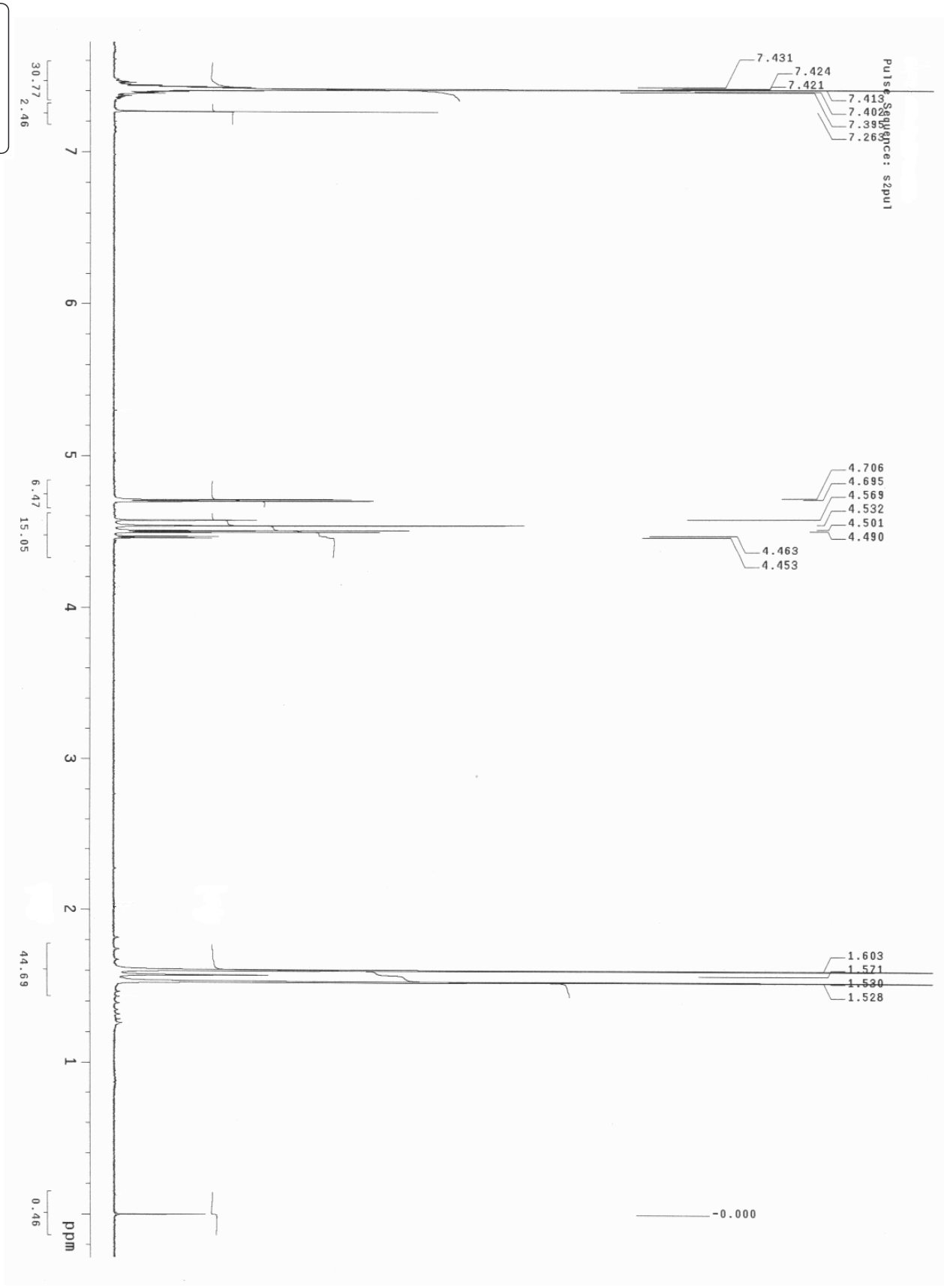


(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrofuranose (**5f**) [300 MHz, $CDCl_3$].

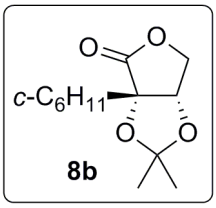


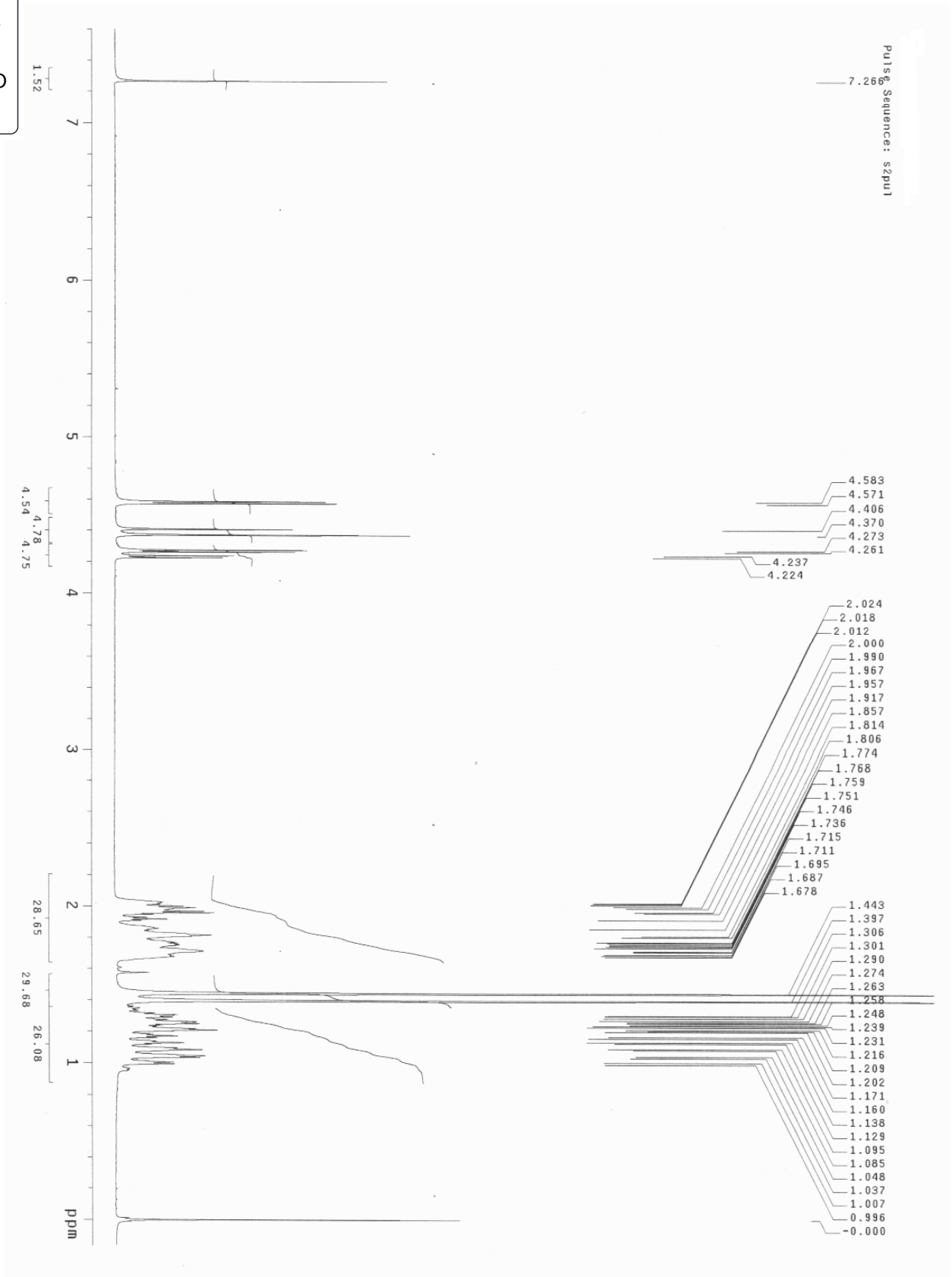
(±)-2,3-*O*-Isopropylidene-2-*C*-phenyl-erythrono-1,4-lactone (**8a**) [300 MHz, $CDCl_3$].



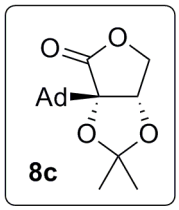


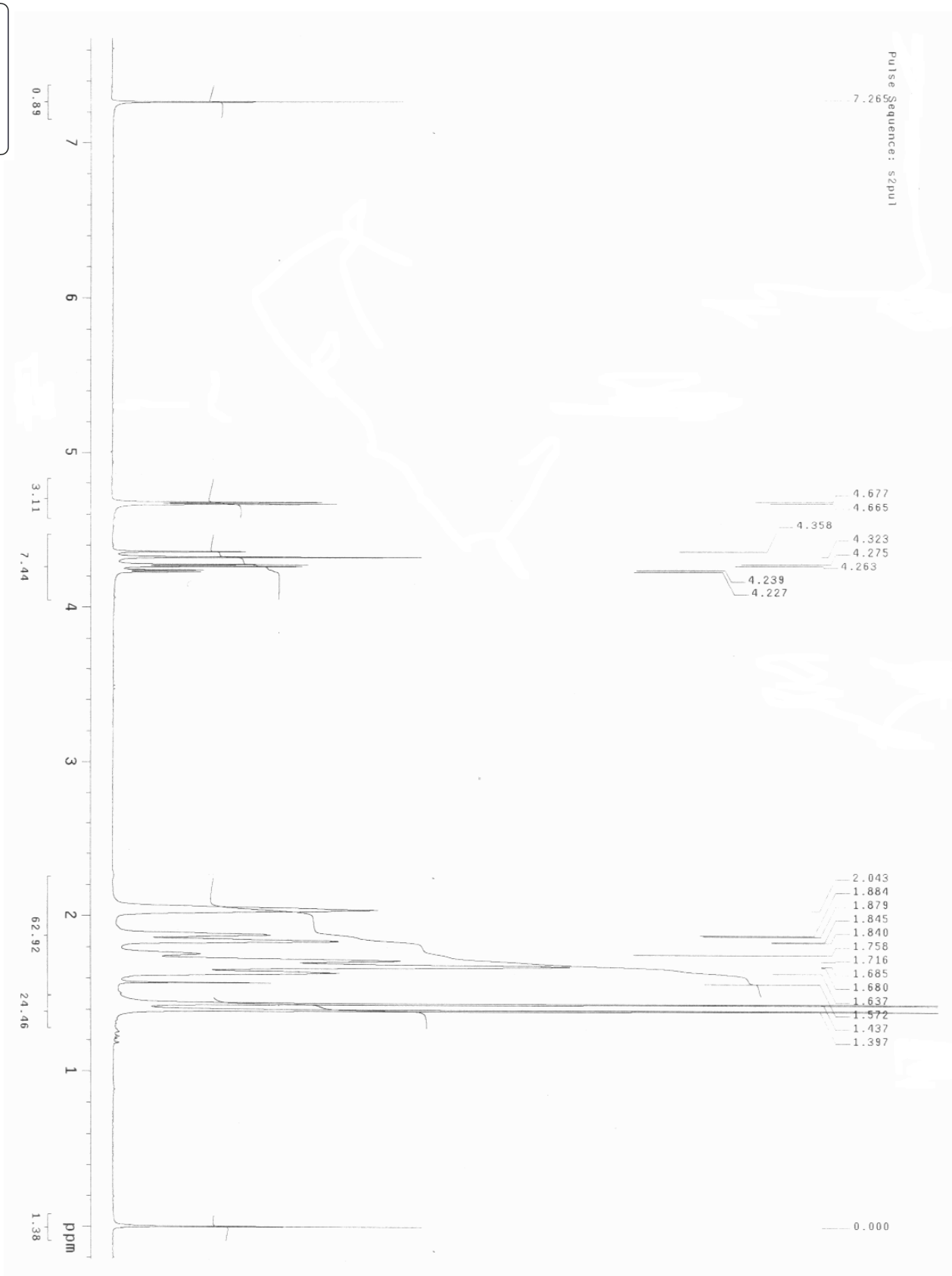
(±)-2,3-*O*-Isopropylidene-2-*C*-cyclohexyl-erythrono-1,4-lactone (**8b**) [300 MHz, $CDCl_3$].



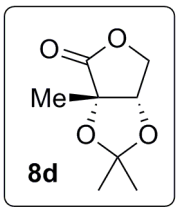


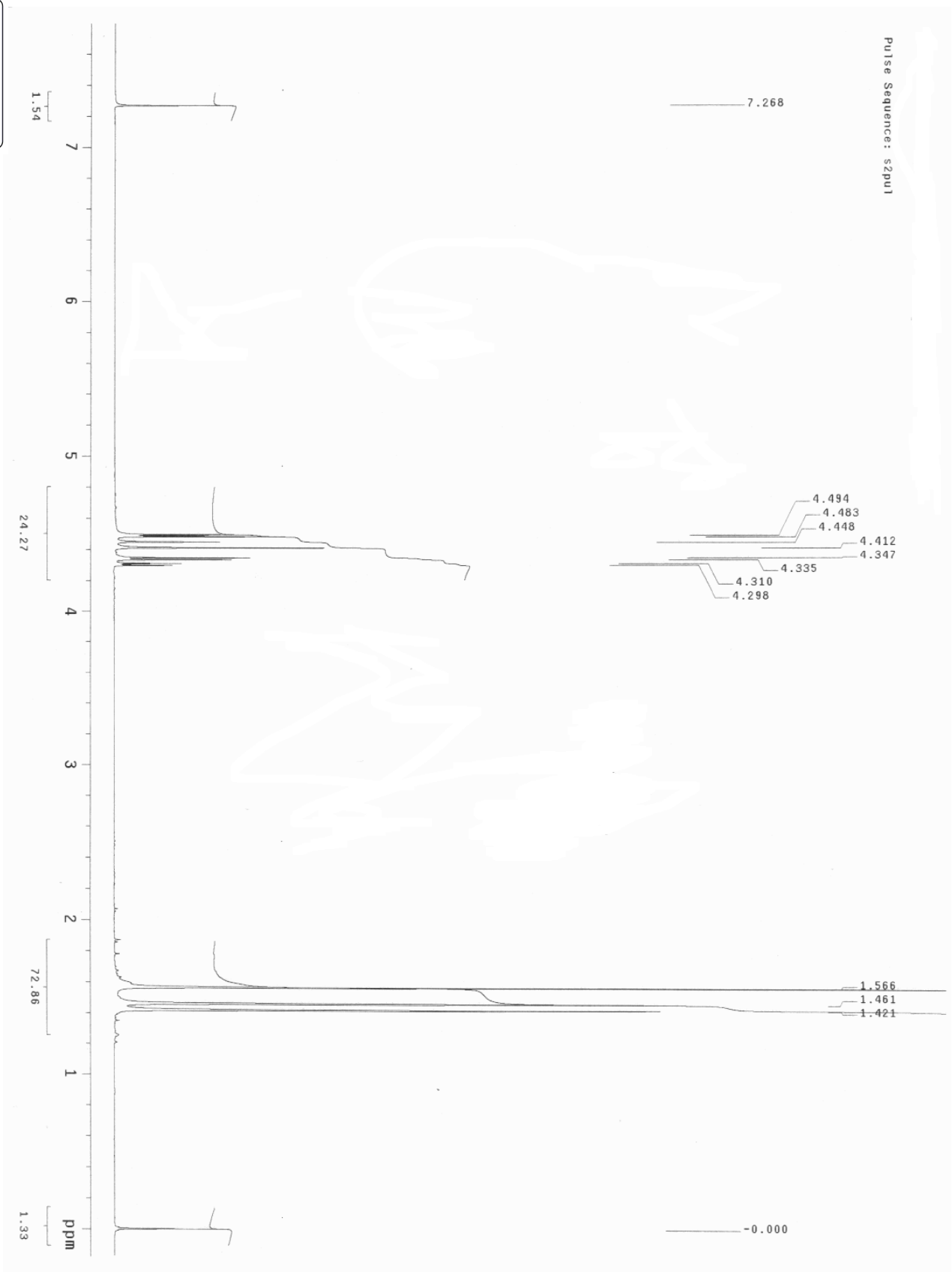
(±)-2,3-*O*-Isopropylidene-2-*C*-(1-adamantyl)-erythrono-1,4-lactone (**8c**) [300 MHz, $CDCl_3$].



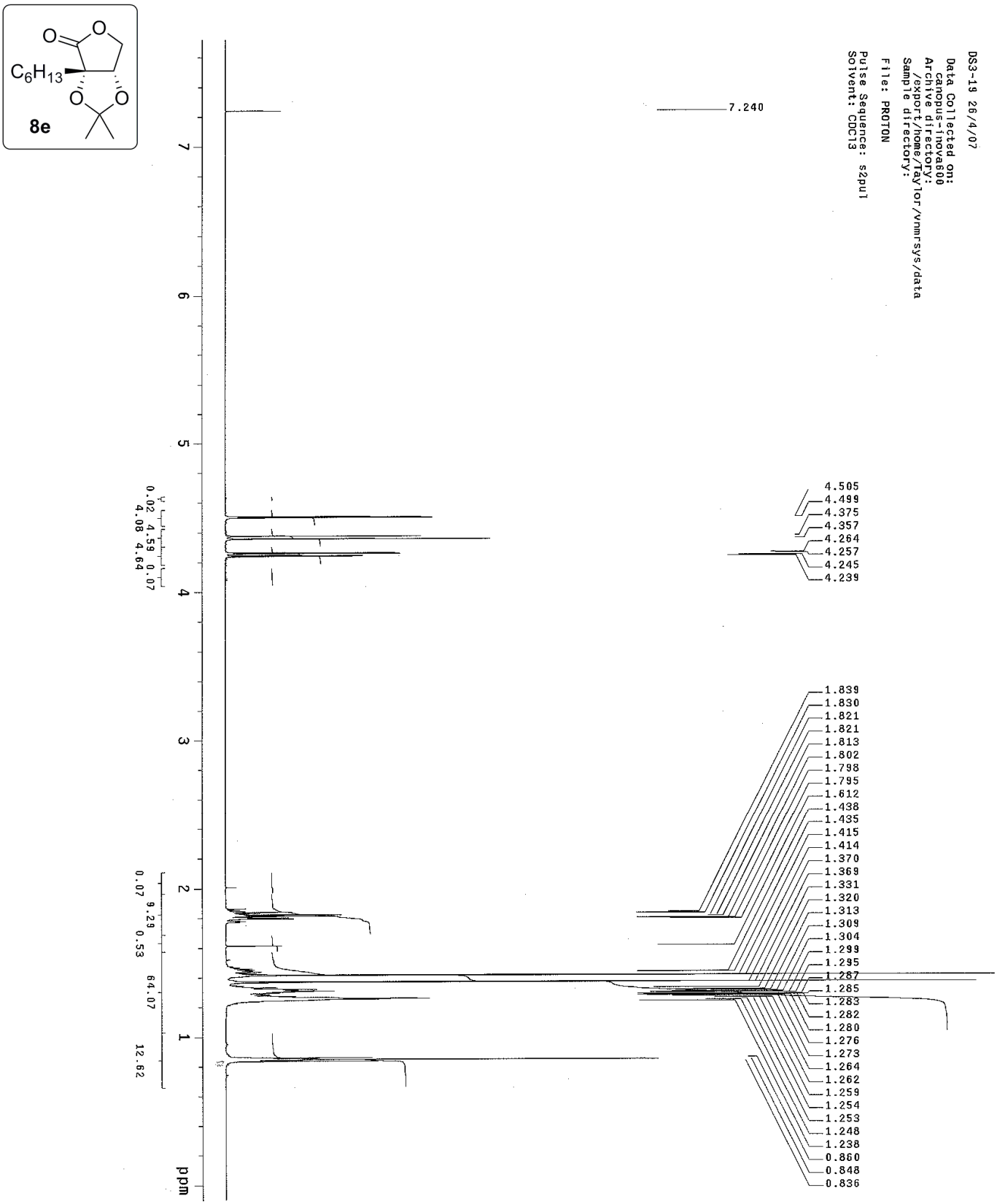


(±)-2,3-*O*-Isopropylidene-2-*C*-methyl-erythrono-1,4-lactone (**8d**) [300 MHz, $CDCl_3$].

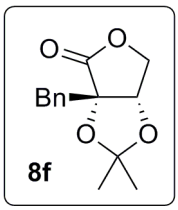


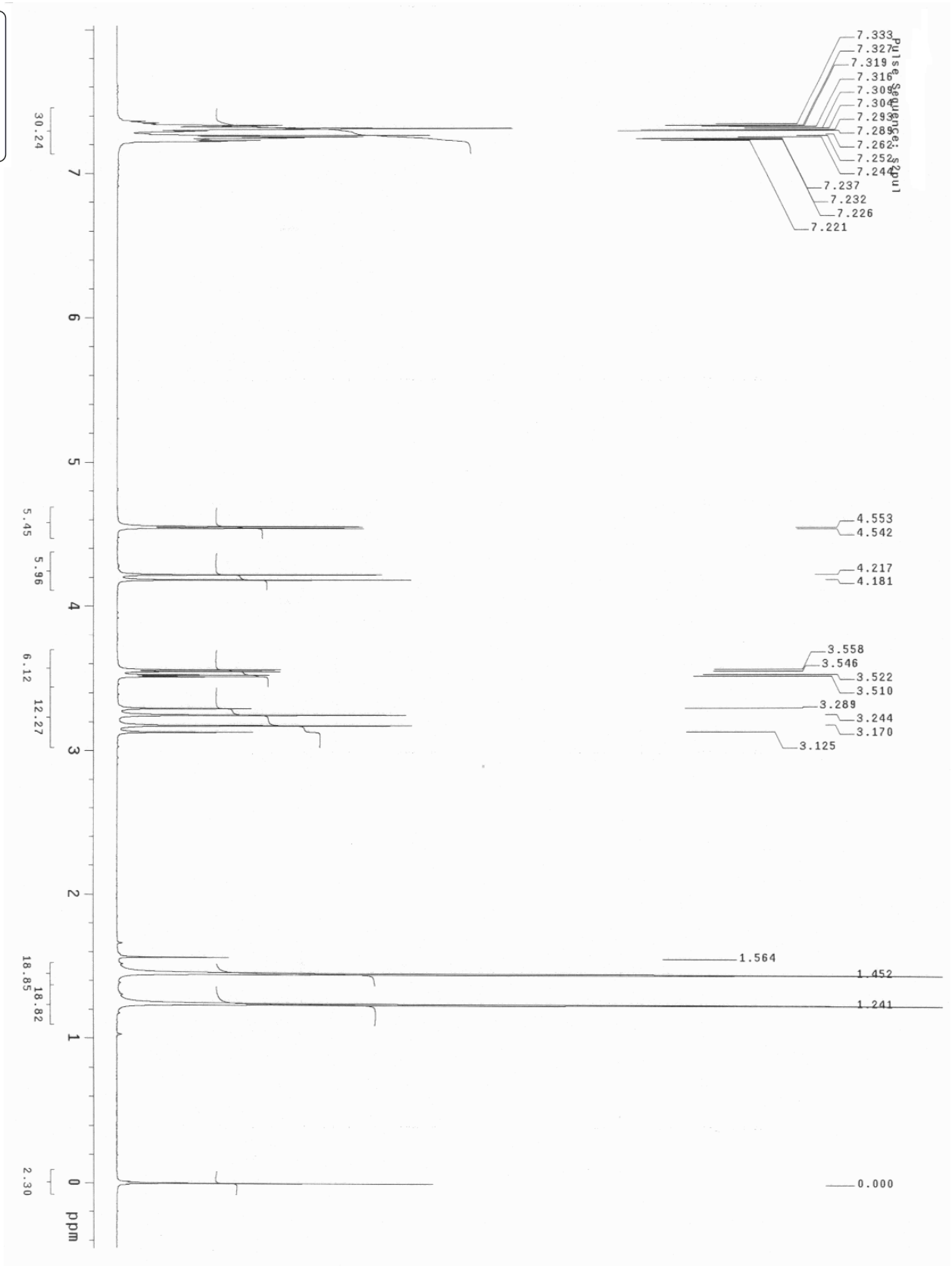


(±)-2,3-*O*-Isopropylidene-2-*C*-hexyl-erythrono-1,4-lactone (**8e**) [600 MHz, $CDCl_3$].

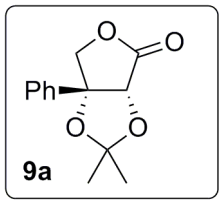


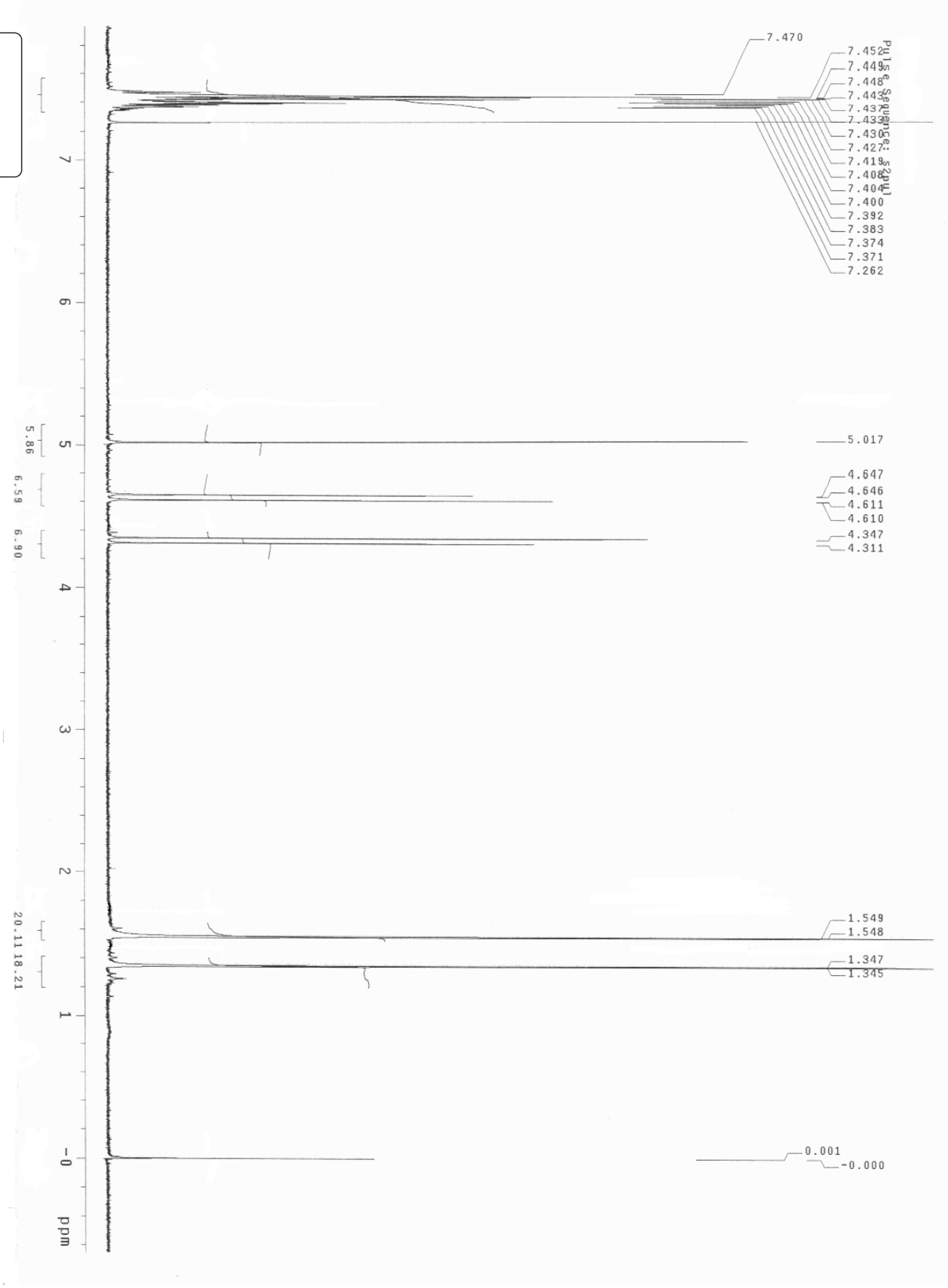
(±)-2,3-*O*-Isopropylidene-2-*C*-benzyl-erythrono-1,4-lactone (**8f**) [300 MHz, $CDCl_3$].



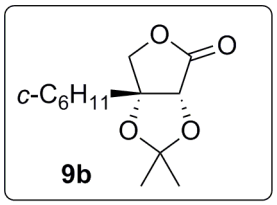


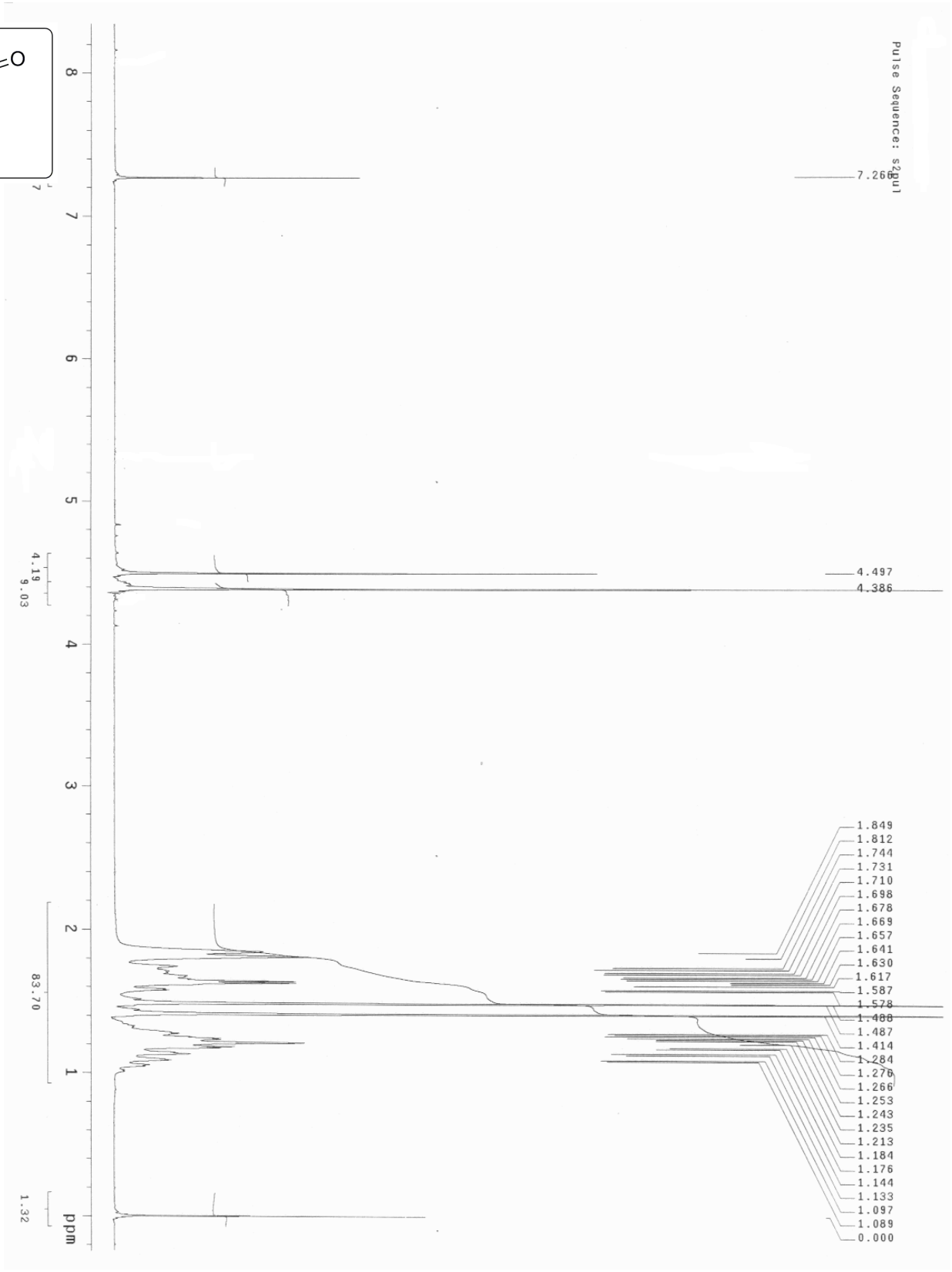
(±)-2,3-*O*-Isopropylidene-3-*C*-phenyl-erythrono-1,4-lactone (**9a**) [300 MHz, $CDCl_3$].



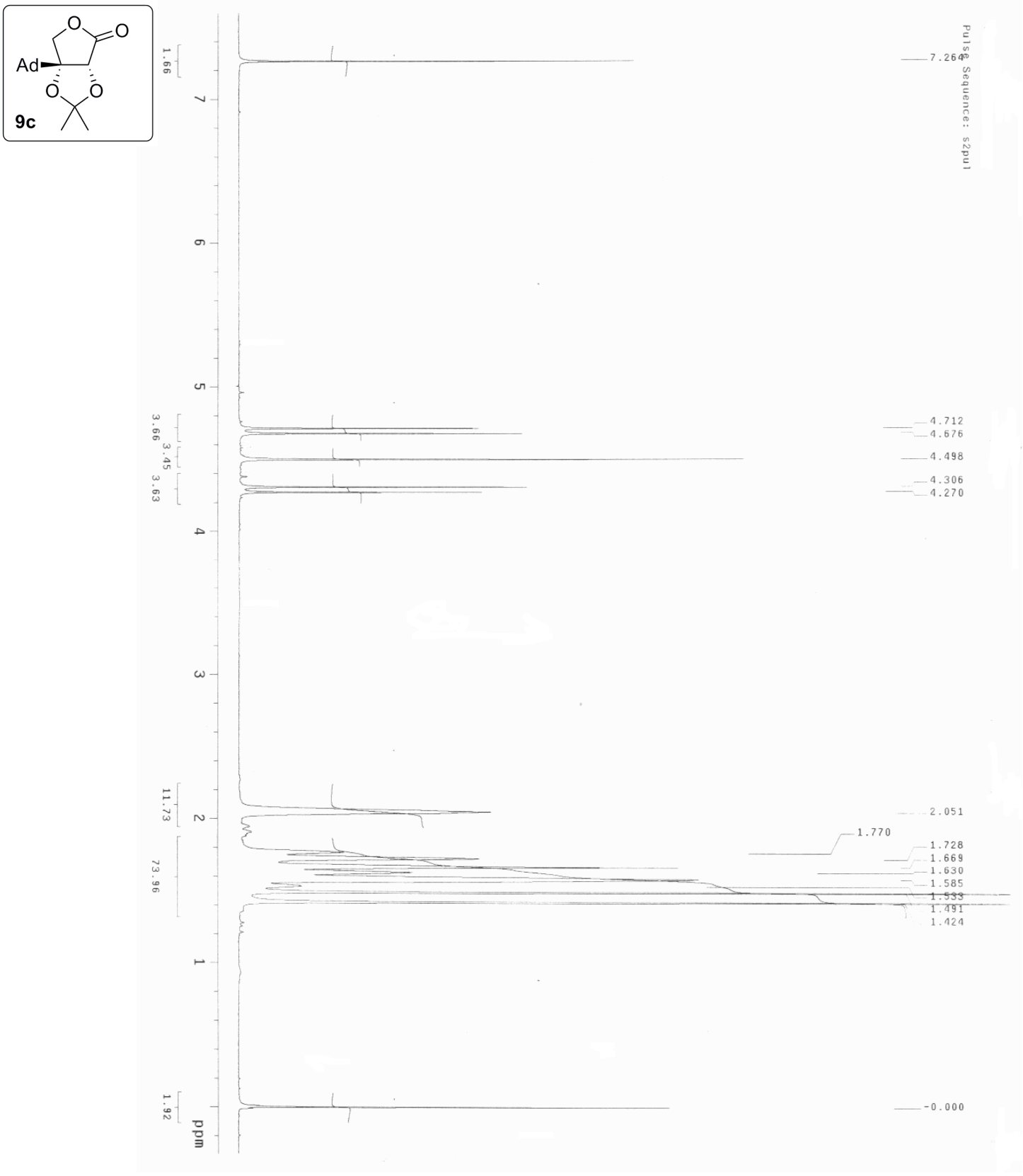


(±)-2,3-*O*-Isopropylidene-3-*C*-cyclohexyl-erythrono-1,4-lactone (**9b**) [300 MHz, $CDCl_3$].

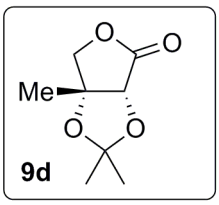


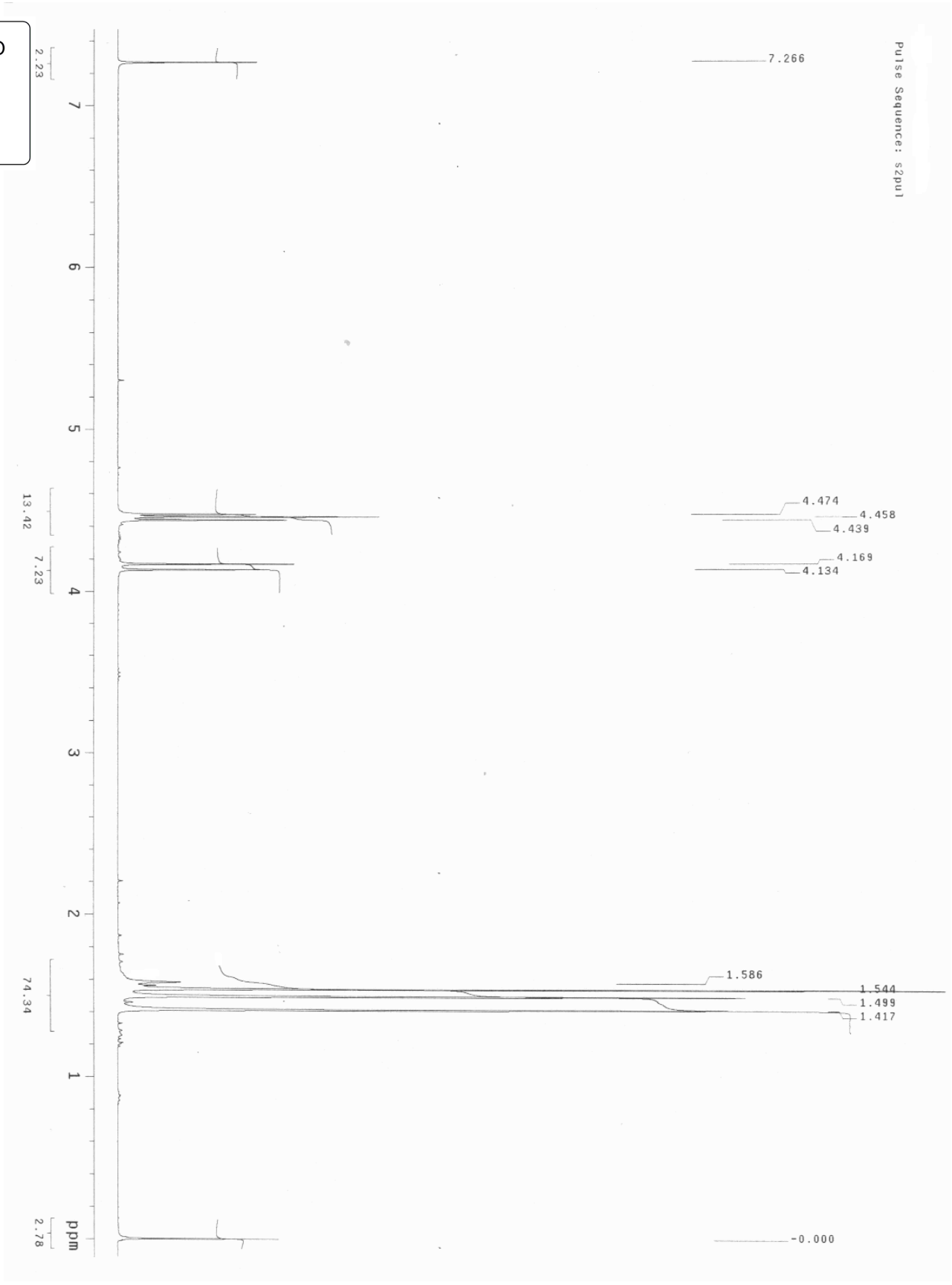


(±)-2,3-*O*-Isopropylidene-3-*C*-(1-adamantyl)-erythrono-1,4-lactone (**9c**) [300 MHz, $CDCl_3$].

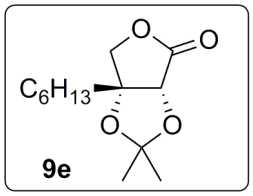


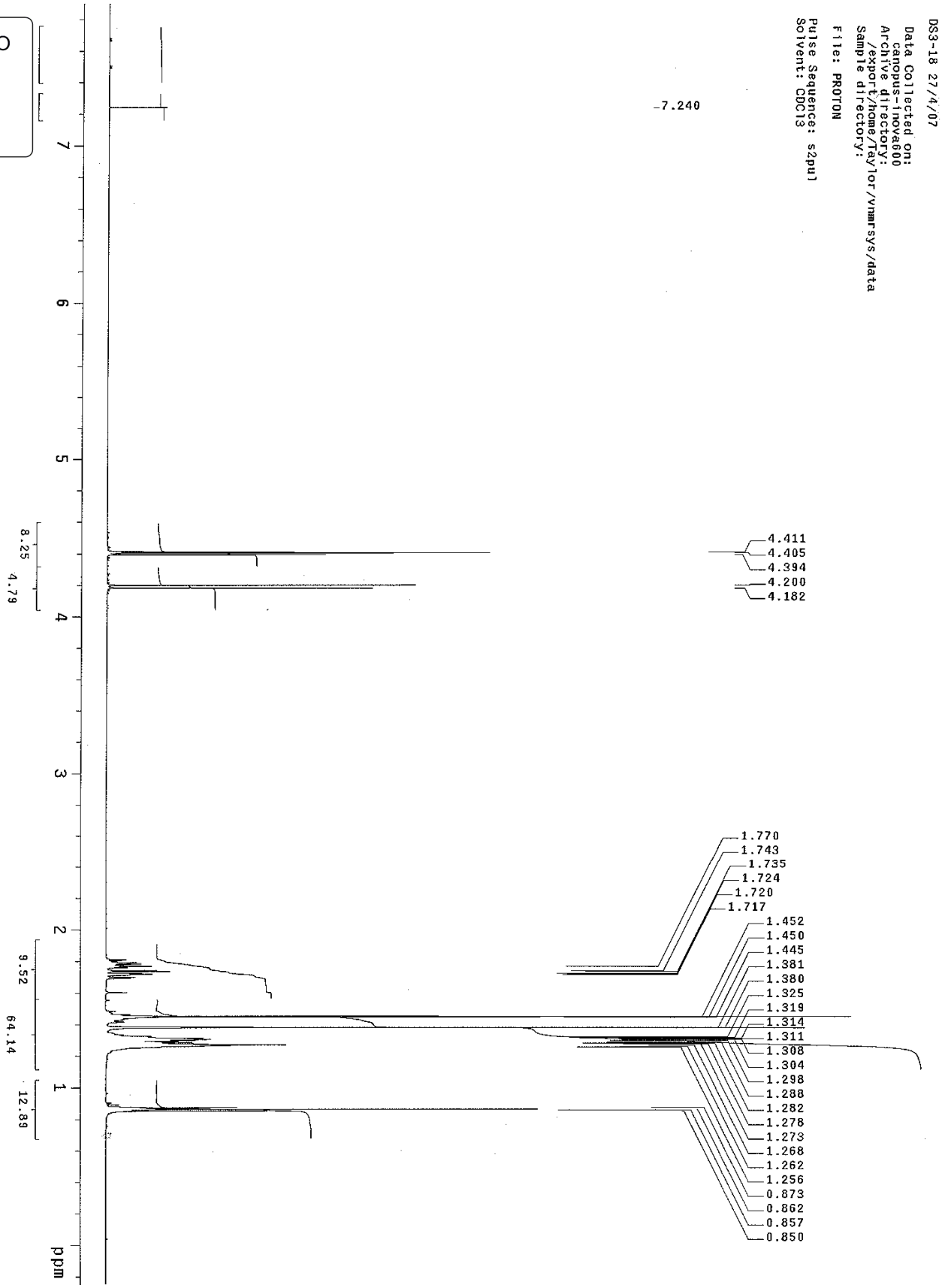
(±)-2,3-*O*-Isopropylidene-3-*C*-methyl-erythrono-1,4-lactone (**9d**) [300 MHz, $CDCl_3$].



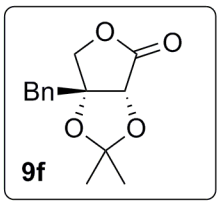


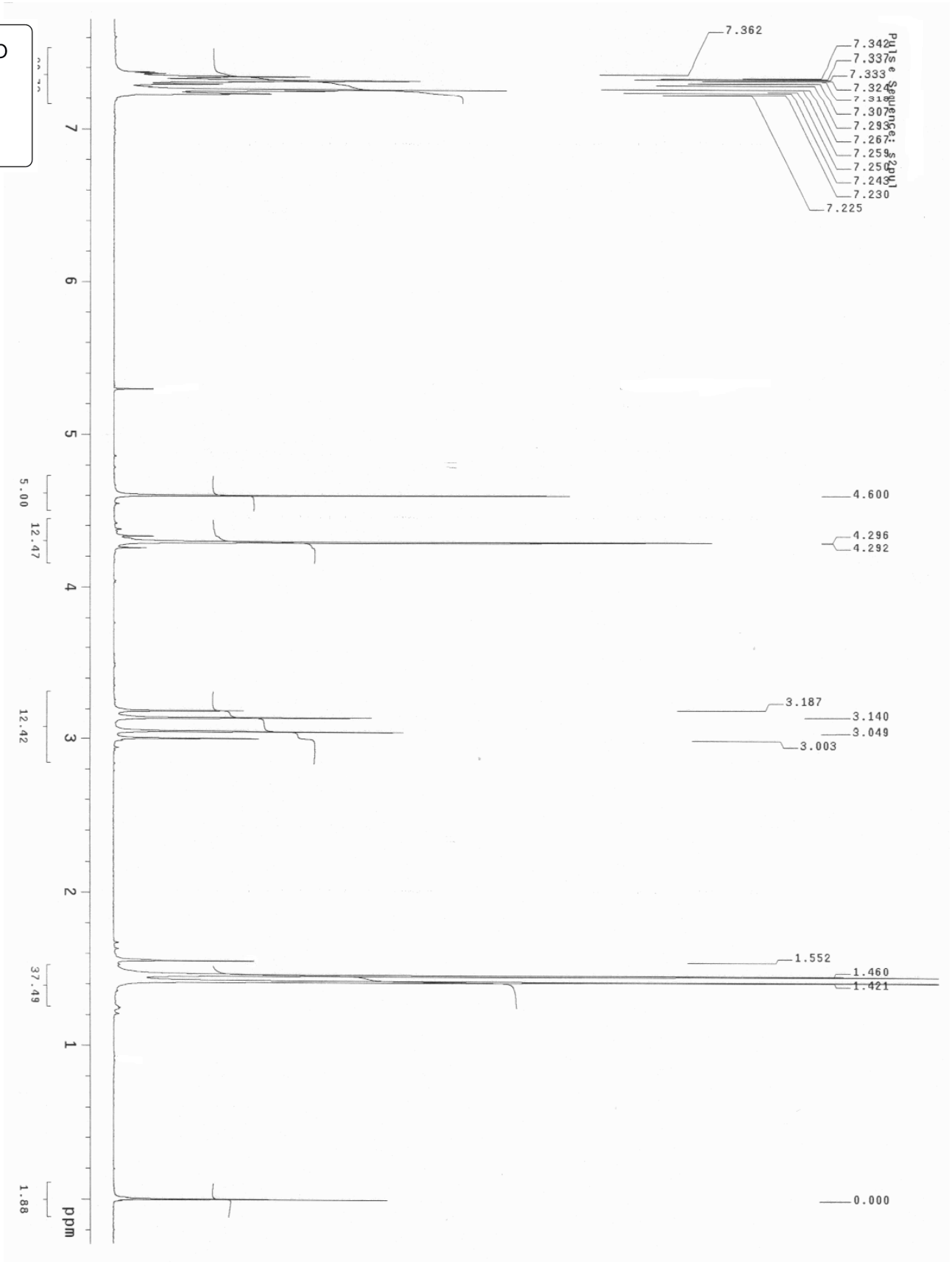
(±)-2,3-*O*-Isopropylidene-3-*C*-hexyl-erythrono-1,4-lactone (**9e**) [600 MHz, $CDCl_3$].



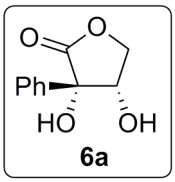


(±)-2,3-*O*-Isopropylidene-3-*C*-benzyl-erythrono-1,4-lactone (**9f**) [300 MHz, $CDCl_3$].

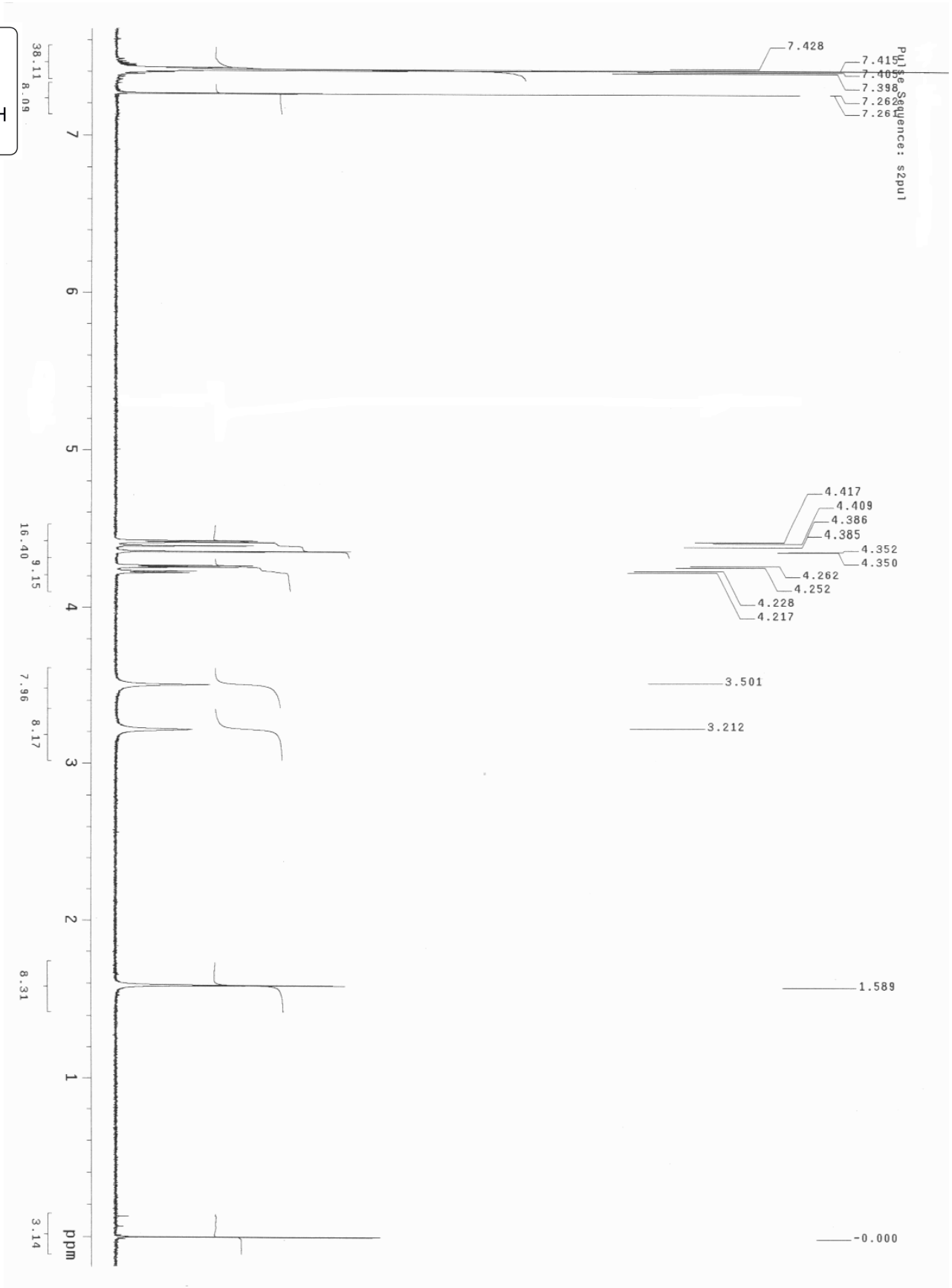




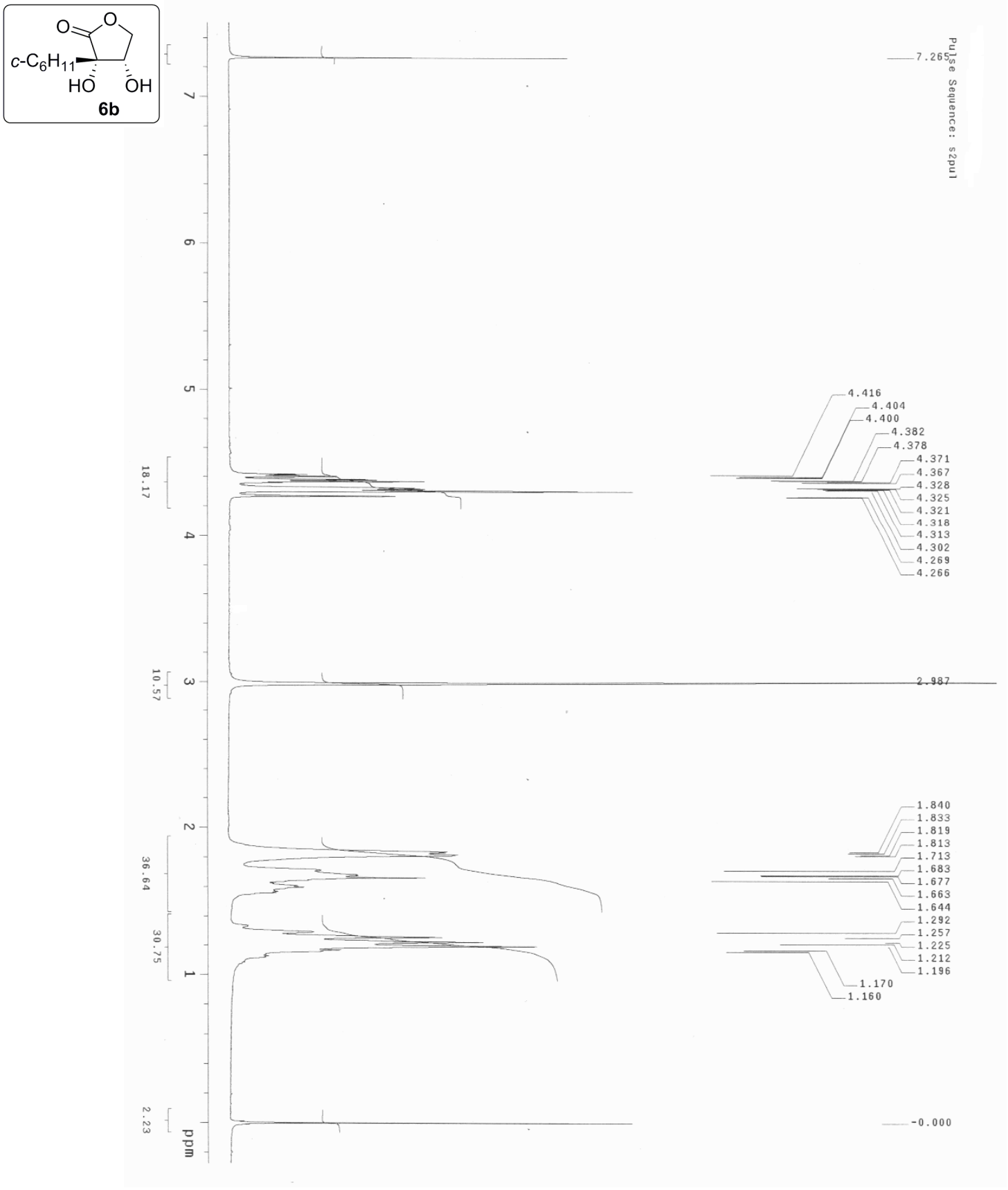
(±)-2-*C*-Phenyl-erythrono-1,4-lactone (**6a**) [300 MHz, $CDCl_3$].



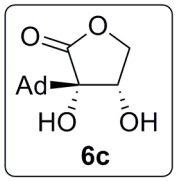
6a

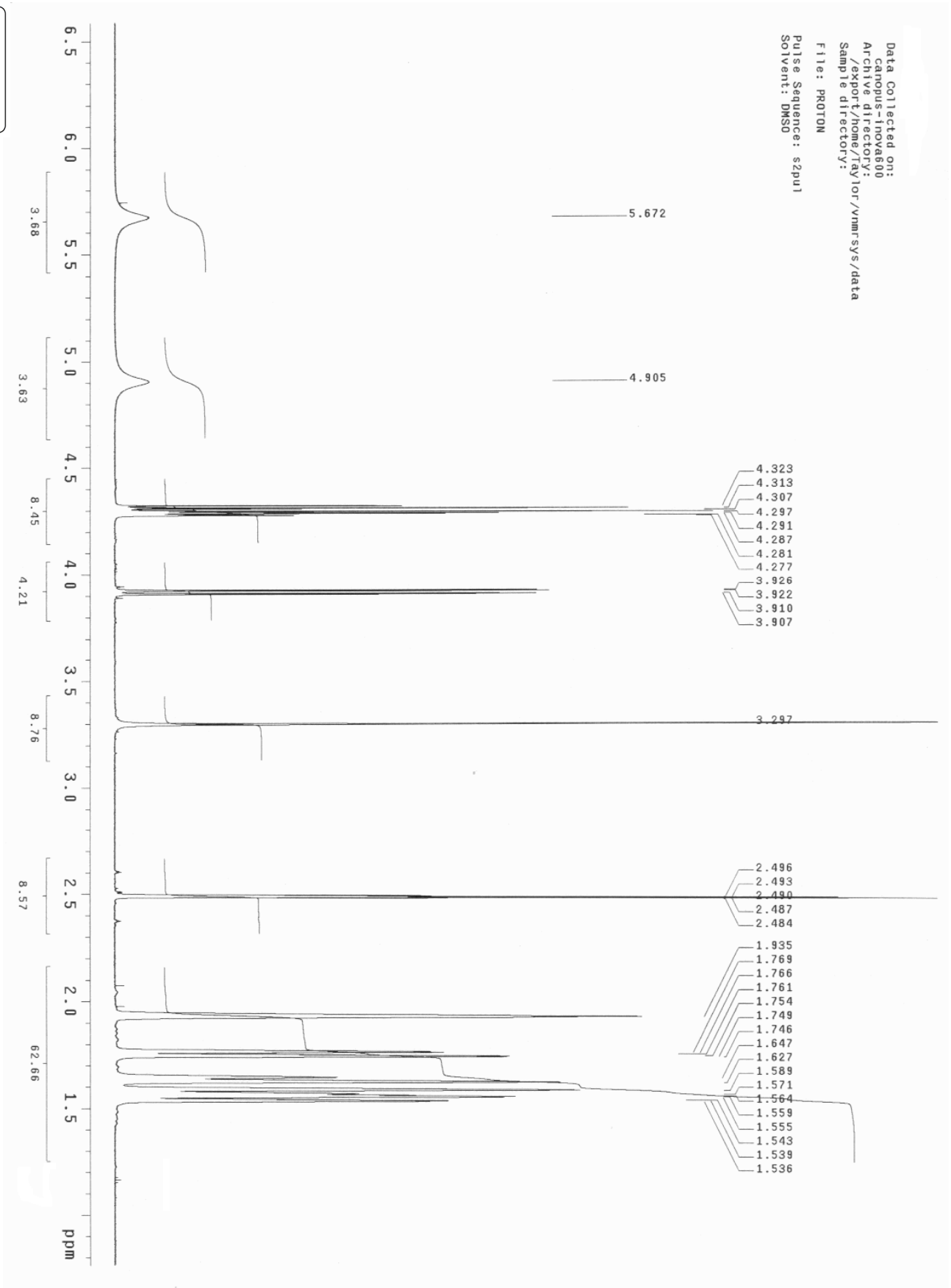


(±)-2-*C*-Cyclohexyl-erythrono-1,4-lactone (**6b**) [300 MHz, $CDCl_3$].

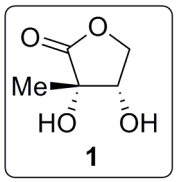


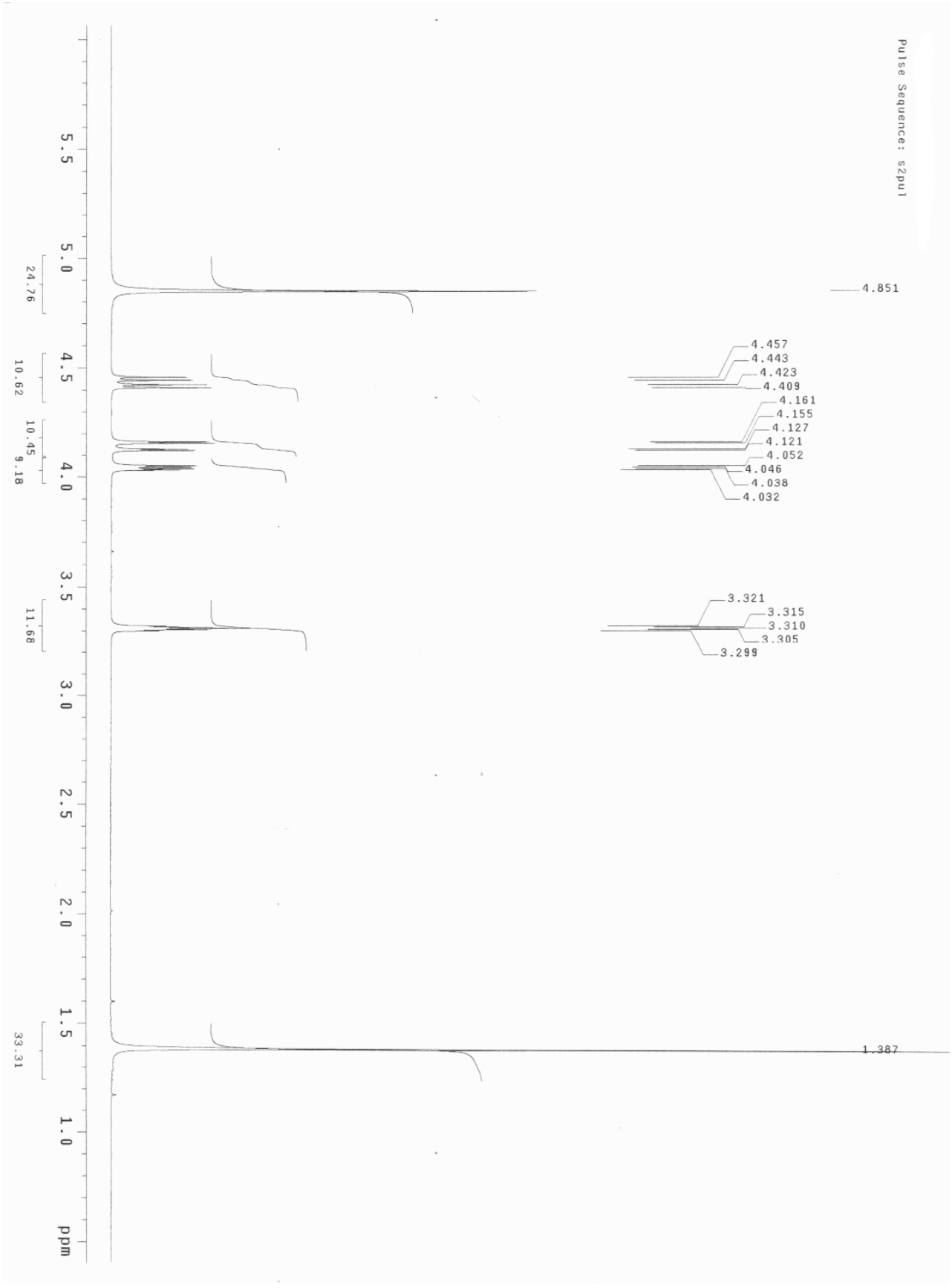
(±)-2-*C*-(1-Adamantyl)-erythrono-1,4-lactone (**6c**) [600 MHz, DMSO-d_6].



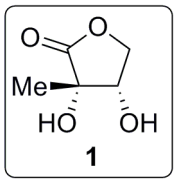


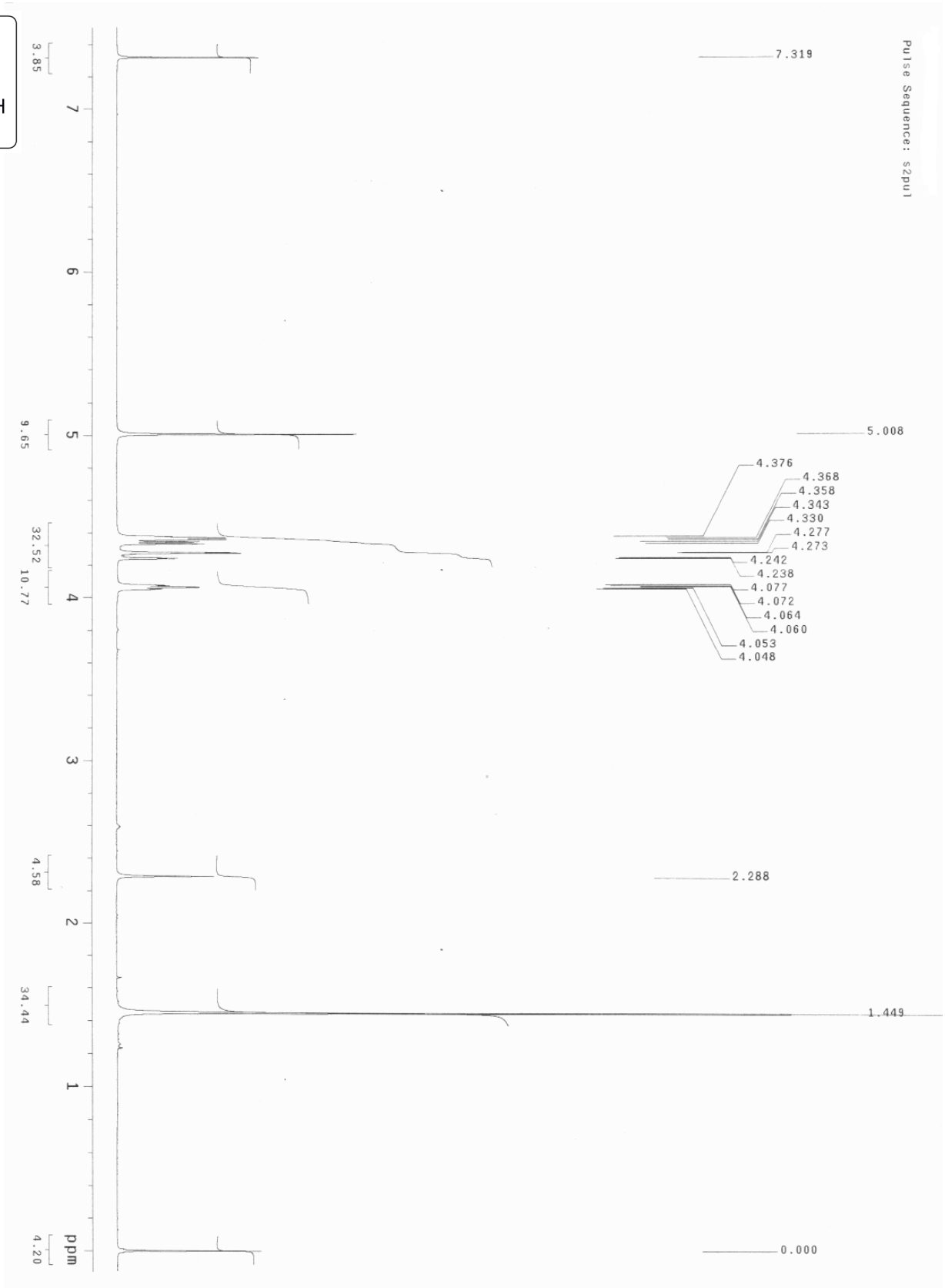
(±)-2-*C*-D-Methyl-erythrono-1,4-lactone (**1**) [300 MHz, CD_3OD].



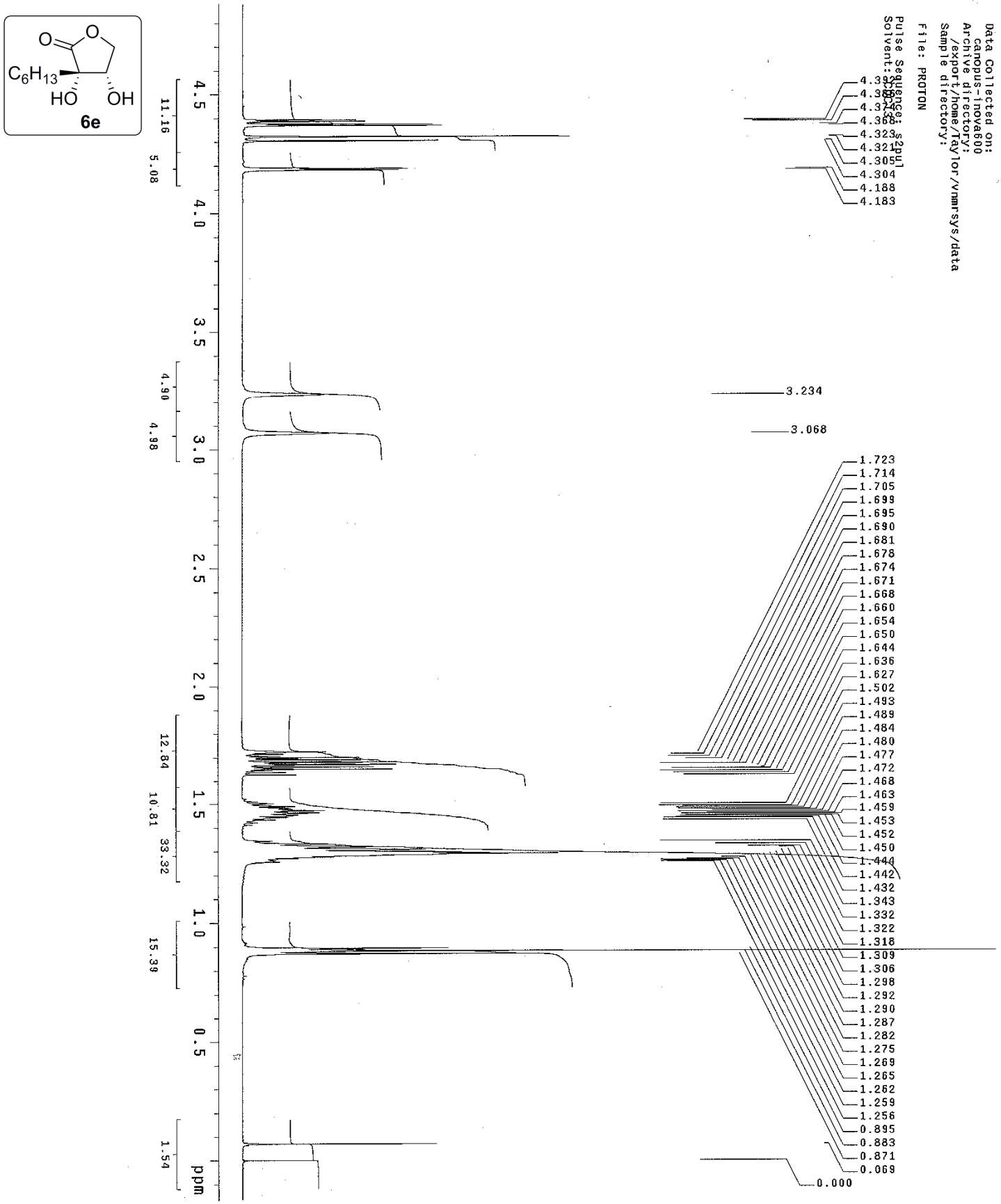


(±)-2-*C*-D-Methyl-erythrono-1,4-lactone (**1**) [300 MHz, $CDCl_3$ + 2 drop DMSO-d_6].

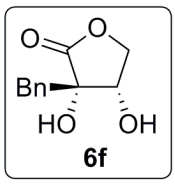


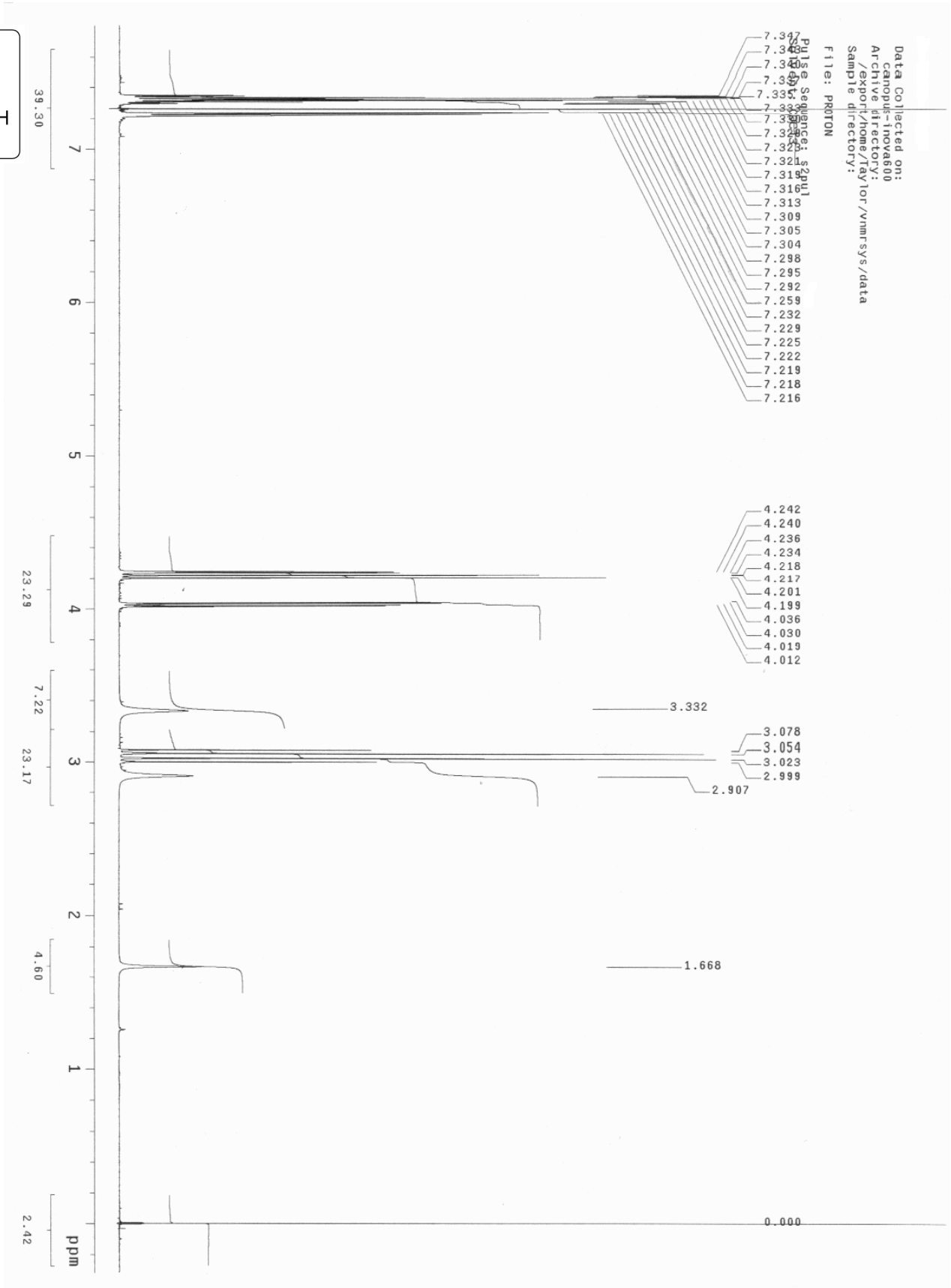


(±)-2-*C*-Hexyl-erythrono-1,4-lactone (**6e**) [600 MHz, $CDCl_3$].

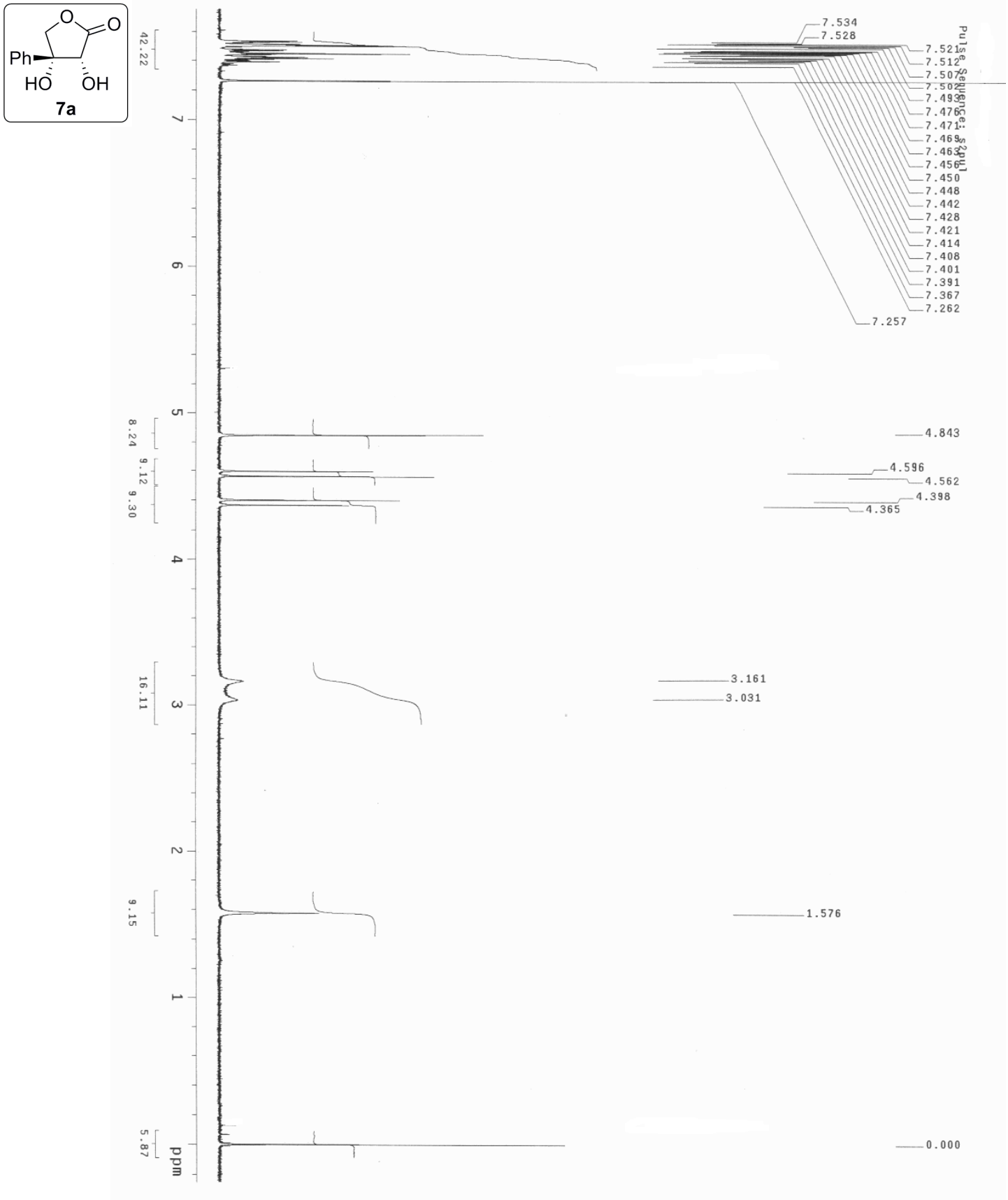


(±)-2-*C*-Benzyl-erythrono-1,4-lactone (**6f**) [600 MHz, $CDCl_3$].

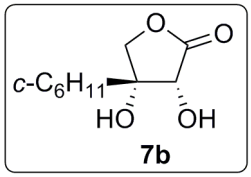


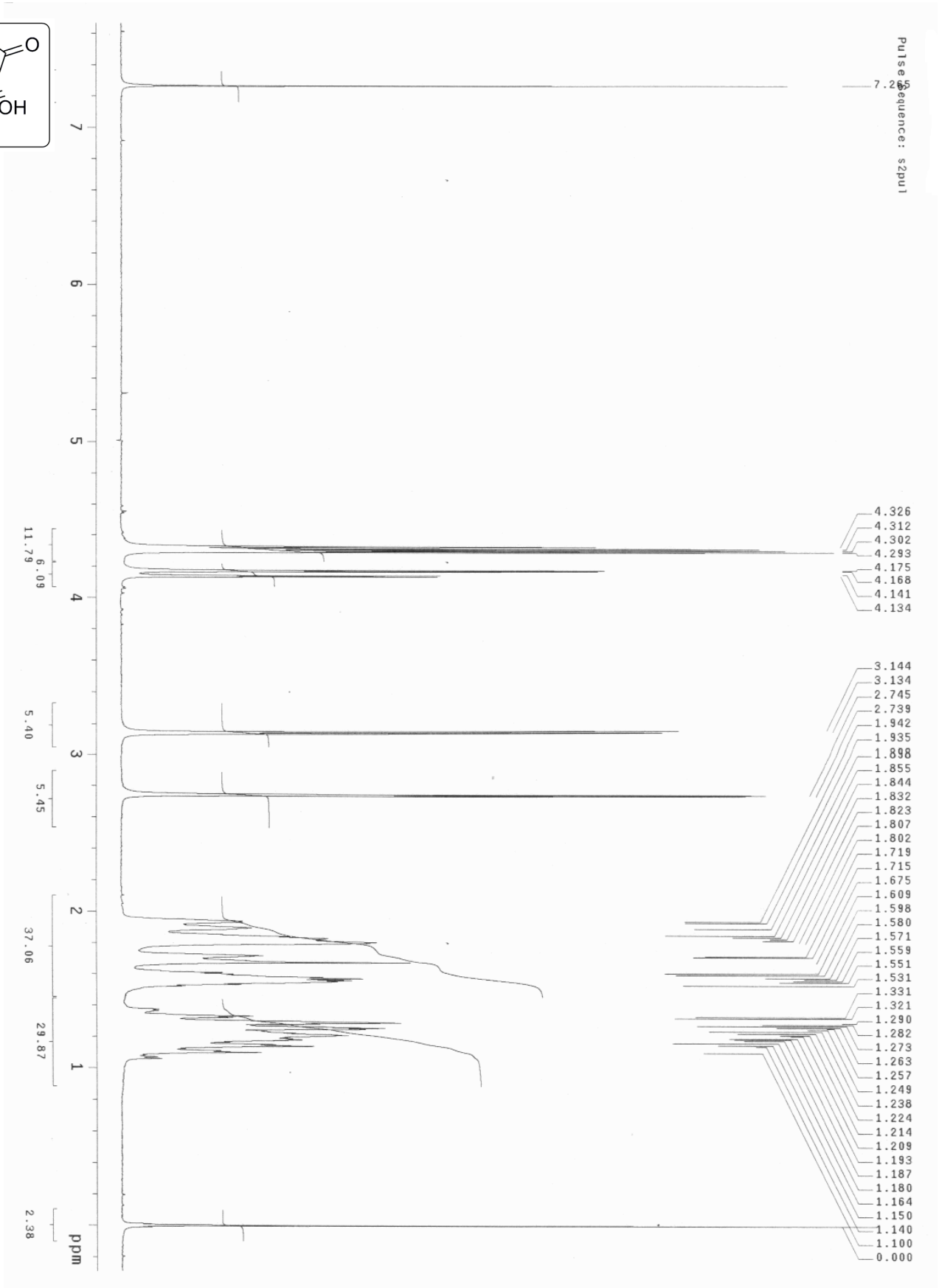


(±)-3-*C*-Phenyl-erythrono-1,4-lactone (**7a**) [300 MHz, $CDCl_3$].

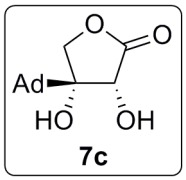


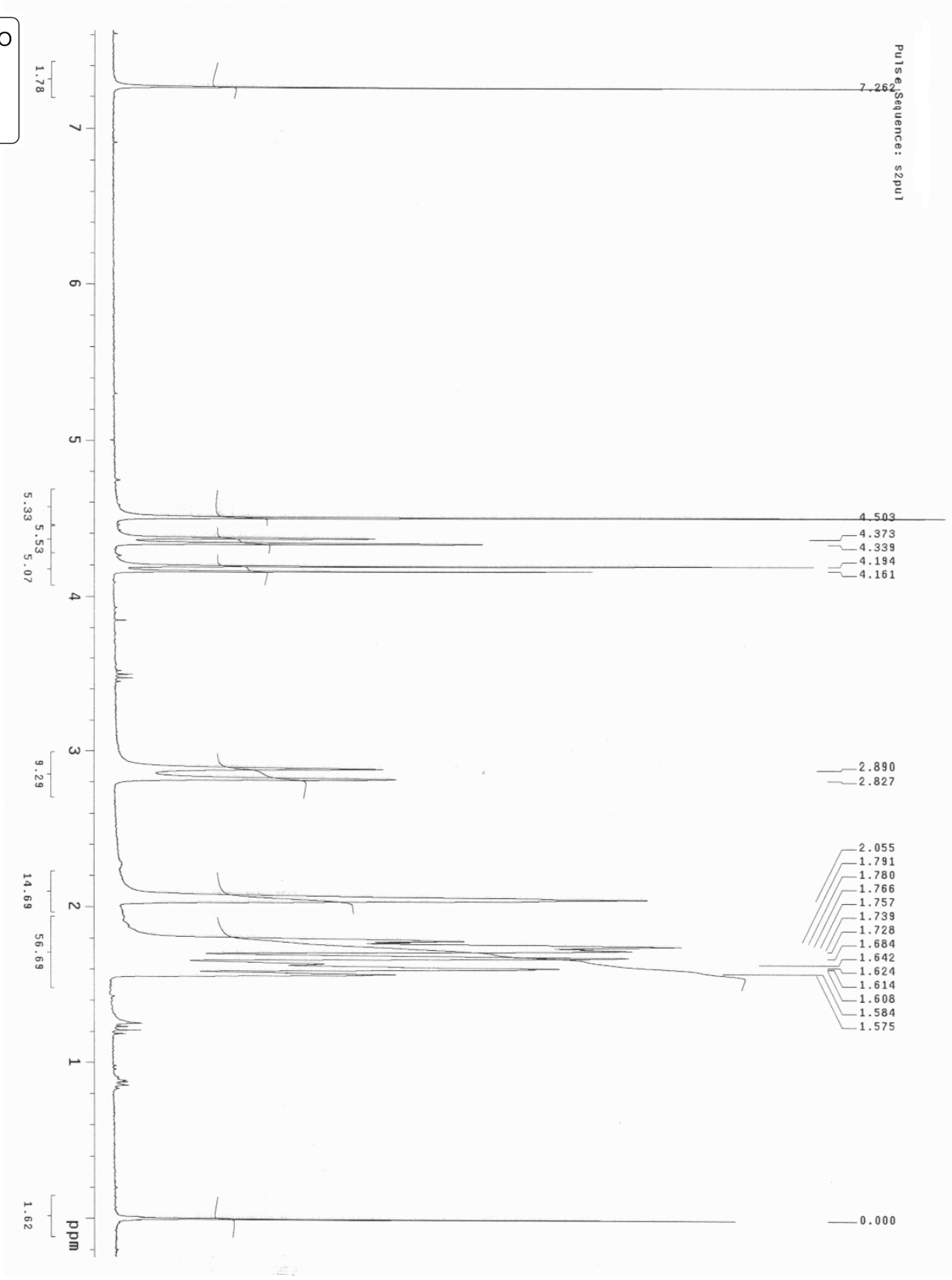
(±)-3-*C*-Cyclohexyl-erythrono-1,4-lactone (**7b**) [300 MHz, $CDCl_3$].



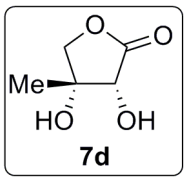


(±)-3-*C*-(1-Adamantyl)-erythrono-1,4-lactone (**7c**) [300 MHz, $CDCl_3$].

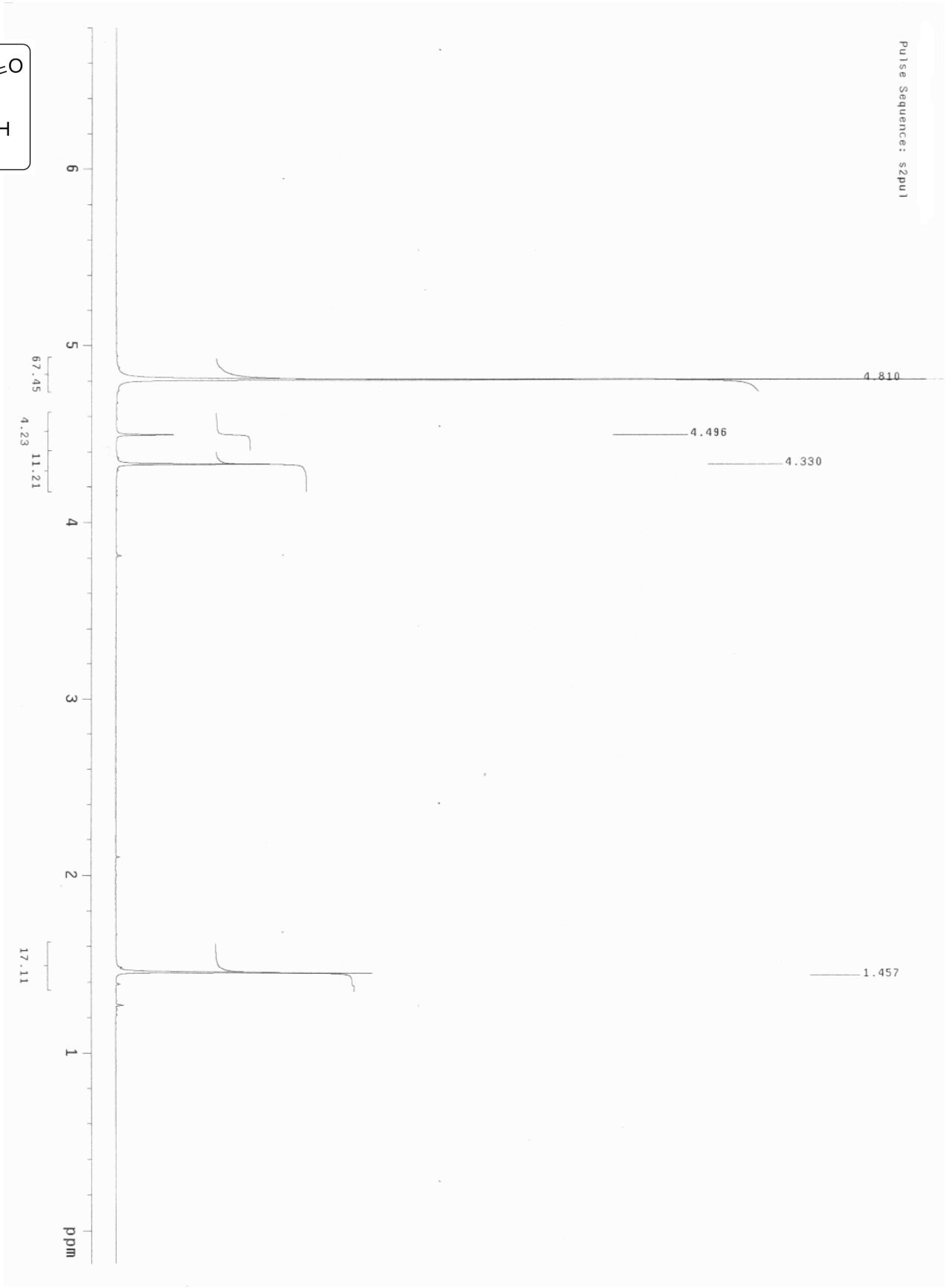




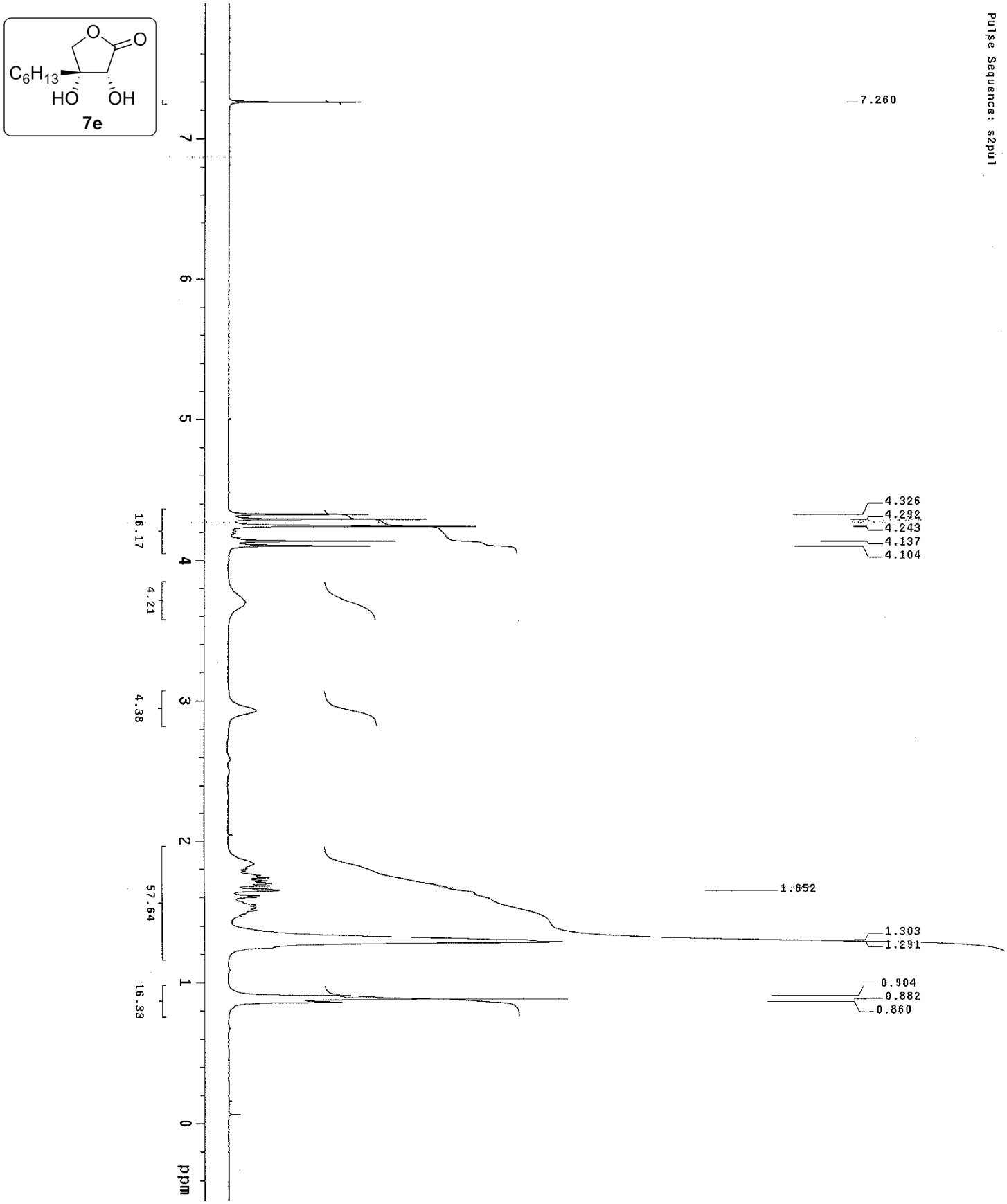
(±)-3-*C*-Methyl-erythrono-1,4-lactone (**7d**) [300 MHz, D_2O].



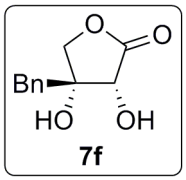
7d



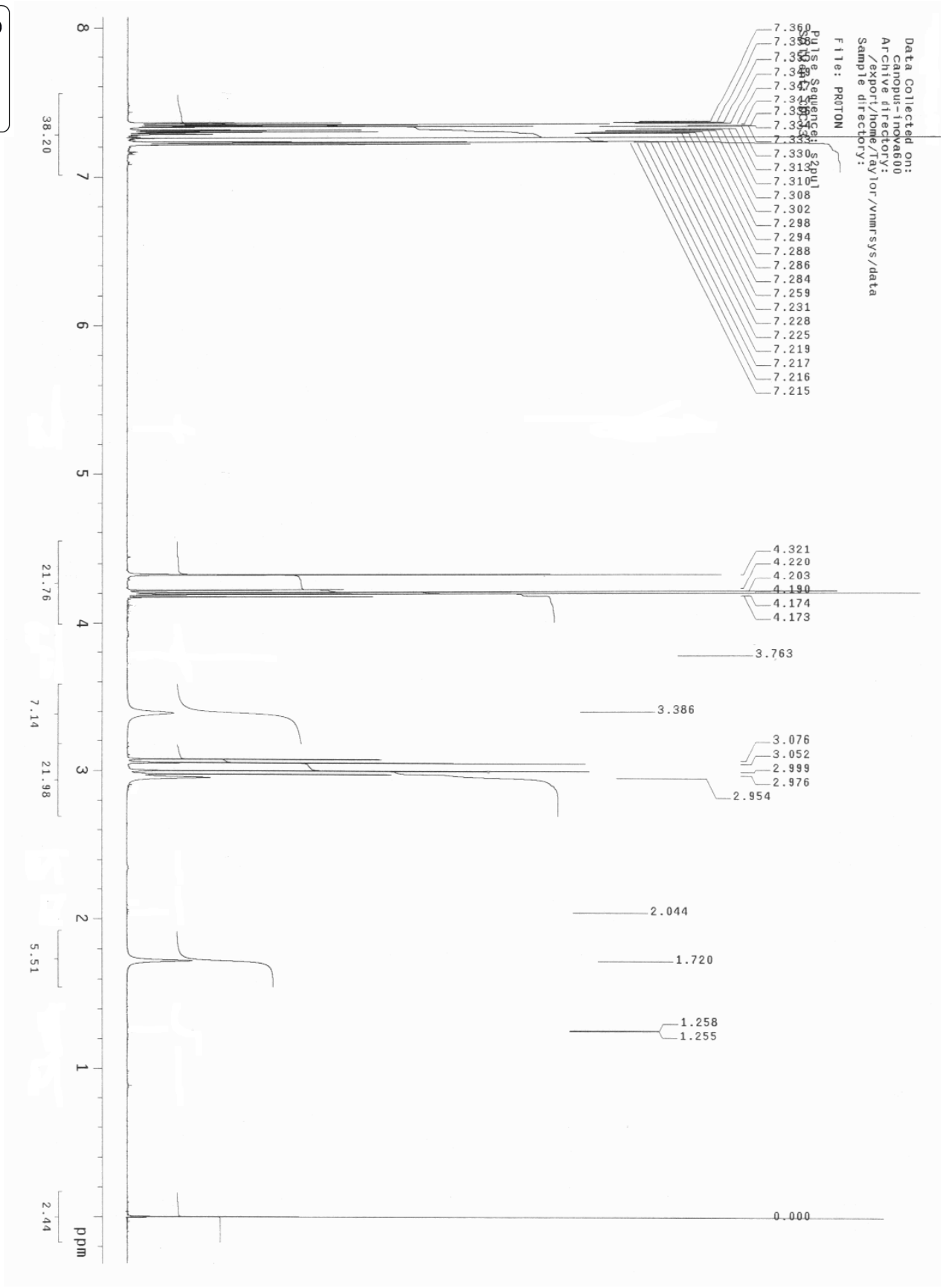
(±)-3-*C*-Hexyl-erythrono-1,4-lactone (**7e**) [300 MHz, $CDCl_3$].



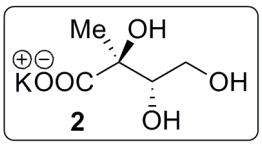
(±)-3-*C*-Benzyl-erythrono-1,4-lactone (**7f**) [600 MHz, $CDCl_3$].



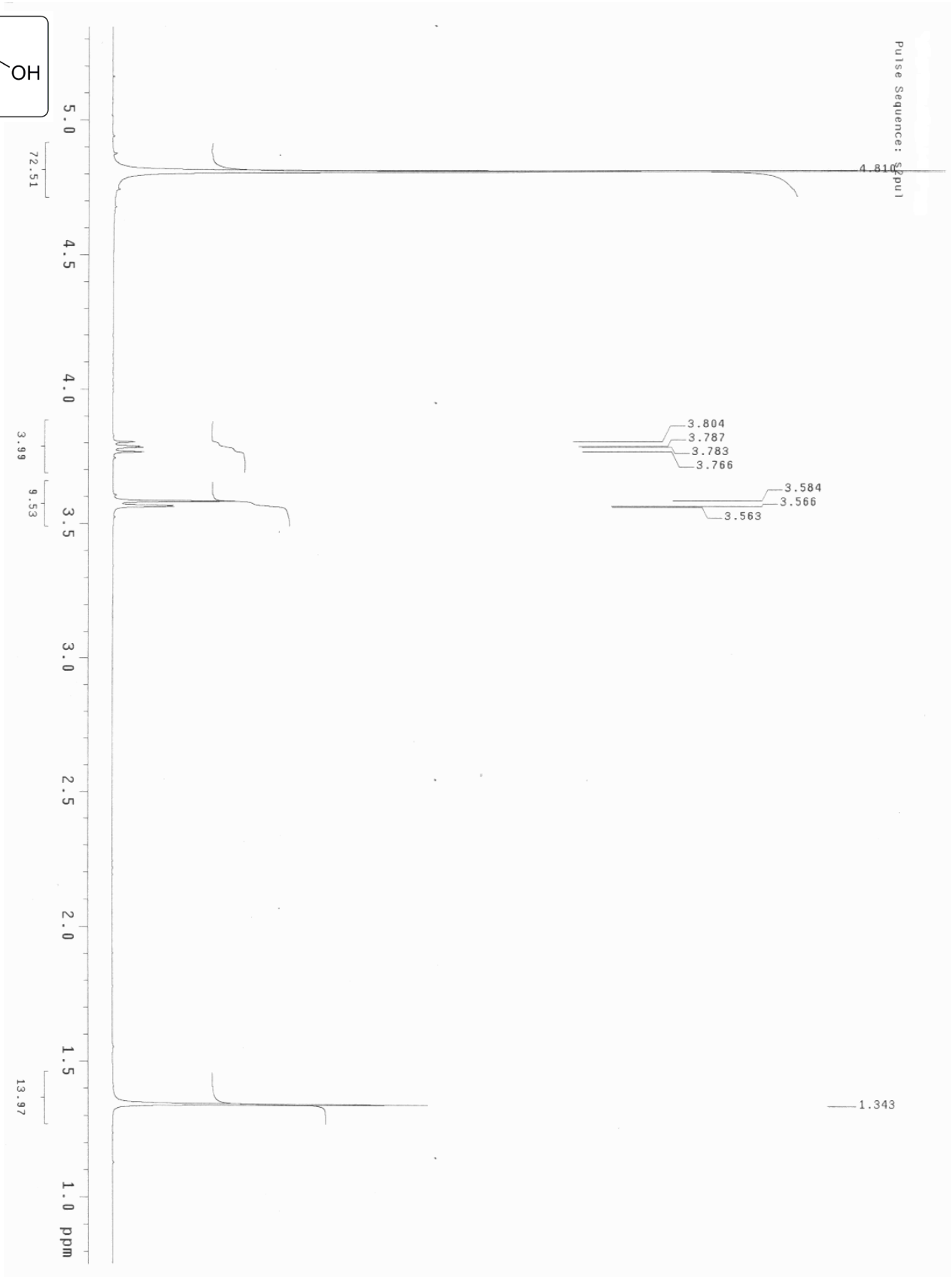
7f



(±)-Potassium 2,3,4-trihydroxy-2-methylbutanoate (**2**) [300 MHz, D_2O].



2



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