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Stereoselective preparation of key intermediates for the synthesis of iso-, neuro- and phyto-prostane family members in high yield: Inaugural asymmetric synthesis of 17-E2c-dihomo- and 17-F2c-dihomo-isoprostanes.

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Supporting Information

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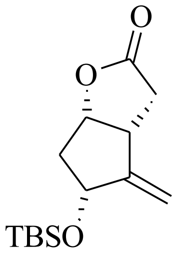
Experimental

All solvents were of commercial quality and were purified by distillation over the drying agents indicated: THF and Et_2O (Na/benzophenone), CH_2Cl_2 and hexane (CaH_2), toluene (Na/K). All other solvents and reagents were purchased from Aldrich, Alfa Aesar, TCI, and Fluorochem and used as received. All moisture-sensitive reactions were carried out under a positive static atmosphere of Ar in flame-dried glassware. Syringes, needles and the other glassware were dried at 140 °C for at least one night and allowed to cool in a desiccator over P_2O_5 before use. Routine monitoring of reactions was performed using silica gel 60 mesh (0.25 mm) aluminium-supported TLC plates (purchased from Merck). Compounds were visualized by UV irradiation at a wavelength of 254 nm or stained by exposure to a 0.5% solution of vanillin in H_2SO_4/EtOH, followed by charring. Flash column chromatography (FCC) was performed on silica gel (40−63 μm). Yields are reported for isolated compounds with >96% purity established by NMR unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, and coupling constants (J) are in hertz (Hz). The solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ-C 77.00; residual $CHCl_3$ in $CDCl_3$: δ-H 7.26; CD_2Cl_2: δ-C 53.8; residual CH_2Cl_2 in CD_2Cl_2: δ-H 5.32 ppm). COSY, DEPT, and NOESY spectra were recorded using a standard pulse program library. The number of H-atoms attached to each C-atom (s= 0H, d = 1H, t = 2H, q = 3H) was determined by DEPT experiments. Optical rotations were recorded on a digital polarimeter at 589 nm, with concentration (c) in g/100 mL. Mass spectrometry was performed by LTQ-XL using electrospray ionization (ESI) mode [$M+H^+$ or $M+Na^+$ adducts for positive mode and $M-H^+$ for the negative mode]. High Resolution Mass Spectra were recorded on a Thermo Q-Exactive Plus mass spectrometer. IR spectra (in cm^{-1}) were recorded either on NaCl film (for solids) or neat (for liquids) on an Alpha Bruker FTIR spectrometer.

(3aR,5R,6aS)-5-((tert-butyldimethylsilyl)oxy)-4-methylenehexahydro-2H-cyclopenta[b]furan-2-one, (**8a**)

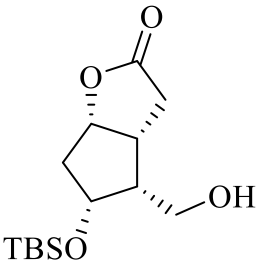


Imidazole (28 mg, 0.407 mmol) and PPh_3 (126 mg, 0.481 mmol) were added at room temperature to a magnetically stirred solution of alcohol **2a** (107 mg, 0.371 mmol) in dry THF (1 mL) under Ar atmosphere. Reaction was cooled to 0°C with an ice bath and I_2 (113 mg, 0.442 mmol) was added in three portions. The cooling bath was removed and the reaction mixture was stirred at rt until complete conversion of the starting material. The reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ (7 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 7 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 85:15 as eluent) to afford the iodide derivative as a white foam (139 mg, Yield = 95%). TLC (SiO_2): R_f=0.28 (Hexane:AcOEt, 8:2). $[\alpha]^{20}_{D}$ = -24.7 (*c* = 0.88, CH_2Cl_2). IR: υ max (CH_2Cl_2):): 2960, 2944, 2866, 1699, 1207, 1029,650 cm^{-1} ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm)= 4.94 (dt, *J* = 7.2, 3.1 Hz, 1H), 4.01 (q, *J* = 6.0 Hz, 1H), 3.22 (d, *J* = 6.0 Hz, 2H), 2.83 (dd, *J* = 10.0, 18.1 Hz, 1H), 2.67-2.64 (m, 1H) 2.50 (dd, *J* = 5.7 Hz, 1H), 2.38-2.31 (m, 1H), 2.03-2.01 (m, 1H), 1.84 (t, *J* = 6.0 Hz, 1H), 0.89 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 176.40 (s), 82.32 (d), 76.93 (d), 54.80 (d), 42.32 (d), 40.23 (t), 34.76 (t), 25.56 (q), 17.73 (s), 8.22 (t), -4.69 (q), -4.82 (q). ESI: 397.02 $[M+H]^+$. HRMS $[M+H]^+$: calcd for $C_{14}H_{26}IO_3Si$ *m/z* 397.0691, *m/z* found: 397.0695.

The corresponding iodide (118 mg, 0.298 mmol) was dissolved in dry PhMe (3 mL) under Ar atmosphere. DBU was added (89 µL, 0.596 mmol) and the reaction was heated to 60°C for 16h. Then, the reaction mixture was quenched with a saturated solution of NH_4Cl (5 mL) and was diluted with CH_2Cl_2. Layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 6 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) to afford the product **8a** (77 mg, yield = 96%) as a white foam. R_f= 0.31 (Hexane:AcOEt 8:2). $[\alpha]^{20}_{D}$ = -7.3 (*c* = 0.56, CH_2Cl_2). IR: υ max (CH_2Cl_2): 2953, 2930, 2856, 1752, 1189, 1029, 887 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm)= 5.17 (s, 1H), 5.07-5.02 (m, 2H), 4.50-4.45(m, 1H), 3.35-3.25 (m, 1H) 2.91 (dd, *J* = 18.2, 11.25 Hz, 1H), 2.63 (dd, *J* = 18.2, 3.69 Hz, 1H), 2.14-2.05 (m, 2H), 0.90

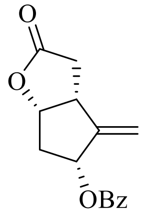
(bs, 9H), 0.10 (s, 3H), 0.09(s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm)= 176.62 (s), 154.46 (s), 109.38 (t), 82.97 (d), 74.95 (d), 41.46 (t), 40.90 (d), 35.98 (t), 25.54 (q), 17.92 (s), -4.93 (q), -5.02 (q). ESI: 269.5 $[M+H]^+$, 291.6 $[M+Na]^+$. HRMS $[M+H]^+$: calcd for $C_{14}H_{25}O_3Si$ *m/z* 269.1558 *m/z* found 269.1554.

(3aR,4R,5R,6aS)-5-((tert-butyldimethylsilyl)oxy)-4-(hydroxymethyl)hexahydro-2H-cyclopenta[b]furan-2-one (**4a**)



A solution of **8a** (338 mg, 1.26 mmol) in dry THF (13 mL) was cooled to -30°C under Ar atmosphere. After 10 min, $BH_3{\cdot}DMS$ (2M in THF, 760 μL, 1.52 mmol) was added. The reaction mixture was then warmed to 0°C and stirred for 6h. The reaction was quenched with a solution of K_2CO_3 (435 mg, 3.15 mmol) in H_2O (4 mL) and H_2O_2 (10M solution in H_2O, 330 μL, 3.30 mmol). The resulting mixture was stirred for 8h at room temperature then H_2O (4 mL), brine (12 mL), phosphate buffer at pH = 6.8 (12 mL) and CH_2Cl_2 were added. Layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 x 20 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 1:1 as eluent) to afford compound **4a** (320 mg, yield = 93%) as a white foam. R_f= 0.36 (Hexane:AcOEt, 1:1). $[\alpha]^{20}_D$ = -32.0 (*c* = 0.53, CH_2Cl_2). IR: υ max (CH_2Cl_2): 3290, 2940, 2927, 2846, 1761, 1649, 1092, 817, 771 cm^{-1}. ^{1}H-NMR (300 MHz; $CDCl_3$): δ 5.11 (t, *J* = 7.4 Hz, 1H), 4.33 (t, *J* = 3.5 Hz, 1H), 3.93 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.81 (dd, *J* = 10.4, 7.3, 1H), 3.18-3.07 (m, 1H), 2.75 (dd, *J* = 18.5, 4.9 Hz, 1H), 2.53 (dd, *J* = 18.5, 11.7 Hz, 1H), 2.19-2.09 (m, 2H), 1.94-1.85 (m, 2H), 0.87 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 177.78 (s), 84.63 (d), 73.79 (d), 59.69 (t), 49.72 (d), 42.00(t), 38.41 (d), 30.30 (t), 25.52 (q), 17.83 (s), -4.85 (q), -5.49 (q). ESI: 287.2 $[M+H]^+$; 309.3 $[M+Na]^+$; HRMS $[M+H]^+$: calcd for $C_{14}H_{27}O_4Si$ *m/z* 287.1673, *m/z* found: 287.1675.

(3aR,5R,6aS)-4-methylene-2-oxohexahydro-2H-cyclopenta[b]furan-5-yl benzoate (**8b**)



The alkene **8b** was obtained as a white solid (Yield =90% over two steps) following the procedure described above for compound **8a**: Imidazole (41 mg, 0.597 mmol) and PPh_3 (185 mg, 0.706 mmol) were added at room temperature to a magnetically stirred solution of alcohol **2b** (150 mg, 0.543 mmol) in dry THF (1 mL) under Ar atmosphere. Reaction was cooled to 0°C with an ice bath and I_2 (165 mg, 0.652 mmol) was added in three portions. The cooling bath was removed and the reaction mixture was stirred at rt until complete conversion of the starting material. The reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ (10 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) to afford the iodide derivative as a white solid (194 mg, Yield = 93%). The corresponding iodide was purified by chromatography on silica gel column (Hexane/EtOAc 85:15 as eluent). The spectroscopical data match with those reported in literature.[1] ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.01 (dd, *J* = 6.3, 0.6 Hz, 2H), 7.66-7.53 (m, 1H), 7.46 (dt, *J* = 6.3, 1.4 Hz, 2H), 5.29 (dt, *J* = 6.3, 4.0 Hz, 1H), 5.10 (dt, *J* = 6.5, 1.7 Hz, 1H), 3.39 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.25 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.06-2.79 (m, 2H), 2.69-2.53 (m, 2H), 2.47-2.28 (m, 2H). The elimination of the iodide led to alkene **8b**. The corresponding iodide (150 mg, 0.389 mmol) was dissolved in dry PhMe (5 mL) under Ar atmosphere. DBU was added (116 μL, 0.778 mmol) and the reaction was heated to 60°C for 16h. Then, the reaction mixture was quenched with a saturated solution of NH_4Cl (8 mL) and was diluted with CH_2Cl_2. Layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) to afford the product **8b** (97 mg, yield = 97%) as a white solid. mp: 93-96°C; R*f*: 0.26 (Hexane:AcOEt, 8:2). $[\alpha]^{20}_D = -40.0$ (*c* = 0.44, CH_2Cl_2). IR: υ max (CH_2Cl_2): 3060, 2993, 2971, 1762, 1708, 1451, 1270, 1053, 719 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.01 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.55 (m, 1H), 7.45 (ddt, *J* = 8.3, 6.6, 1.2 Hz, 2H),

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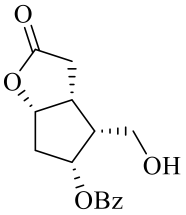
[1] R. Bansal, G. F. Cooper and E. J. Corey, *J. Org. Chem.* 1991, **56**, 1329

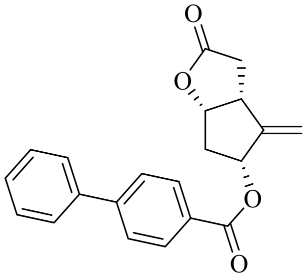
5.86 (d, *J* = 5.2 Hz, 1H), 5.60 (dd, *J* = 2.2, 0.9 Hz, 1H), 5.33 (dd, *J* = 1.8, 1.0 Hz, 1H), 5.19 (t, *J* = 6.1 Hz, 1H), 3.52 (m, 1H), 3.05 (dd, *J*= 18.2, 10.7 Hz, 1H), 2.62 (dd, *J*= 18.2, 2.5 Hz, 1H), 2.51 (d, *J*= 15.8 Hz, 1H), 2.30 (dt, *J*= 15.8, 5.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 176.22 (s), 165.77 (s), 150.93 (s), 133.10 (d), 129.65 (d), 129.58 (d), 128.38 (s), 116.16 (t), 84.06 (q), 74.40 (q), 42.26 (q), 38.74 (t), 37.07 (t). ESI**:** 259.12 $[M+H]^+$, HRMS $[M+H]^+$: calcd for $C_{15}H_{15}O_4$: *m/z* 259.0965, found: *m/z* 259.0962.

(3aR,4R,5R,6aS)-4-(hydroxymethyl)-2-oxohexahydro-2H-cyclopenta[b]furan-5-yl benzoate (**4b**)



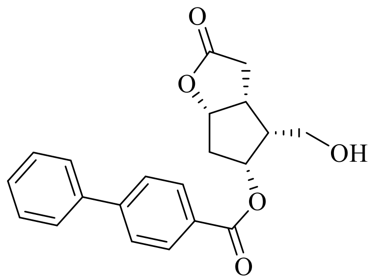
The alcohol **4b** was obtained as a white foam (Yield= 76%), following the procedure described above for compound **4a**. A solution of **8b** (95 mg, 0.38 mmol) in dry THF (4 mL) was cooled to -30°C under Ar atmosphere. After 10 min, $BH_3{\cdot}DMS$ (2M in THF, 230 μL, 0.46 mmol) was added. The reaction mixture was then warmed to 0°C and stirred for 12h. The reaction was quenched with a solution of K_2CO_3 (131 mg, 0.95 mmol) in H_2O (2 mL) and H_2O_2 (10M solution in H_2O, 100 μL, 1 mmol). The resulting mixture was stirred for 8h at room temperature then H_2O (3 mL), brine (5 mL), phosphate buffer at pH = 6.8 (5 mL) and CH_2Cl_2 (5ml)were added. Layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 1:1 as eluent) to afford compound **4b** (80 mg, yield = 76%) as a white foam. R_f: 0.29 (Hexane/EtOAc 1:1). $[\alpha]^{20}_D$ = -37.6 (*c* = 1.04, CH_2Cl_2). IR: υ max (CH_2Cl_2): 3440, 2954, 2930, 2856, 1752, 1641, 1471, 1093, 832, 776 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl3): δ (ppm) = 7.98 (d, *J* = 7.1 Hz, 2H), 7.64-7.52 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.64 (t, *J* = 4.1 Hz, 1H), 5.23 (t, *J* = 7.0 Hz, 1H), 3.70 (d, *J* = 7.7 Hz, 2H), 3.26 (ddd, *J* = 10.6, 8.5, 4.4 Hz, 1H), 2.78 (bs, 1H), 2.70 – 2.45 (m, 4H), 2.18 (ddt, *J* = 16.0, 4.5, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 177.01 (s), 166.82 (s), 133.56 (d), 129.70 (d), 128.80 (d), 128.54 (s), 84.27 (d), 76.24 (d), 58.56 (t), 49.19 (d), 42.52 (d), 39.48 (d), 38.23 (t), 29.73 (t). ESI: 277.05 $[M+H]^+$, HRMS $[M+H]^+$: calcd for $C_{15}H_{17}O_5$*:* *m/z* 277.1071, found: *m/z* 277.1072.

(3aR,5R,6aS)-4-methylene-2-oxohexahydro-2H-cyclopenta[b]furan-5-yl[1,1'-biphenyl]-4-carboxylate (**8c**)



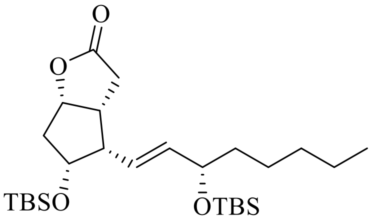
The alkene **8c** was obtained as a white solid (Yield = 86% over two steps) following the procedure described above for compound **8a**: Imidazole (106 mg, 1.56 mmol) and PPh_3 (485 mg, 1.85 mmol) were added at room temperature to a magnetically stirred solution of alcohol **2c** (500 mg, 1.42 mmol) in dry THF (1 mL) under Ar atmosphere. Reaction was cooled to 0°C with an ice bath and I_2 (433 mg, 1.70 mmol) was added in three portions. The cooling bath was removed and the reaction mixture was stirred at rt until complete conversion of the starting material. The reaction mixture was quenched with a saturated solution of $Na_2S_2O_3$ (40 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) to afford the iodide derivative as a white solid (440 mg, Yield = 93%). The corresponding iodide was purified by chromatography on silica gel column (Hexane/EtOAc 85:15 as eluent). mp: 163-165°C, R*f*: 0.22 (Hexane/EtOAc 85:15), $[\alpha]^{20}_{D} = -76.7$ (*c* = 0.3, CH_2Cl_2), IR: υ max (CH_2Cl_2): 3063, 2988, 2967, 1755, 1710, 1453, 1265, 1058, 726 cm^{-1}. ^{1}H-NMR (300 MHz, CDC13): δ (ppm)= 8.09 (dd, *J* = 6.7, 1.9 Hz, 2H), 7.71-7.63 (m, 4H), 7.52-7.42 (m, 3H), 5.32 (dt, *J* = 6.3, 3.84 Hz, 1H), 5.12 (dt, *J* = 6.43, 1.7 Hz, 1H), 3.41 (dd, *J* = 10.1, 5.2 Hz, 1H), 3.25 (dd, *J* = 10.3, 7.5 Hz, 1H), 3.04-2.83 (m, 2H), 2.70-2.58 (m, 2H), 2.44-2.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 175.96 (s), 165.66 (s), 146.06 (s), 139.74 (s), 130.13 (d), 128.83 (d), 128.12 (d), 127.89 (s), 127.17 (d), 127.11 (d), 83.61 (d), 79.34 (d), 53.98 (d), 44.27 (d), 37.84 (t), 35.66 (t), 6.78 (t). ESI**:** 463.10 $[M+H]^+$, HRMS $[M+H]^+$: calcd for $C_{21}H_{20}IO_4$: *m/z* 463,0401 found: *m/z* 463.0404. The elimination of the iodide led to alkene **8c**. The corresponding iodide (230 mg, 0.497 mmol) was dissolved in dry PhMe (6.5 mL) under Ar atmosphere. DBU was added (148 μL, 0.994 mmol) and the reaction was heated to 60°C for 16h. Then, the reaction mixture was quenched with a saturated solution of NH_4Cl (10 mL) and was diluted with CH_2Cl_2. Layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 12 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) to afford the product **8c** (152 mg, yield = 92%) as a white solid. mp: 60-64°C; R_f: 0.26 (Hexane:AcOEt, 8:2). $[\alpha]^{20}_D$ = -36.0 (*c* = 0.50, CH_2Cl_2). IR: υ max (CH_2Cl_2): 3065, 2988, 2976, 1758, 1706, 1447, 1053, 755 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm)= 8.09 (d, *J* = 6.6 Hz, 2H), 7.55 (m, 4H), 7.45 (m, 3H), 5.88 (d, *J* = 5.2 Hz, 1H), 5.60 (m, 1H), 5.34 (s, 1H), 5.18 (t, *J* = 6.1 Hz, 1H), 3.53 (ddt, *J* = 10.46, 6.86, 1.86 Hz, 1H), 3.06 (dd *J*= 18.14, 10.72 Hz, 1H), 2.64 (dd, *J*= 18.1, 2.4 Hz, 1H), 2.53 (d, *J* = 15.8 Hz, 1H), 2.29 (dt, *J*= 15.8, 5.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 176.28 (s), 165.64 (s), 150.99 (s), 145.77 (s), 139.85 (s), 130.13 (d), 128.81 (d), 128.42 (s), 128.03 (d), 127.16 (d), 127.04 (d), 116.18 (t), 84.11 (d), 76.45 (d), 42.28 (d), 38.78 (t), 37.14 (t). ESI**:** 335.19 $[M+H]^+$, HRMS $[M+H]^+$: calcd for $C_{21}H_{19}O_4$: *m/z* 335.1278, found: *m/z* 335.1274.

(3aR,4R,5R,6aS)-4-(hydroxymethyl)-2-oxohexahydro-2H-cyclopenta[b]furan-5-yl[1,1'-biphenyl]-4-carboxylate (**4c**)



The alcohol **4c** was obtained as a white foam (Yield= 93%), following the procedure described above for compound **4a**. A solution of **8c** (101 mg, 0.30 mmol) in dry THF (1 mL) was cooled to -30°C under Ar atmosphere. After 10 min, $BH_3\cdot DMS$ (2M in THF, 182 μL, 0.36 mmol) was added. The reaction mixture was then warmed to 0°C and stirred for 12h. The reaction was quenched with a solution of K_2CO_3 (105 mg, 0.76 mmol) in H_2O (5 mL) and H_2O_2 (10M solution in H_2O, 50 μL, 0.5 mmol). The resulting mixture was stirred for 8h at room temperature then H_2O (2 mL), brine (3 mL), phosphate buffer at pH = 6.8 (4 mL) and CH_2Cl_2 (5 mL)were added. Layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 x 24 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc 1:1 as eluent) to afford compound **4c** (99 mg, yield = 93%) as a white foam R$_f$: 0.31 (Hexane/EtOAc 1:1), $[\alpha]^{20}_{D} = -49.4$ ($c = 1.25$, CH_2Cl_2). IR: υ max (CH_2Cl_2): 3441, 2949, 2939, 2851, 1746, 1650, 1473, 1088, 829, 775 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm)= 7.95 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.39-7.28 (m, 3H), 5.57 (bs, 1H), 5.20 (s, 1H), 5.15 (t, *J* = 7.1 Hz, 1H), 3.61 (d, *J* = 6.1 Hz, 2H), 3.16 (dt, *J* = 16.1, 9.8 Hz, 1H), 2.69 (m, 1H), 2.57 (t, *J* = 10.8 Hz, 2H), 2.41 (bs, 1H), 2.10 (dt, *J* =15.8, 5.7 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 177.01 (s), 166.88 (s), 146.33 (s), 139.64 (s), 130.31 (d), 128.85 (d), 128.18 (d), 127.21 (d), 127.17 (d), 84.30 (d), 77.36 (d), 76.22 (d), 58.62 (t), 49.35 (d), 39.50 (t), 38.22 (d), 29.77 (t). ESI**:** 353.21 $[M+H]^+$; HRMS $[M+H]^+$: calcd for $C_{21}H_{21}O_5$: *m/z* 353.1384, found: *m/z* 353.1380.

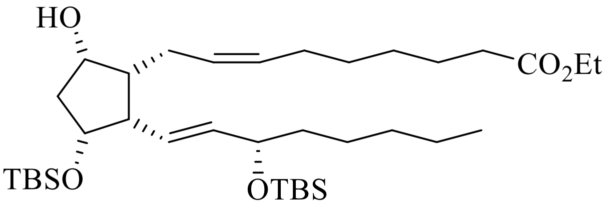
(3aR,4S,5R,6aS)-5-((tert-butyldimethylsilyl)oxy)-4-((S,E)-3-((tert-butyldimethylsilyl)oxy)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one (**9**)



Compound **9** was synthesized using a modified literature procedure.[15a] The alcohol **4a** (100 mg, 0.351 mmol) was dissolved in dry DCM (5 mL) under Ar atmosphere. DMP (170 mg, 0.402 mmol), was added at rt. After 1.5h the reaction mixture was diluted with a MTBE/Hexane solution (7:3, 40 mL) and quenched with the addition of a saturated solution of $Na_2S_2O_3$ (15 mL) and a saturated solution of $NaHCO_3$ (30 mL). Layers were separated and the aqueous layer was extracted with a MTBE/Hexane 7:3 mixture (3 x 15 mL). Combined organic layers were dried on Na_2SO_4, filtered and concentrated under vacuum. The crude aldehyde was used for the next step without further purification. A solution of Heptyne (55 μL, 0.420 mmol) in dry THF under Ar atmosphere was cooled to -78°C. Then n-ButhylLithium (solution 2.2M in hexane, 175 μL, 0.385 mmol) was added dropwise and the reaction was maintained at -78°C for 1h. Subsequently, a solution of the aldehyde previously prepared (0.348 mmol) in dry THF (1 mL) was added *via cannula* and the resulting mixture was stirred for additional 30 minutes at -78°C. The reaction was quenched at -78°C with a saturated solution of NH_4Cl (15 mL) and diluted with Et_2O (15 mL). Layers were separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). Combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue, without further purification, was dissolved in a stirred solution of MeOH/H_2O 1:1 (2 mL) and Au catalyst (20 mg, 6% mol) was added. The reaction was stirred at rt until complete conversion (TLC, Hexane/EtOAc 7:3). Then, the reaction was concentrated under vacuum and the residue was purified by chromatography on silica gel column (Hexane/EtOAc 8:2 as eluent) affording the enone derivative as a pale-yellow oil (86 mg, yield = 88%). R_f : TLC (SiO_2) 0.40 (Hexane/ EtOAc 7:3), $[\alpha]^{20}_{D}$ = +15.0 (*c* = 0.30, CH_2Cl_2). IR: υ max (liquid film) 2955, 2872, 1738, 1696, 1627, 1459, 1435, 1199, 978, 711, 440 cm^{-1}. ^{1}H-NMR (300 MHz; CD_2Cl_2) δ (ppm): 6.96 (dd, *J* =12.3, 6.1 Hz, 1H), 6.17 (dd, *J* = 12.0, 0.6 Hz, 1H), 5.14 (t, *J* = 5.4 Hz, 1H), 4.31 (t, *J* = 2.4 Hz, 1H), 3.19 (m, 1H), 2.78 (dd, *J* = 14.1, 4.0 Hz, 1H), 2.70-2.72 (m, 1H), 2.60-2.51 (m, 3H), 2.21 (d, *J* = 5.7 Hz, 1H), 2.03-2.0 (m, 1H), 1.62 (t, *J* = 5.7 Hz, 2H), 1.36-1.30 (m, 4H), 0.93 (t, *J* = 5.1 Hz, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H).^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) = 202.10 (s), 177.20 (s), 143.12 (d), 133.46 (d), 85.15 (d), 77.26 (d), 50.83 (d), 42.81 (t), 42.02 (d), 39.87 (t), 31.85(t), 31.57(t), 25.80 (q), 24.26 (t), 22.88 (t), 18.24 (s), 14.15 (q),-4.80 (q), -5.25 (q). ESI: 381.24 $[M+H]^+$, 403.51 $[M+Na]^+$. HRMS $[M+H]^+$: calcd for $C_{21}H_{37}O_4Si$: *m/z* 381.2456, found: *m/z* 381.2460. The purified enone (65 mg, 0.171 mmol) was dissolved in dry THF (1.8 mL) under Ar atmosphere and cooled at -40°C. Then (-)-Dip-Cl (solution 2.3M in Heptane, 365 μL, 0.842 mmol) was added dropwise. The temperature was warmed to -25°C and stirred at this temperature for 6h. The reaction mixture was quenched with solid $NaHCO_3$ (270 mg) and MeOH (730 μL) and stirred overnight at rt. Subsequently the solution was concentrated under vacuum, diluted with: water (3 mL), a saturated solution of $NaHCO_3$ (5 mL), and DCM (10 mL). Layers were separated and the aqueous layer was extracted with DCM (3 x 7 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc from 7:3 to 1:1 as eluent) to afford the allylic alcohol intermediate (52 mg, yield = 80%) as a pale-yellow oil. R_f : TLC (SiO_2) 0.29 (Hexane/ EtOAc 6:4), $[\alpha]^{20}_{D}$ = 5.5 (*c* = 0.26 CH_2Cl_2). IR υmax: 3425, 2955, 2931, 2857, 1758, 1463, 1361, 1254, 1187, 1093, 1035, 904, 836, 776 cm^{-1}.^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm)= 5.84 (dd, *J* = 15.5, 8.4 Hz, 1H), 5.62 (dd, *J* = 15.6, 7.0 Hz, 1H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.19 (t, *J* = 3.5 Hz, 1H), 4.11 (q, *J* = 6.5 Hz, 1H), 3.14-3.01 (m, 1H), 2.84 (dd, *J* = 18.5, 4.9 Hz, 1H), 2.56-2.44 (m, 2H), 2.17 (d, *J* = 15.1 Hz, 1H), 1.99-1.82 (m, 1H), 1.77-1.52 (m, 3H), 1.39-1.27 (m, 6H), 0.92-0.88 (m, 12H), 0.07 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 177.48 (s), 136.62 (d), 127.44 (d), 84.67 (d), 76.91 (d), 72.89 (d), 50.49 (d), 42.17 (t), 41.57 (d), 37.14 (t), 31.63 (t), 31.04 (t), 25.57 (q), 25.07 (t), 22.46 (t), 17.92 (s) 13.91 (q), -4.82 (q), -5.29 (q). ESI: 383.44 $[M+H]^+$, 405.38 $[M+Na]^+$; HRMS $[M+H]^+$: calcd. for $C_{21}H_{39}O_4Si$: *m/z* 383.2612, found: *m/z* 383.2611.

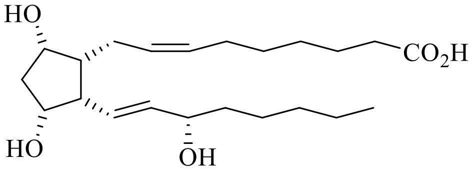
The allylic alcohol intermediate (200 mg, 0.523 mmol) was dissolved in dry DCM (4 mL) under Ar atmosphere at rt. Imidazole (90 mg, 1.3 mmol) and TBS-Cl (95 mg, 0.628 mmol) were added. The reaction was stirred at rt for 12h and then quenched with the addition of H_2O (4 mL) and a saturated solution of $NaHCO_3$ (4 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 10 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc from 9:1 to 8:2 as eluent) to afford the product **9** (250 mg, yield = 96%) as a pale-yellow oil. R_f: TLC (SiO_2) 0.42 (Hexane/ EtOAc 8:2), $[\alpha]^{20}_{D}$ = -3.8 (*c* = 1.93, CH_2Cl_2). IR υmax: 2925, 2857, 1765, 1574, 1457, 1256, 1086, 832, 773 cm^{-1}. ^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm)= 5.70 (dd, *J* = 8.2, 7.5 Hz, 1H), 5,52 (dd, *J* = 8.4, 7.2 Hz, 1H), 5.09 (t, *J* = 7.2 Hz, 1H), 4.18 (t, *J* = 3 Hz, 1H), 4.05 (q, *J* = 6.6 Hz, 1H), 3.0-3.14 (m, 1H), 2.83 (dd, *J* = 17.1, 4.9 Hz, 1H), 2.52-2.46 (m, 2H), 2.16 (d, *J* = 15.1 Hz, 1H), 1.92-1.71 (m, 1H), 1.55-1.27 (m, 9H), 0.91-0.88 (m, 20H), 0.06-0.02 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)= 177.57 (s), 137.62 (d), 125.98 (d), 84.64 (d), 76.57 (d), 73.89 (d), 50.41 (d), 42,25 (t), 41.69 (d), 38.13 (t), 31.66 (t), 31.02 (t), 25.78 (q), 25.59 (q), 24.89 (t), 22.50 (t), 18.12 (s), 17.91 (s), 13.93 (q), -4.25 (q), -4.73 (q), -4.82(q) , -5.27 (q). ESI: 497.55 $[M+H]^+$, 519.20 $[M+Na]^+$; HRMS: calcd for $C_{27}H_{53}O_4Si_2$: *m/z* 497.3477, found: *m/z* 497.3479.

Ethyl(Z)-9-((1R,2S,3R,5S)-3-((tert-butyldimethylsilyl)oxy)-2-((S,E)-3-((tert-butyldimethylsilyl)oxy)oct-1-en-1-yl)-5-hydroxycyclopentyl)non-7-enoate (**10**)



Compound **9** (75mg; 0.151mmol) was dissolved in dry DCM (2 ml) under Ar atmosphere and the solution was cooled at -78°C. DIBALH (1M in Hexane, 181 μl, 0.181mmol) was added dropwise and the reaction was stirred for 1h at the same temperature. Then, the reaction mixture, was quenched with a saturated solution of Rochelle salt (5 ml) and then stirred for 6h at rt. Subsequently the reaction was diluted with H_2O (5ml). The layers were separated and the aqueous layer was extracted with DCM (3x10ml). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude lactole, without further purification, was dissolved in PhMe dry (3ml) and added *via cannula* to the ylide solution at -20°C previously prepared. (*Ylide* *preparation*: Phosphonium salt **11** (295 mg, 0.564 mmol) was dissolved in dry THF (4 mL) under Ar atmosphere. The resulting suspension was cooled to 0°C and KHMDS (0.5M solution in PhMe, 1.13 mL, 0.565 mmol) was added dropwise and stirred at rt for 1h). The reaction mixture was stirred at -20°C for 0.5h, then was warmed to rt and, after 4h, the resulting mixture was quenched with a saturated solution of NH_4Cl (5 mL) and Et_2O (5 mL). Layers were separated and the aqueous layer was extracted with Et_2O (3 x 5 mL). Combined organic layers were washed with brine (5ml), dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc from 98:2 to 9:1 as eluent) to afford product **10** as a colourless oil (74mg, Yield = 77%). R_f: TLC (SiO_2) 0.31 (Hexane/ EtOAc 9:1), $[\alpha]^{20}_{D}$ = -8.1 (*c* = 3.4, CH_2Cl_2). IR υ max: 3517, 2954, 2928, 2856, 1737, 1462, 1252, 836, 775 cm^{-1}. ^1H-NMR (300 MHz; $CDCl_3$), δ (ppm): 5.65 (dd, *J* = 10.2, 5.3 Hz, 1H), 5.48-5.33 (m, 3H), 4.19-4.06 (m, 4H), 2.64-2.51 (m, 2H), 2.27 (p, *J* = 7.5 Hz, 3H), 2.18-15 (m, 6H), 1.61 (p, *J* = 7.2 Hz; 2H), 1.54-1.22 (m, 15 H), 0.93-0.85 (m, 21 H), 0.06-0.01 (m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.66 (s), 136.75 (d), 130.00 (d), 129.04 (d), 128.16 (d), 76.91 (d), 73.86 (d), 73.59 (d), 60.01 (t), 50.52 (d), 47.41 (d), 42.92 (t), 38.51 (t), 34.21 (t), 31.74 (t), 29.25 (t), 28.73 (t), 27.07 (t), 25.78 (q), 25.74 (q), 24.91 (t), 24.81 (t) , 24.54 (t), 22.49 (t), 18.07 (s), 17.98 (s), 14.13 (q), 13.95 (q), -4.13 (q), -4.84 (q), -4.92 (q), -5.02 (q). ESI: 639.51 $[M+H]^+$; HRMS $[M+H]^+$: calcd for $C_{36}H_{71}O_5Si_2$: *m/z* 639.4835, found: *m/z* 639.4837.

(Z)-9-((1R,2S,3R,5S)-3,5-dihydroxy-2-((S,E)-3-hydroxyoct-1-en-1-yl)cyclopentyl)non-7-enoic acid (**7**)

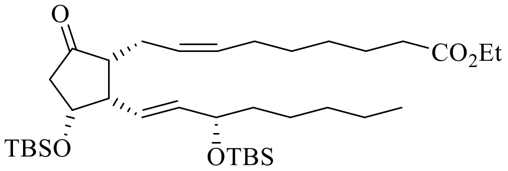


Compound **10** (40 mg, 0.063 mmol) was dissolved in MeCN (4 mL) and then, HF (48% solution in H_2O, M= 27.6, 68 μL) was added and the reaction mixture was stirred at rt for 18h. Then, the reaction mixture was quenched with SiO_2 (150mg), filtered and concentrated under vacuum. The residue was purified by chromatography on silica gel column (Hexane/EtOAc from 3:7 to a 1:9 as eluent) affording the desired 17-F_{2c}-dihomo-IsoP-ethylesther as a colorless oil (24 mg, yield =

93%). R*f*: 0.30 (Hexane/EtOAc 2:8). $[\alpha]^{20}_{D}$ = -5.3 (*c* = 0.43, EtOAc). IR υmax: 3355, 2930, 2858, 1761, 1409, 1376, 1266, 1096, 1042, 985, 737, 701 cm^{-1}. ^{1}H-NMR (300 MHz; CD_3CN) δ (ppm): 5.79 (dd, *J* = 15.4, 10.5, 1H), 5.52-5.34 (m, 3H), 4.14-4.00 (m, 4H), 2.85 (bs, 1H), 2.75 (bs, 1H), 2.66-2.53 (m, 2H), 2.32-2.13 (m, 4H), 2.11-2.03 (m, 2H), 1.97 (dt, *J* = 5.0, 2.5 Hz, 1H), 1.91-1.74 (m, 1H), 1.61-1.56 (m, 3H), 1.45-1.32 (m, 12H), 1.23 (t, *J* = 7.1, 3H), 0.91 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (75 MHz, CD_3CN): δ (ppm)= 173.37 (s), 137.07 (d), 129.64 (d), 129.15 (d), 127.68 (d), 73.96 (d), 71.89 (d), 71.66 (d), 59.8 (t), 50.49 (d), 47.15 (d), 42.83 (t), 37.41 (t), 33.76 (t), 31.64 (t), 29.06 (t), 28.41 (t), 26.84 (t), 24.95 (t), 24.60 (t), 23.98 (t), 22.4 (t), 13.58 (q), 13.36 (q). ESI: 411.44 $[M+H]^+$, 433.50 $[M+Na]^+$; HRMS $[M+H]^+$: calcd for $C_{24}H_{43}O_5$: *m/z* 411.3105 found: *m/z* 411.3108.

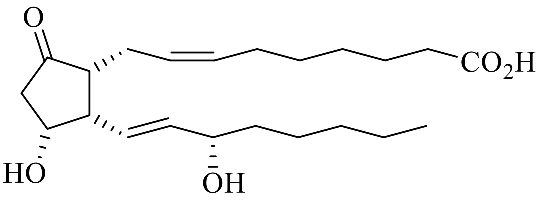
The 17-F_{2c}-AdrenoP-ethylesther (20 mg, 0.048 mmol) was dissolved in MTBE (1 ml) then, H_2O (100μL) and the *lipase* CAL-B (20 mg) were added. The reaction was stirred at rt for 18h and then the enzyme was filtered and washed with DCM (2 ml), CH_3CN (2 mL) and MTBE (2 mL). The residue was purified by chromatography on silica gel column (from EtOAc to EtOAc/*i*-PrOH 95:5 as eluent) to afford the product **7** (16 mg, Yield = 86%) as a colourless oil. R*f*: (EtOAc) = 0.31. $[\alpha]^{20}_{D}$ = -4.6 (*c* = 0.26, EtOAc). IR υmax: 3389, 2930, 2858, 1712, 1409, 1376, 1266, 1104, 1044, 985, 737, 703 cm^{-1}.^{1}H-NMR (300 MHz; CD_3CN) δ (ppm): 5.79 (dddd, *J* = 11.5, 10.5, 0.9 Hz, 1H), 5.51-5.31 (m, 3H), 4.14-4.0 (m, 3H), 2.68-2.55 (m, 1H), 2.34-2.15 (m, 4H), 2.08-2.01 (m, 2H), 1.95 (dt, *J* = 5.2, 2.6 Hz, 1H), 1.88-1.76 (m, 1H), 1.57-1.50 (m, 3H), 1.51-1.30 (m, 12H), 0.97-0.89 (m, 3H). ^{13}C NMR (75 MHz, CD_3CN): δ (ppm)= 174.32 (s), 136.96 (d), 129.65 (d), 129.18 (d), 127.84 (d), 73.98 (d), 71.93 (d), 71.78 (d), 50.48 (d), 47.14 (d), 42.8 (t), 37.38 (t), 33.23 (t), 31.62 (t), 28.99 (t), 28.36 (t), 26.81 (t), 24.94 (t), 24.47 (t), 23.98 (t), 22.39 (t), 13.36 (q). ESI-MS: 381.25 $[M-H]^-$, 763.08 $[2M-H]^+$.; HRMS $[M+H]^+$: calcd for $C_{22}H_{39}O_5$: *m/z* 383.2792 found: *m/z* 383.2796.

Ethyl(Z)-9-((1R,2S,3R)-3-((tert-butyldimethylsilyl)oxy)-2-((S,E)-3-((tert-butyldimethylsilyl)oxy)oct-1-en-1-yl)-5-oxocyclopentyl)non-7-enoate (**12**)



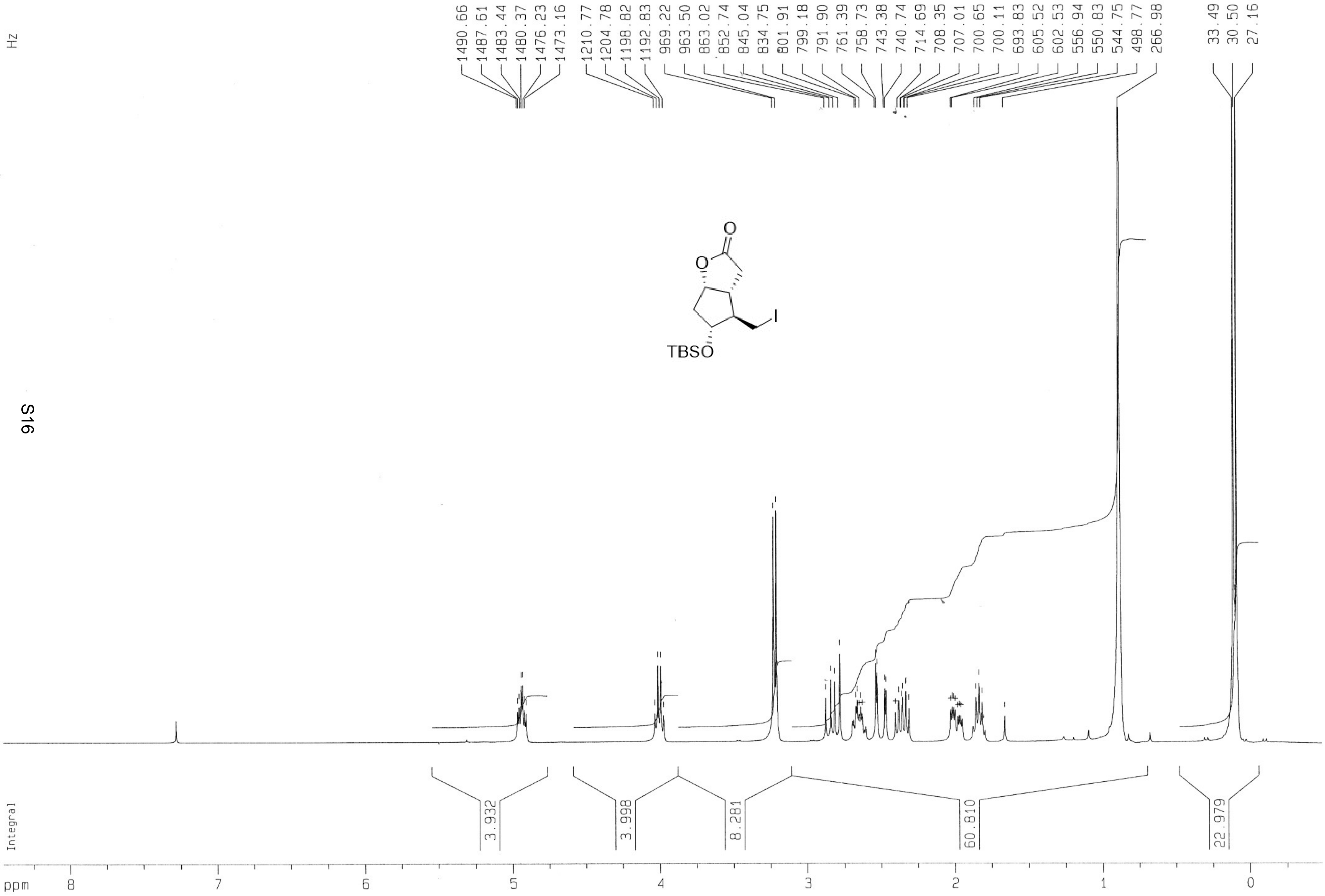
Compound **10** (50mg, 0.078 mmol), was dissolved in dry DCM (2ml), then DMP (40 mg, 0.094 mmol) was added and the reaction was stirred at rt for 1.5h. Then, the solution was diluted with Et_2O (5 mL), and filtered on a pad of silica gel using Hexane/EtOAc 92:8 as eluent affording compound **12** (47 mg, yield= 95%) as a pale-yellow oil. R_f: 0.45 (Hexane:AcOEt, 98:2). $[\alpha]^{20}_D$ = -28.5 (c = 0.94, CH_2Cl_2). IR υmax: 2927, 2856, 1735, 1463, 1178, 1109, 1028, 955, 772 cm^{-1}. ^{1}H-NMR (300 MHz; CD_3CN): δ (ppm)= 5.62-5.33 (m, 4H), 4.49 (td, J = 6.8, 5.2 Hz, 1H), 4.17 (q, J = 5.8 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.08-3.01 (m, 1H), 2.54 (dd, J = 18.5, 7.0 Hz, 1H), 2.44 (dt, J = 14.2, 6.3 Hz, 1H), 2.34-2.25 (m, 2H), 2.12-1.95 (m, 4H), 1.58 (dt, J = 14.7, 7.3 Hz, 2H), 1.53-1.43 (m, 2H), 1.42-1.31 (m, 10H), 1.22 (t, J =7.2 Hz, 3H), 0.96-0.83 (m, 22H), 0.10-0.02 (m, 12H). ^{13}C NMR (75 MHz, CD_3CN): δ (ppm)= 215.6 (s), 173.2 (s), 137.94 (d), 130.18 (d), 127.77 (d), 124.87 (d), 73.13 (d), 71.24 (d), 59.76 (t), 53.17 (d), 49.16 (d), 45.36 (t), 38.31 (t), 33.78 (t), 31.6 (t), 28.98 (t), 28.47 (t), 26.92 (t), 25.3 (q), 25.27 (q), 24.64 (t), 24.58 (t), 23.98 (t), 22.36 (t), 17.79 (s), 17.73 (s), 13.62 (q),13.37 (q), -4.9 (q), -5.42 (q), -5.42 (q), -5.53 (q). ESI: 637.40 $[M+H]^+$, 659.55 $[M+Na]^+$; HRMS $[M+H]^+$, calcd for $C_{36}H_{69}O_5Si_2$: m/z 637.4648, found: m/z 637.4650.

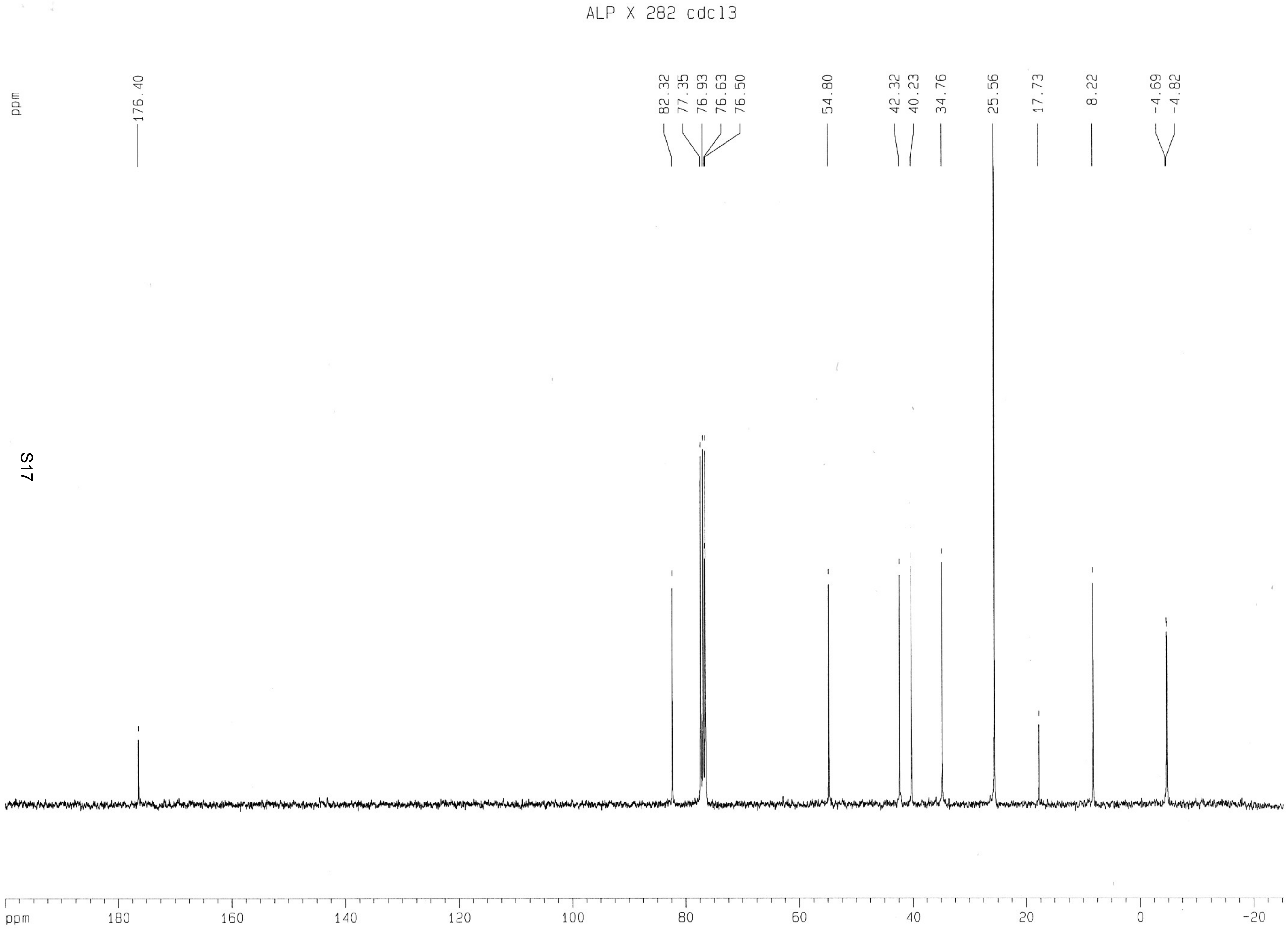
(Z)-9-((1R,2S,3R)-3-hydroxy-2-((S,E)-3-hydroxyoct-1-en-1-yl)-5-oxocyclopentyl)non-7-enoic acid (**6**)



Compound **12** (45 mg, 0.071 mmol) was dissolved in MeCN (4.8 mL) in a polyethylene test tube, then HF (48% solution in H_2O, M= 27.6, 52 μL) was added at rt. After 8h, the reaction was quenched with SiO_2 (100 mg), concentrated under vacuum and the residue was purified by chromatography on silica gel column (EtOAc/Hexane from 1:1 to 6:4 as eluent) to afford the 17-E_{2c}-dihomo-Isop-ethylester (23 mg, yield = 82%) as a pale-yellow oil. R$_f$: 0.18 (Hexane/EtOAc 1:1). $[\alpha]^{20}_D$ = -39.6 (*c* = 0.26 , EtOAc). IR υmax: 3375, 2927, 2856, 1735, 1459, 1185, 1106, 1035 cm^{-1}. ^{1}H-NMR (300 MHz; CD_3CN): δ (ppm)= 5.65 (dd, *J* =15.3, 5.81 1H), 5.49-5.38 (m, 3H), 4.43-4.33 (m, 1H), 4.13-3.98 (m, 3H), 3.12-3.04 (m, 1H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.70 (d, *J* = 4.9 Hz, 1H), 2.93 (d, *J* = 5.2 Hz, 1H),2.69 (d, *J* = 4.9, 1H), 2.59(dd, *J* = 30.4, 7.6 Hz, 1H), 2.48-2.26 (m, 4H), 2.23-1.95 (m, 3H), 1.59 (p, *J* = 6.9 Hz, 2H), 1.47-1.30 (m, 10H), 1.23 (t, *J* = 7.1 Hz, 2H), 0.93-089 (m, 3H). ^{13}C NMR (75 MHz, CD_3CN): δ (ppm)= 215.41 (s), 173.38 (s), 139.21 (d), 130.4 (d), 127.56 (d), 123.98 (d), 71.5 (d), 69.28 (d), 59.83 (t) , 53.95 (d), 48.86 (d), 44.11 (t), 37.34 (t), 33.79 (t), 31.62 (t), 28.99 (t), 28.44 (t), 26.89 (t), 24.93 (t), 24.63 (t), 23.36 (t), 22.41 (t), 13.61 (q), 13.37 (q). ESI: 409.35 $[M+H]^+$, 431.20 $[M+Na]^+$. HRMS $[M+H]^+$: calcd for $C_{22}H_{41}O_5$: *m/z* 409.2949, found: *m/z* 409.2946. The ethyl ester obtained (13 mg, 0.032 mmol) was dissolved in MTBE (0.5 mL) and then, H_2O (50 μL) and lipase CAL-B (13 mg) were added, the reaction mixture was stirred at rt for 18h. Then, enzyme was filtered and washed with DCM (2 mL), CH_3CN (2 mL) and MTBE (2 mL) and the resulting solution was concentrated *in vacuo*. the residue was purified by chromatography on silica gel column (Hexane/EtOAc from 2:8 to pure EtOAc) to afford the product **6** as a pale-yellow oil (9.8 mg, yield= 81%). R$_f$: Hexane:AcOEt 2:8 = 0.27. $[\alpha]^{20}_D$ = -37.4 (*c* = 0.19 , EtOAc). IR υmax: 3386, 2929, 2857, 1732, 1459, 1406, 1267, 1075, 974, 736 cm^{-1} .^{1}H-NMR (300 MHz; CD_3COCD_3): δ (ppm)= 5.69 (dd, *J* = 20.9, 5.6, 1H), 5.56 (dd, *J* = 16.1, 9.8 1H), 5.46-5.36 (m, 2H), 4.49 (td, *J* = 7.6, 5.5 Hz, 1H), 4.10 (q, *J* = 6.2 Hz, 1H), 3.14-3.10 (m, 1H), 2.99-2.76 (bs, 2H), 2.61-1.97 (m, 10H), 1.72-1.17 (m, 14H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CD_3COCD_3): δ (ppm)= 215.92 (s), 175.02 (s), 140.47 (d), 131.32 (d), 129.13 (d), 125.27 (d), 72.73 (d), 70.87 (d), 55.03 (d), 50.37 (d), 45.69 (t), 38.87 (t), 34.56 (t), 33.06 (t), 30.46 (t), 29.94 (t), 28.21 (t), 26.29 (t), 25.95 (t), 24.88 (t), 23.73 (t), 14.71 (q). ESI-MS: 379.25 $[M-H]^-$; HRMS $[M+H]^+$: calcd for $C_{22}H_{37}O_5$: *m/z* 381.2636, found: *m/z* 381.2634.

ALP X 282 cdcl3 aprile 1

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76.63
76.50
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34.76
25.56
17.73
8.22
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-4.82
ppm
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140
120
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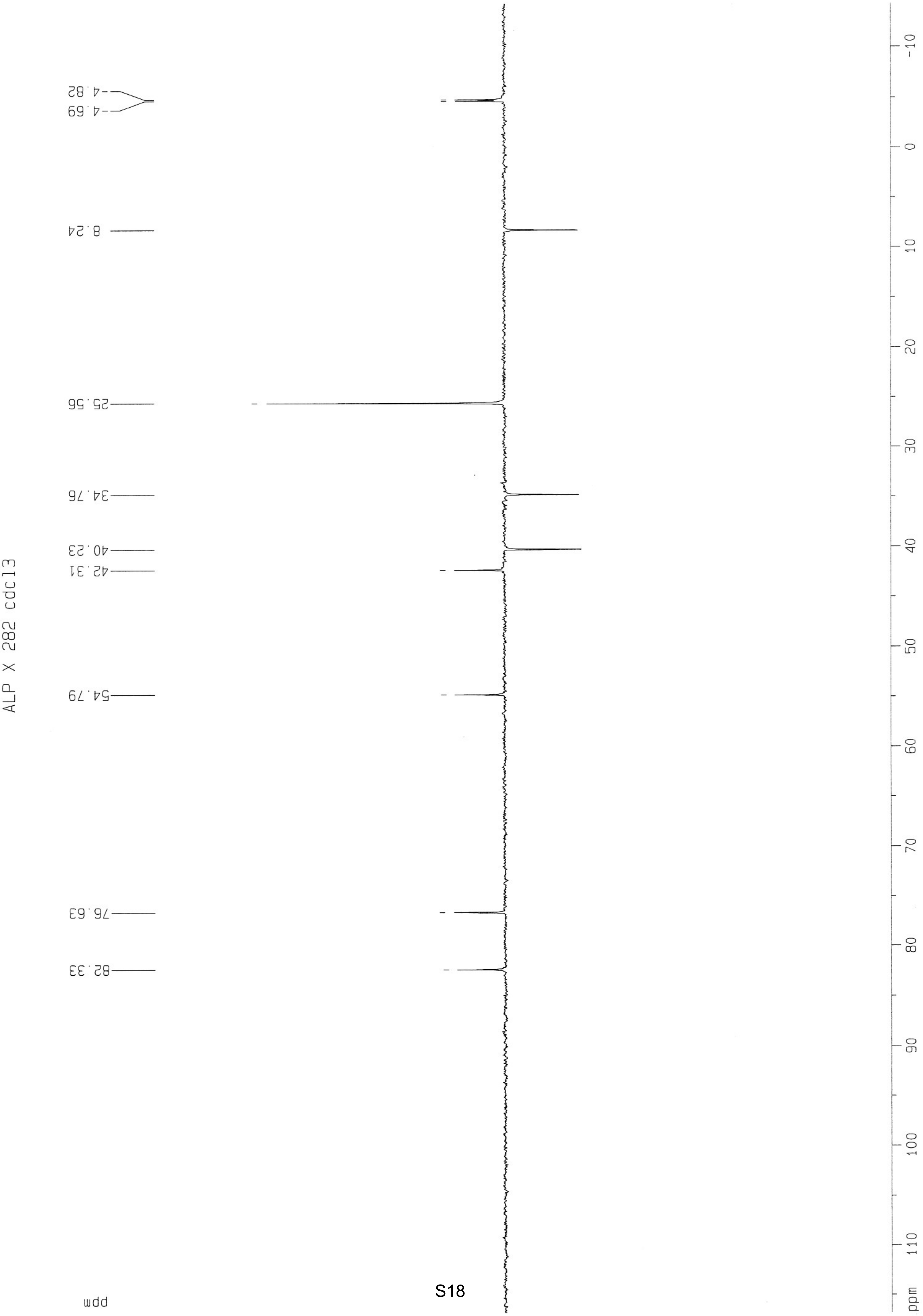
80
60
40
20
0
-20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8.24
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34.76
40.23
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54.79
76.63
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ppm
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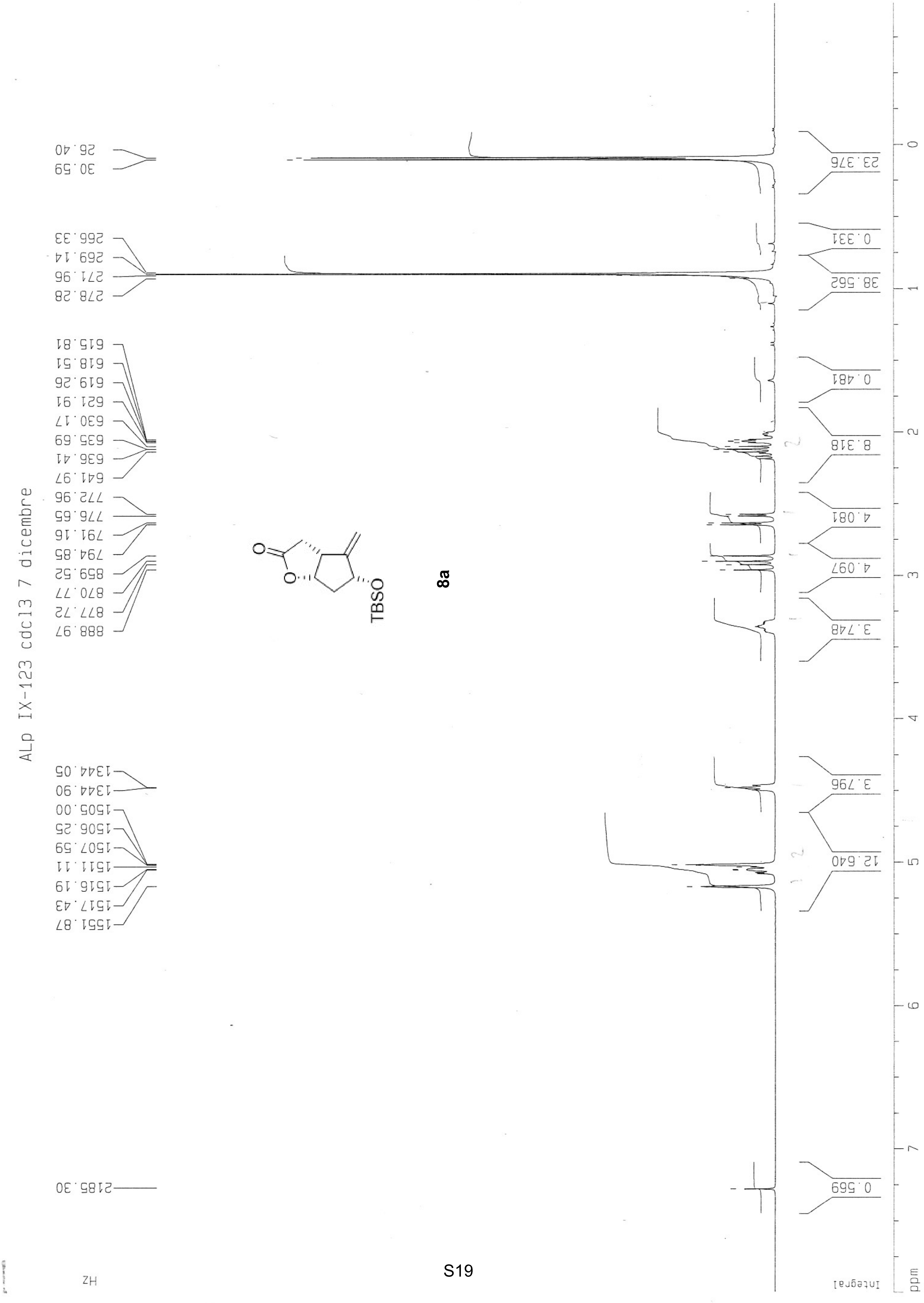
0
10
20
30
40
50
60
70
80
90
100
110
ppm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26.40
30.59
266.33
269.14
271.96
278.28
615.81
618.51
619.26
621.91
630.17
635.69
636.41
641.97
772.96
776.65
791.16
794.85
859.52
870.77
877.72
888.97
1344.05
1344.90
1505.00
1506.25
1507.59
1511.11
1516.19
1517.43
1551.87
2185.30
Hz
TBSO
O
O
8a
23.376
0.331
38.562
0.481
8.318
4.081
4.097
3.748
3.796
12.640
0.569
Integral
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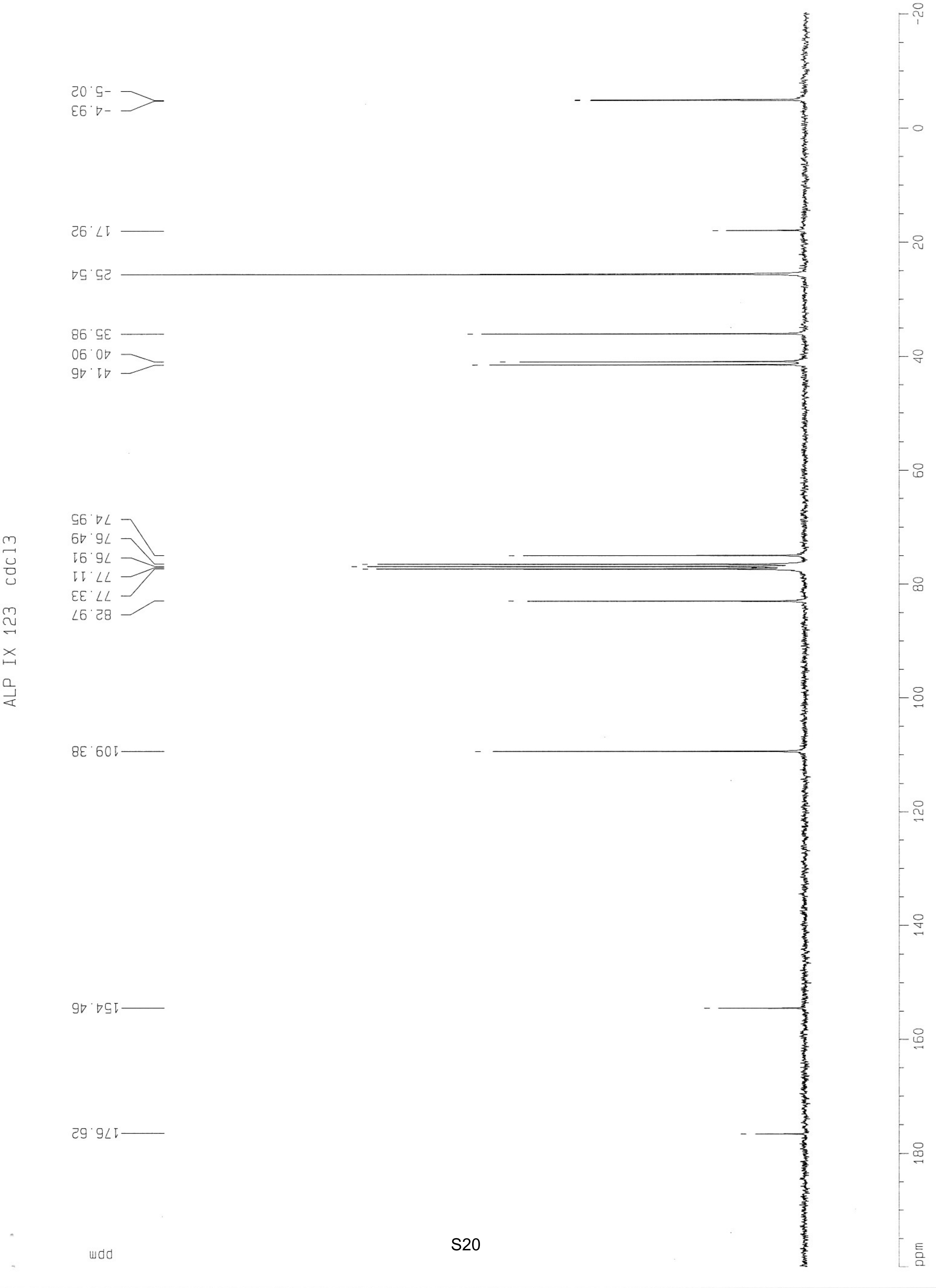
1
2
3
4
5
6
7
ppm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40.90
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74.95
76.49
76.91
77.11
77.33
82.97
109.38
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176.62
ppm
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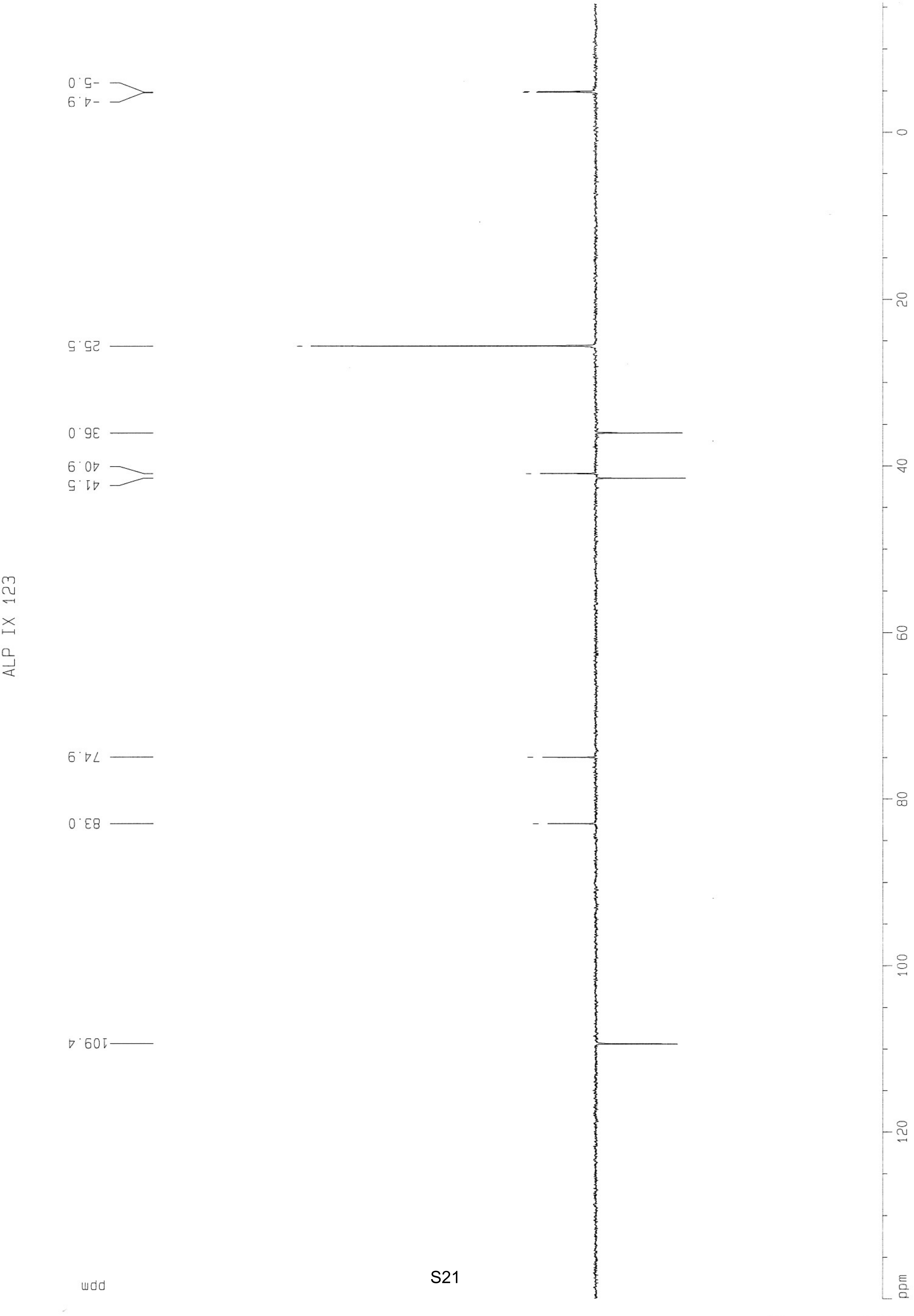
20
40
60
80
100
120
140
160
180
ppm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41.5
74.9
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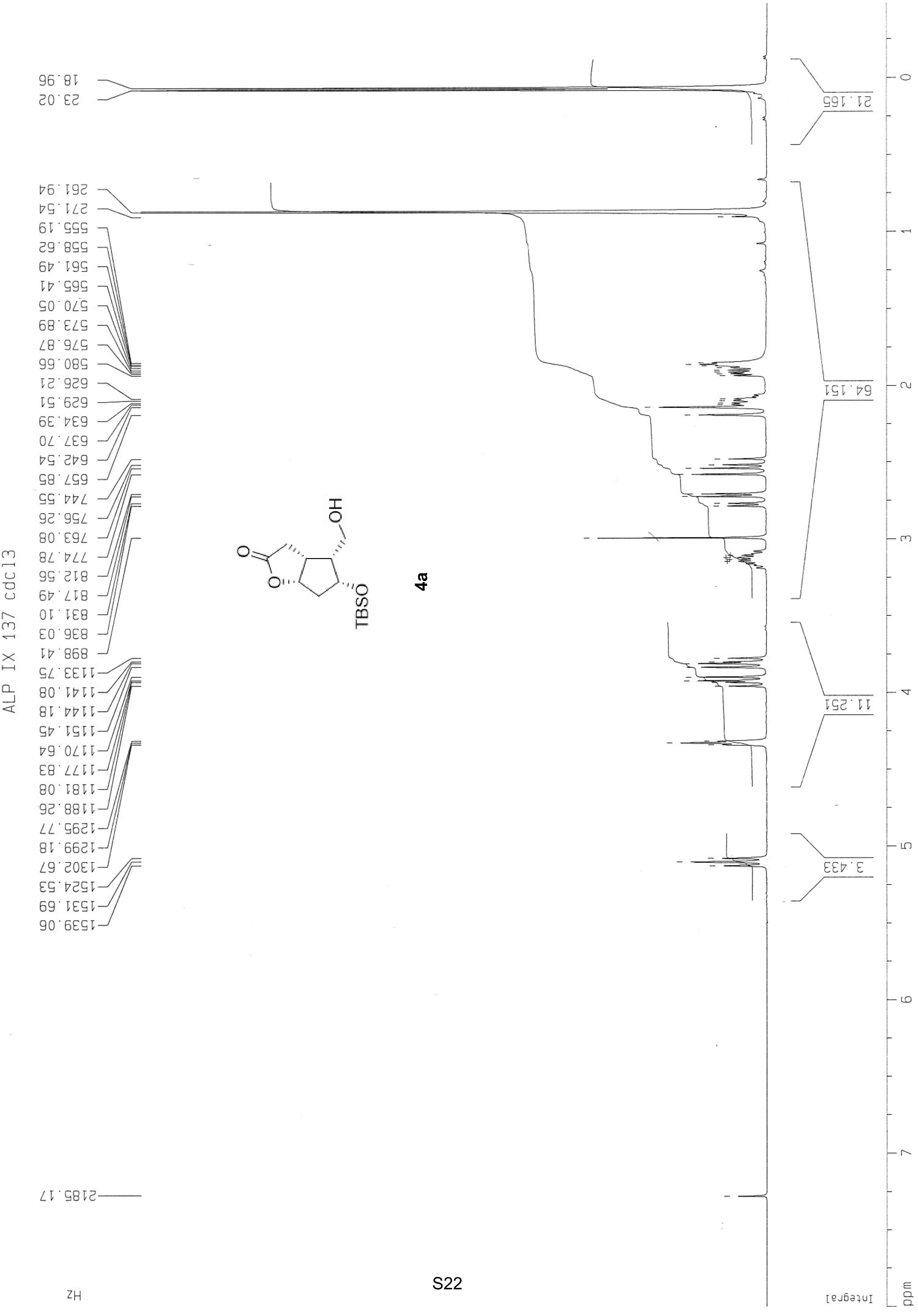
109.4
ppm
0
20
40
60
80
100
120
ppm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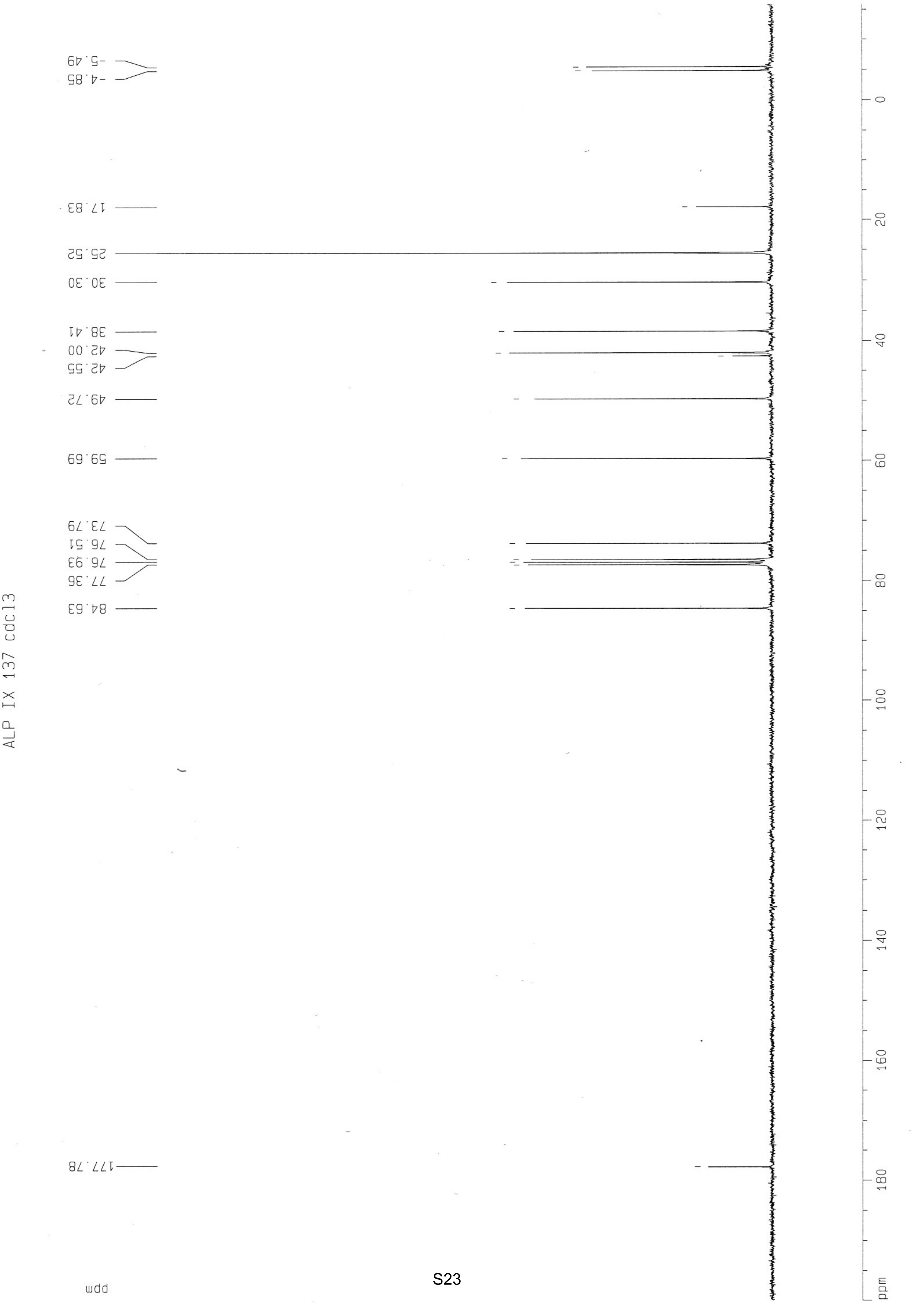
23.02
261.94
271.54
555.19
558.62
561.49
565.41
570.05
573.89
576.87
580.66
626.21
629.51
634.39
637.70
642.54
657.85
744.55
756.26
763.08
774.78
812.56
817.49
831.10
836.03
898.41
1133.75
1141.08
1144.18
1151.45
1170.64
1177.83
1181.08
1188.26
1295.77
1299.18
1302.67
1524.53
1531.69
1539.06
2185.17
Hz
21.165
64.151
11.251
3.433
Integral
7
6
5
4
3
2
1
0
ppm
TBSO
OH
O
O
4a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38.41
42.00
42.55
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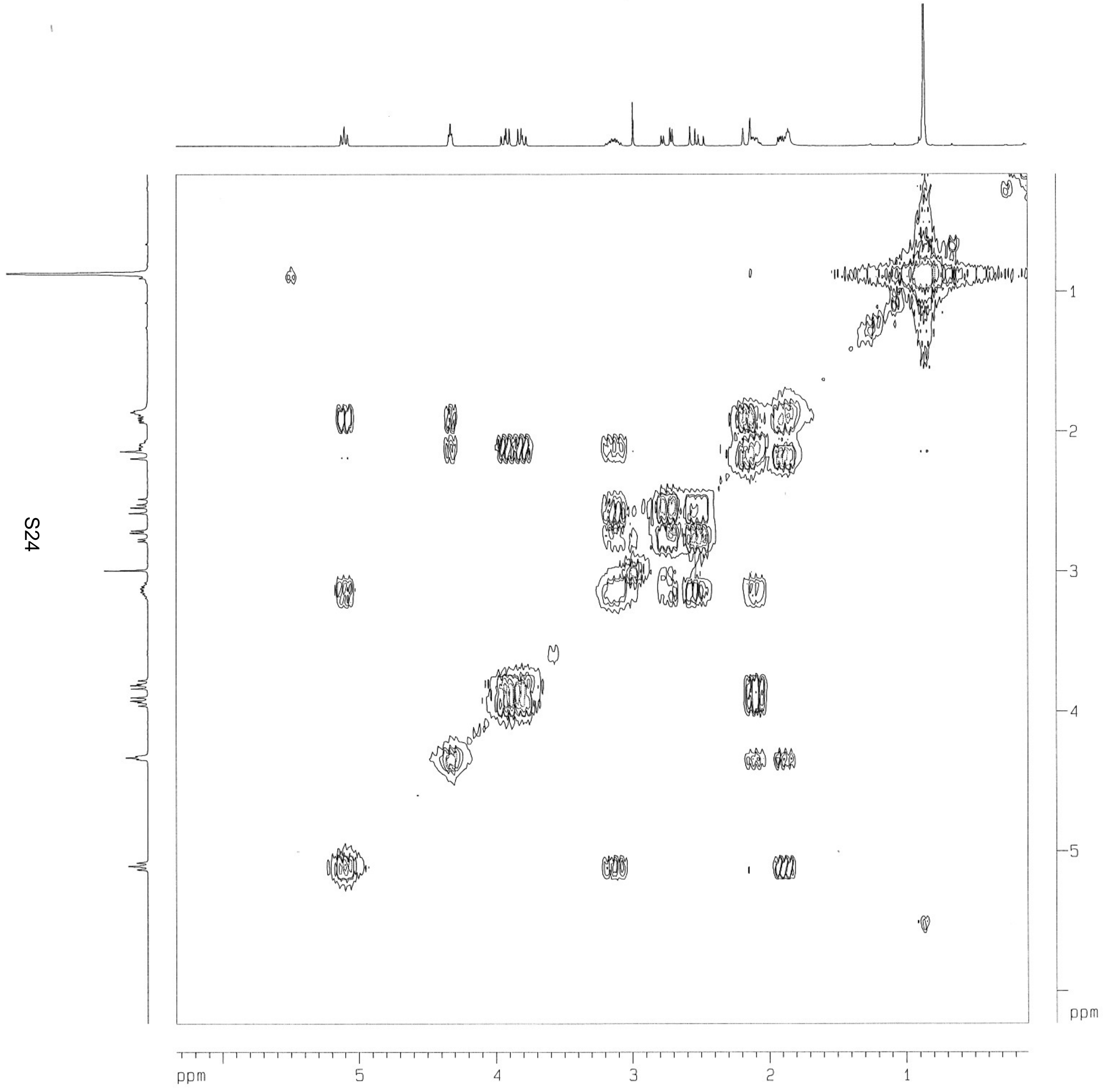
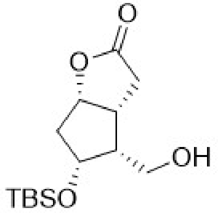
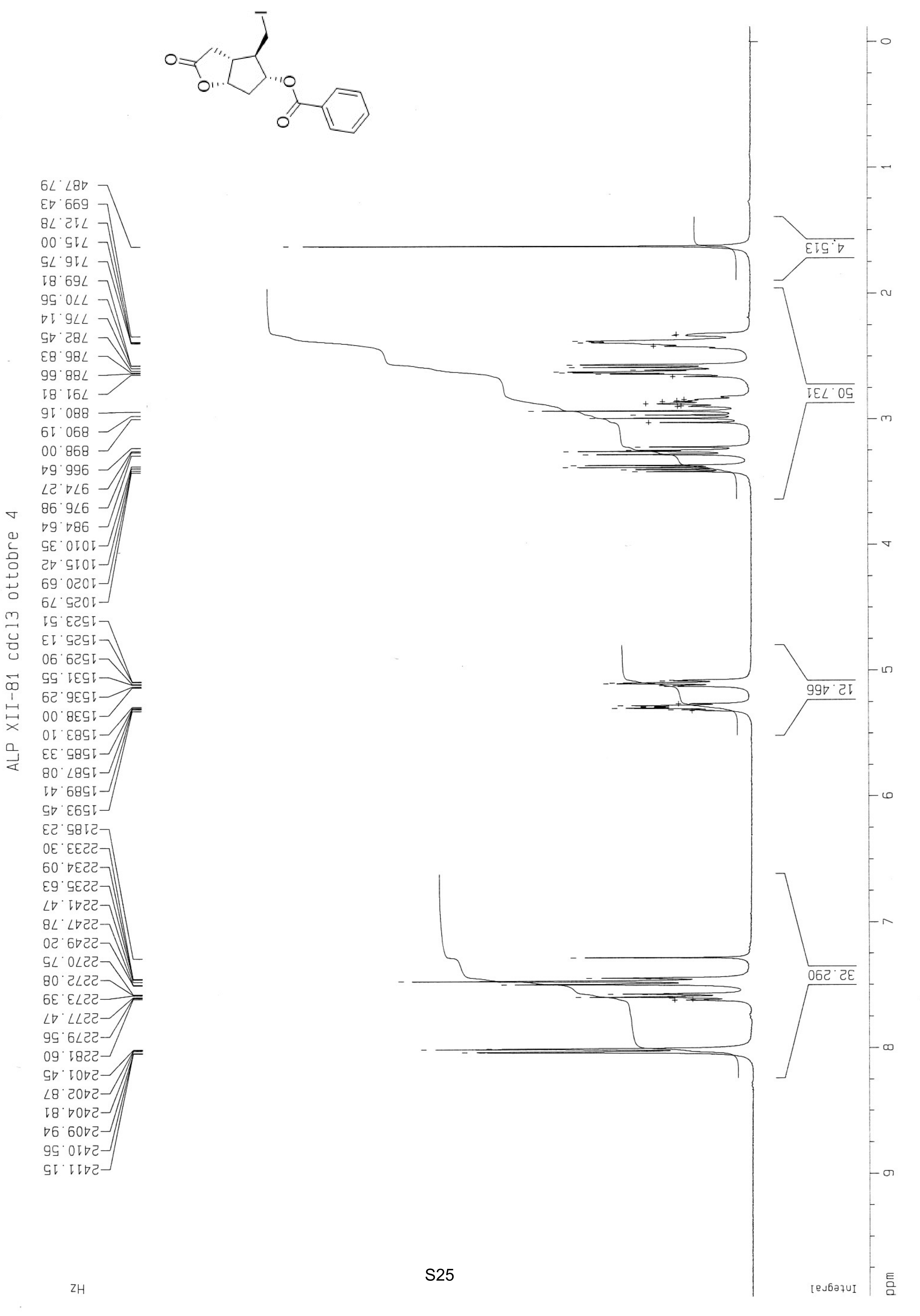
59.69
73.79
76.51
76.93
77.36
84.63
177.78
ppm
0
20
40
60
80
100
120
140
160
180
ppm

ALP IX 137






ALP XII-81 cdcl3 ottobre 4
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712.78
715.00
716.75
769.81
770.56
776.14
782.45
786.83
788.66
791.81
880.16
890.19
898.00
966.64
974.27
976.98
984.64
1010.35
1015.42
1020.69
1025.79
1523.51
1525.13
1529.90
1531.55
1536.29
1538.00
1583.10
1585.33
1587.08
1589.41
1593.45
2185.23
2233.30
2234.09
2235.63
2241.47
2247.78
2249.20
2270.75
2272.08
2273.39
2277.47
2279.56
2281.60
2401.45
2402.87
2404.81
2409.94
2410.56
2411.15
Hz
4.513
50.731
12.466
32.290
Integral
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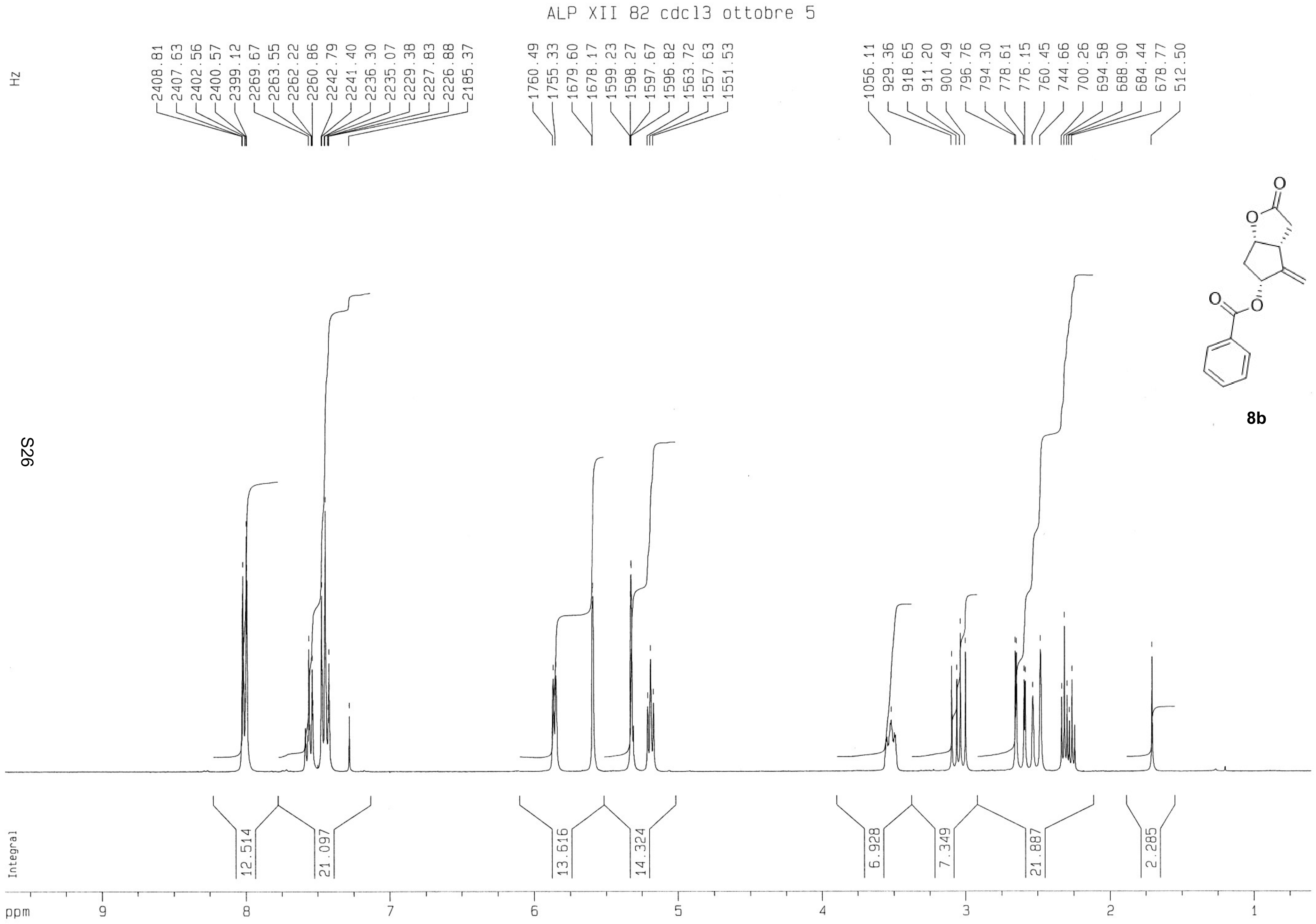
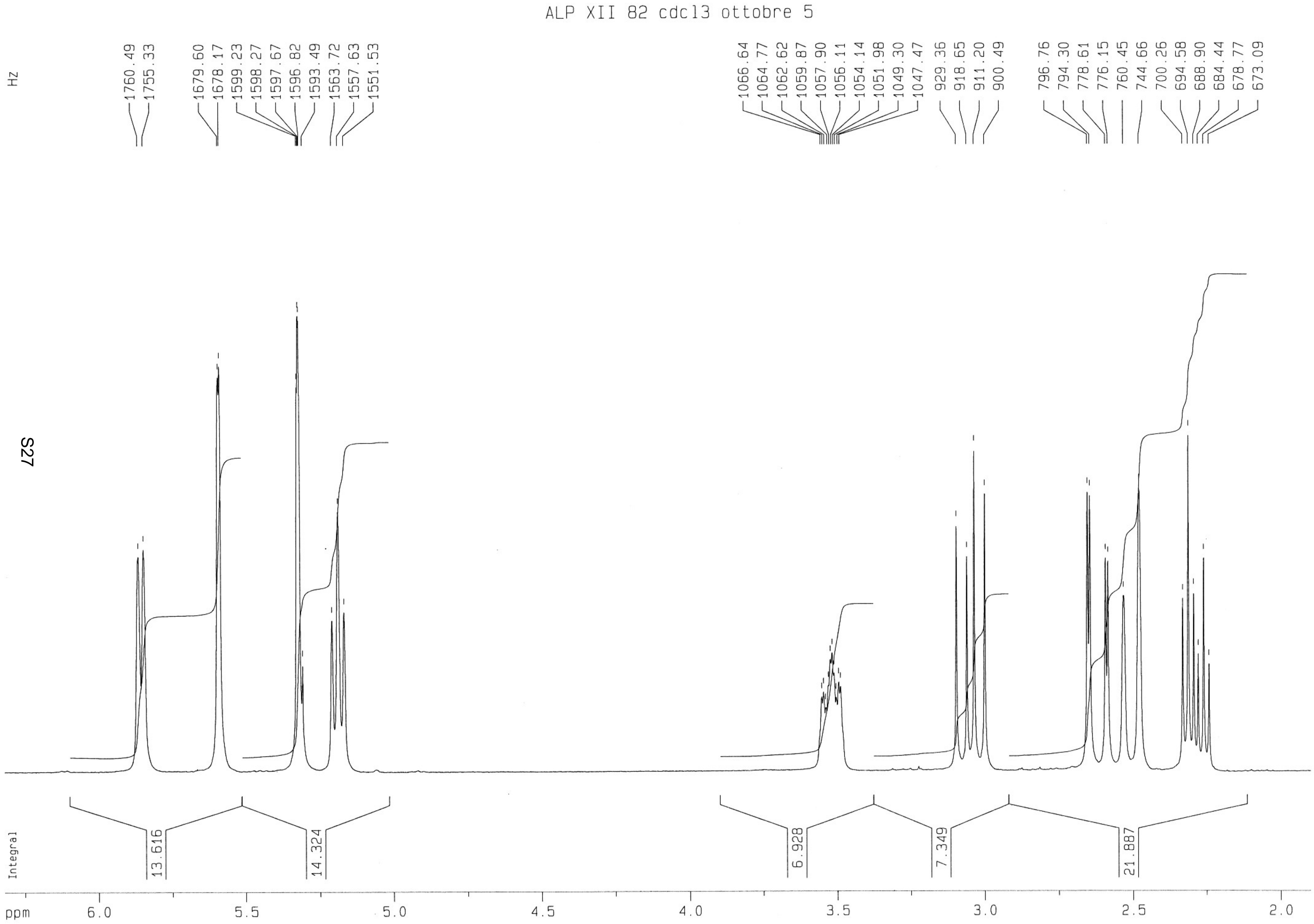
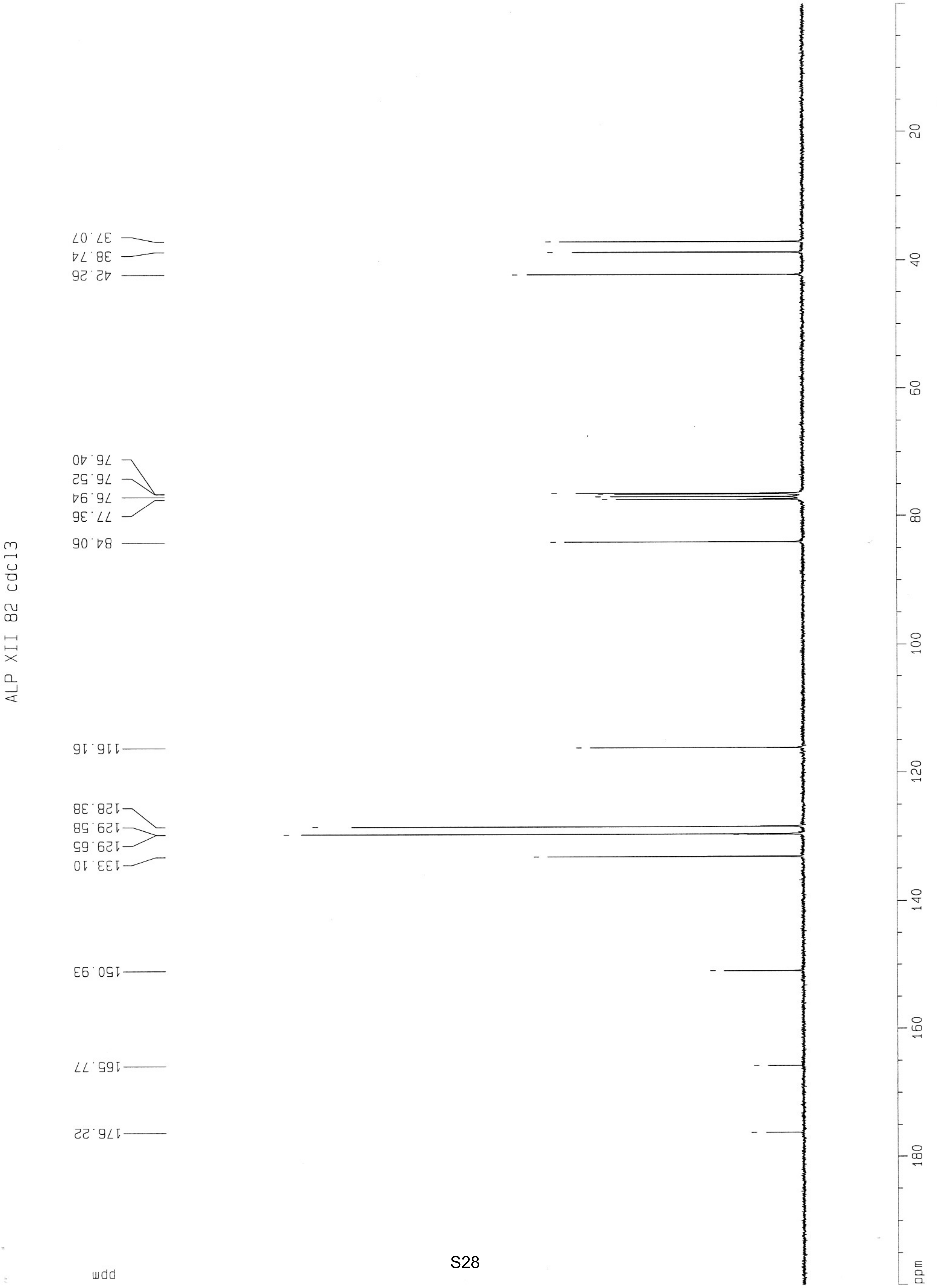
1
2
3
4
5
6
7
8
9
ppm


ALP XII 82 cdcl3 ottobre 5
Hz
2408.81
2407.63
2402.56
2400.57
2399.12
2269.67
2263.55
2262.22
2260.86
2242.79
2241.40
2236.30
2235.07
2229.38
2227.83
2226.88
2185.37
1760.49
1755.33
1679.60
1678.17
1599.23
1598.27
1597.67
1596.82
1563.72
1557.63
1551.53
1056.11
929.36
918.65
911.20
900.49
796.76
794.30
778.61
776.15
760.45
744.66
700.26
694.58
688.90
684.44
678.77
512.50
Integral
12.514
21.097
13.616
14.324
6.928
7.349
21.887
2.285
ppm
9
8
7
6
5
4
3
2
1

8b


ALP XII 82 cdcl3 ottobre 5
Hz
1760.49
1755.33
1679.60
1678.17
1599.23
1598.27
1597.67
1596.82
1593.49
1563.72
1557.63
1551.53
1066.64
1064.77
1062.62
1059.87
1057.90
1056.11
1054.14
1051.98
1049.30
1047.47
929.36
918.65
911.20
900.49
796.76
794.30
778.61
776.15
760.45
744.66
700.26
694.58
688.90
684.44
678.77
673.09
Integral
13.616
14.324
6.928
7.349
21.887
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


ALP XII 82 cdcl3
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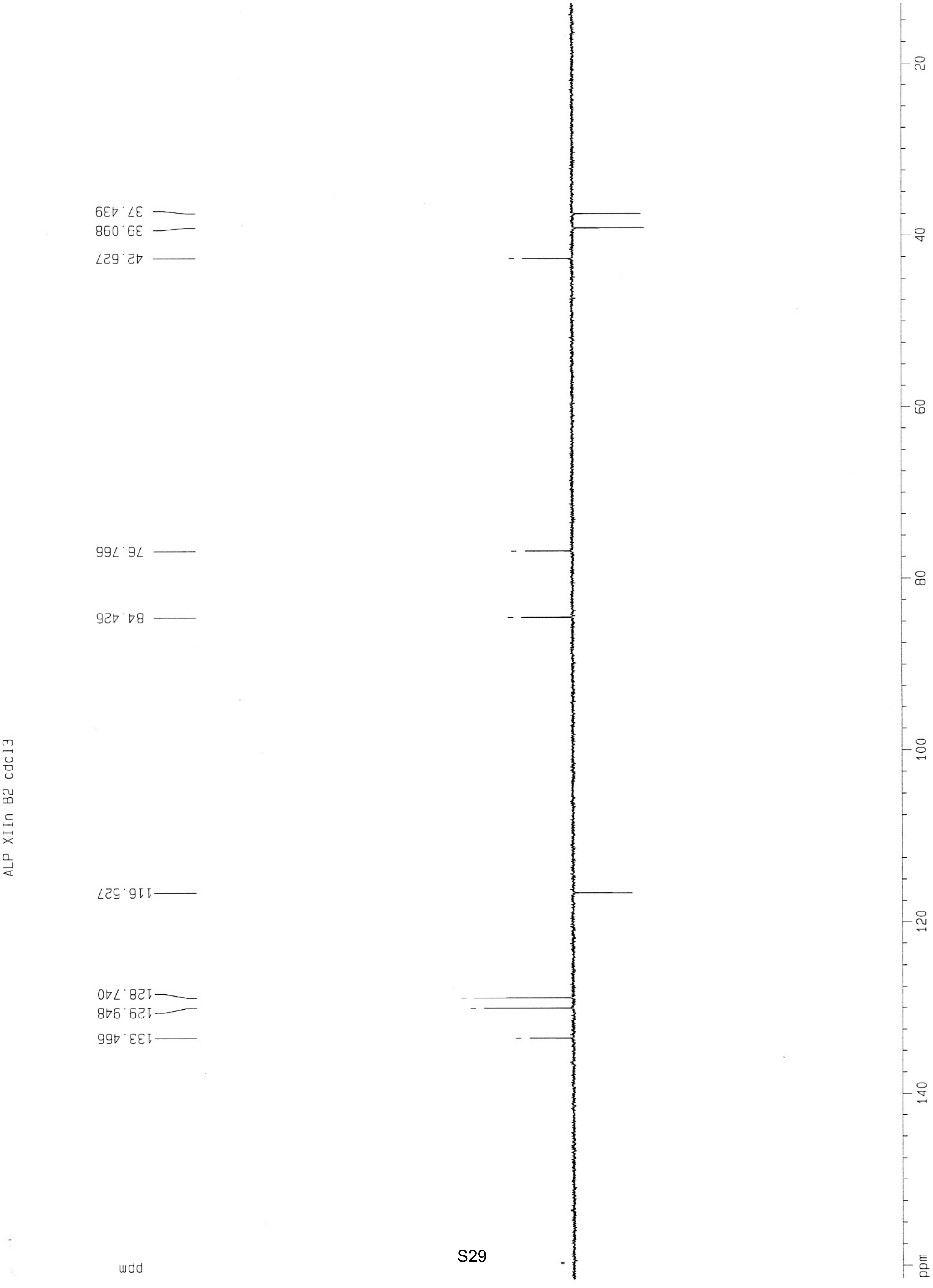
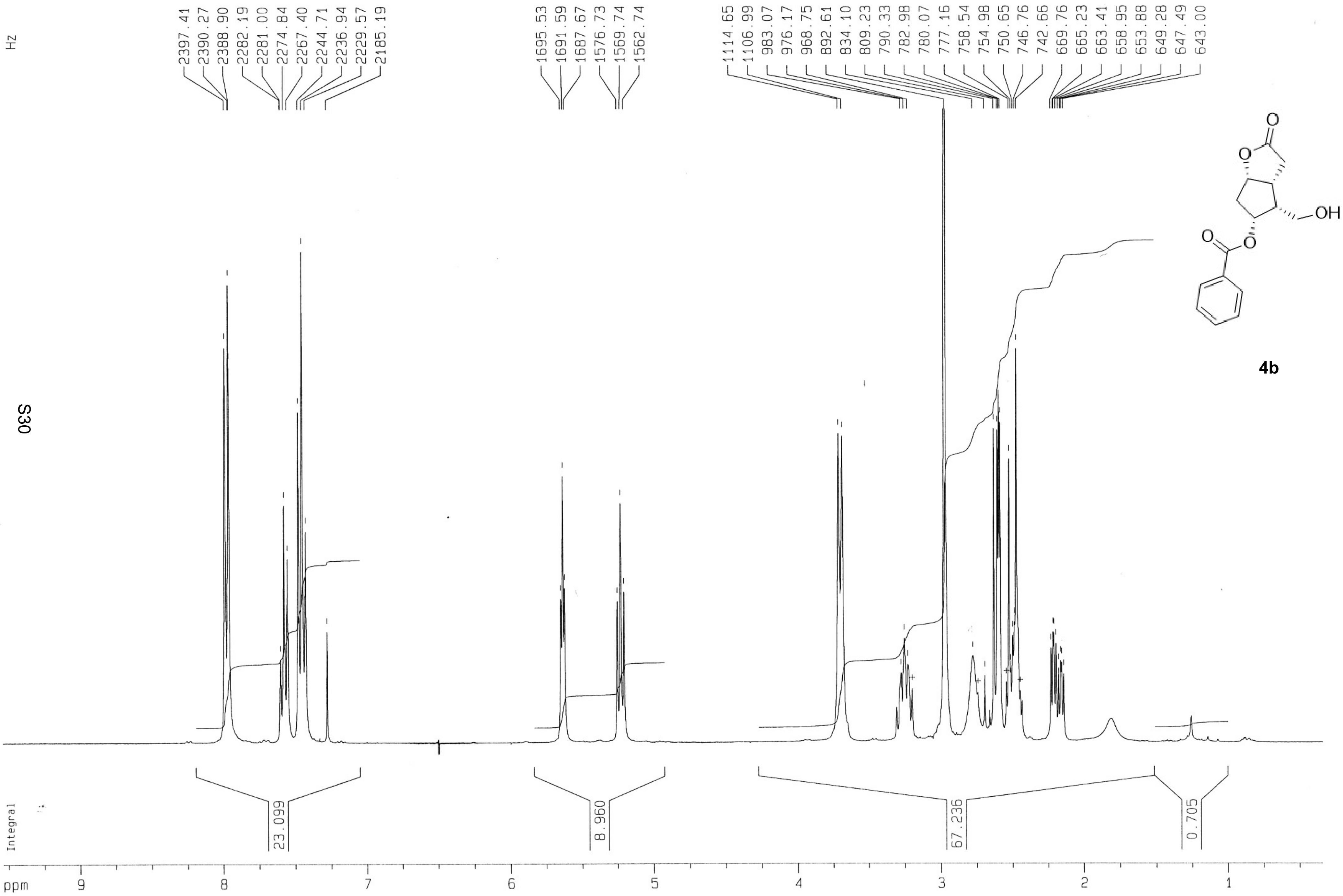
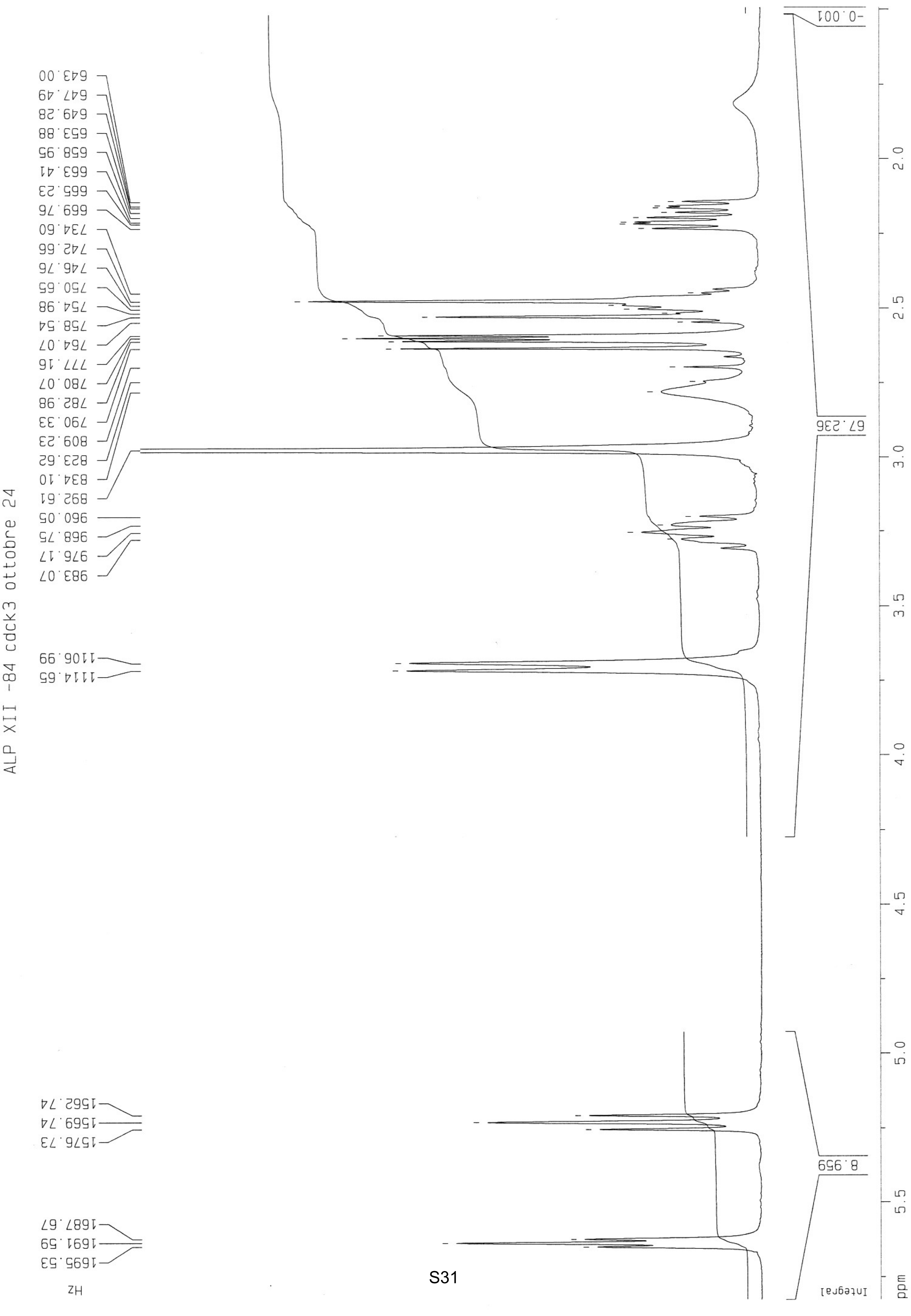
165.77
150.93
133.10
129.65
129.58
128.38
116.16
84.06
77.36
76.94
76.52
76.40
42.26
38.74
37.07
ppm
180
160
140
120
100
80
60
40
20
ppm

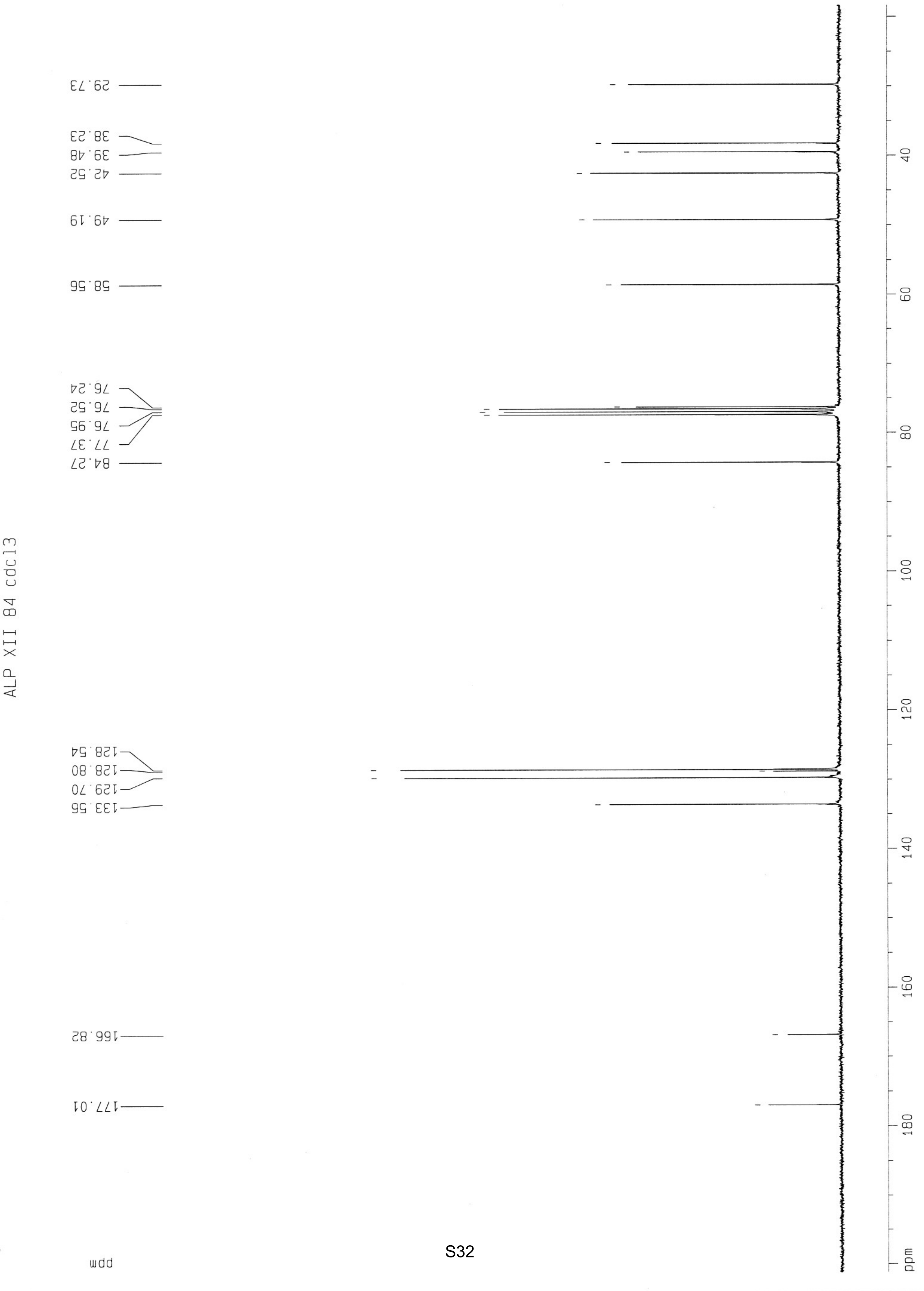

ALP XIIn B2 cdcl3
37.439
39.098
42.627
76.766
84.426
116.527
128.740
129.948
133.466
20
40
60
80
100
120
140
ppm
ppm

ALP XII -84 cdck3 ottobre 24



4b


ALP XII -84 cdck3 ottobre 24
643.00
647.49
649.28
653.88
658.95
663.41
665.23
669.76
734.60
742.66
746.76
750.65
754.98
758.54
764.07
777.16
780.07
782.98
790.33
809.23
823.62
834.10
892.61
960.05
968.75
976.17
983.07
1106.99
1114.65
1562.74
1569.74
1576.73
1687.67
1691.59
1695.53
Hz
-0.001
67.236
8.959
Integral
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
ppm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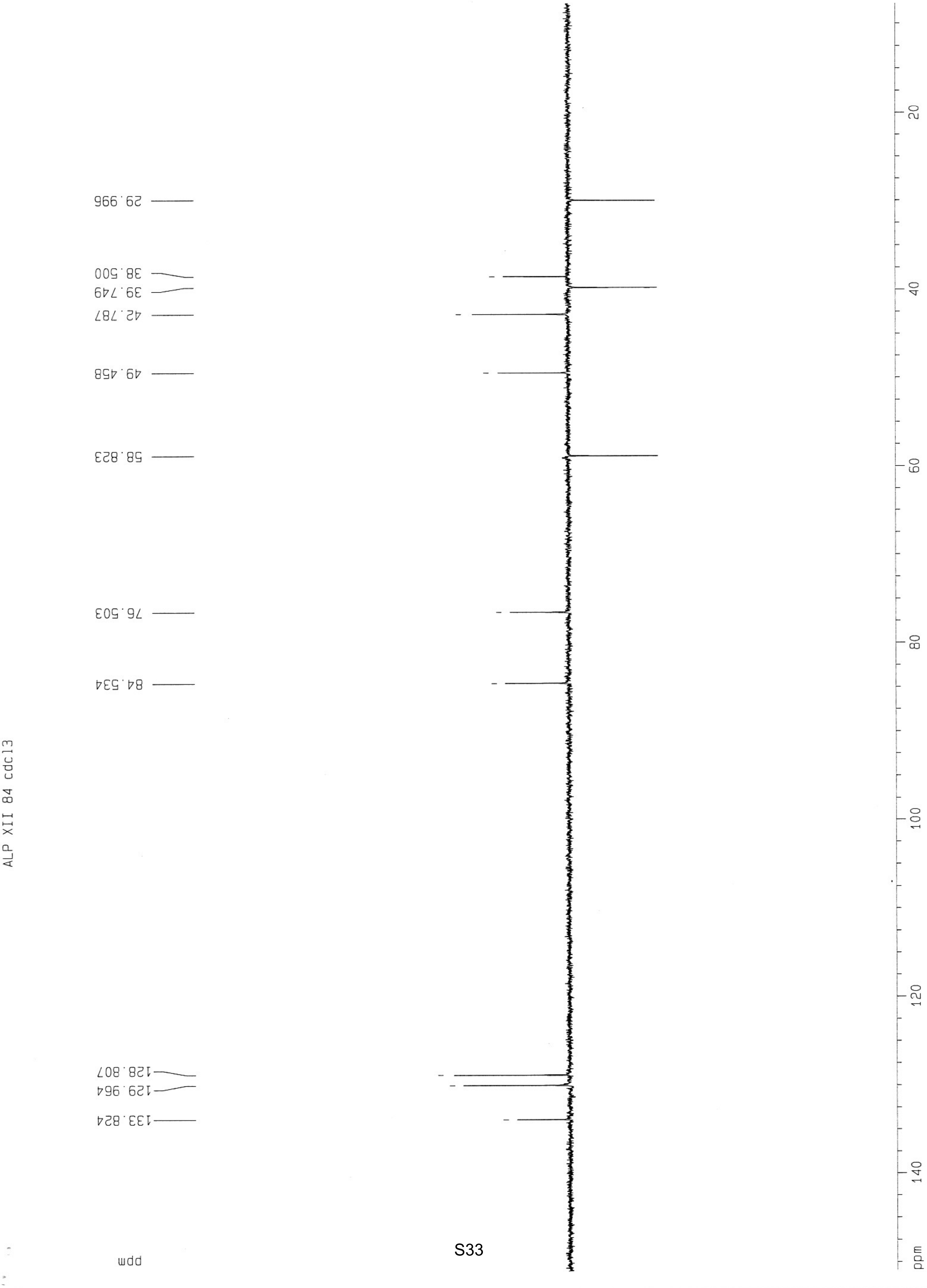
38.23
39.48
42.52
49.19
58.56
76.24
76.52
76.95
77.37
84.27
128.54
128.80
129.70
133.56
166.82
177.01
ppm
40
60
80
100
120
140
160
180
ppm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42.787
49.458
58.823
76.503
84.534
128.807
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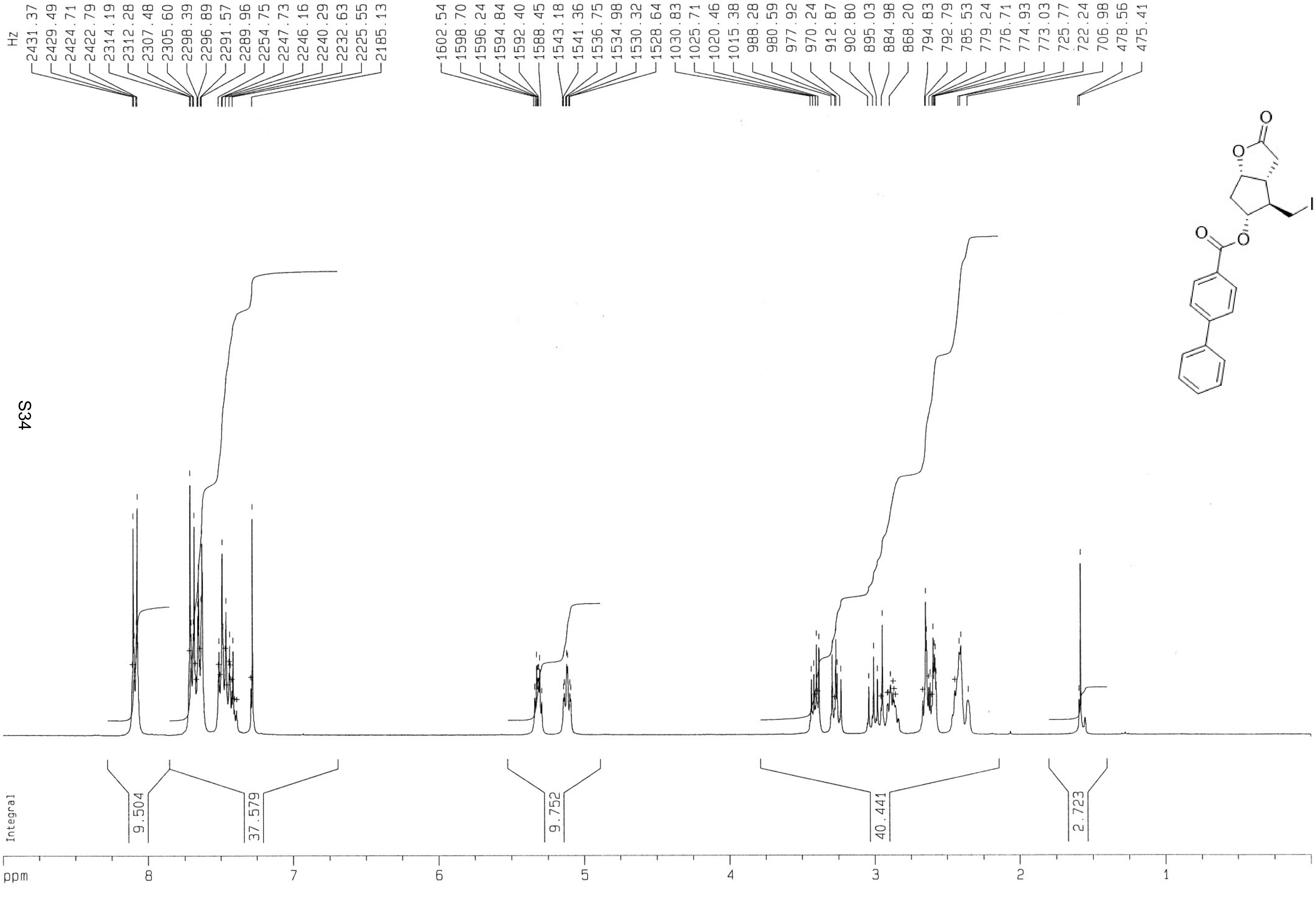
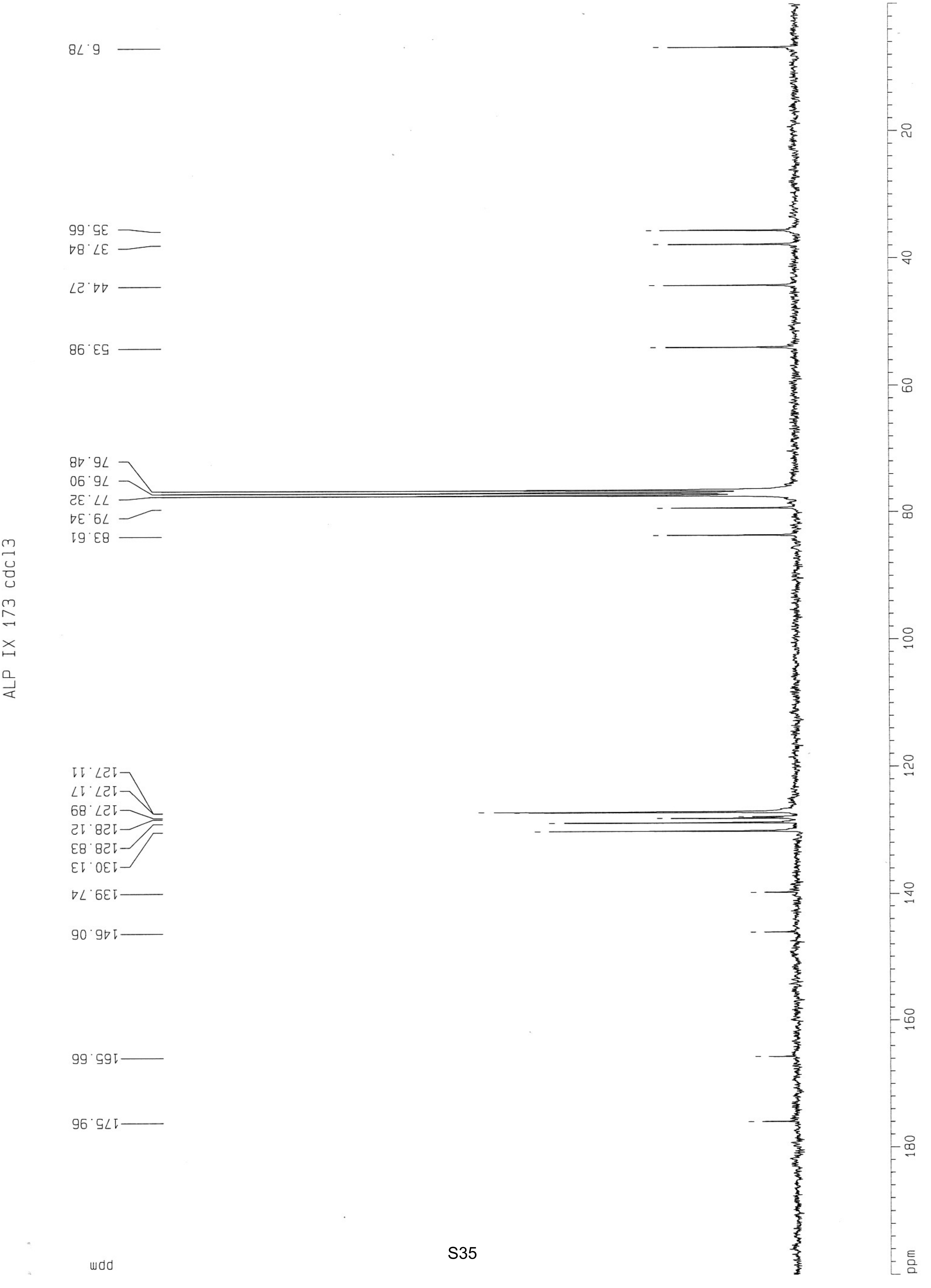
133.824
ppm
20
40
60
80
100
120
140
ppm

ALP IX 173 cdcl3 novembre 6

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37.84
44.27
53.98
76.48
76.90
77.32
79.34
83.61
127.11
127.17
127.89
128.12
128.83
130.13
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146.06
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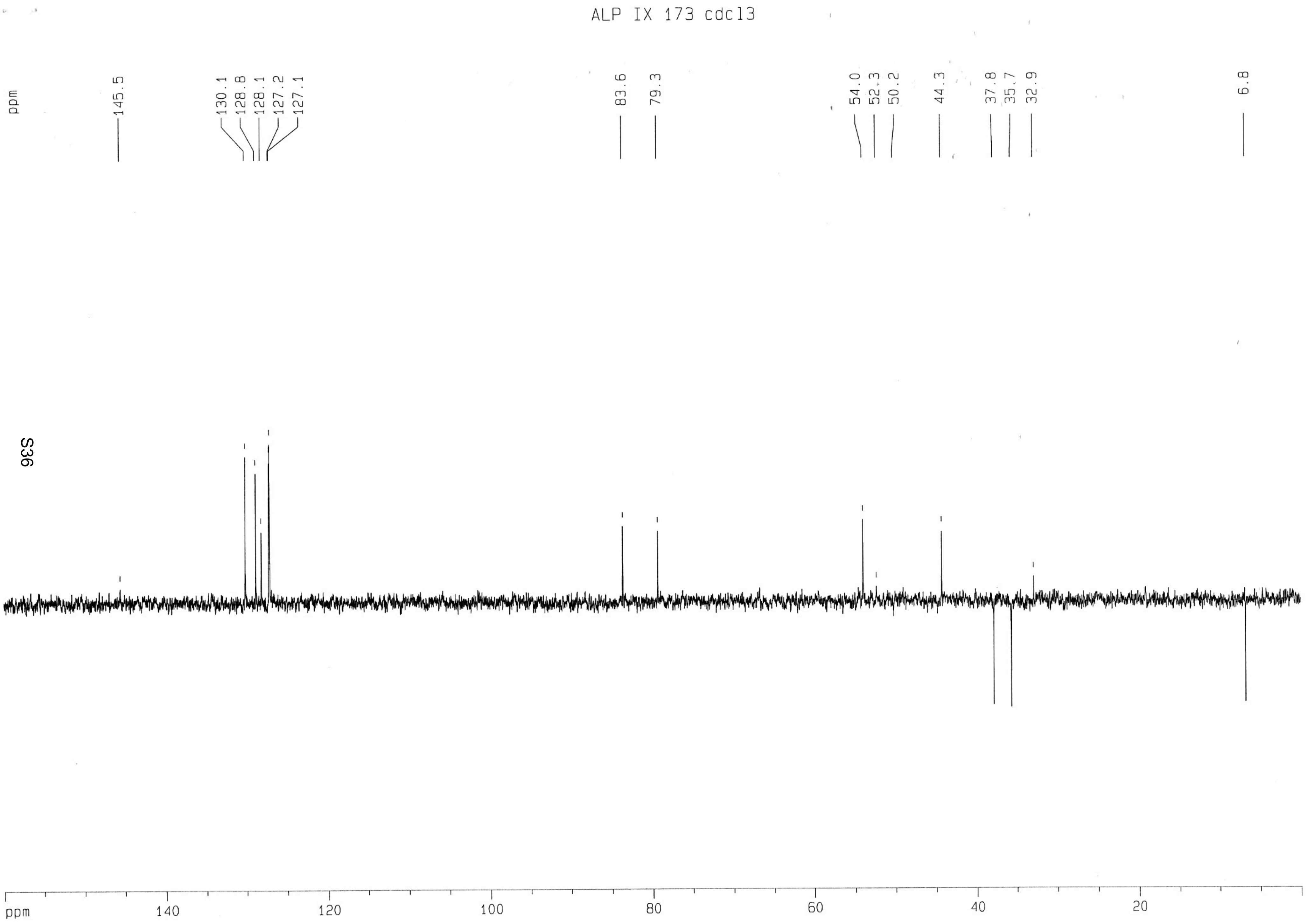
60
80
100
120
140
160
180
ppm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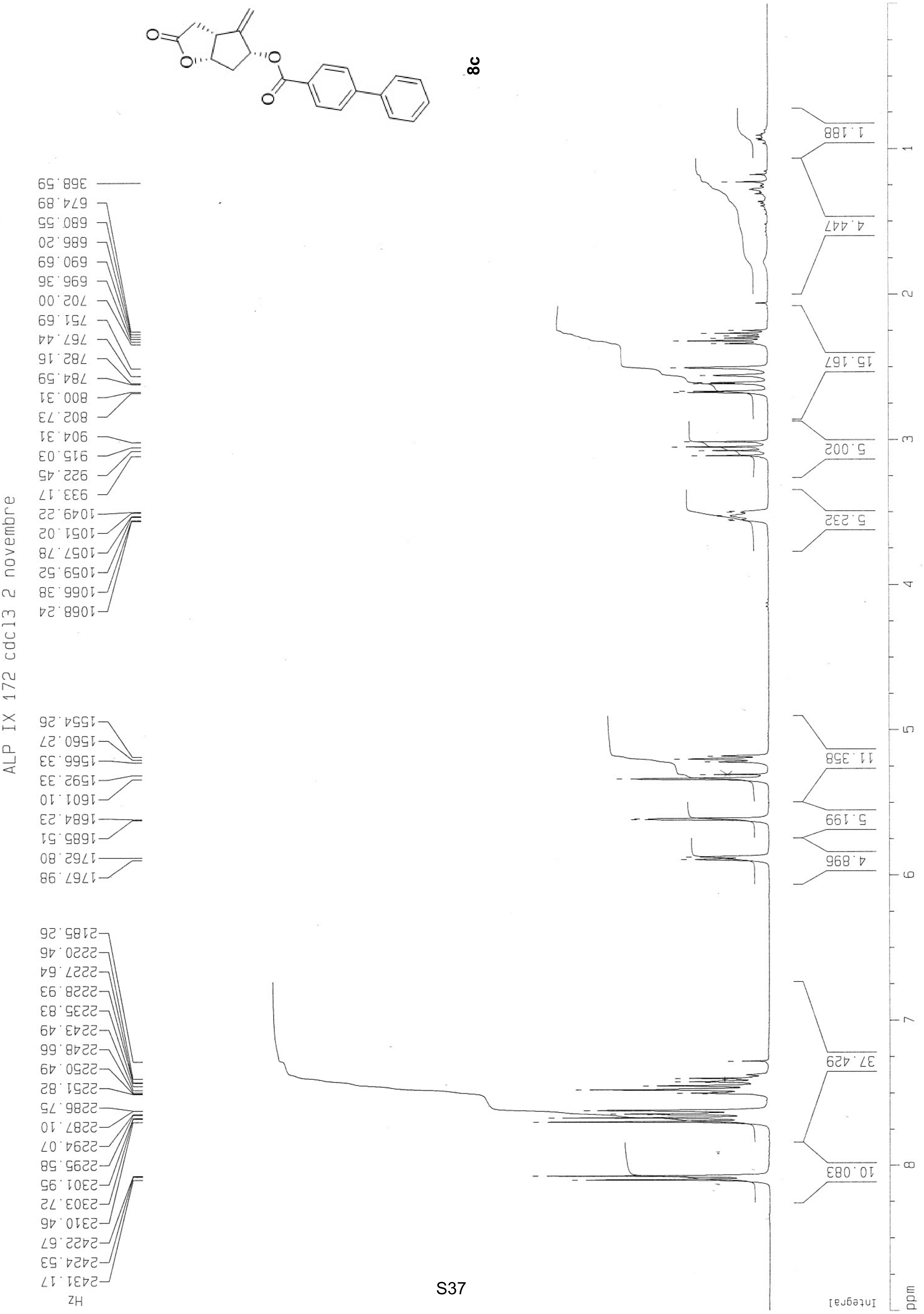
128.8
128.1
127.2
127.1
83.6
79.3
54.0
52.3
50.2
44.3
37.8
35.7
32.9
6.8
ppm
140
120
100
80
60
40
20


8c
ALP IX 172 cdcl3 2 novembre
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696.36
702.00
751.69
767.44
782.16
784.59
800.31
802.73
904.31
915.03
922.45
933.17
1049.22
1051.02
1057.78
1059.52
1066.38
1068.24
1554.26
1560.27
1566.33
1592.33
1601.10
1684.23
1685.51
1762.80
1767.98
2185.26
2220.46
2227.64
2228.93
2235.83
2243.49
2248.66
2250.49
2251.82
2286.75
2287.10
2294.07
2295.58
2301.95
2303.72
2310.46
2422.67
2424.53
2431.17
Hz
1.188
4.447
15.167
5.002
5.232
11.358
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4.896
37.429
10.083
Integral
1
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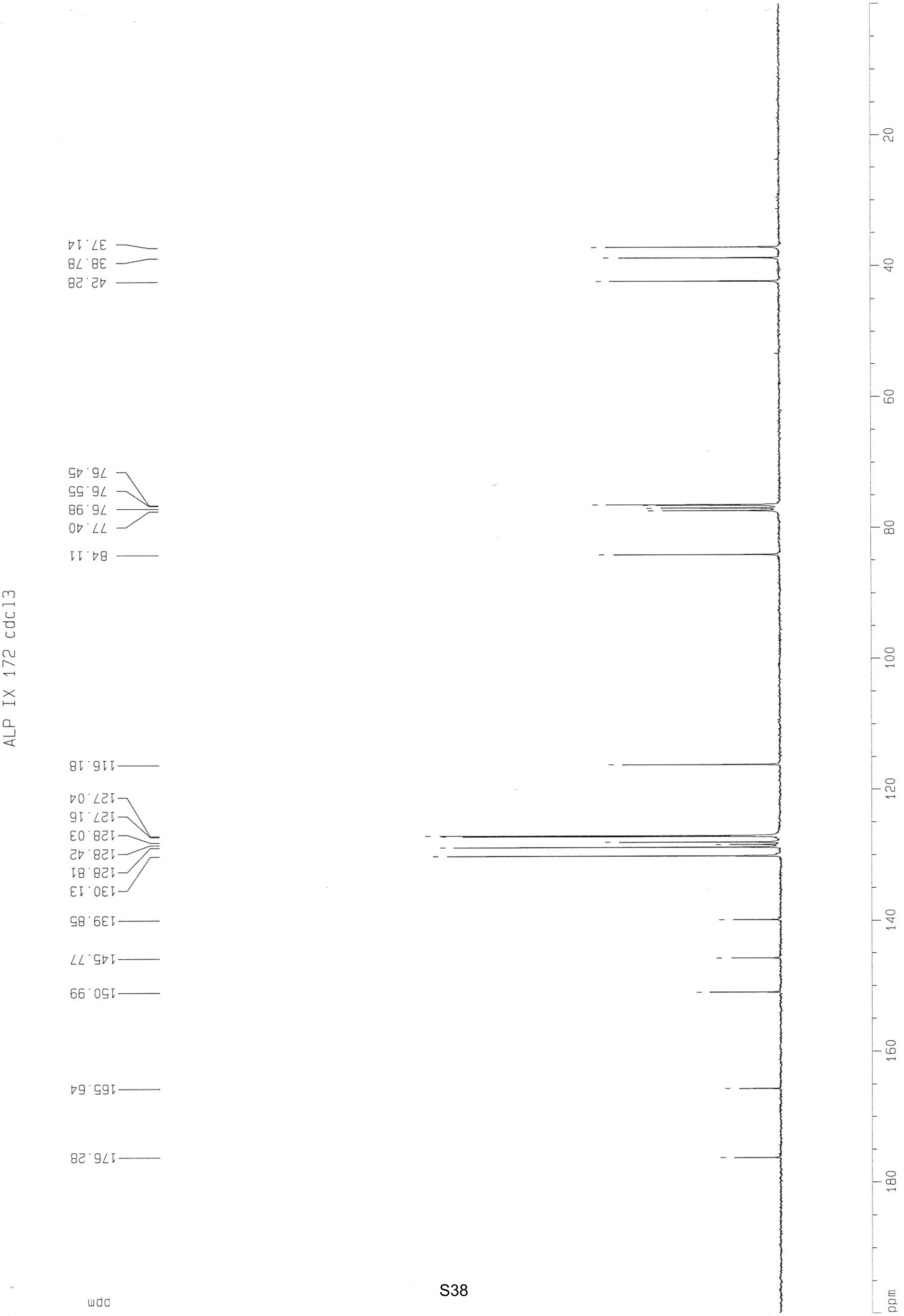
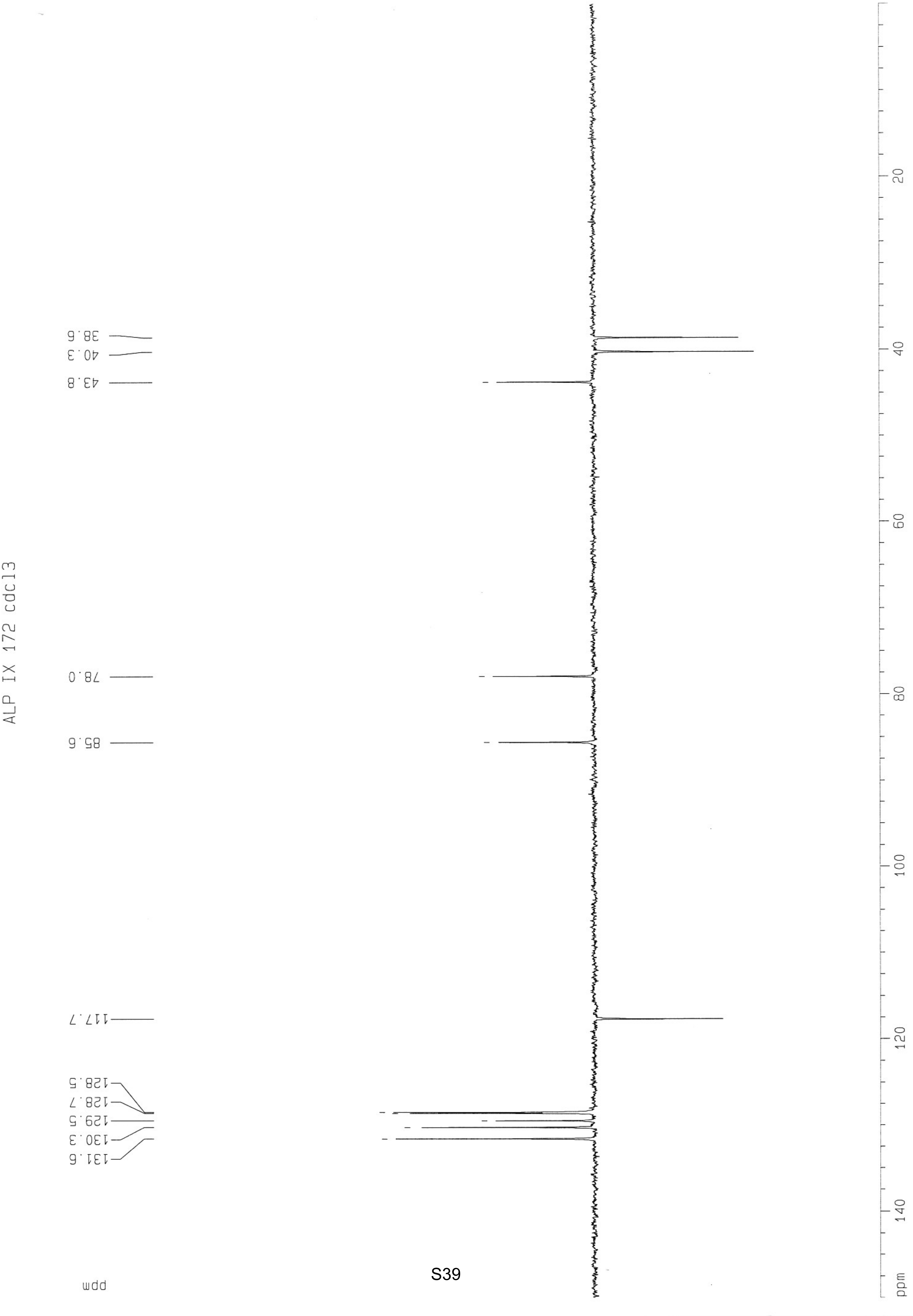
4
5
6
7
8
ppm


ALP IX 172 cdcl13
37.14
38.78
42.28
76.45
76.55
76.98
77.40
84.11
116.18
127.04
127.16
128.03
128.42
128.81
130.13
139.85
145.77
150.99
165.64
176.28
ppm
20
40
60
80
100
120
140
160
180
ppm


ALP IX 172 cdcl3
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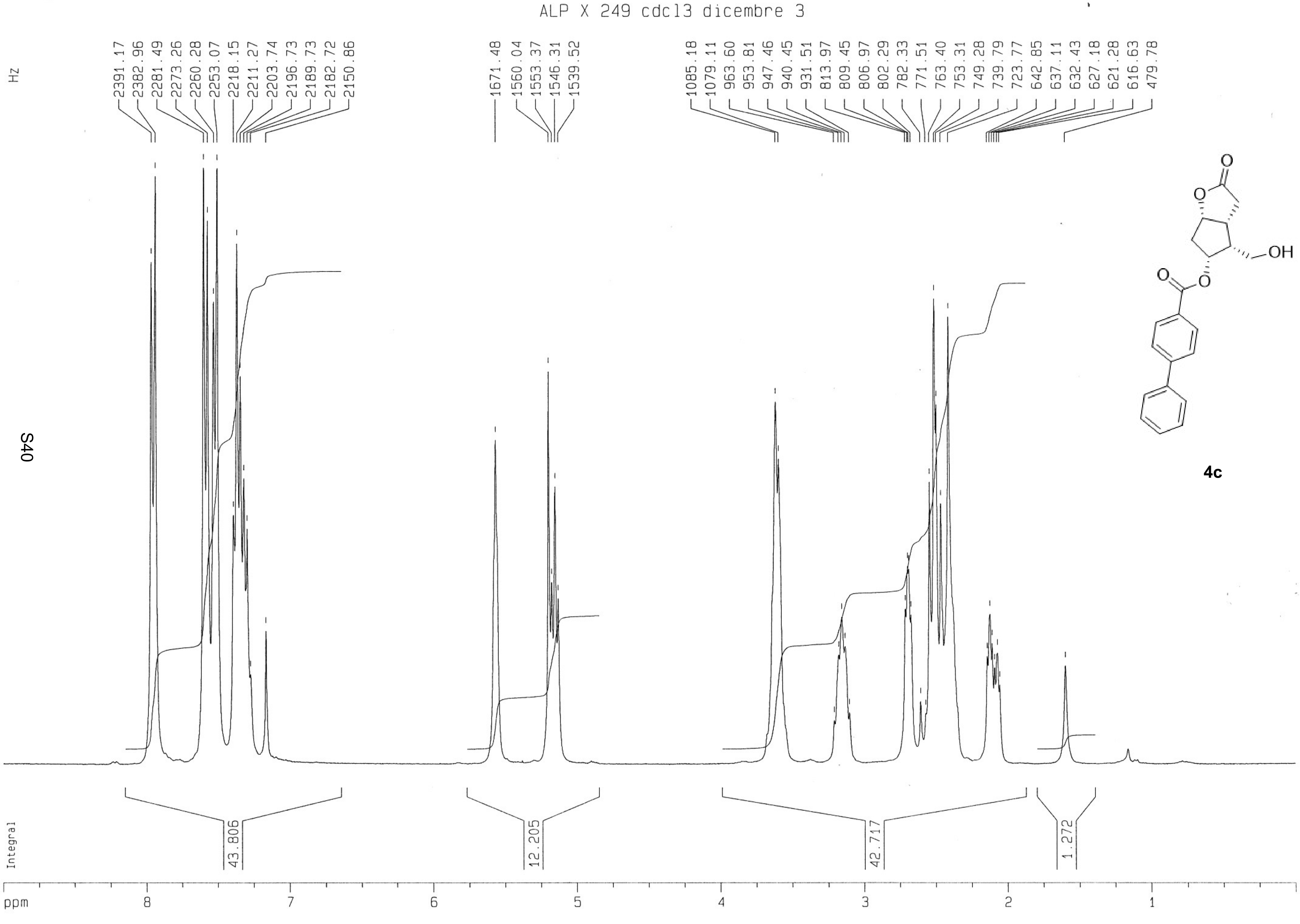
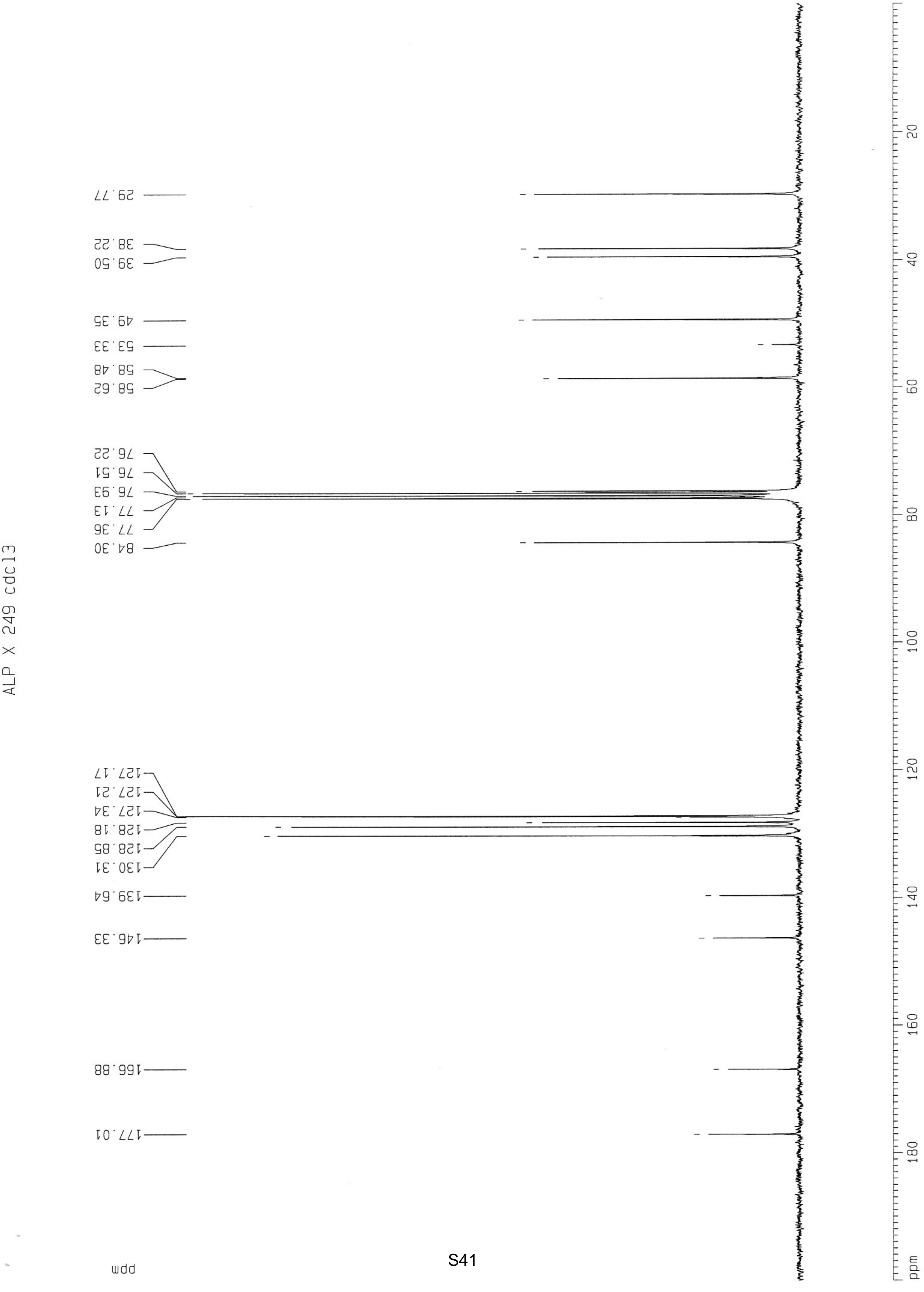
40.3
43.8
78.0
85.6
117.7
128.5
128.7
129.5
130.3
131.6
ppm
20
40
60
80
100
120
140
ppm


ALP X 249 cdcl3 dicembre 3
Hz
2391.17
2382.96
2281.49
2273.26
2260.28
2253.07
2218.15
2211.27
2203.74
2196.73
2189.73
2182.72
2150.86
1671.48
1560.04
1553.37
1546.31
1539.52
1085.18
1079.11
963.60
953.81
947.46
940.45
931.51
813.97
809.45
806.97
802.29
782.33
771.51
763.40
753.31
749.28
739.79
723.77
642.85
637.11
632.43
627.18
621.28
616.63
479.78
O
O
OH
O
O
Integral
43.806
12.205
42.717
1.272
ppm
8
7
6
5
4
3
2
1

4c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166.88
146.33
139.64
130.31
128.85
128.18
127.34
127.21
127.17
84.30
77.36
77.13
76.93
76.51
76.22
58.62
58.48
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49.35
39.50
38.22
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ppm
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40
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120
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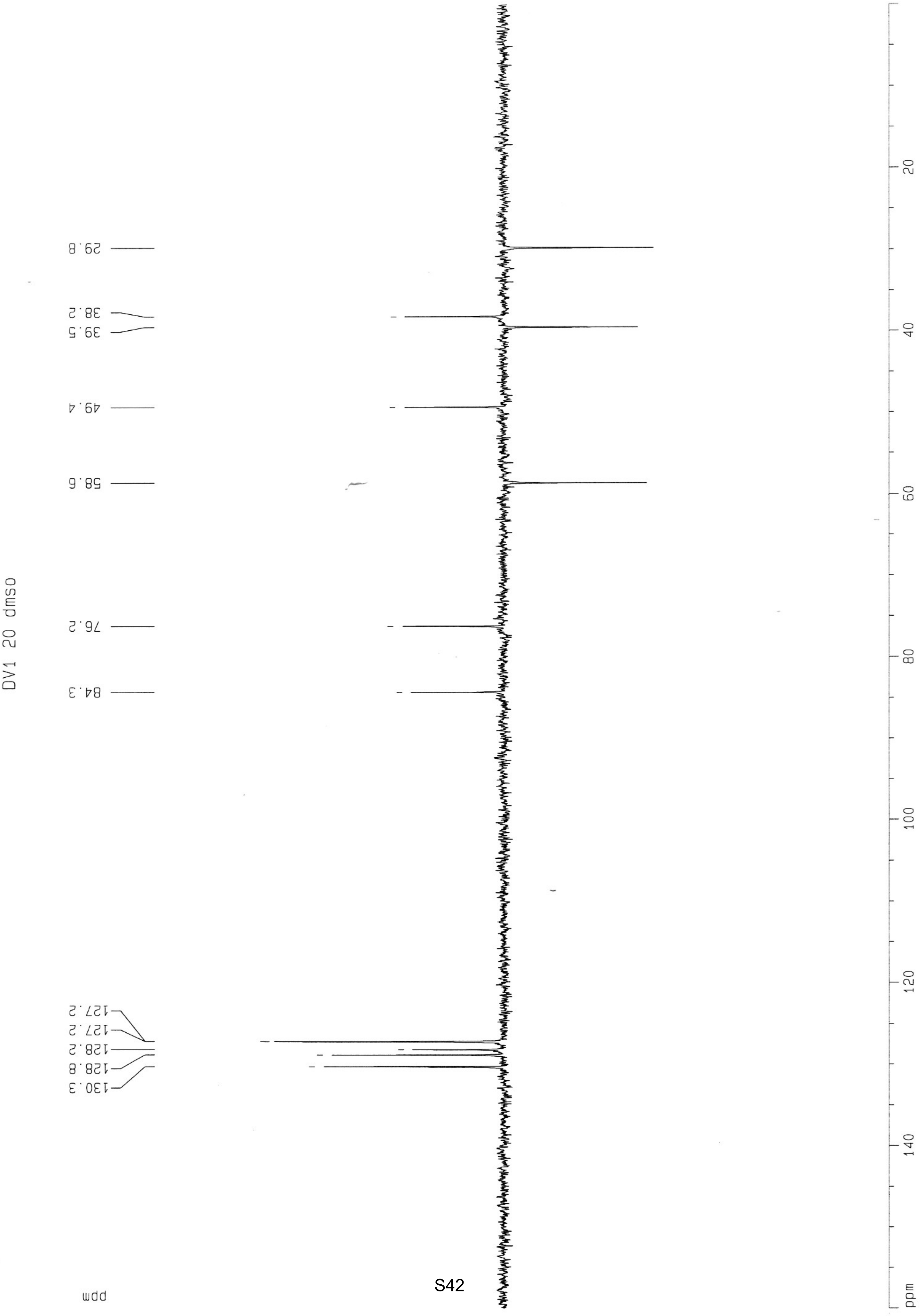
160
180
ppm


DV1 20 dmso
29.8
38.2
39.5
49.4
58.6
76.2
84.3
127.2
127.2
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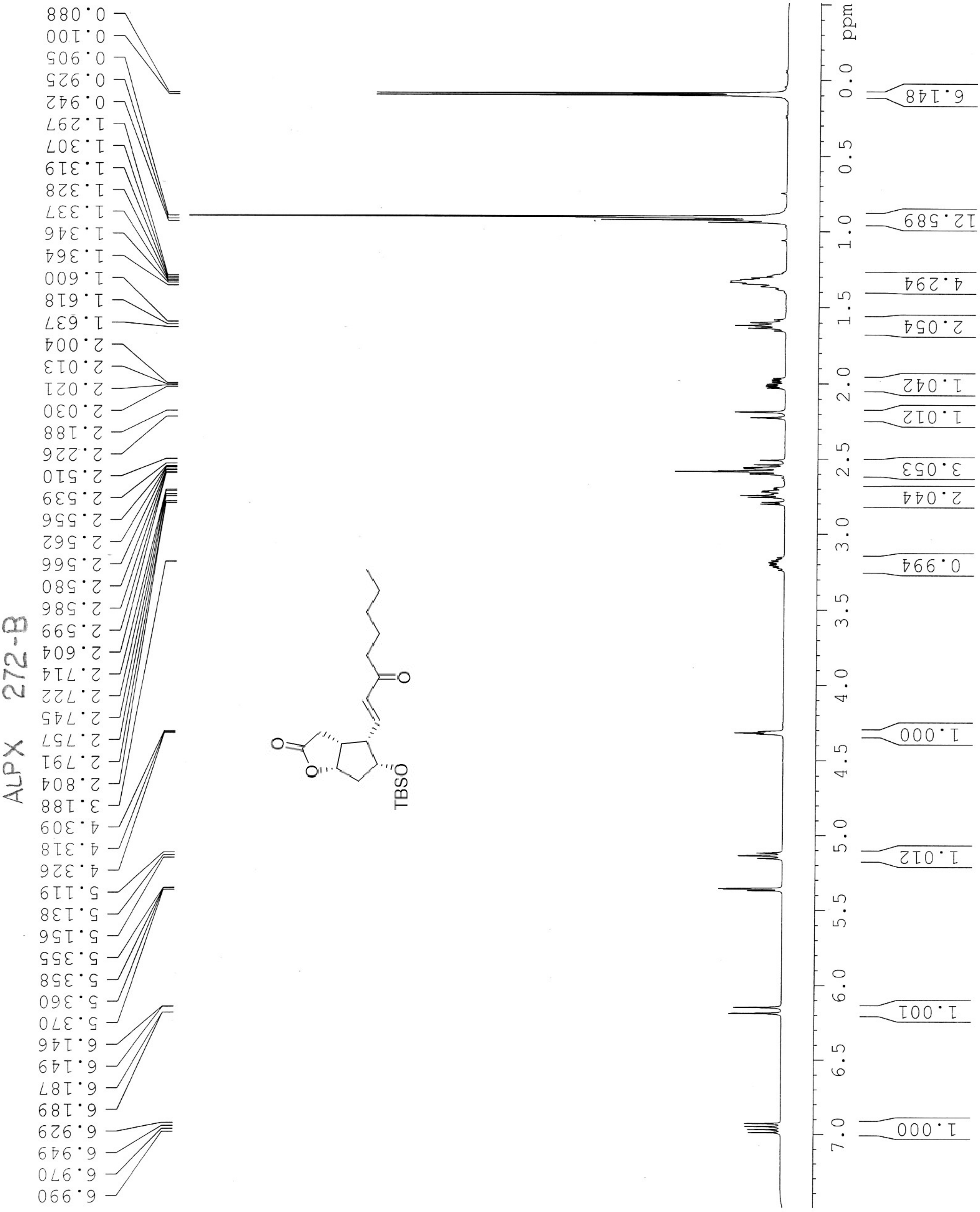
100
120
140
ppm


ALPX 272-B
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0.100
0.905
0.925
0.942
1.297
1.307
1.319
1.328
1.337
1.346
1.364
1.600
1.618
1.637
2.004
2.013
2.021
2.030
2.188
2.226
2.510
2.539
2.556
2.562
2.566
2.580
2.586
2.599
2.604
2.714
2.722
2.745
2.757
2.791
2.804
3.188
4.309
4.318
4.326
5.119
5.138
5.156
5.355
5.358
5.360
5.370
6.146
6.149
6.187
6.189
6.929
6.949
6.970
6.990
O
O
O
TBSO
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
6.148
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1.042
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3.053
2.044
0.994
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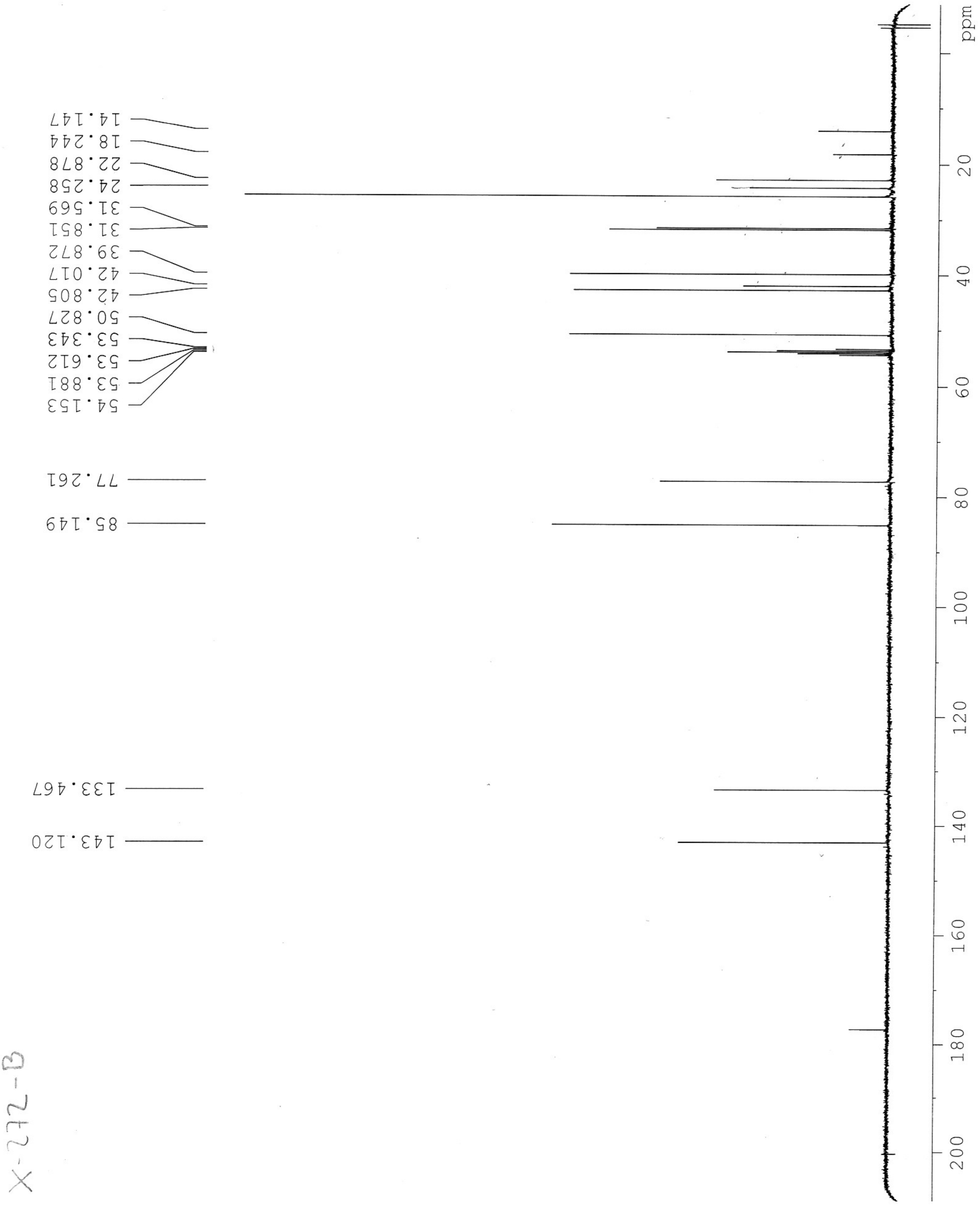
1.012
1.001
1.000


X-272-B
14.147
18.244
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31.851
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42.805
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53.343
53.612
53.881
54.153
77.261
85.149
133.467
143.120
ppm
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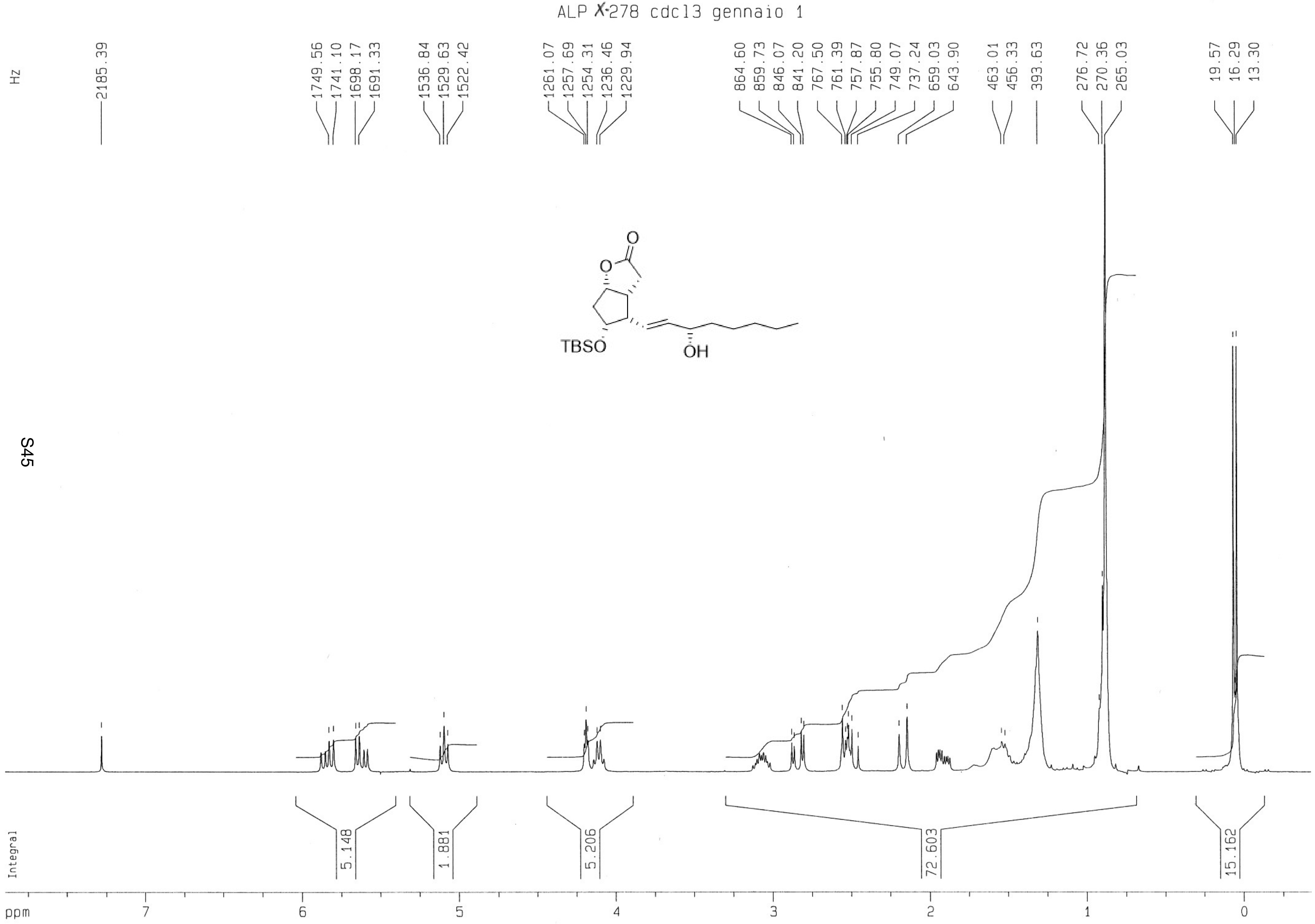
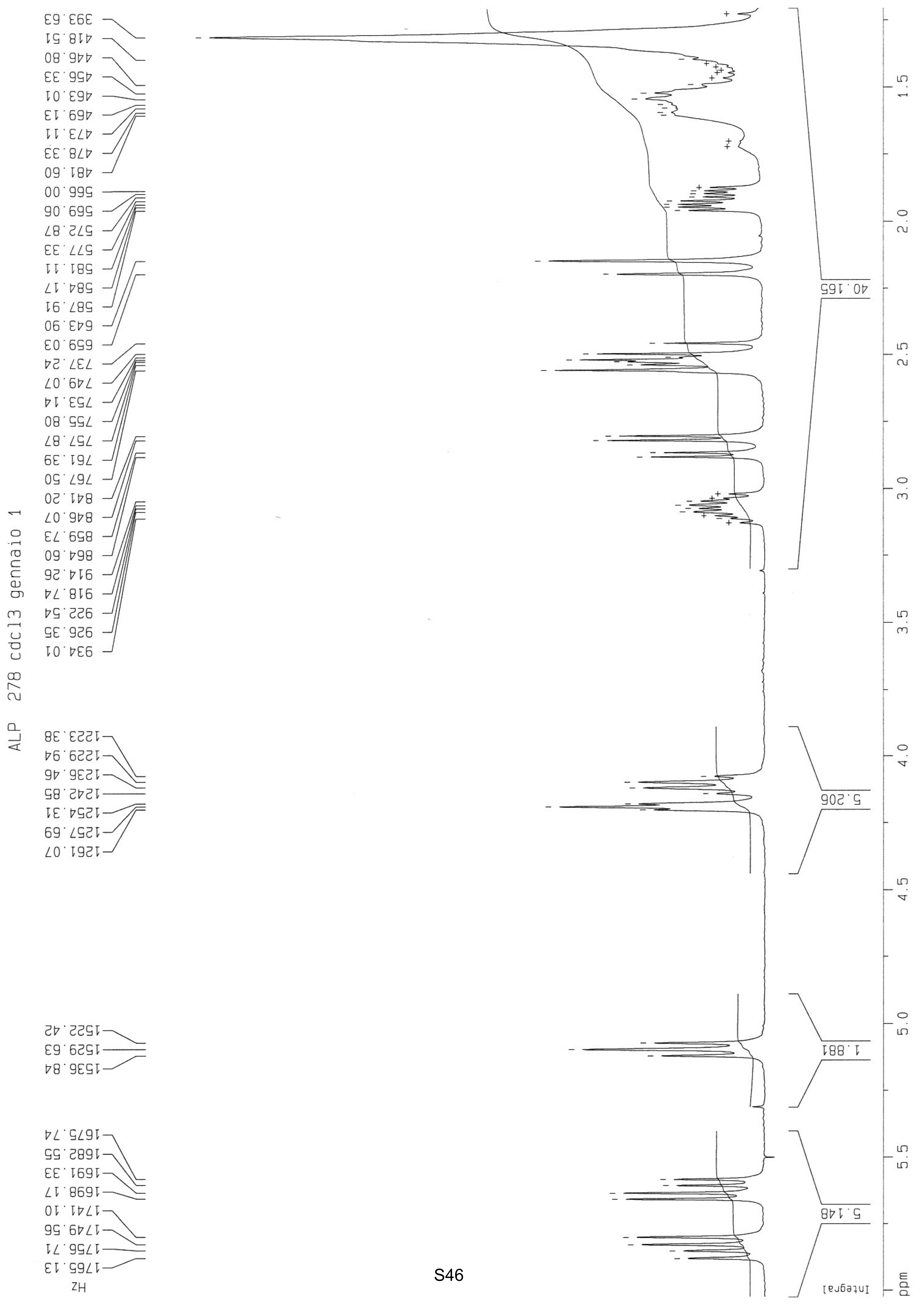
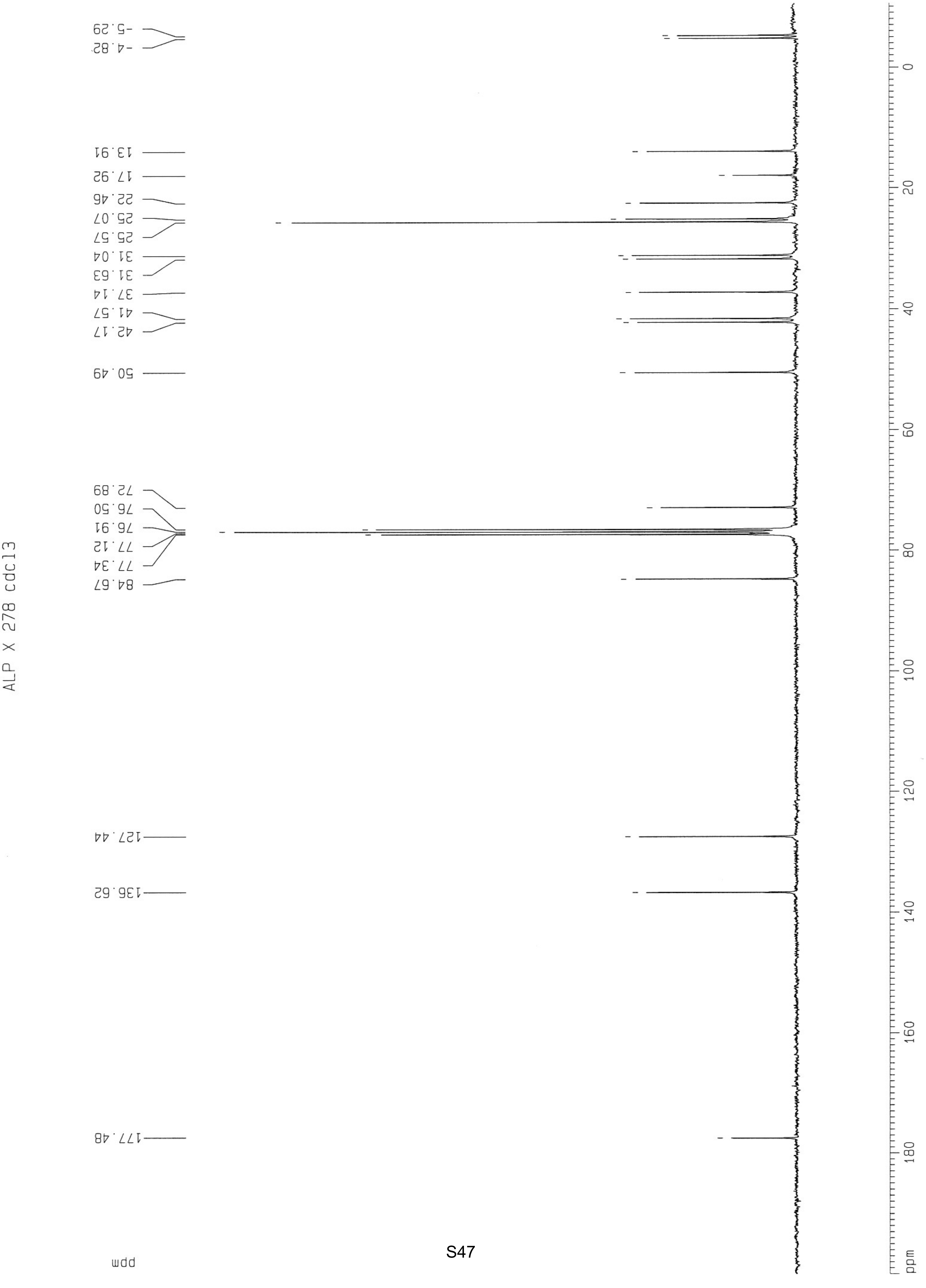
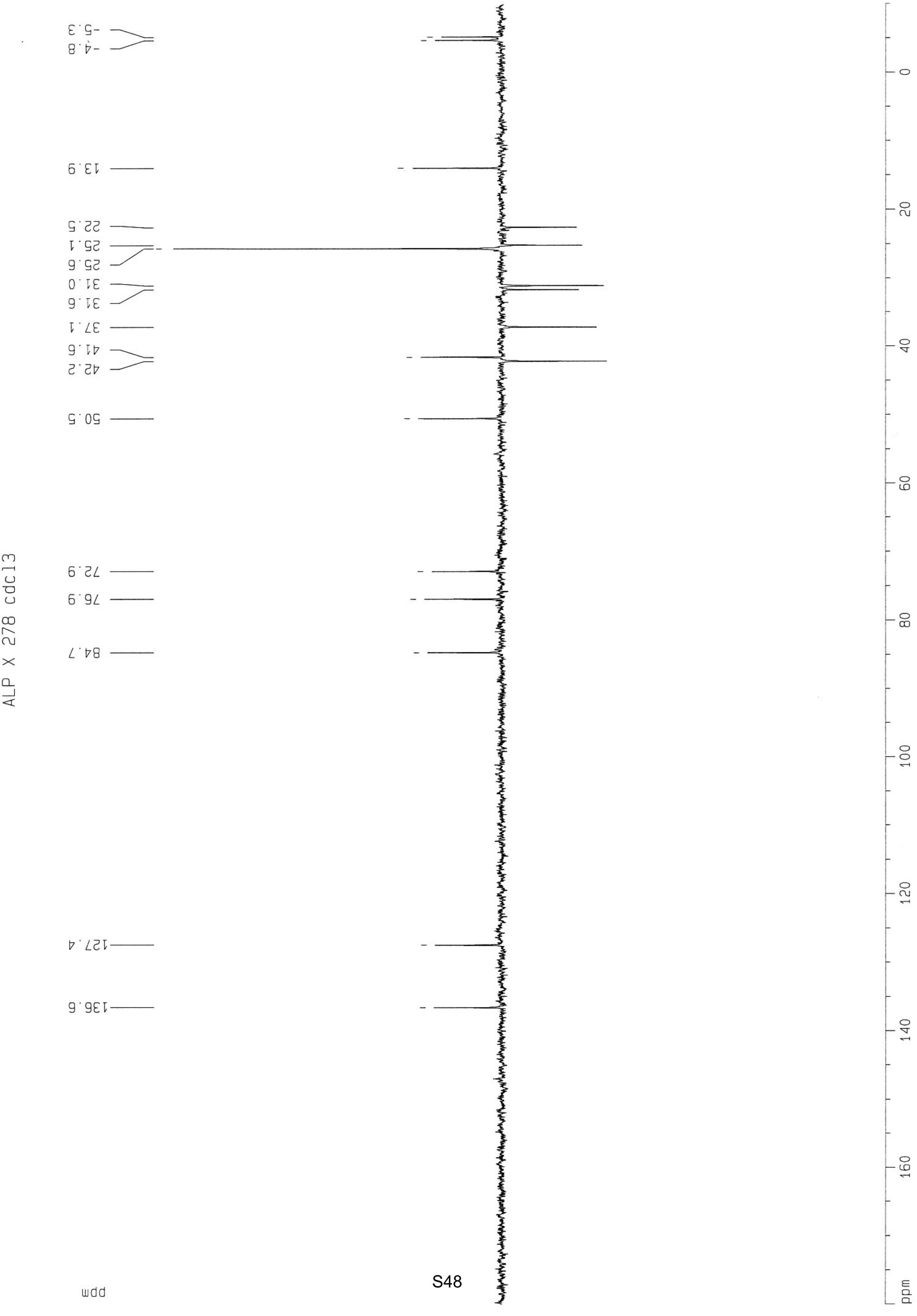
40
60
80
100
120
140
160
180
200

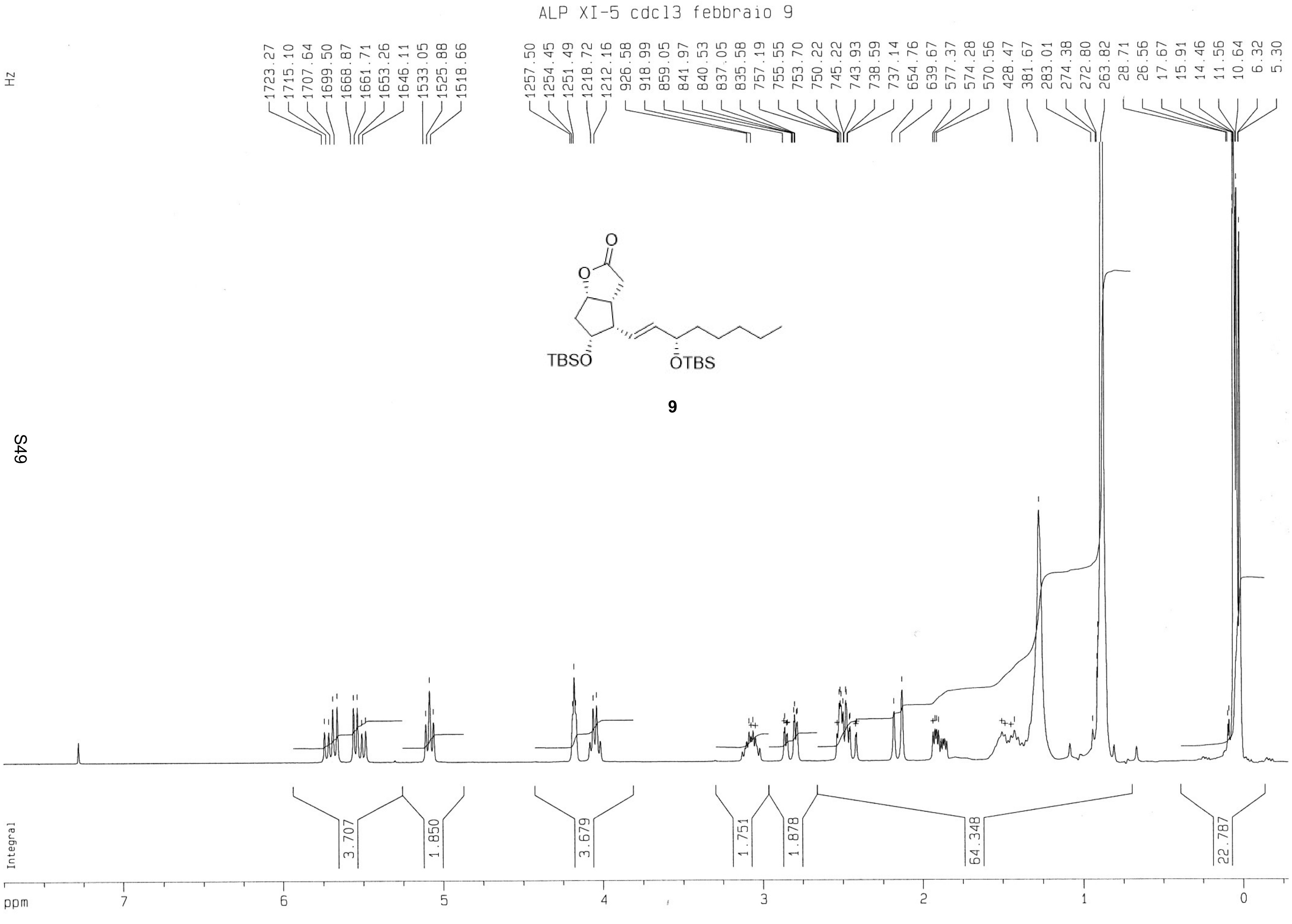

ALP X-278 cdcl3 gennaio 1
Hz
2185.39
1749.56
1741.10
1698.17
1691.33
1536.84
1529.63
1522.42
1261.07
1257.69
1254.31
1236.46
1229.94
864.60
859.73
846.07
841.20
767.50
761.39
757.87
755.80
749.07
737.24
659.03
643.90
463.01
456.33
393.63
276.72
270.36
265.03
19.57
16.29
13.30
O
TBSO
OH
Integral
5.148
1.881
5.206
72.603
15.162
ppm
7
6
5
4
3
2
1
0


ALP 278 cdcl3 gennaio 1
393.63
418.51
446.80
456.33
463.01
469.13
473.11
478.33
481.60
566.00
569.06
572.87
577.33
581.11
584.17
587.91
643.90
659.03
737.24
749.07
753.14
755.80
757.87
761.39
767.50
841.20
846.07
859.73
864.60
914.26
918.74
922.54
926.35
934.01
1223.38
1229.94
1236.46
1242.85
1254.31
1257.69
1261.07
1522.42
1529.63
1536.84
1675.74
1682.55
1691.33
1698.17
1741.10
1749.56
1756.71
1765.13
Hz
40.165
5.206
1.881
5.148
Integral
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
ppm

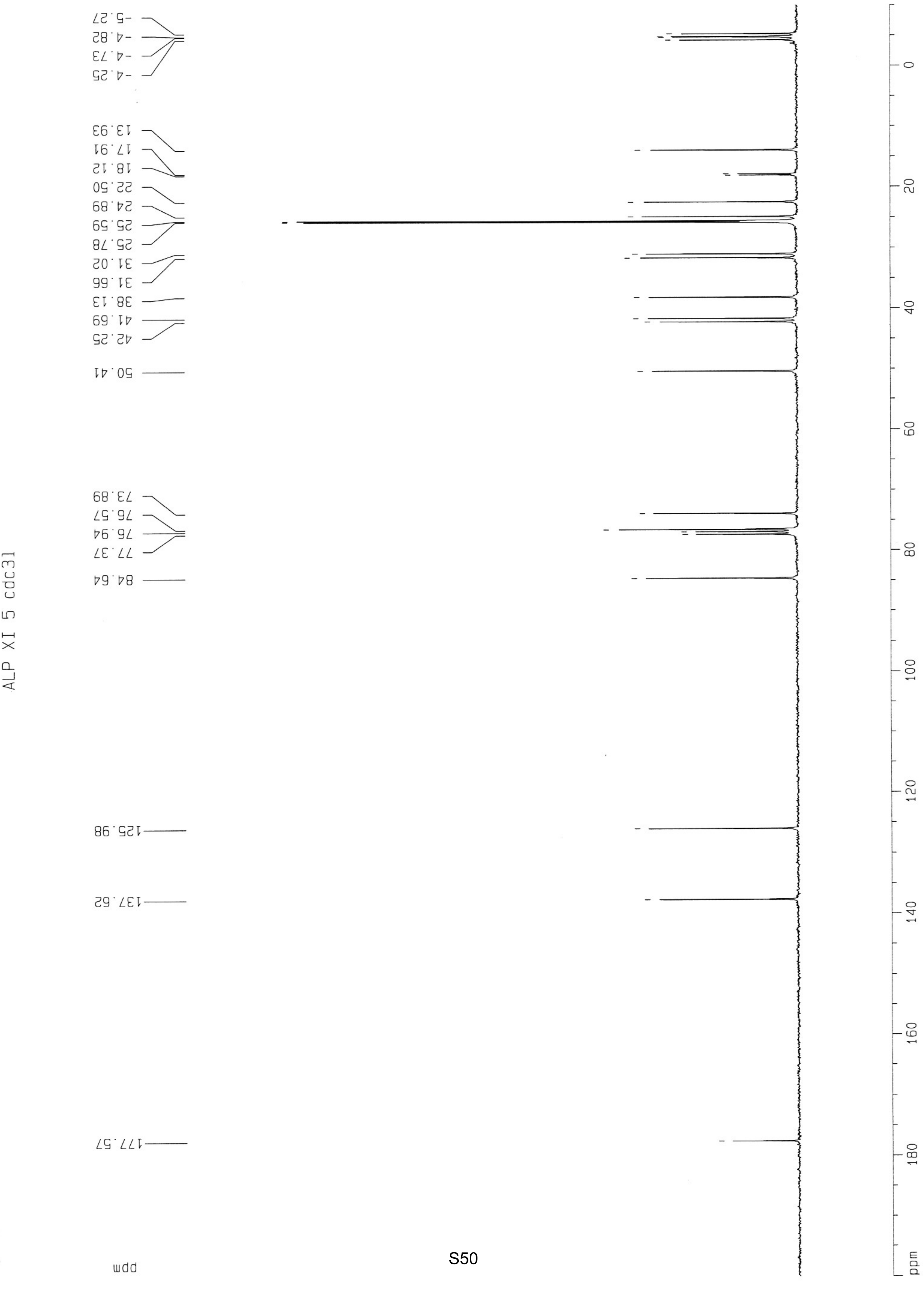

ALP X 278 cdcl3
-5.29
-4.82
13.91
17.92
22.46
25.07
25.57
31.04
31.63
37.14
41.57
42.17
50.49
72.89
76.50
76.91
77.12
77.34
84.67
127.44
136.62
177.48
ppm
0
20
40
60
80
100
120
140
160
180
ppm

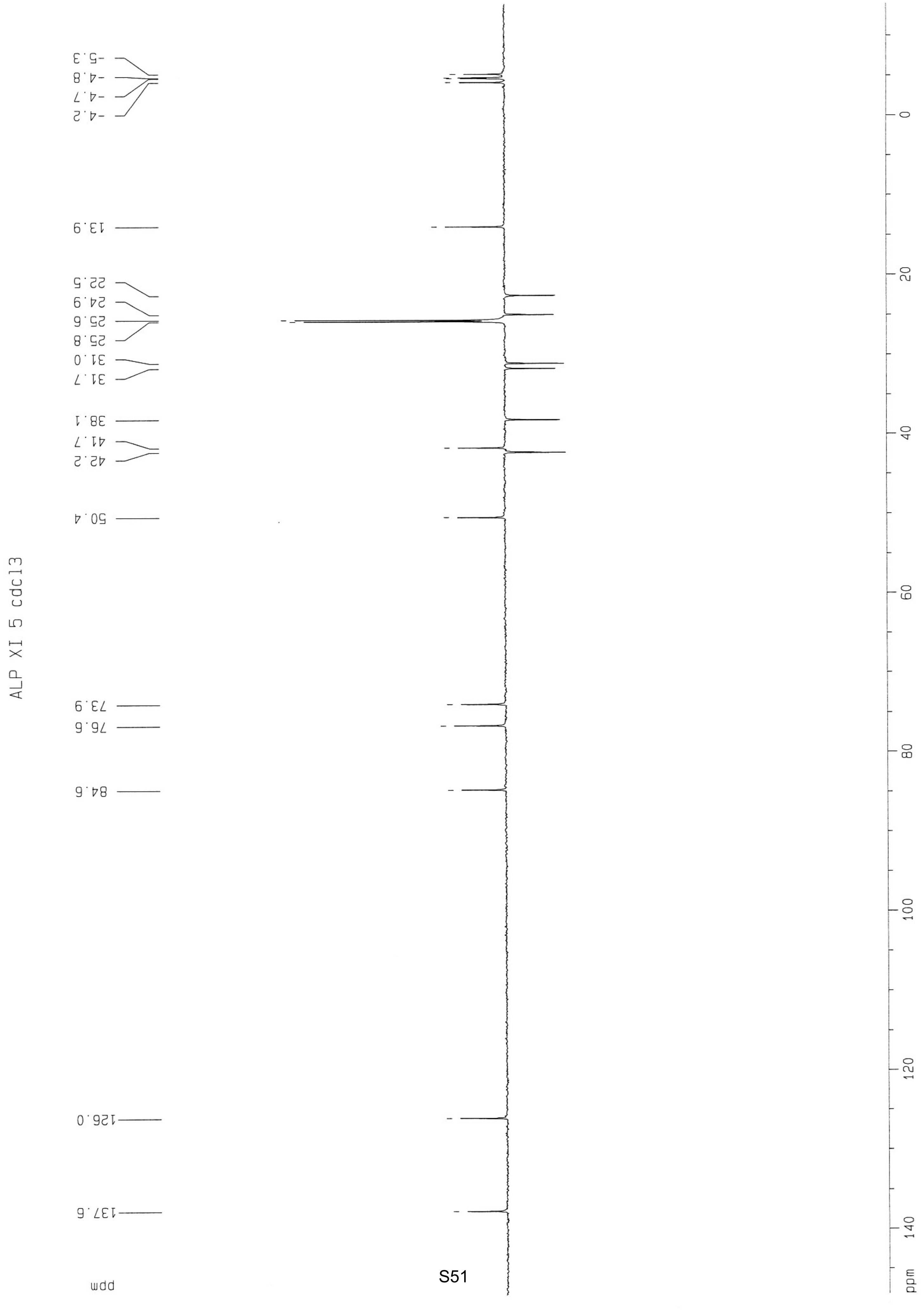


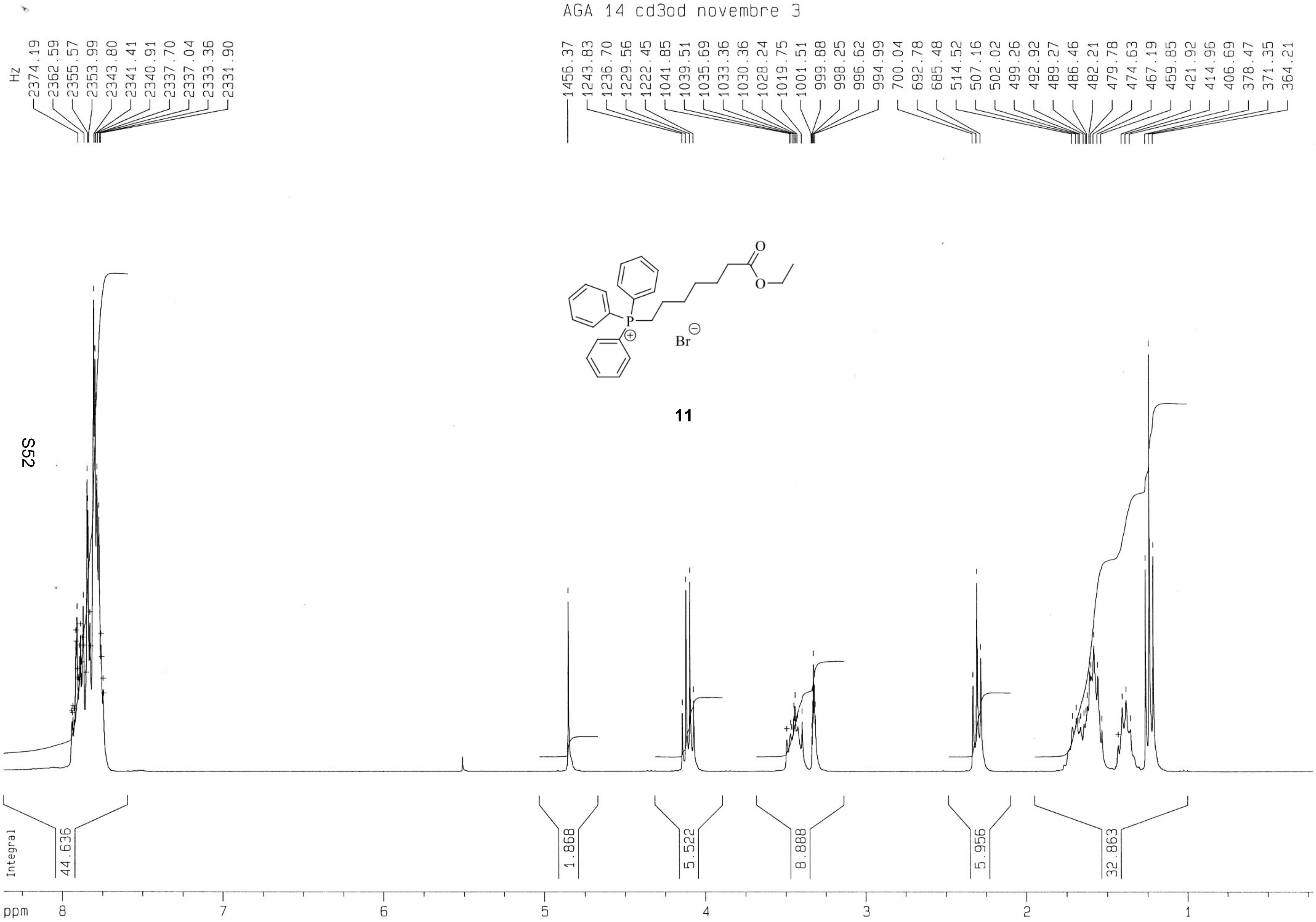
ALP X 278 cdcl3
-5.3
-4.8
13.9
22.5
25.1
25.6
31.0
31.6
37.1
41.6
42.2
50.5
72.9
76.9
84.7
127.4
136.6
ppm
0
20
40
60
80
100
120
140
160
ppm


ALP XI-5 cdcl3 febbraio 9
Hz
1723.27
1715.10
1707.64
1699.50
1668.87
1661.71
1653.26
1646.11
1533.05
1525.88
1518.66
1257.50
1254.45
1251.49
1218.72
1212.16
926.58
918.99
859.05
841.97
840.53
837.05
835.58
757.19
755.55
753.70
750.22
745.22
743.93
738.59
737.14
654.76
639.67
577.37
574.28
570.56
428.47
381.67
283.01
274.38
272.80
263.82
28.71
26.56
17.67
15.91
14.46
11.56
10.64
6.32
5.30
O
TBSO
OTBS
Integral
3.707
1.850
3.679
1.751
1.878
64.348
22.787
ppm
7
6
5
4
3
2
1
0

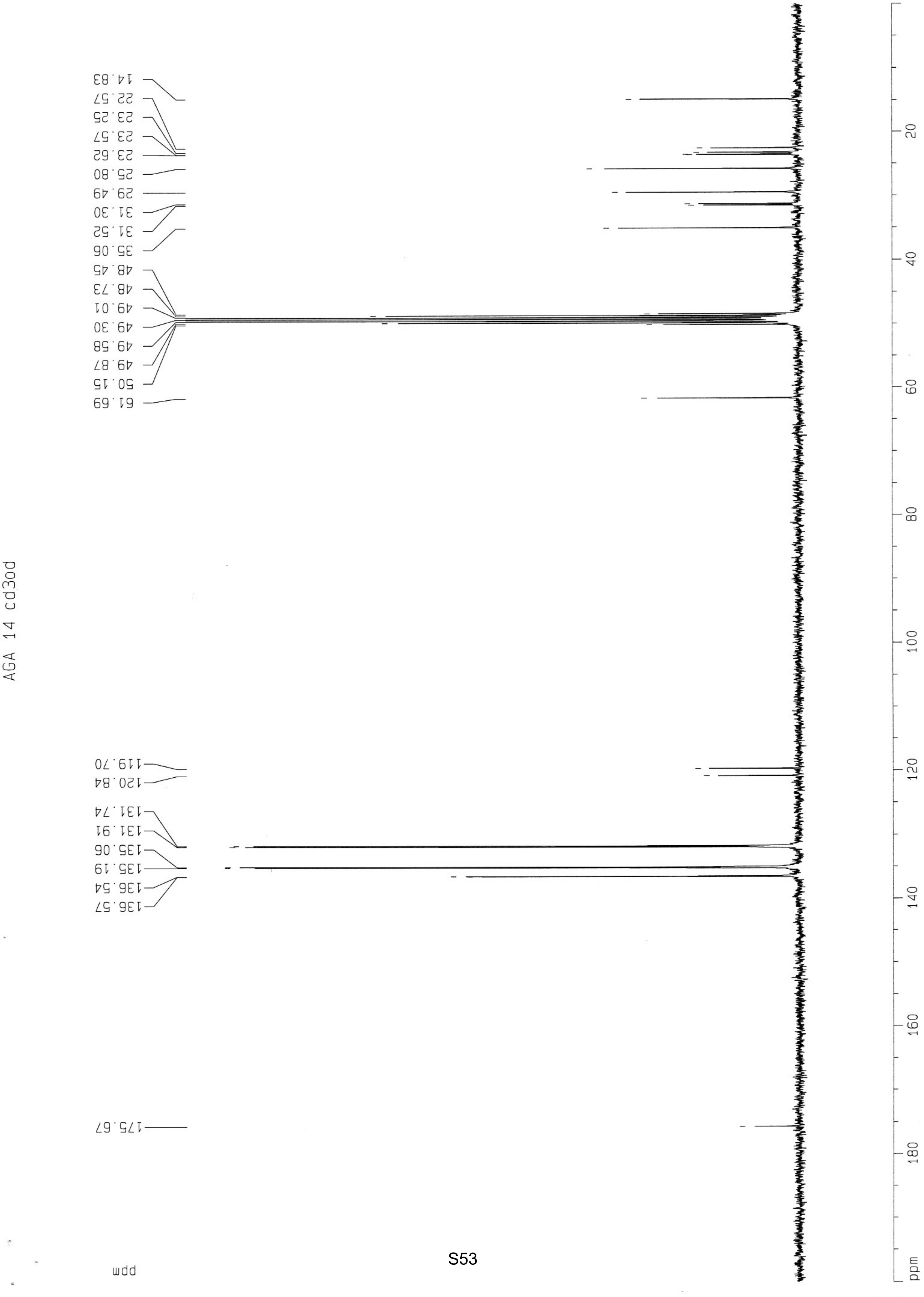
9


ALP XI 5 cdc31
-5.27
-4.82
-4.73
-4.25
13.93
17.91
18.12
22.50
24.89
25.59
25.78
31.02
31.66
38.13
41.69
42.25
50.41
73.89
76.57
76.94
77.37
84.64
125.98
137.62
177.57
ppm
0
20
40
60
80
100
120
140
160
180
ppm

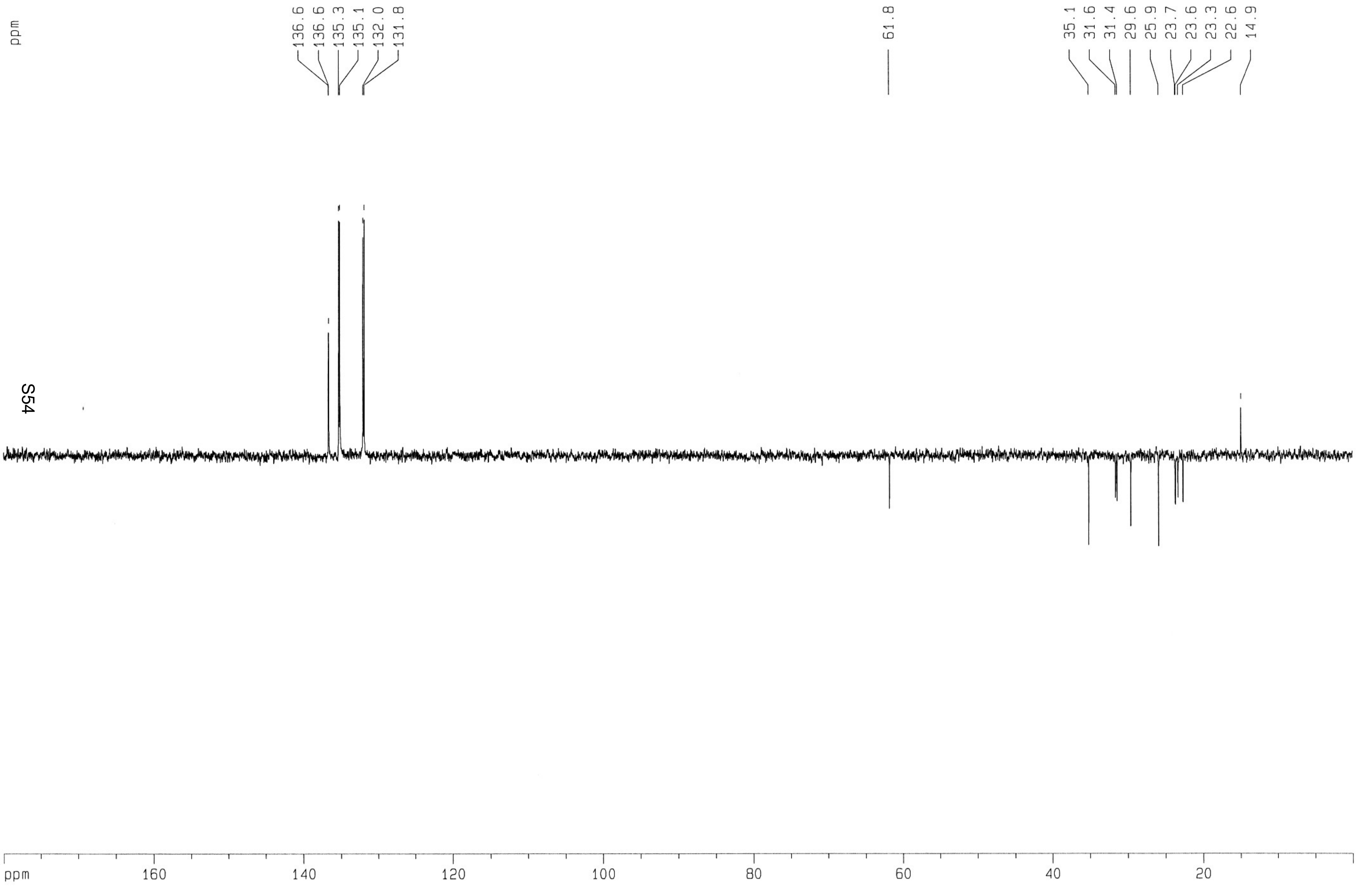

ALP XI 5 cdcl3
-5.3
-4.8
-4.7
-4.2
13.9
22.5
24.9
25.6
25.8
31.0
31.7
38.1
41.7
42.2
50.4
73.9
76.6
84.6
126.0
137.6
ppm
0
20
40
60
80
100
120
140
ppm


AGA 14 cd3od novembre 3
Hz
2374.19
2362.59
2355.57
2353.99
2343.80
2341.41
2340.91
2337.70
2337.04
2333.36
2331.90
1456.37
1243.83
1236.70
1229.56
1222.45
1041.85
1039.51
1035.69
1033.36
1030.36
1028.24
1019.75
1001.51
999.88
998.25
996.62
994.99
700.04
692.78
685.48
514.52
507.16
502.02
499.26
492.92
489.27
486.46
482.21
479.78
474.63
467.19
459.85
421.92
414.96
406.69
378.47
371.35
364.21
O
O
P
Br
Integral
44.636
1.868
5.522
8.888
5.956
32.863
ppm
8
7
6
5
4
3
2
1

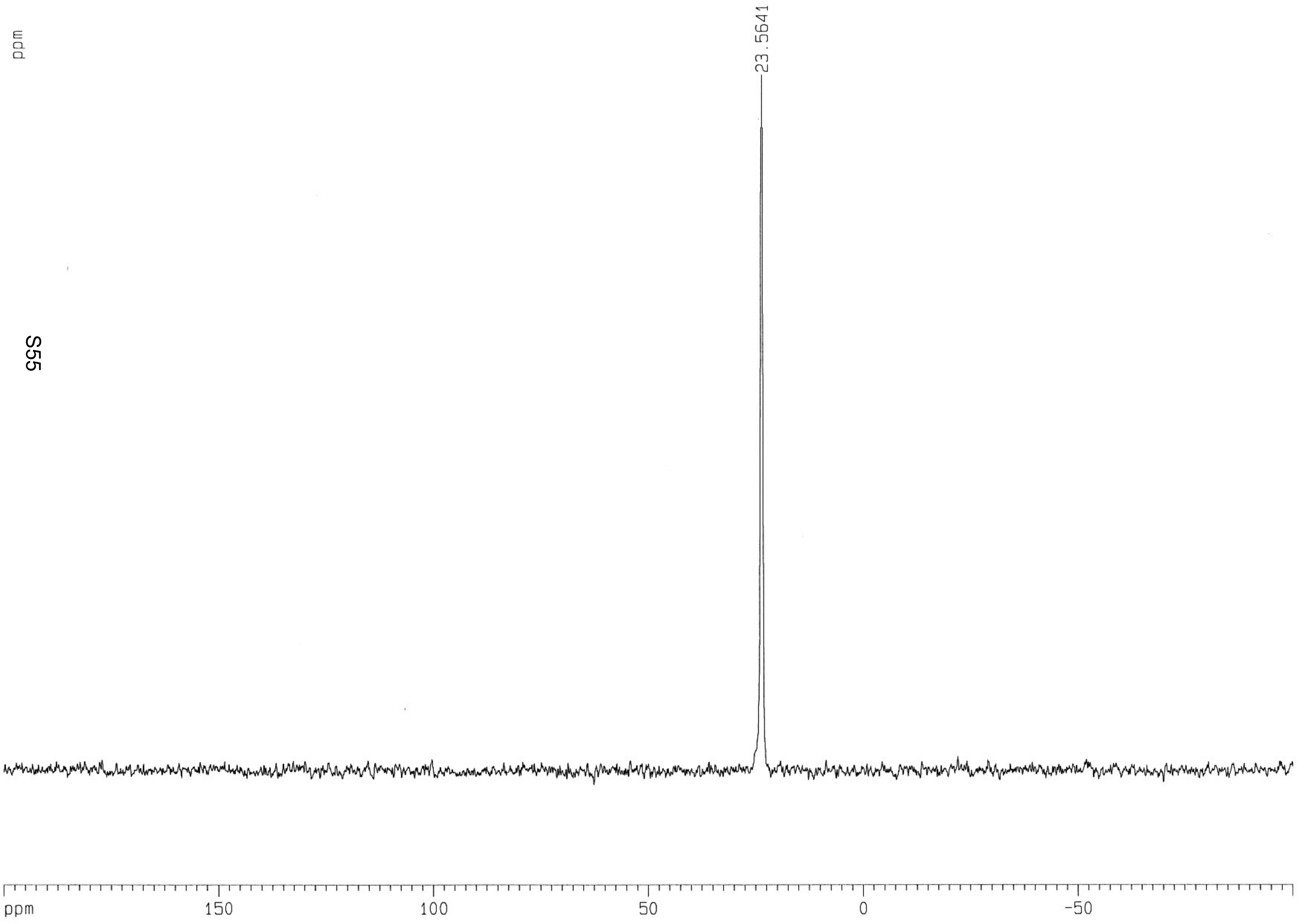
11


AGA 14 cd3od
14.83
22.57
23.25
23.57
23.62
25.80
29.49
31.30
31.52
35.06
48.45
48.73
49.01
49.30
49.58
49.87
50.15
61.69
119.70
120.84
131.74
131.91
135.06
135.19
136.54
136.57
175.67
ppm
20
40
60
80
100
120
140
160
180
ppm

AGA 14 cd3od


136.6
136.6
135.3
135.1
132.0
131.8
61.8
35.1
31.6
31.4
29.6
25.9
23.7
23.6
23.3
22.6
14.9
ppm
160
140
120
100
80
60
40
20
ppm

AGA 14 cd3od



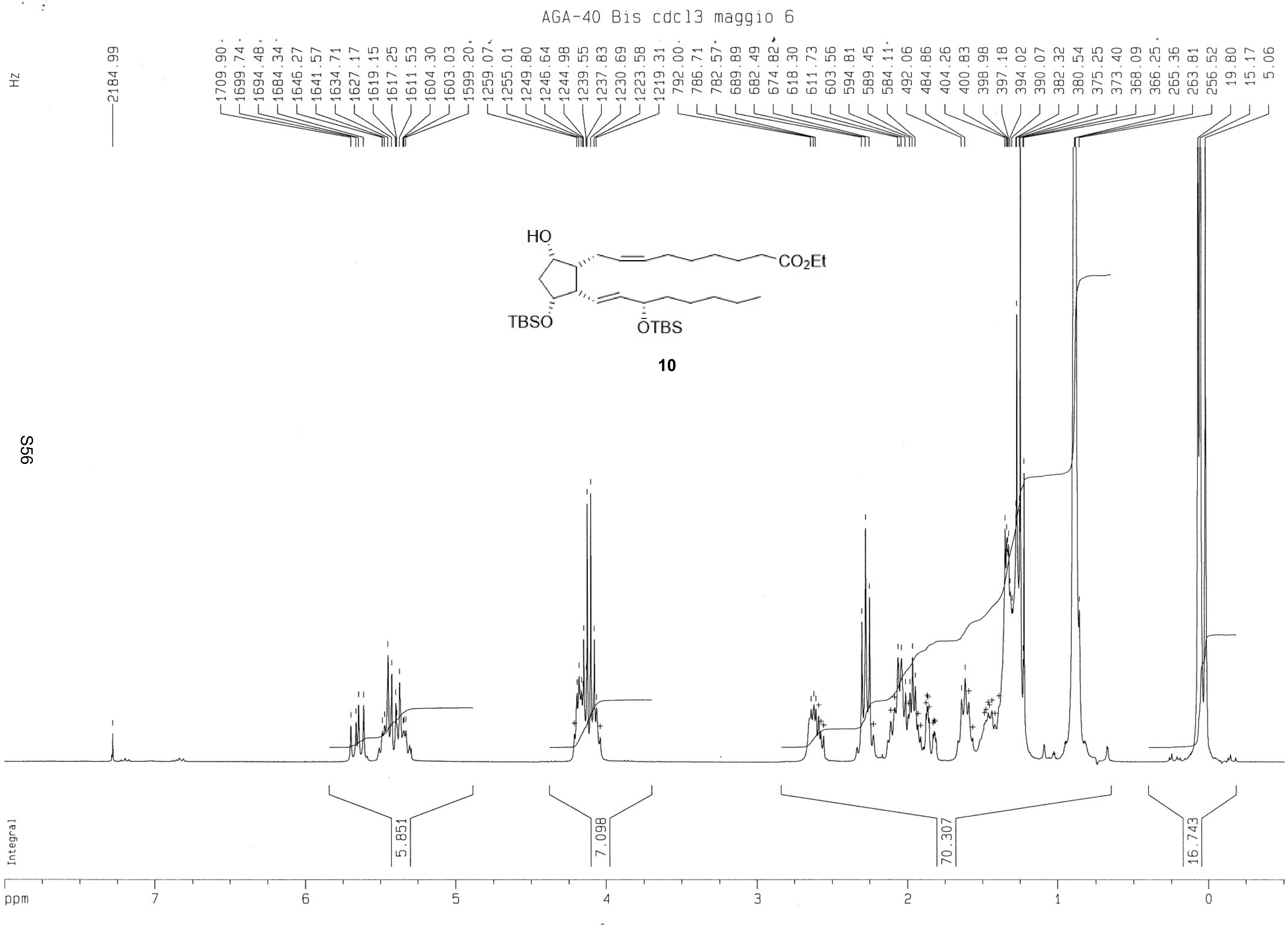
```
Current Data Parameters
NAME              fosforo
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121115
Time                15.21
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     40
DS                      2
SWH             48661.801 Hz
FIDRES           1.485040 Hz
AQ              0.3367412 sec
RG                 5792.6
DW                 10.275 usec
DE                   6.00 usec
TE                  298.2 K
D1             5.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  31P
P1                   6.70 usec
PL1                 -2.00 dB
SFO1          121.5009107 MHz

F2 - Processing parameters
SI                  16384
SF            121.4948840 MHz
WDW                    EM
SSB                     0
LB                  20.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.00 cm
CY                   0.00 cm
F1P               200.000 ppm
F1               24298.98 Hz
F2P              -100.000 ppm
F2              -12149.49 Hz
PPMCM            13.63636 ppm/cm
HZCM           1656.74841 Hz/cm
```


AGA-40 Bis cdcl3 maggio 6
Hz
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1699.74
1694.48
1684.34
1646.27
1641.57
1634.71
1627.17
1619.15
1617.25
1611.53
1604.30
1603.03
1599.20
1259.07
1255.01
1249.80
1246.64
1244.98
1239.55
1237.83
1230.69
1223.58
1219.31
792.00
786.71
782.57
689.89
682.49
674.82
618.30
611.73
603.56
594.81
589.45
584.11
492.06
484.86
404.26
400.83
398.98
397.18
394.02
390.07
382.32
380.54
375.25
373.40
368.09
366.25
265.36
263.81
256.52
19.80
15.17
5.06
HO
CO_2Et
TBSO
OTBS
10
Integral
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16.743
ppm
7
6
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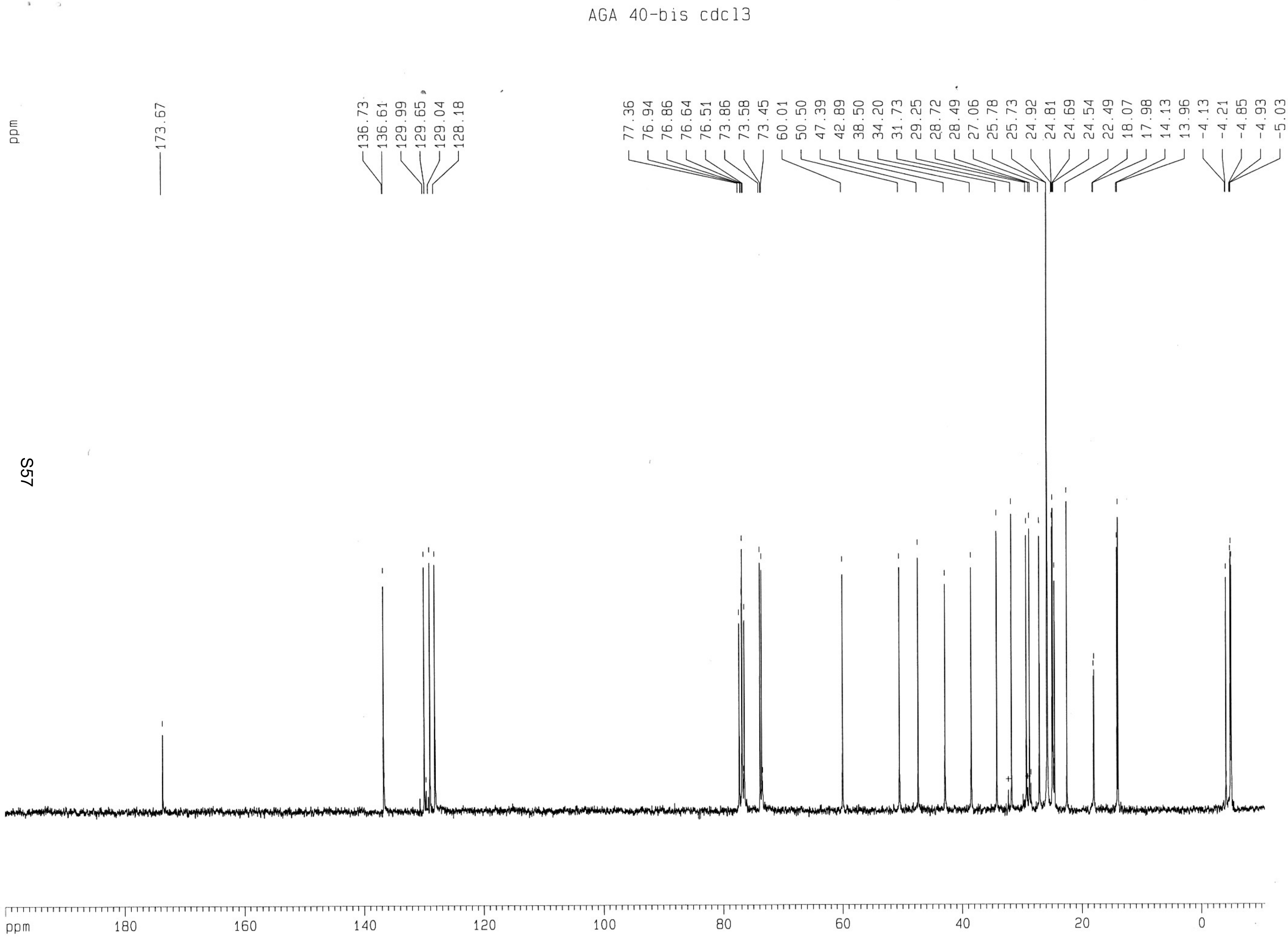
4
3
2
1
0


AGA 40-bis cdcl3
ppm
173.67
136.73
136.61
129.99
129.65
129.04
128.18
77.36
76.94
76.86
76.64
76.51
73.86
73.58
73.45
60.01
50.50
47.39
42.89
38.50
34.20
31.73
29.25
28.72
28.49
27.06
25.78
25.73
24.92
24.81
24.69
24.54
22.49
18.07
17.98
14.13
13.96
-4.13
-4.21
-4.85
-4.93
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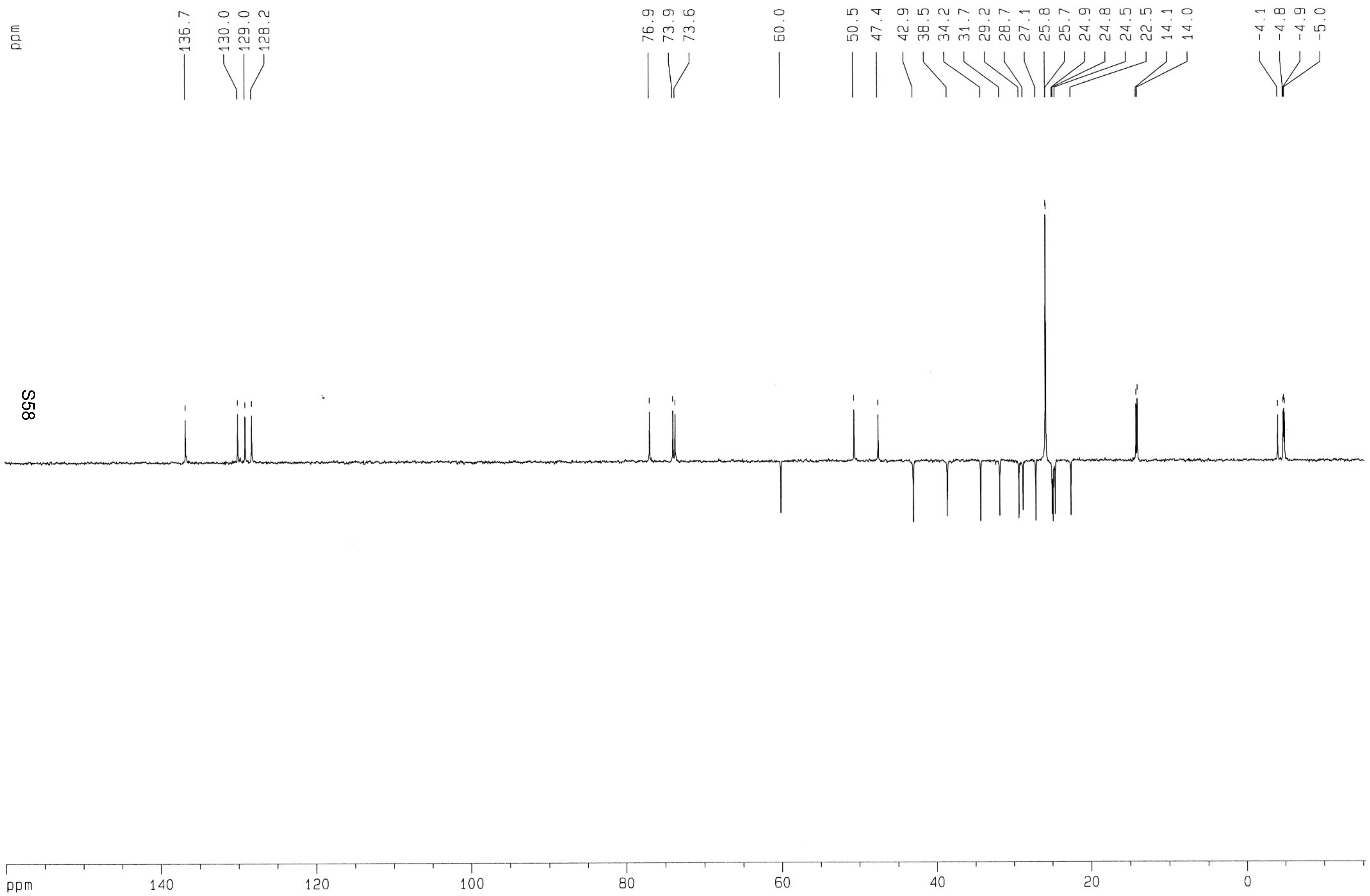
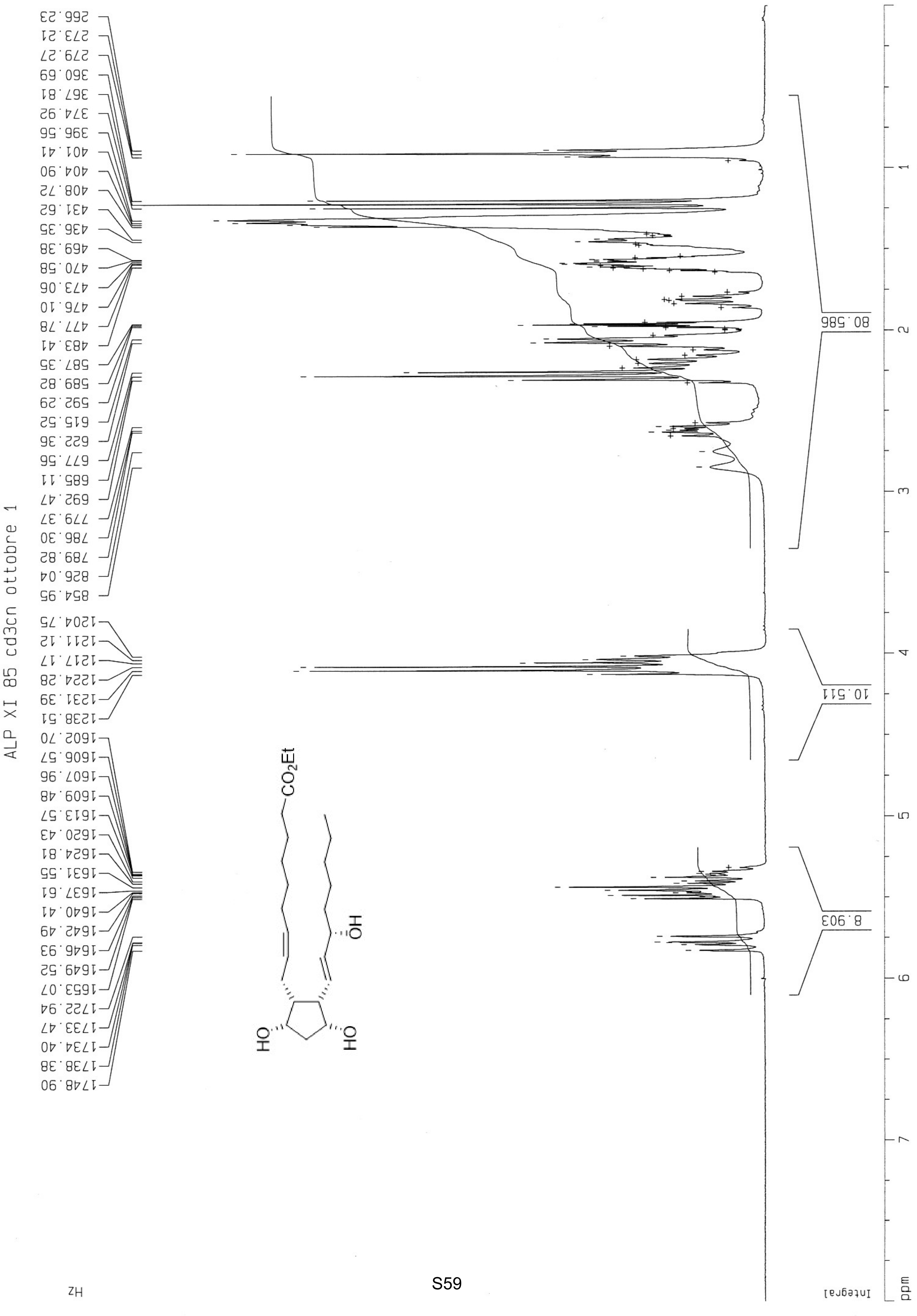
ppm
180
160
140
120
100
80
60
40
20
0

AGA 40-bis cdcl3




ALP XI 85 cd3cn ottobre 1
266.23
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279.27
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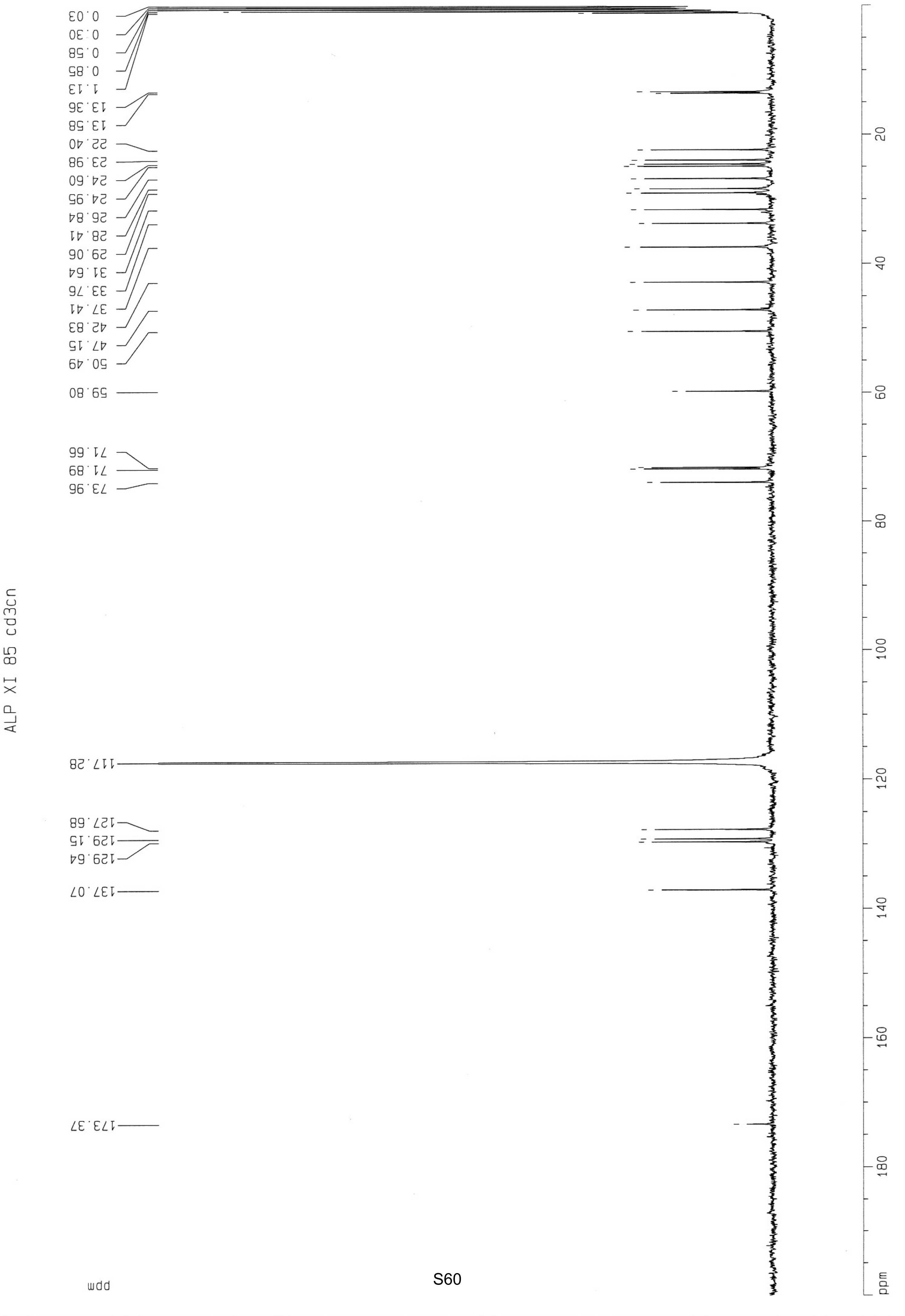
367.81
374.92
396.56
401.41
404.90
408.72
431.62
436.35
469.38
470.58
473.06
476.10
477.78
483.41
587.35
589.82
592.29
615.52
622.36
677.56
685.11
692.47
779.37
786.30
789.82
826.04
854.95
1204.75
1211.12
1217.17
1224.28
1231.39
1238.51
1602.70
1606.57
1607.96
1609.48
1613.57
1620.43
1624.81
1631.55
1637.61
1640.41
1642.49
1646.93
1649.52
1653.07
1722.94
1733.47
1734.40
1738.38
1748.90
Hz
CO2Et
HO
HO
OH
80.586
10.511
8.903
Integral
1
2
3
4
5
6
7
ppm


ALP XI 85 cd3cn
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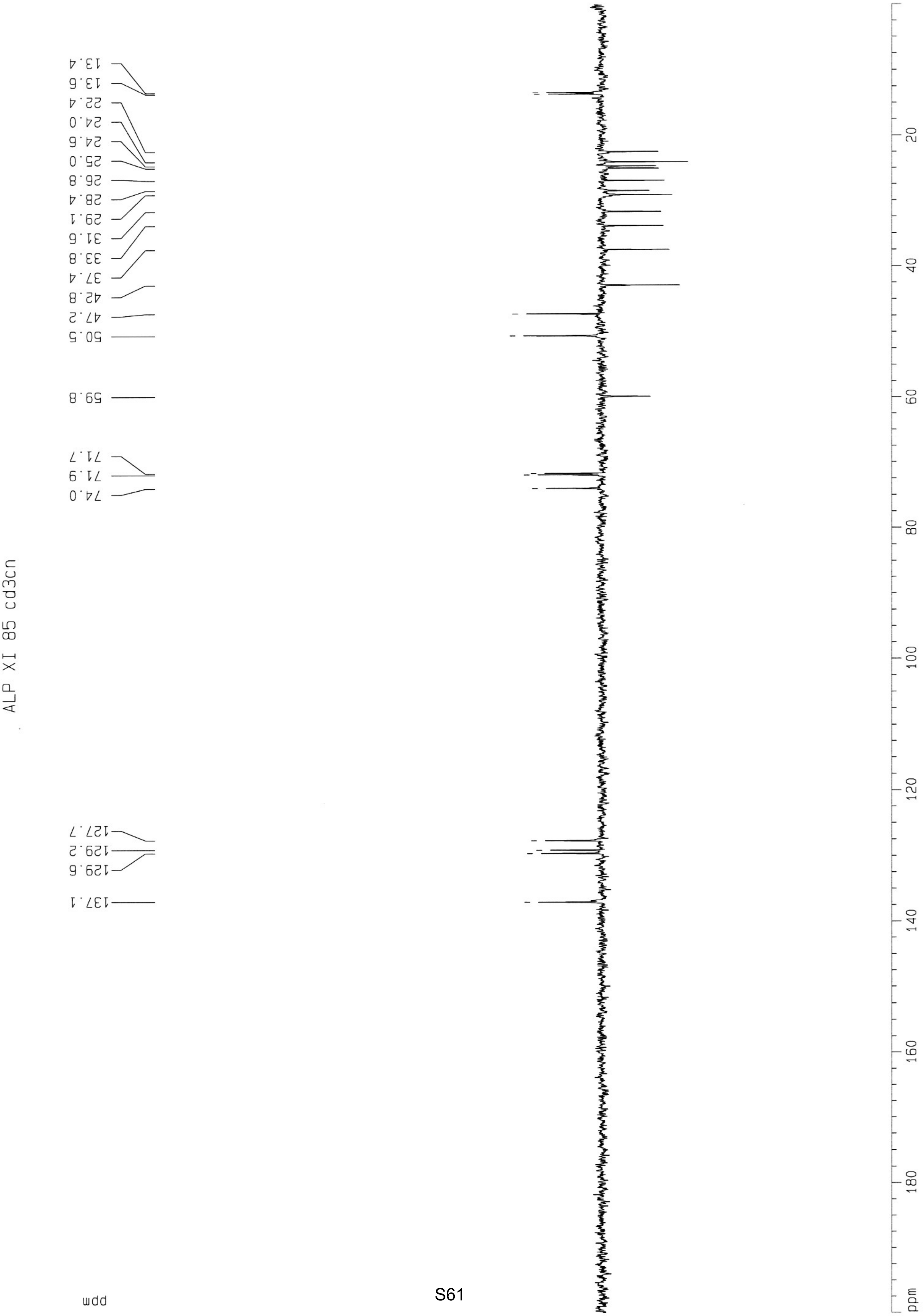
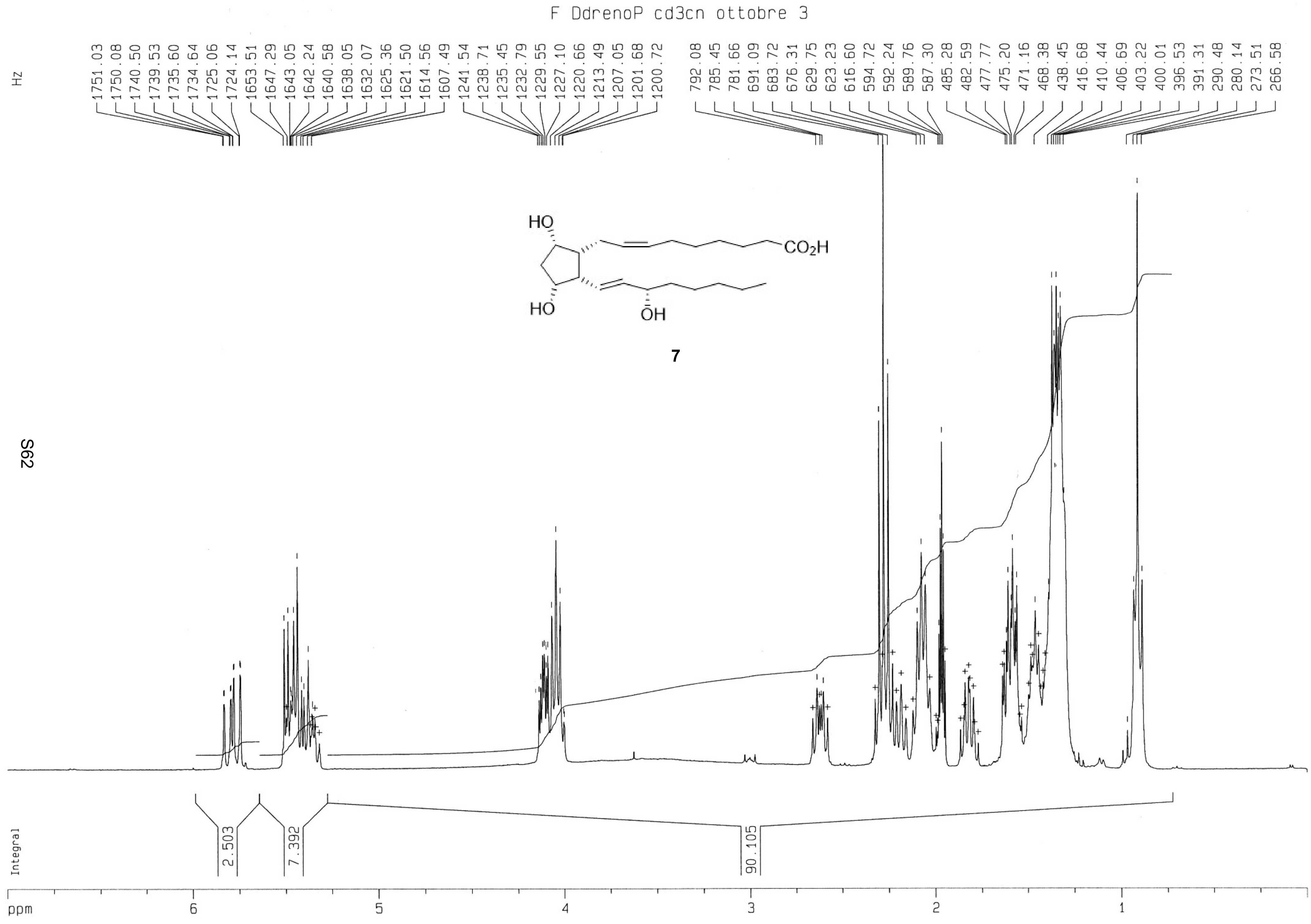
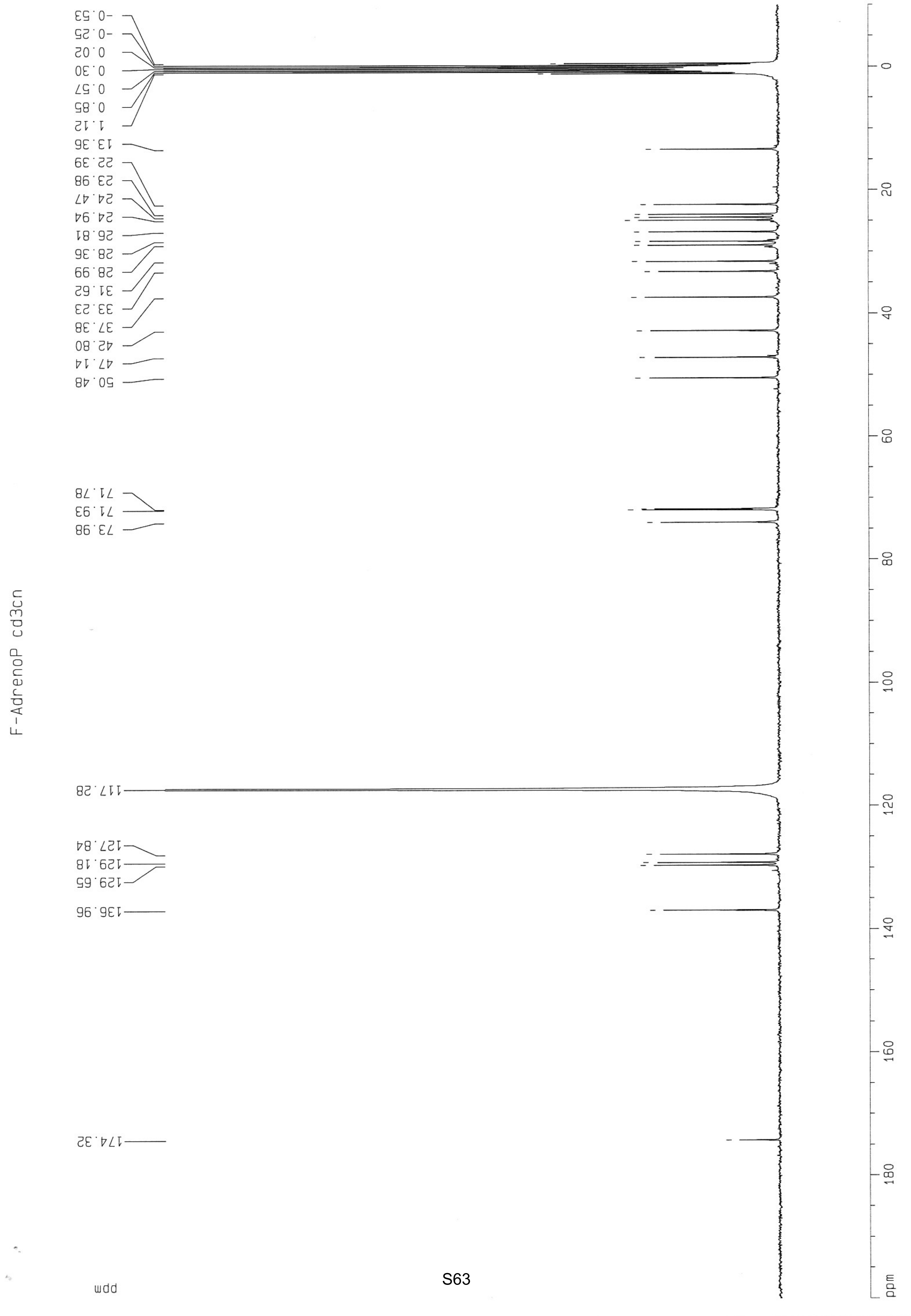
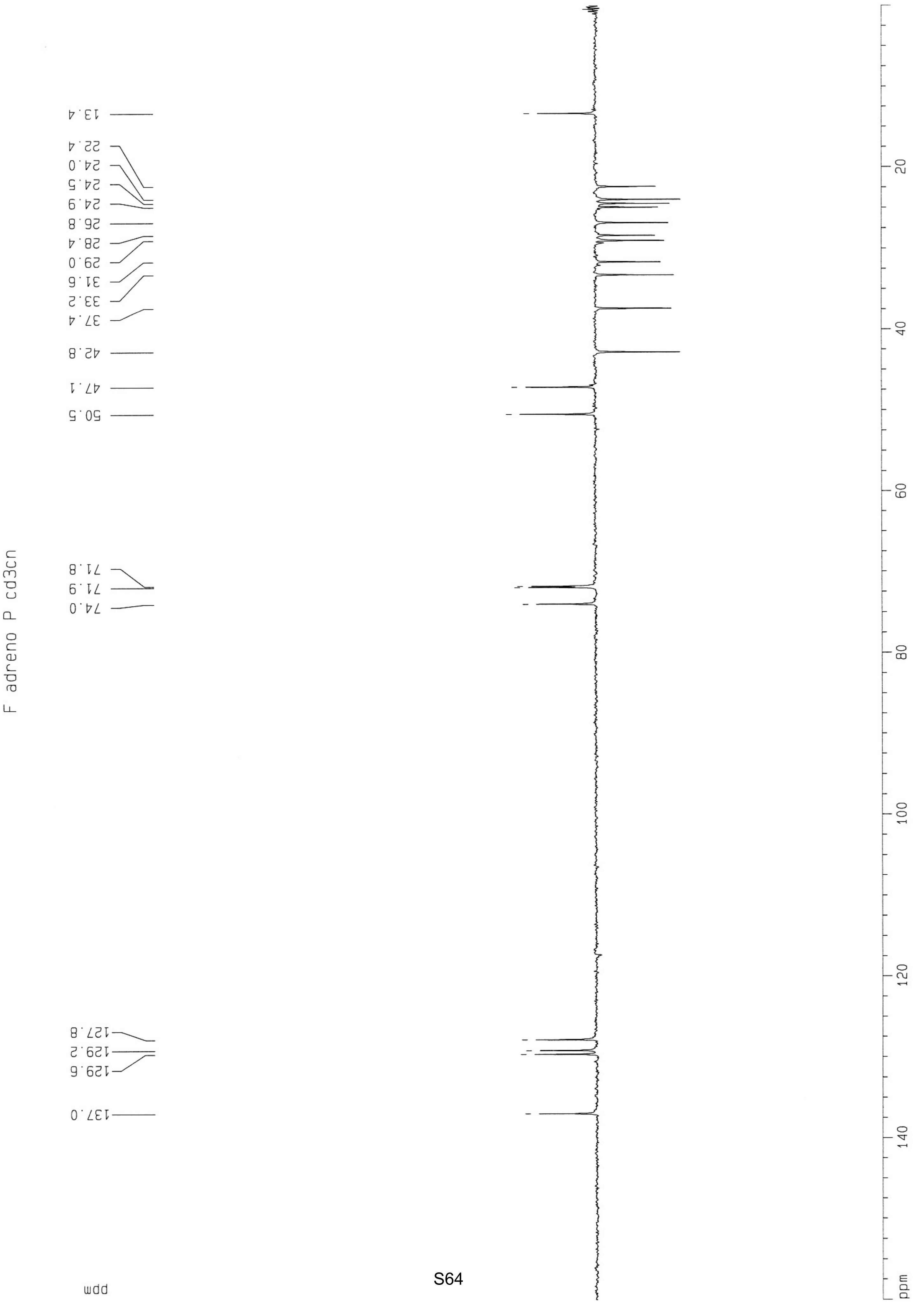
0.58
0.85
1.13
13.36
13.58
22.40
23.98
24.60
24.95
26.84
28.41
29.06
31.64
33.76
37.41
42.83
47.15
50.49
59.80
71.66
71.89
73.96
117.28
127.68
129.15
129.64
137.07
173.37
ppm
20
40
60
80
100
120
140
160
180
ppm

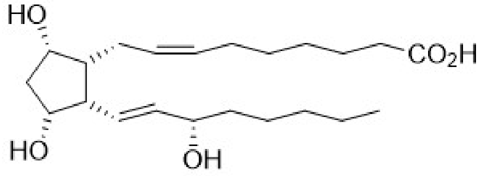

ALP XI 85 cd3cn
13.4
13.6
22.4
24.0
24.6
25.0
26.8
28.4
29.1
31.6
33.8
37.4
42.8
47.2
50.5
59.8
71.7
71.9
74.0
127.7
129.2
129.6
137.1
ppm
20
40
60
80
100
120
140
160
180
ppm

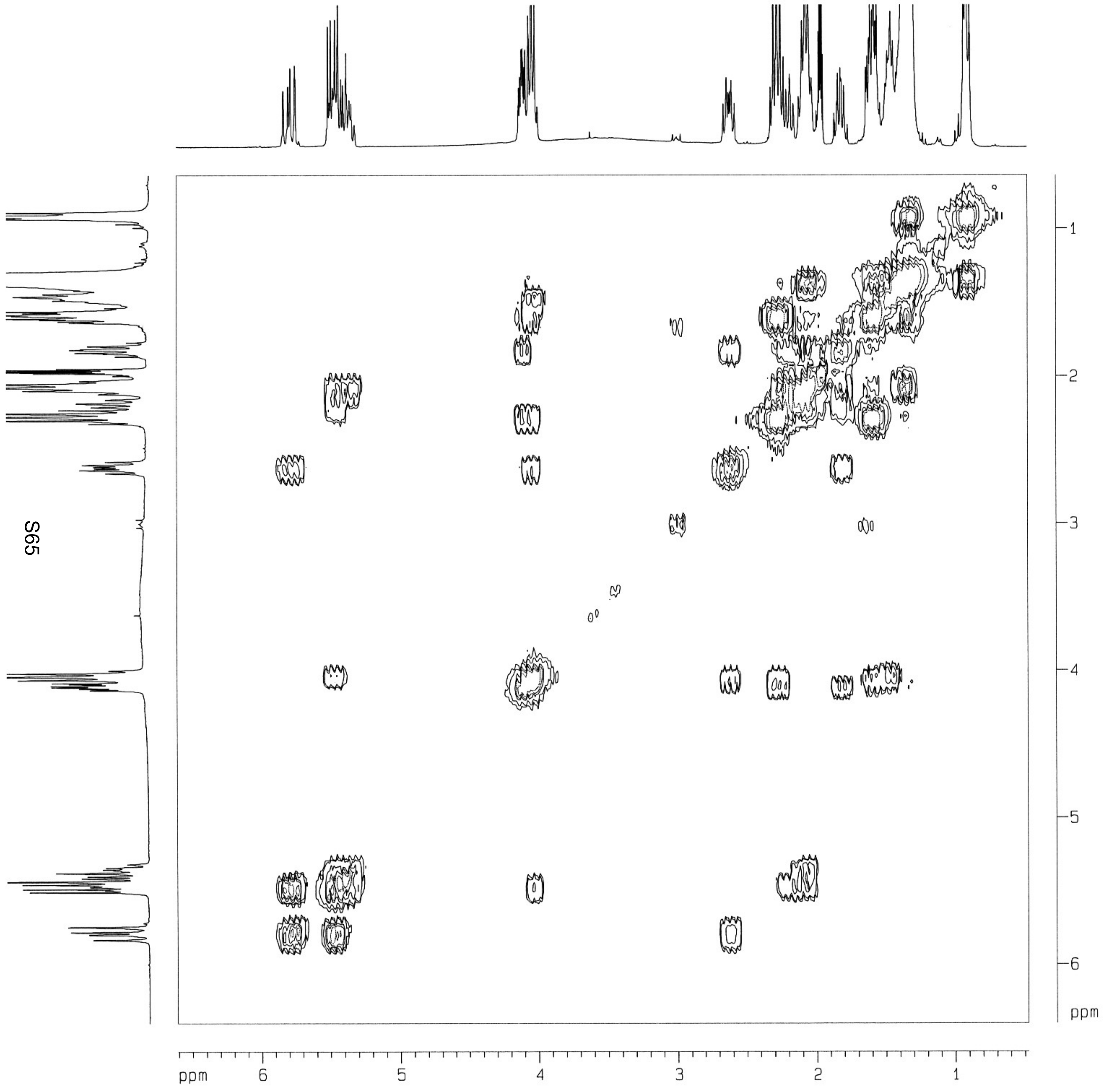

F DdrenoP cd3cn ottobre 3
Hz
1751.03
1750.08
1740.50
1739.53
1735.60
1734.64
1725.06
1724.14
1653.51
1647.29
1643.05
1642.24
1640.58
1638.05
1632.07
1625.36
1621.50
1614.56
1607.49
1241.54
1238.71
1235.45
1232.79
1229.55
1227.10
1220.66
1213.49
1207.05
1201.68
1200.72
792.08
785.45
781.66
691.09
683.72
676.31
629.75
623.23
616.60
594.72
592.24
589.76
587.30
485.28
482.59
477.77
475.20
471.16
468.38
438.45
416.68
410.44
406.69
403.22
400.01
396.53
391.31
290.48
280.14
273.51
266.58
HO
HO
OH
CO2H
7
Integral
2.503
7.392
90.105
ppm
6
5
4
3
2
1


F-AdrenoP cd3cn
-0.53
-0.25
0.02
0.30
0.57
0.85
1.12
13.36
22.39
23.98
24.47
24.94
26.81
28.36
28.99
31.62
33.23
37.38
42.80
47.14
50.48
71.78
71.93
73.98
117.28
127.84
129.18
129.65
136.96
174.32
ppm
0
20
40
60
80
100
120
140
160
180
ppm

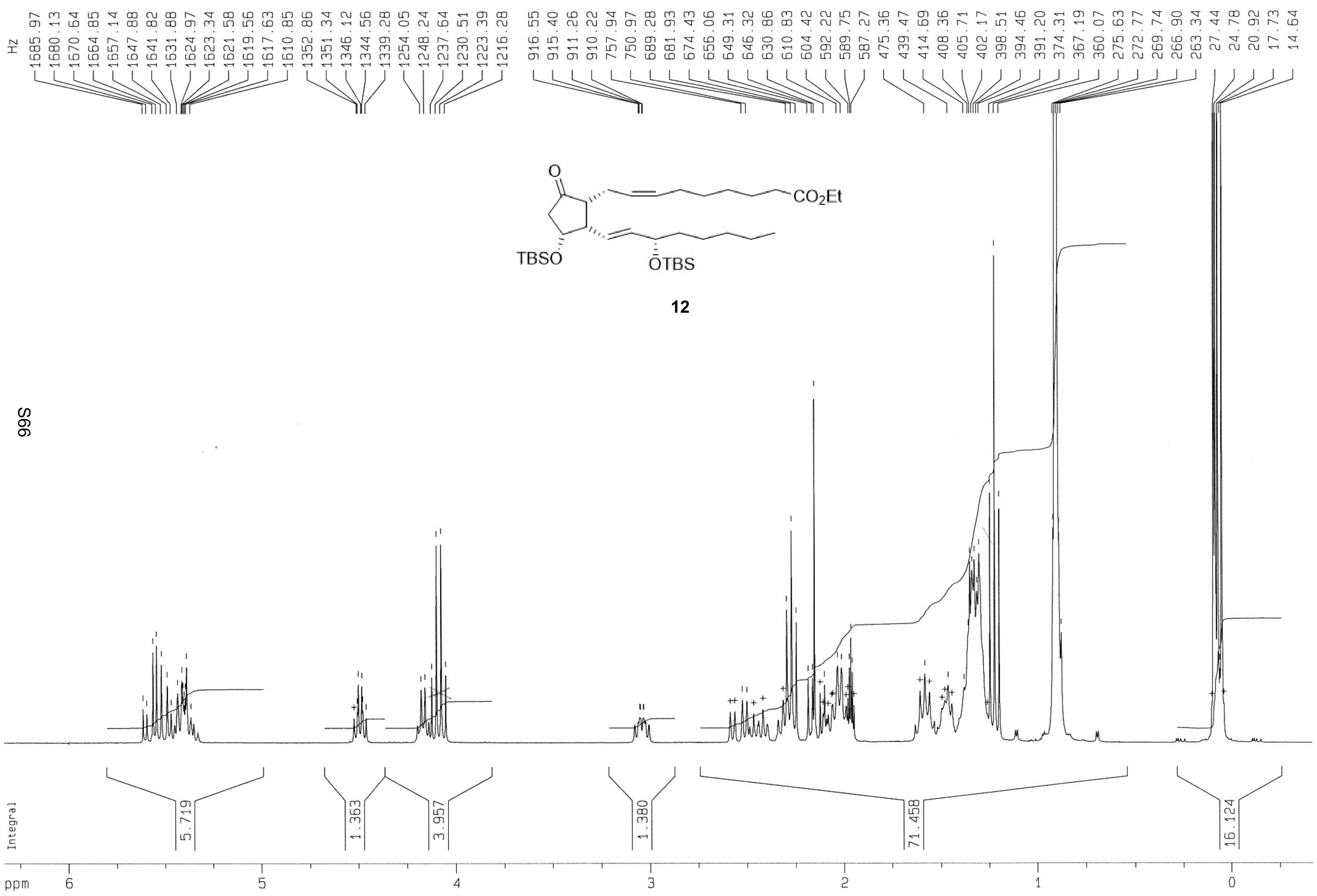

F adreno P cd3cn
13.4
22.4
24.0
24.5
24.9
26.8
28.4
29.0
31.6
33.2
37.4
42.8
47.1
50.5
71.8
71.9
74.0
127.8
129.2
129.6
137.0
ppm
20
40
60
80
100
120
140
ppm

ALP adreno pf cd3cn

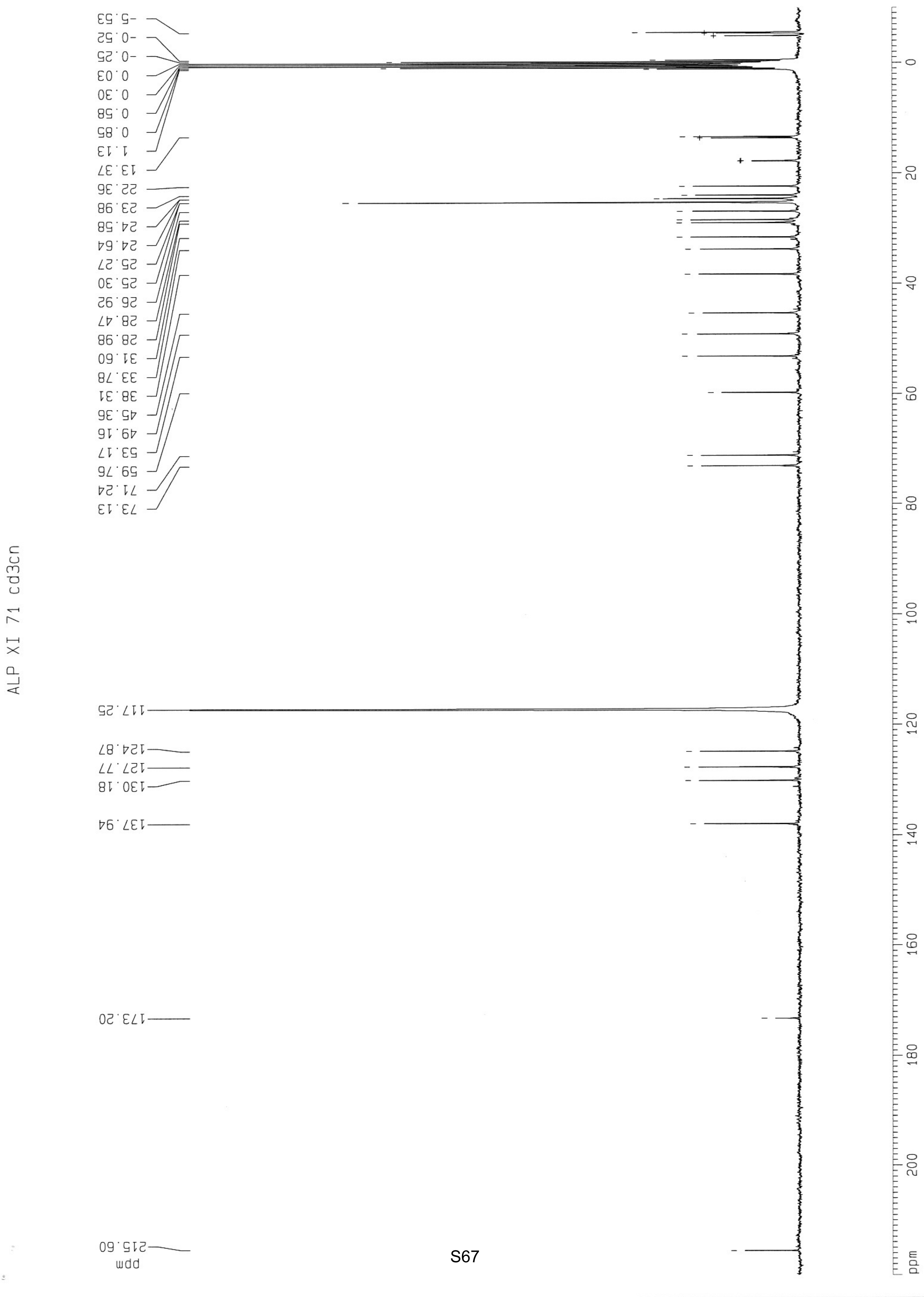


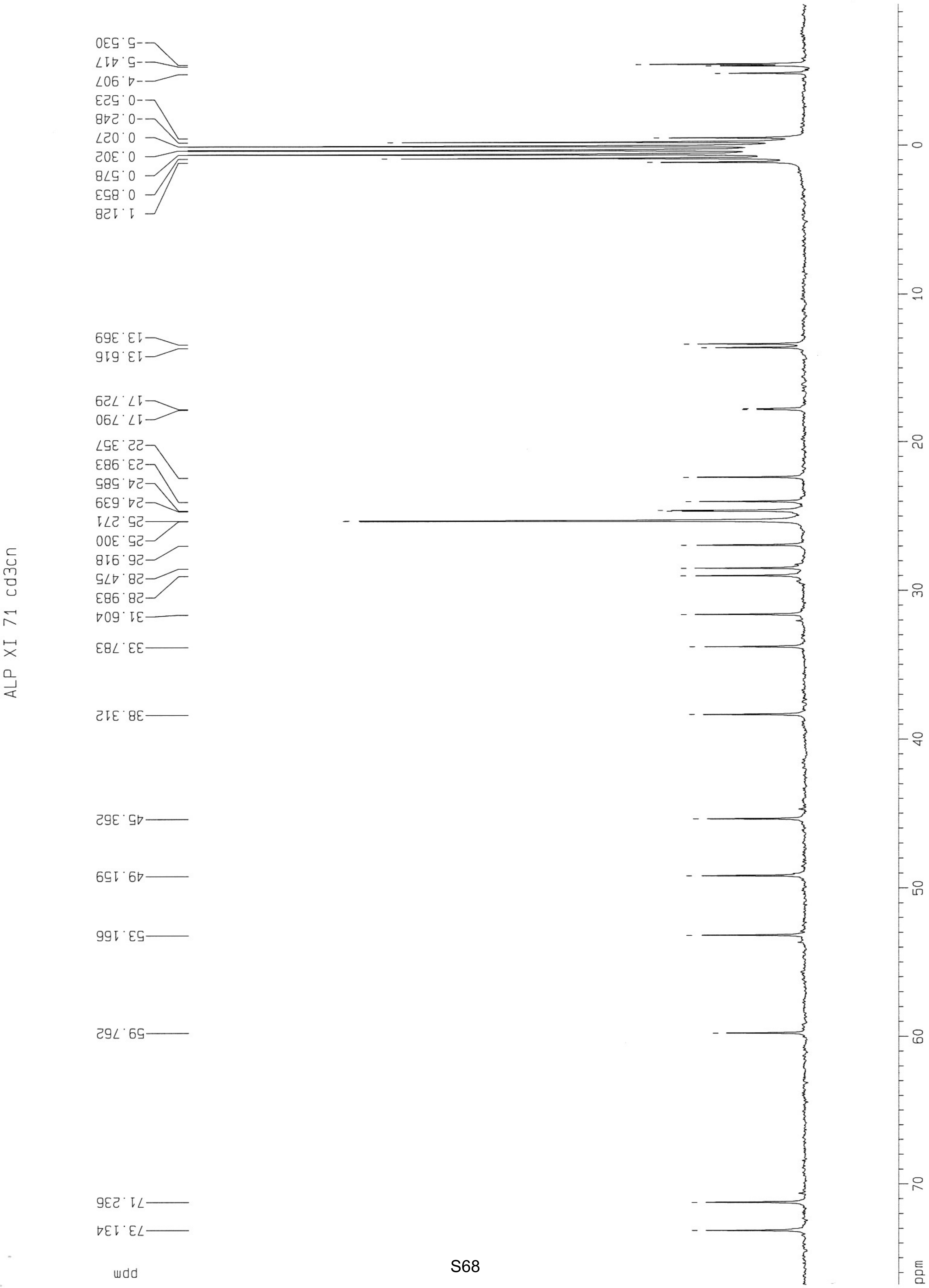


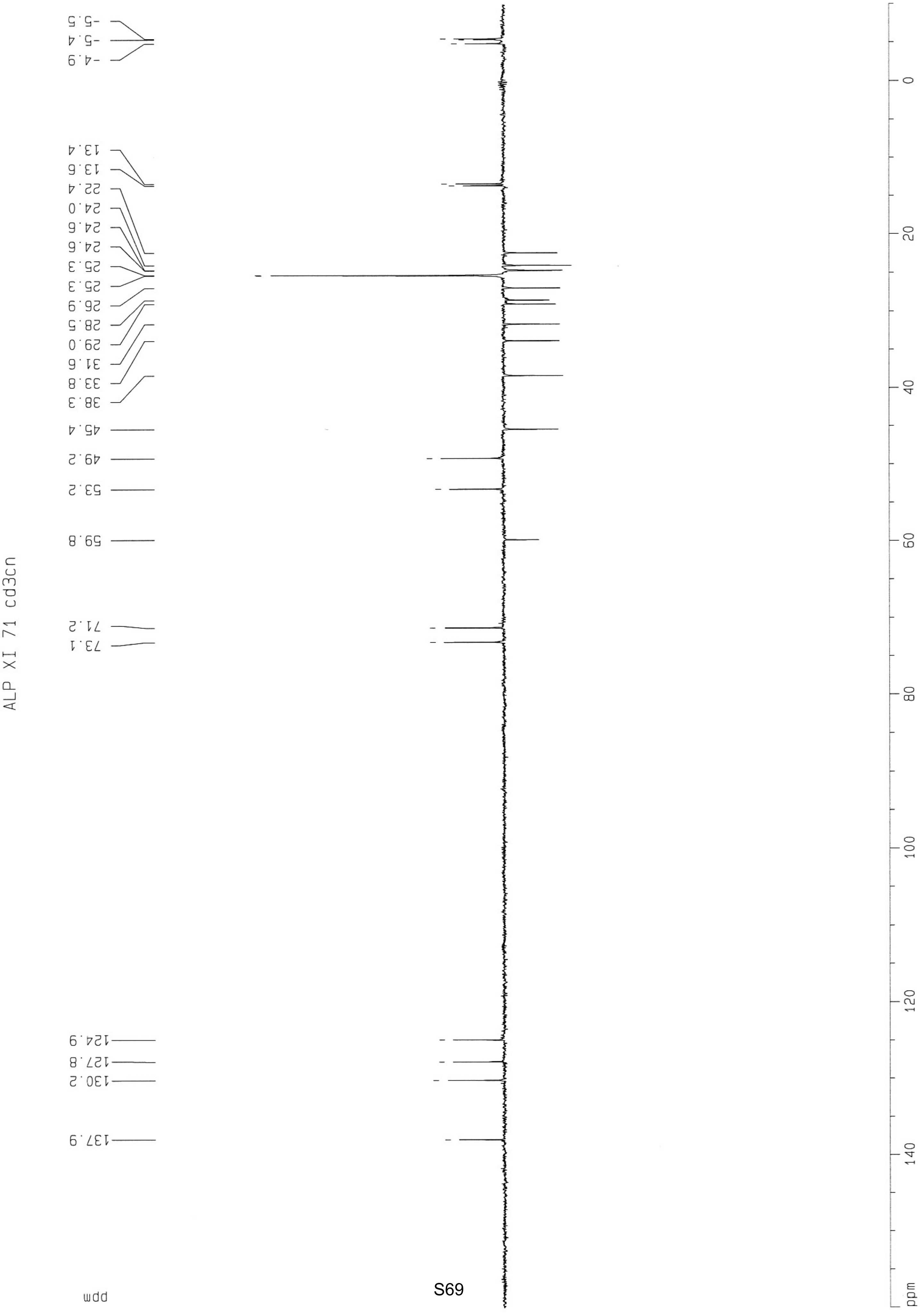
ALP-XI-71 cd3cn luglio 5

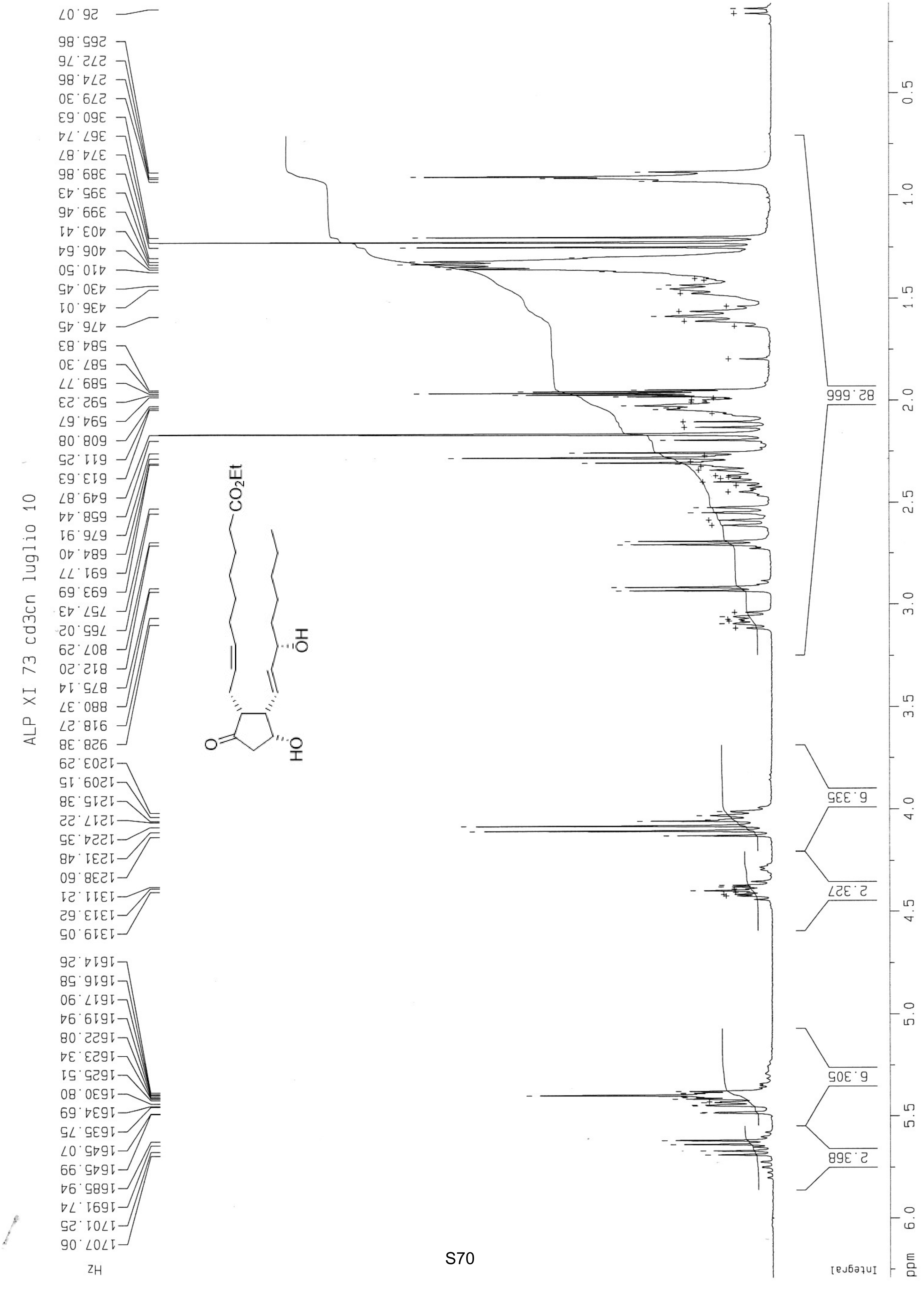


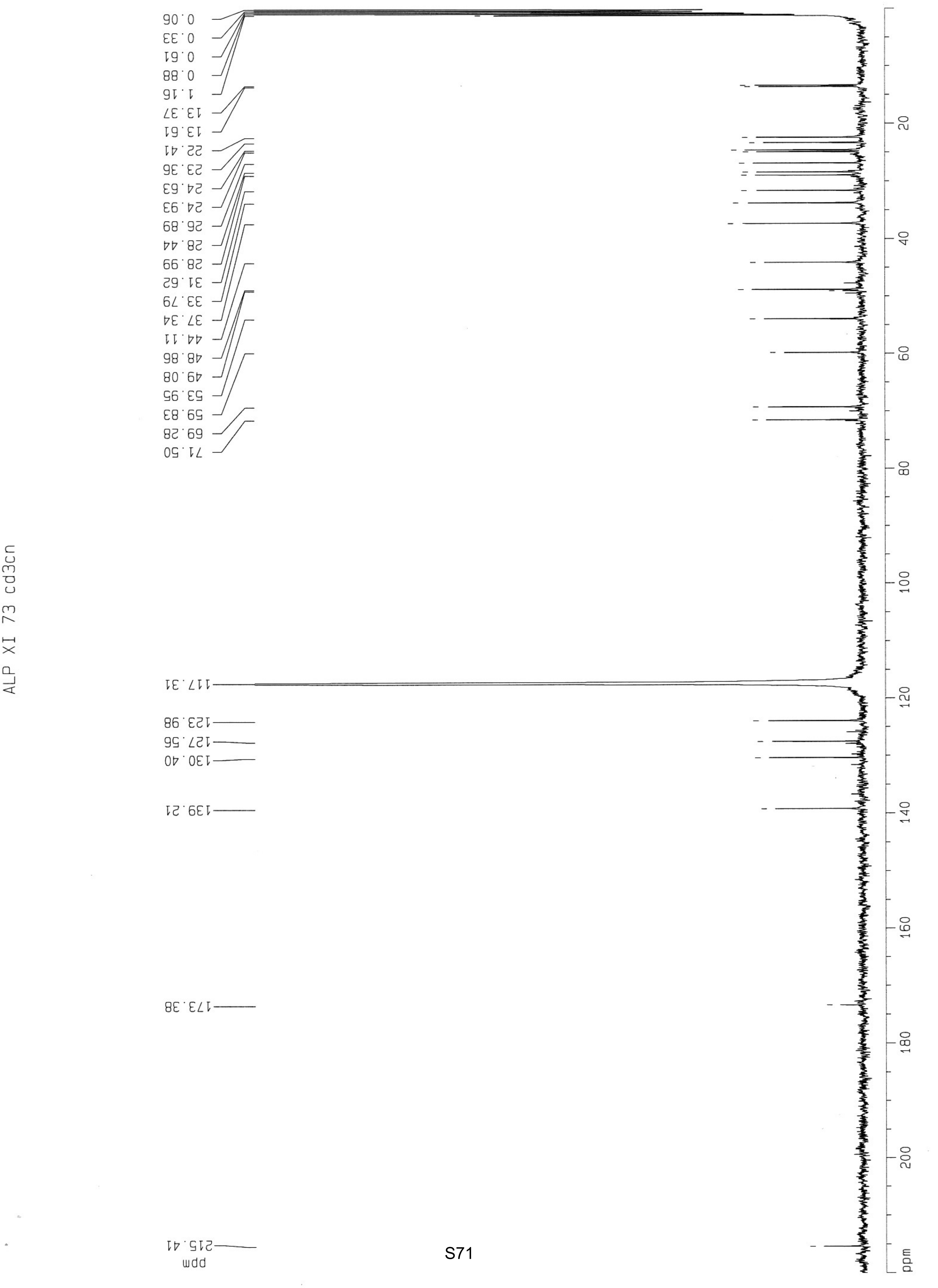
12

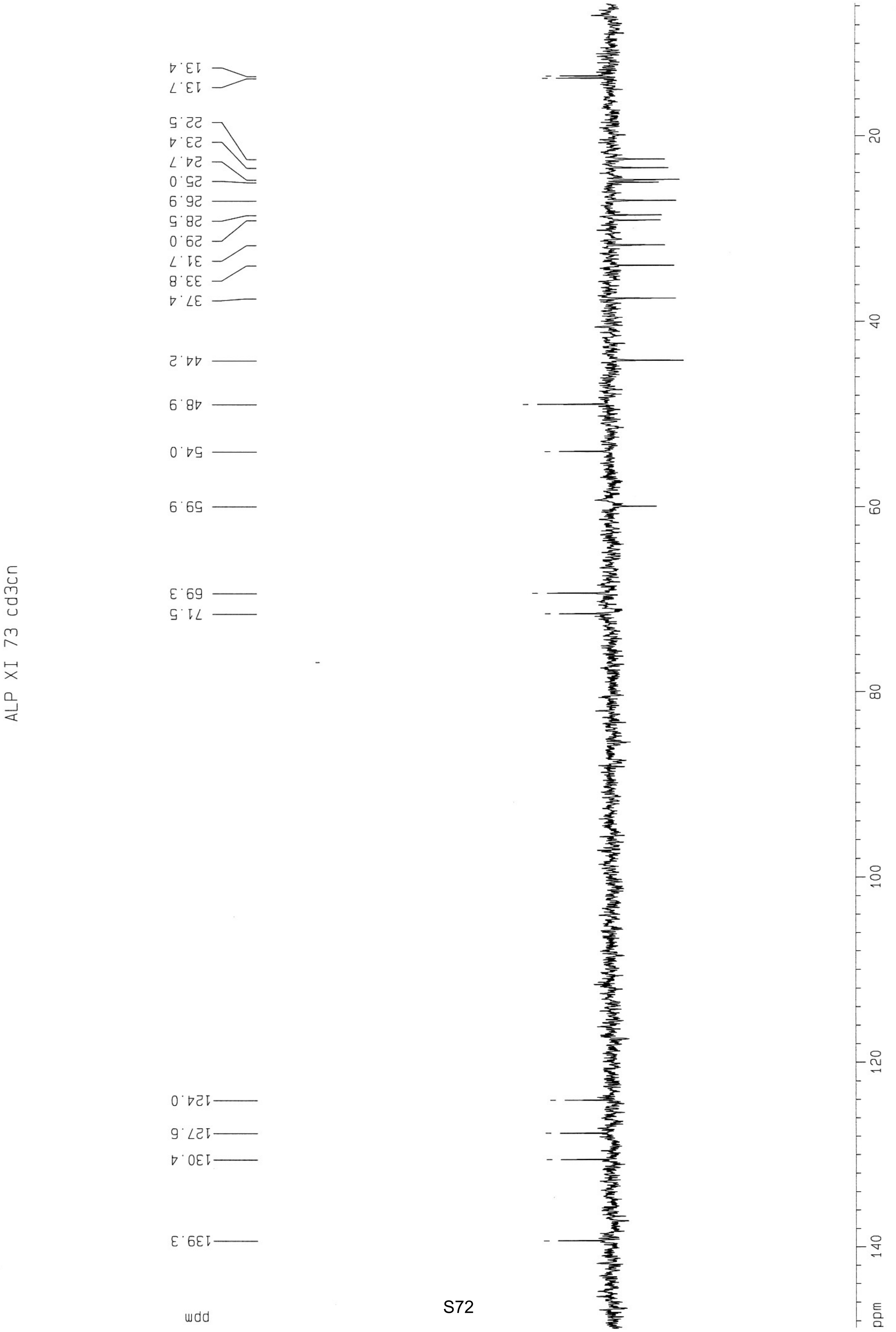

ALP XI 71 cd3cn
-5.53
-0.52
-0.25
0.03
0.30
0.58
0.85
1.13
13.37
22.36
23.98
24.58
24.64
25.27
25.30
26.92
28.47
28.98
31.60
33.78
38.31
45.36
49.16
53.17
59.76
71.24
73.13
117.25
124.87
127.77
130.18
137.94
173.20
215.60
ppm
0
20
40
60
80
100
120
140
160
180
200
ppm


ALP XI 71 cd3cn
-5.530
-5.417
-4.907
-0.523
-0.248
0.027
0.302
0.578
0.853
1.128
13.369
13.616
17.729
17.790
22.357
23.983
24.585
24.639
25.271
25.300
26.918
28.475
28.983
31.604
33.783
38.312
45.362
49.159
53.166
59.762
71.236
73.134
ppm
0
10
20
30
40
50
60
70
ppm

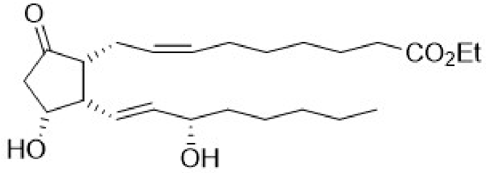

ALP XI 71 cd3cn
-5.5
-5.4
-4.9
13.4
13.6
22.4
24.0
24.6
24.6
25.3
25.3
26.9
28.5
29.0
31.6
33.8
38.3
45.4
49.2
53.2
59.8
71.2
73.1
124.9
127.8
130.2
137.9
ppm
0
20
40
60
80
100
120
140
ppm

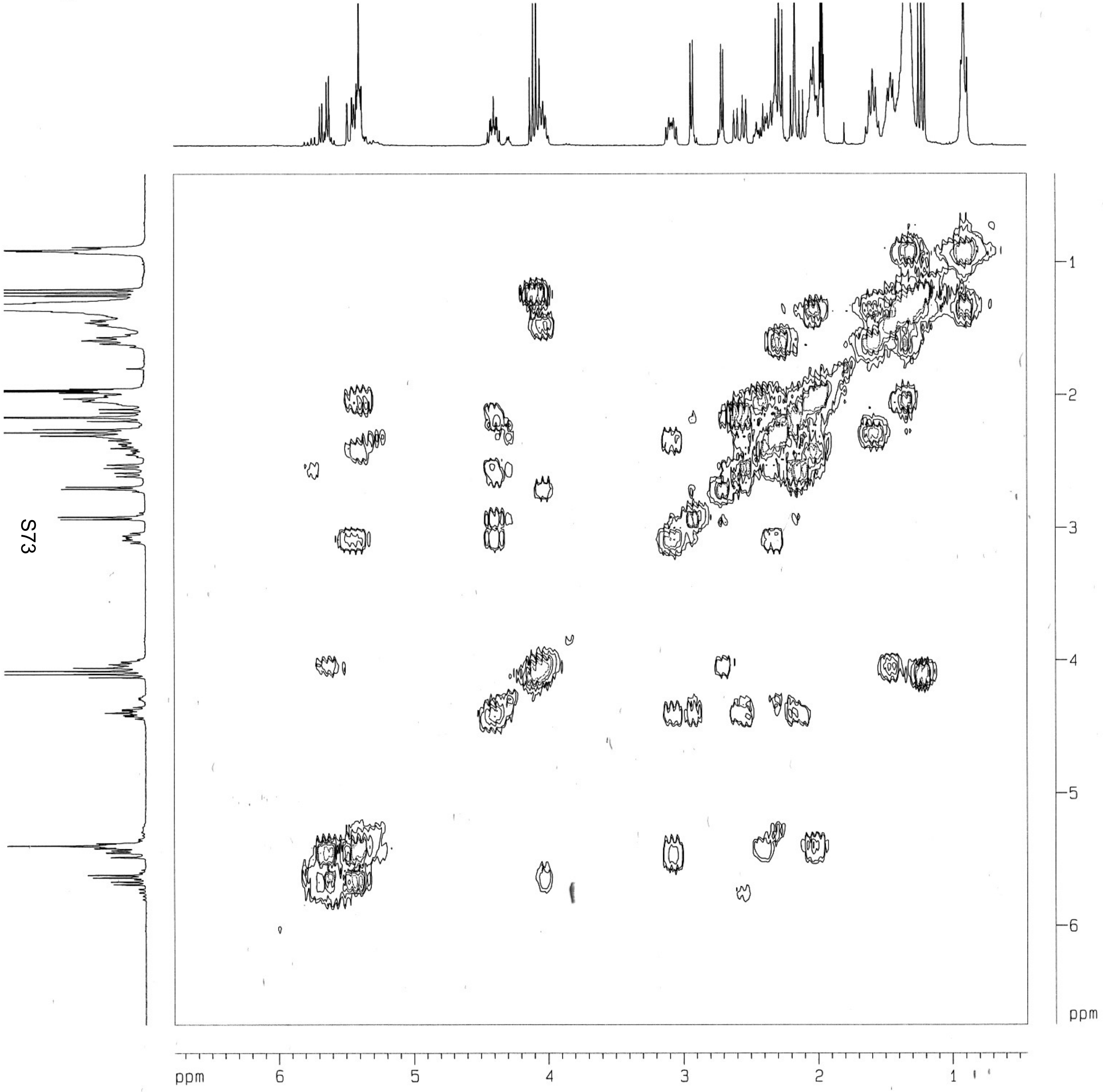

ALP XI 73 cd3cn luglio 10
CO$_2$Et
OH
HO
O
26.07
265.86
272.76
274.86
279.30
360.63
367.74
374.87
389.86
395.43
399.46
403.41
406.64
410.50
430.45
436.01
476.45
584.83
587.30
589.77
592.23
594.67
608.08
611.25
613.63
649.87
658.44
676.91
684.40
691.77
693.69
757.43
765.02
807.29
812.20
875.14
880.37
918.27
928.38
1203.29
1209.15
1215.38
1217.22
1224.35
1231.48
1238.60
1311.21
1313.62
1319.05
1614.26
1616.58
1617.90
1619.94
1622.08
1623.34
1625.51
1630.80
1634.69
1635.75
1645.07
1645.99
1685.94
1691.74
1701.25
1707.06
Hz
82.666
6.335
2.327
6.305
2.368
Integral
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
ppm

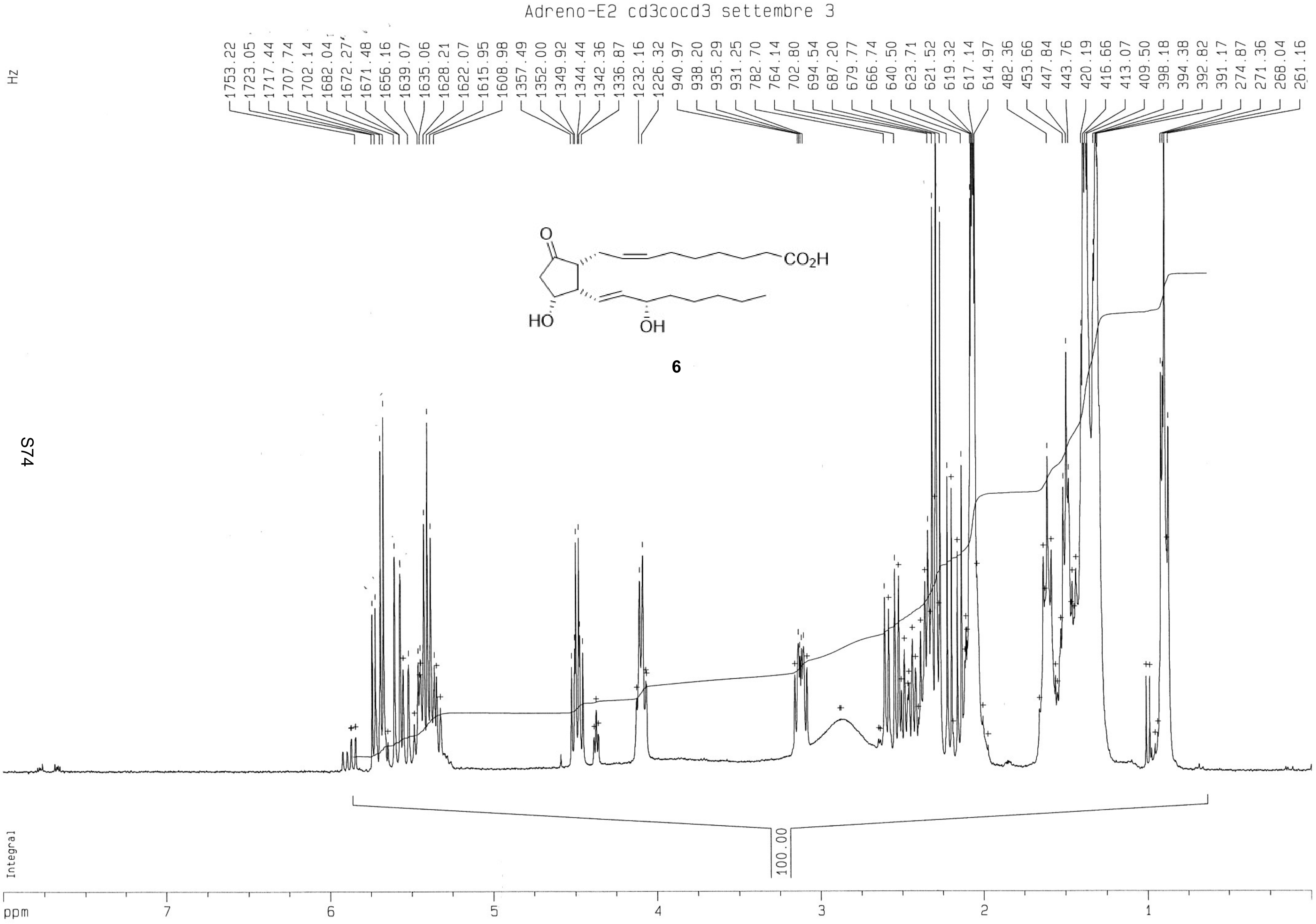

ALP XI 73 cd3cn
0.06
0.33
0.61
0.88
1.16
13.37
13.61
22.41
23.36
24.63
24.93
26.89
28.44
28.99
31.62
33.79
37.34
44.11
48.86
49.08
53.95
59.83
69.28
71.50
117.31
123.98
127.56
130.40
139.21
173.38
215.41
ppm
20
40
60
80
100
120
140
160
180
200
ppm

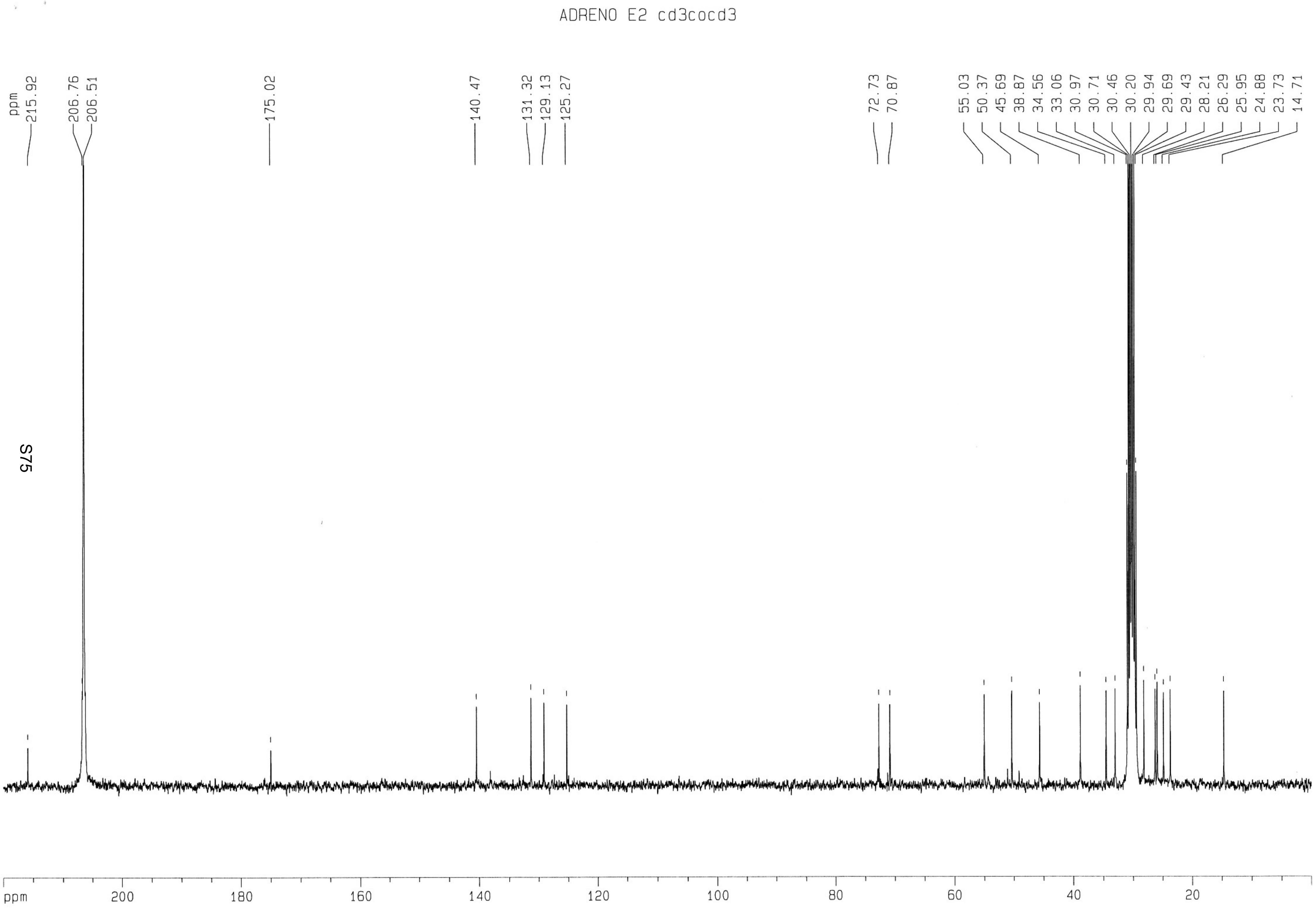

ALP XI 73 cd3cn
13.4
13.7
22.5
23.4
24.7
25.0
26.9
28.5
29.0
31.7
33.8
37.4
44.2
48.9
54.0
59.9
69.3
71.5
124.0
127.6
130.4
139.3
ppm
20
40
60
80
100
120
140
ppm

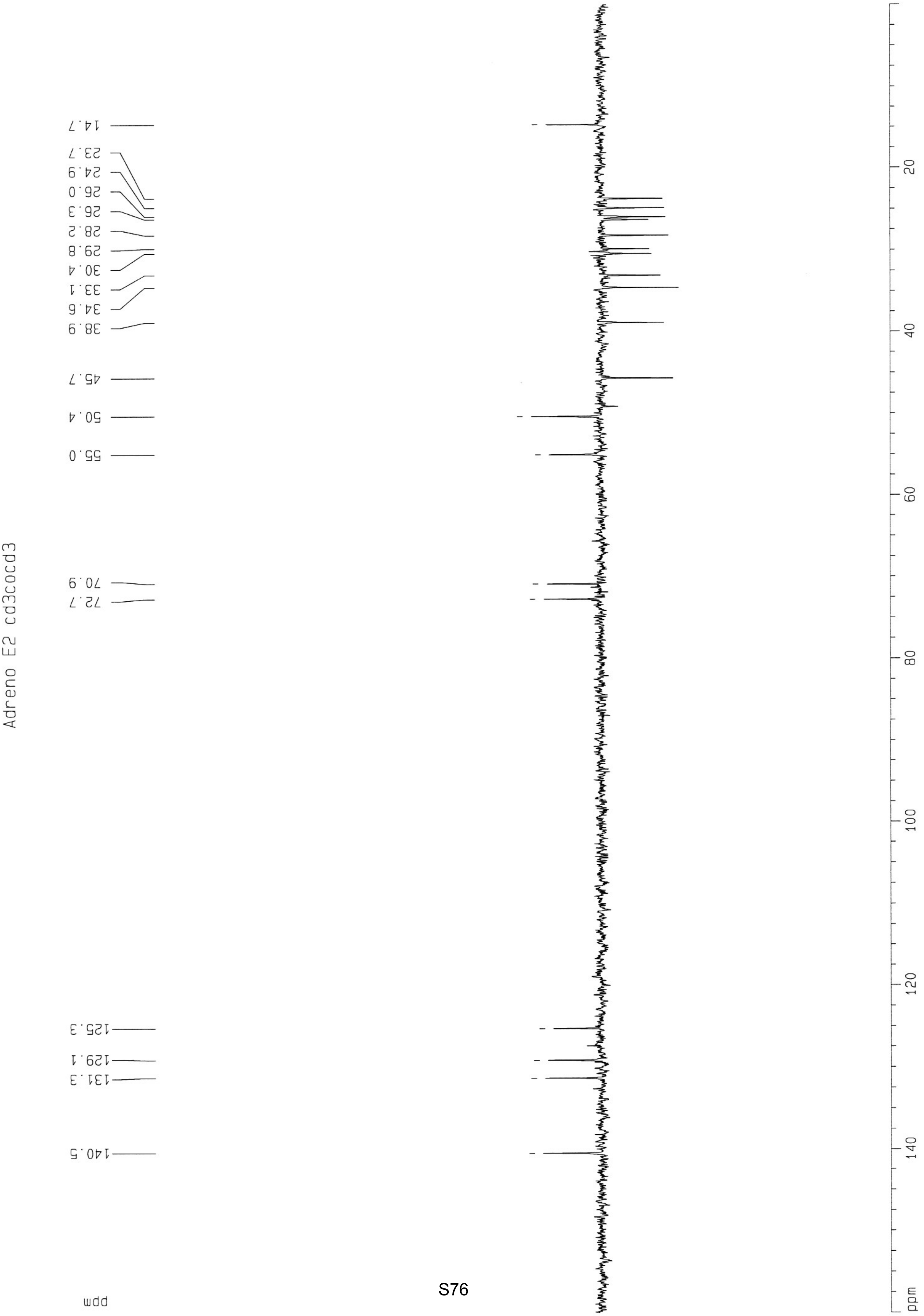
ALP XI






Adreno-E2 cd3cocd3 settembre 3
Hz
1753.22
1723.05
1717.44
1707.74
1702.14
1682.04
1672.27
1671.48
1656.16
1639.07
1635.06
1628.21
1622.07
1615.95
1608.98
1357.49
1352.00
1349.92
1344.44
1342.36
1336.87
1232.16
1226.32
940.97
938.20
935.29
931.25
782.70
764.14
702.80
694.54
687.20
679.77
666.74
640.50
623.71
621.52
619.32
617.14
614.97
482.36
453.66
447.84
443.76
420.19
416.66
413.07
409.50
398.18
394.38
392.82
391.17
274.87
271.36
268.04
261.16
O
CO2H
HO
OH
6
Integral
100.00
ppm
7
6
5
4
3
2
1


ADRENO E2 cd3cocd3
ppm
215.92
206.76
206.51
175.02
140.47
131.32
129.13
125.27
72.73
70.87
55.03
50.37
45.69
38.87
34.56
33.06
30.97
30.71
30.46
30.20
29.94
29.69
29.43
28.21
26.29
25.95
24.88
23.73
14.71
ppm
200
180
160
140
120
100
80
60
40
20

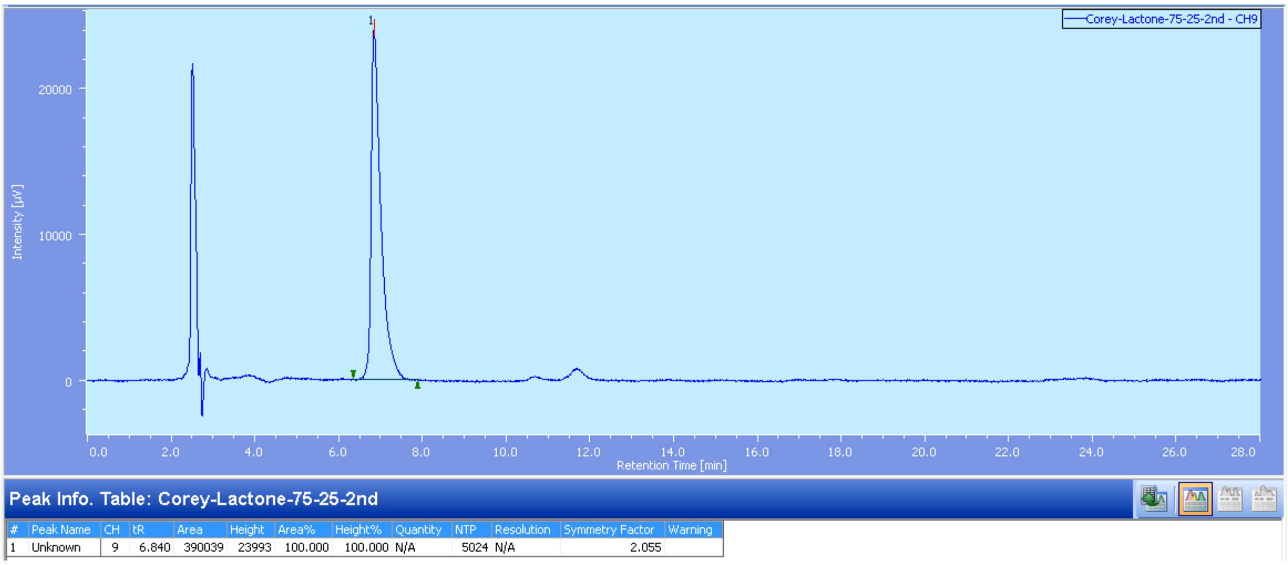


Adreno E2 cd3cocd3
14.7
23.7
24.9
26.0
26.3
28.2
29.8
30.4
33.1
34.6
38.9
45.7
50.4
55.0
70.9
72.7
125.3
129.1
131.3
140.5
ppm
20
40
60
80
100
120
140
ppm

Idroboration with BH_3*DMS on Compound **8a**

Column: Hypersil LiChroCART 250-4; 4.6 x 250 (5 µ) Direct Phase.
Flow: 1 mL /min
Eluent: *n*Hexane-*i*PrOH 75:25
UV data: 204 nm

Corey Lactone:

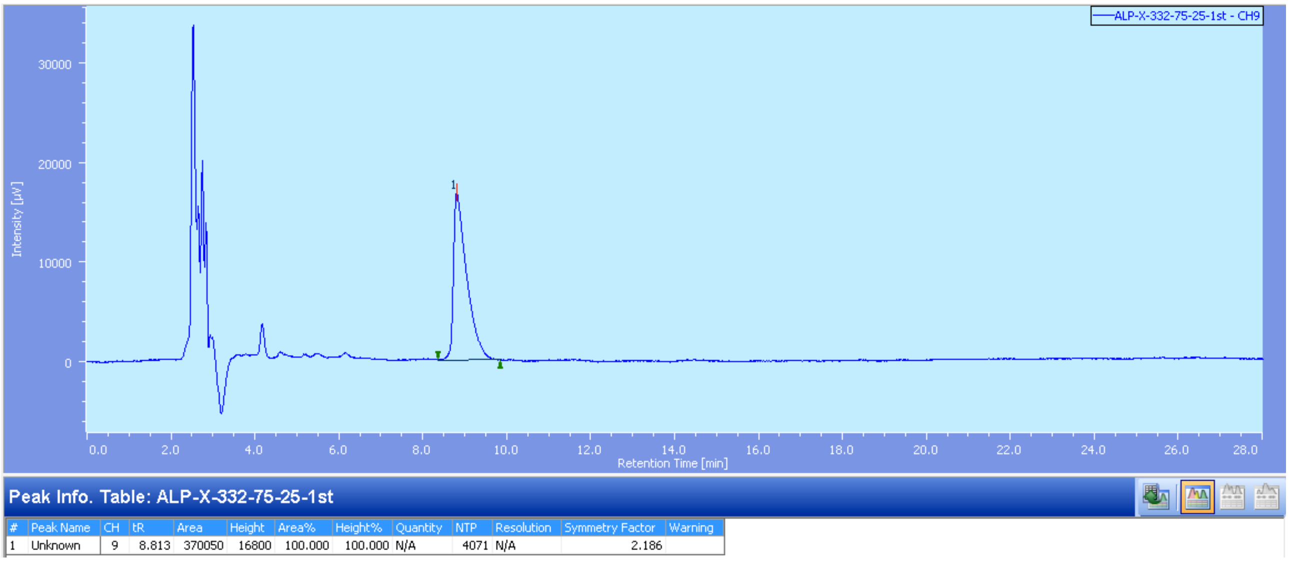


Peak Info. Table: Corey-Lactone-75-25-2nd

#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	6.840	390039	23993	100.000	100.000	N/A	5024	N/A	2.055	

Chromatographic Profile UV at 204 nm with integration results.

epi Corey Lactone:



Peak Info. Table: ALP-X-332-75-25-1st

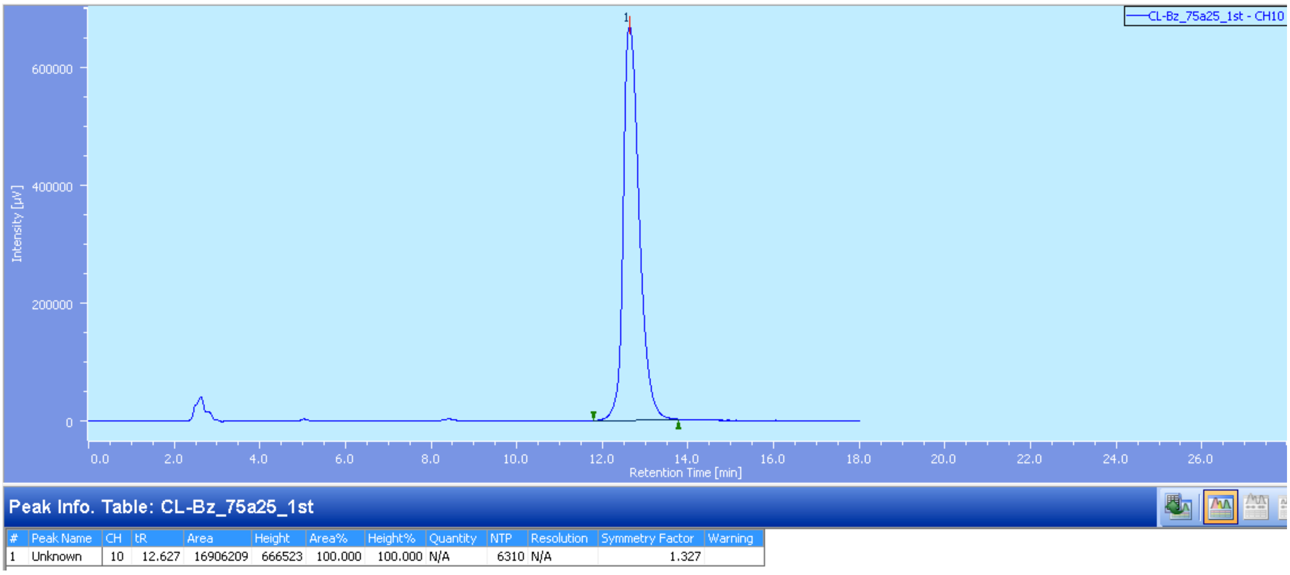
#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.813	370050	16800	100.000	100.000	N/A	4071	N/A	2.186	

Chromatographic Profile UV at 204 nm with integration results.

Idroboration with BH_3*DMS on Compound **8b**

Column: Hypersil LiChroCART 250-4; 4.6 x 250 (5 μ) Direct Phase.
Flow: 1 mL /min
Eluent: *n*Hexane-*i*PrOH 75:25
UV data: 254 nm

Corey Lactone-Bz:

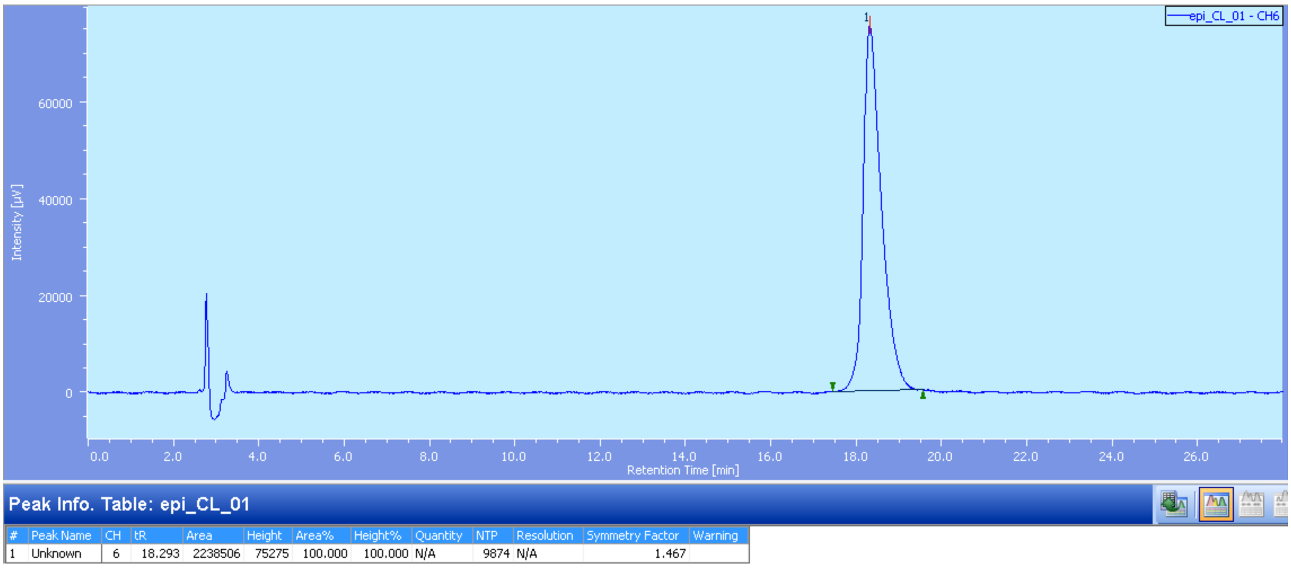


Peak Info. Table: CL-Bz_75a25_1st

#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	12.627	16906209	666523	100.000	100.000	N/A	6310	N/A	1.327	

Chromatographic Profile UV at 254 nm with integration results.

epi Corey Lactone-Bz:



Peak Info. Table: epi_CL_01

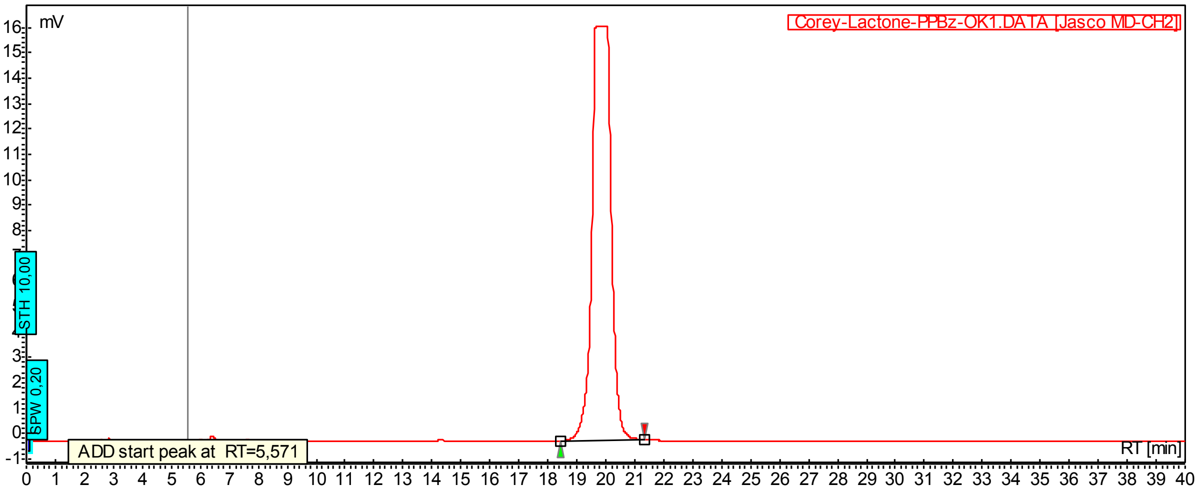
#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	6	18.293	2238506	75275	100.000	100.000	N/A	9874	N/A	1.467	

Chromatographic Profile UV at 254 nm with integration results.

Idroboration with BH$_3$*DMS on compound **8c**

Column: Hypersil LiChroCART 250-4; 4.6 x 250 (5 µ) Direct Phase.
Flow: 1 mL /min
Eluent: *n*Hexane-*i*PrOH 80:20

Corey Lactone Standard PPBz:

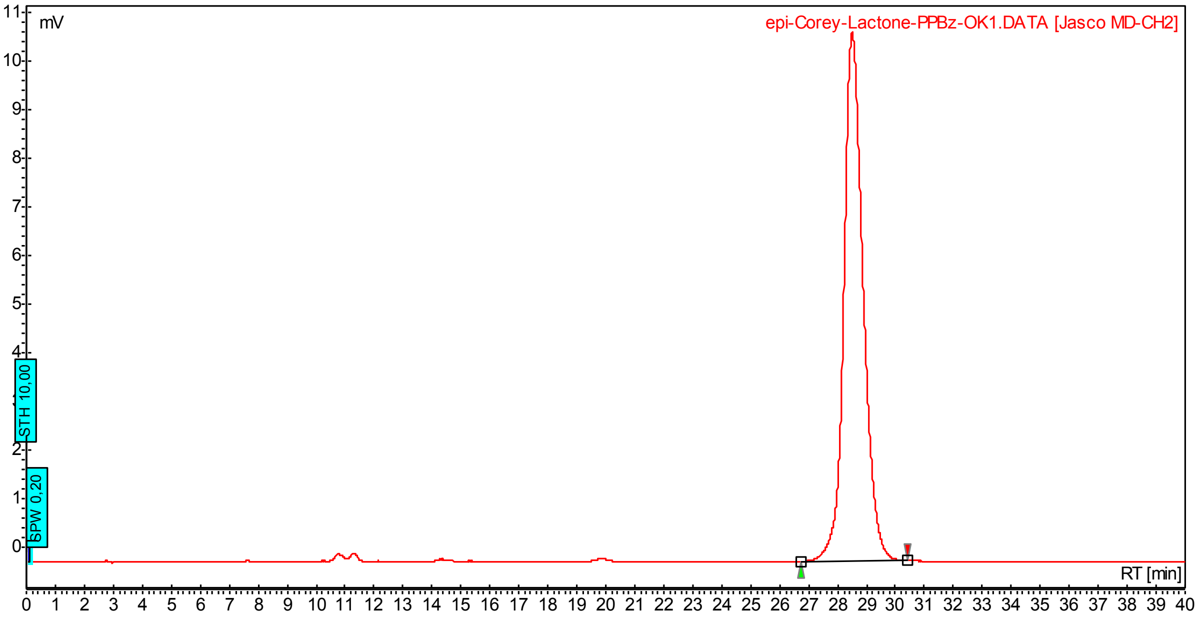


Chromatographic Profile UV at 260 nm

Integration Results

#	Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Corey Lactone	18,44	19,717	21,337	100	16,3	12,6	10
Total					100	16,3	12,6	10

epi-Corey Lactone Standard PPBz:

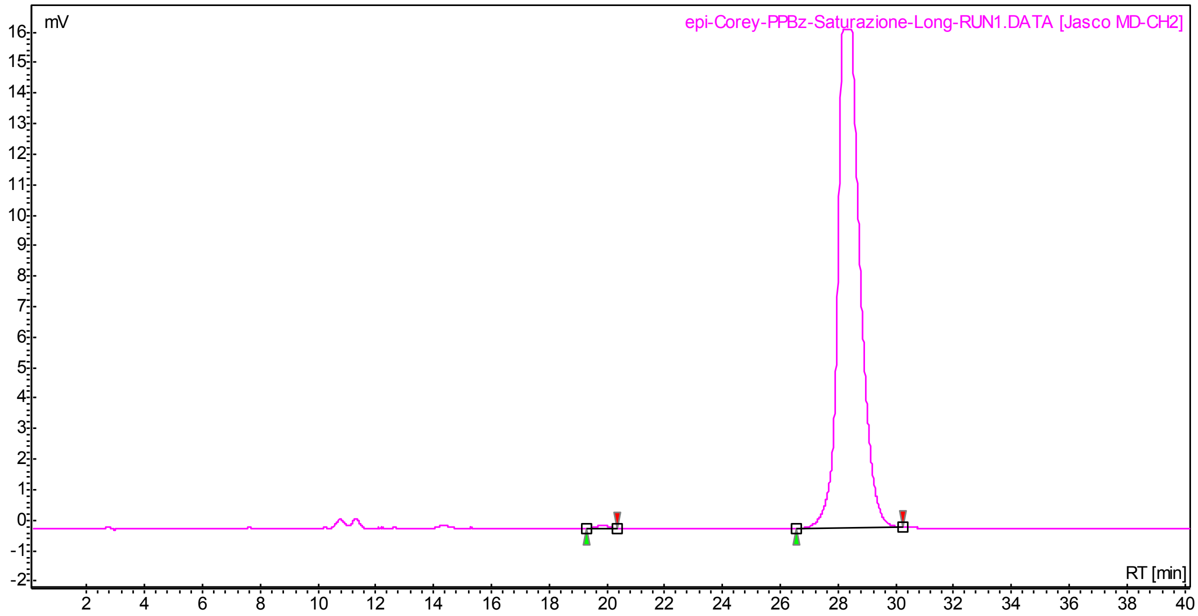


Chromatographic Profile UV at 260 nm

Integration results

#	Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	*epi*-Corey Lactone	26,741	28,5	30,418	100	10,9	8,4	10
Total					100	10,9	8,4	10

D.E. Evaluation.



Chromatographic Profile UV at 260 nm

Integration results.

#	Name	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [mV]	Area [mV.Min]	Area % [%]
1	Corey Lactone	19,307	19,842	20,382	0,36	0,1	0,1	0,36
2	*epi-Corey*	26,587	28,225	30,275	99,64	16,3	14,7	99,64
Total					100	16,4	14,8	100

D.E. = 99.28 %