Supporting Information

for

3α,5α-Cyclocholestan-6β-yl ethers as donors of the cholesterol moiety for the electrochemical synthesis of cholesterol glycoconjugates

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Experimental section including ^{1}H, ^{13}C NMR, and mass spectra

for all new compounds

Experimental

Cyclic voltammograms were recorded with iR compensation at 25 °C using a three-electrode potentiostat (Princeton Applied Research, model Parstat 2273). The experiments were conducted in a 3-mL electrochemical cell with an argon-purge system. The working electrode was a Bioanalytical Systems platinum inlay (1 mm in diameter), the auxiliary electrode was a platinum mesh (contained in a glass tube with a medium porosity glassfrit), and the reference electrode was Ag/0.1 M $AgNO_3$ in acetonitrile. The latter was contained in a Pyrex tube with a cracked softglass tip which was placed inside a Luggin capillary. Before each experiment, the working electrode was polished using Buehler Micropolish Alumina Gamma 3B and a Buehler Microcloth polishing cloth, rinsed with dichloromethane and dried. In all of the measurements, 0.2M solution of tetrabutylammonium tetrafluoroborate ($TBABF_4$) from Aldrich in dichloromethane was used as a supporting electrolyte.

The preparative electrolyses were performed with a potentiostat/galvanostat (Princeton Applied Research, model Parstat 2273) under galvanostatic conditions using a current that was equal in a typical experiment to 7.5 mA and a reaction time of 4000 s. The current applied was the maximum current available for the electrolysis set-up being used (power supply and ohmic resistance). The reactions were monitored by TLC and stopped when no further increase in the concentration of the glycosylation products was observed. A divided H-cell was used in which the cathodic and anodic compartments (3.5 mL of electrolyte each) were separated by a glass frit. In all measurements, 0.1 M solution of tetrabutylammonium tetrafluoroborate ($TBABF_4$) from Aldrich in dichloromethane was used as a supporting electrolyte. The steroid (0.30 mmol) and sugar (0.36 mmol) substrates were introduced into the anodic compartment together with 0.3 g of 3 Å molecular sieves added to eliminate traces of water, whereas anionite (1.5–2 g, Dowex 2 × 8, 200–400 mesh, perchlorate form) was placed in the cathodic compartment to eliminate chloride ions that are formed by the reduction of dichloromethane. The solutions in both compartments were stirred during electrolysis and, additionally, a continuous flow of argon was applied in the anodic compartment. A platinum mesh was used as a cathode and a platinum plate (2 × 1.5 cm) was used as an anode. All measurements were performed at 25 °C.

The sugar (1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose; **7**) [1] and steroidal substrates, 3α,5α-cyclocholestan-6β-ol (*i*-cholesterol; **6a**) [2], 6β-methoxy-3α,5α-cyclocholestane (**6b**) [3], and 6β-ethoxy-3α,5α-cyclocholestane (**6c**) [4], were prepared according to known procedures.

Melting points were determined on a Toledo Mettler-MP70 apparatus. ^1H and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded on a Bruker Avance II spectrometer in $CDCl_3$ solutions with TMS as the internal standard (only selected signals in the ^1H NMR spectra are reported; sugar protons are marked with the 'prime' index). Infrared spectra were recorded on a Nicolet series II Magna-IR 550 FTIR spectrometer in chloroform solutions. Mass spectra were recorded at 70 eV with a time-of-flight (TOF) AMD-604 spectrometer with electrospray ionization (ESI) or AutoSpec Premier (Waters) (EI).

Merck Silica Gel 60, F 256 TLC aluminum sheets were applied for thin-layer chromatographic analysis. For a visualization of the products, a 5% solution of phosphomolybdic acid in ethanol was used. The reaction products were separated by column chromatography performed on a 70–230 mesh silica gel (J. T. Baker).

Synthesis of 6β-benzyloxy-3α,5α-cyclocholestane (**6e**)

To cholesteryl *p*-tosylate (1 g; 1.9 mmol) dissolved in dioxane (50 mL) freshly dried potassium acetate (0.8 g; 5.7 mmol; 3 equiv.) and benzyl alcohol (6.2 g; 57 mmol; 30 equiv.) were added. The reaction mixture was refluxed for 24 h. After cooling it was poured into water (200 mL) and extracted with benzene (3 × 100 mL). The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was subjected to silica gel column chromatography. Elution with CH_2Cl_2/hexane (1:9) afforded 6β-benzyloxy-3α,5α-cyclocholestane (**6e**; 0.43 g; 48%).

6e: Colorless oil; $[\alpha]_D^{20}$ +37.0 (*c* 1.0, $CHCl_3$); Rf = 0.31 (hexane-AcOEt 98:2); IR, ν_{max} (cm^{-1}): 3064, 1496, 1093, 1067; ^{1}H NMR (ppm), δ: 7.35 (m, 4H, H-Ar), 7.27 (m, 1H, H-Ar), 4.66 (d, 1H, *J* = 12.5 Hz, O-CH_2Ph), 4.50 (d, 1H, *J* = 12.5 Hz, O-CH_2Ph), 2.98 (m, 1H, H-6), 1.11 (s, 3H, H-19), 0.93 (d, 3H, *J* = 6.5 Hz, H-21), 0.887 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.883 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.72 (s, 3H, H-18), 0.67 (dd, 1H, *J* = 4.9 Hz, *J* = 4.1 Hz, H-4α), 0.41 (dd, 1H, *J* = 8.0 Hz, *J* = 4.9 Hz, H-4β); ^{13}C NMR (ppm), δ: 140.1 (C), 128.2 (CH), 127.1 (CH), 126.9 (CH), 80.2 (CH), 70.0 (CH_2), 56.6 (CH), 56.4 (CH), 48.1 (CH), 43.3 (C), 42.8 (C), 40.4 (CH_2), 39.5 (CH_2), 36.2 (CH_2), 35.8 (CH), 35.7 (C), 35.4 (CH_2), 33.4 (CH_2), 30.6 (CH), 28.3 (CH_2), 28.0 (CH), 25.0 (CH_2), 24.2 (CH_2), 23.9 (CH_2), 22.84 (CH_2), 22.81 (CH_3), 22.6 (CH_3), 21.8 (CH), 19.5 (CH_3), 18.7 (CH_3), 13.2 (CH_2), 12.3 (CH_3); EI MS, *m/z:* 476 (M^+, 35%), 461 [(M-Me)$^+$, 7%], 385 [(M-Bn)$^+$, 77%], 370 [(M-Bn-Me)$^+$, 67%], 91 (100%).

6β-Isopropyloxy-3α,5α-cyclocholestane (**6d**) was obtained in a similar way (compound **6d** was eluted with hexane).

6d: Colorless oil; $[\alpha]_D^{20}$ +43.4 (*c* 1.0, $CHCl_3$); Rf = 0.39 (hexane-AcOEt 98:2); IR, ν_{max} (cm^{-1}): 1138, 1124, 1041; ^{1}H NMR (ppm), δ: 3.74 (h, 1H, *J* = 6.1 Hz, O-CH$(Me)_2$), 2.93 (m, 1H, H-6), 1.08 (d, 6H, *J* = 6.2 Hz, $(CH_3)_2$CH), 1.02 (s, 3H, H-19), 0.93 (d, 3H, *J* = 6.6 Hz, H-21), 0.881 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.877 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.73 (s, 3H, H-18), 0.58 (dd, 1H, *J* = 4.9 Hz, *J* = 3.9 Hz, H-4α), 0.33 (dd, 1H, *J* = 7.9 Hz, *J* = 4.9 Hz, H-4β); ^{13}C NMR (ppm), δ: 76.9 (CH), 67.1 (CH), 56.6 (CH), 56.4 (CH), 48.2 (CH), 43.2 (C), 42.8 (C), 40.4 (CH_2), 39.6 (CH_2), 36.4 (C), 36.2 (CH_2), 35.9 (CH), 35.8 (CH_2), 33.4 (CH_2), 30.4 (CH), 28.4 (CH_2), 28.0 (CH), 25.1 (CH_2), 24.3 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 22.52 (CH_3), 22.47 (CH_3), 22.3 (CH), 19.6 (CH_3), 18.7 (CH_3), 12.8 (CH_2), 12.2 (CH_3); EI MS, *m/z:* 428 [M^+, 56%], 413 [(M-Me)$^+$, 20%], 386 [(M-propene)$^+$, 17%], 371 [(M-Me-propene)$^+$, 81%], 43 (100%).

6β-(4-Hydroxyphenyloxy)-3α,5α-cyclocholestane (**6g**) was obtained in a similar way (compound **6g** was eluted with a hexane-ethyl acetate (93:7) mixture).

6g: Beige crystalline material, mp 54-56 °C (CH_2Cl_2-hexane); $[\alpha]_D^{20}$ +24.4 (*c* 0.33, $CHCl_3$); Rf = 0.27 (hexane-AcOEt 9:1); IR, ν_{max}(cm^{-1}): 3601, 3340, 1601, 1507, 1175, 827; ^{1}H NMR (ppm), *δ*: 6.79 (d, 2H, *J* = 9.0 Hz, H-Ar), 6.72 (d, 2H, *J* = 9.0 Hz, H-Ar), 4.36 (s, 1H, -OH), 3.64 (m, 1H, H-6), 1.16 (s, 3H, H-19), 0.93 (d, 3H, *J* = 6.5 Hz, H-21), 0.876 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.872 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.73 (s, 3H, H-18), 0.60 (dd, 1H, *J* = 5.1 Hz, *J* = 3.9 Hz, H-4α), 0.34 (dd, 1H, *J* = 7.9 Hz, *J* = 5.1 Hz, H-4β); ^{13}C NMR (ppm), *δ*: 152.4 (C), 150.1 (C), 119.2 (CH), 116.0 (CH), 82.5 (CH), 56.39 (CH), 56.35 (CH), 47.7 (CH), 43.2 (C), 42.7 (C), 40.2 (CH_2), 39.5 (CH_2), 36.6 (C), 36.2 (CH_2), 35.8 (CH), 34.5 (CH_2), 33.4 (CH_2), 30.3 (CH), 28.2 (CH_2), 28.0 (CH), 25.0 (CH_2), 24.1 (CH_2), 23.8 (CH_2), 23.5 (CH), 22.8 (CH_3), 22.7 (CH_2), 22.5 (CH_3), 19.9 (CH_3), 18.7 (CH_3), 12.6 (CH_2), 12.1 (CH_3); EI MS, *m/z:* 478 (M^+, 1%), 369 [(M-*p*-OH-PhO)$^+$, 100%].

Synthesis of 6β-phenyloxy-3α,5α-cyclocholestane (**6f**)

Phenol (10 g; 0.1 mol, 36 equiv.) was melted at 42 °C. Then cholesteryl *p*-tosylate (1.5 g; 2.8 mmol) and freshly dried potassium acetate (0.8 g; 8.2 mmol, 3 equiv.) were added. The stirred reaction mixture was maintained at this temperature for 2 h. After cooling it was poured into 100 mL of 1 M NaOH solution and extracted with benzene (3 × 100 mL). The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness *in vacuo*. The reaction products were separated by silica gel column chromatography. 6β-Phenyloxy-3α,5α-cyclocholestane (**6f**; 0.27 g, 21%) was eluted with hexane. Further elution with a hexane/ethyl acetate (99:1) mixture afforded cholesteryl phenyl ether **12f** (0.41 g; 32%).

6f: White crystals, mp 58-61 °C (AcOEt-hexane); $[\alpha]_D^{20}$ +36.5 (*c* 0.33, $CHCl_3$); Rf = 0.28 (hexane); IR, ν_{max} (cm^{-1}): 3064, 1597, 1243; ^{1}H NMR (ppm), δ: 7.26 (m, 2H, H-Ar), 6.91 (m, 3H, H-Ar), 3.82 (m, 1H, H-6), 1.19 (s, 3H, H-19), 0.94 (d, 3H, *J* = 6.5 Hz, H-21), 0.893 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.889 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.74 (s, 3H, H-18), 0.62 (dd, 1H, *J* = 5.2 Hz, *J* = 3.9 Hz, H-4α), 0.36 (dd, 1H, *J* = 7.9 Hz, *J* = 5.2 Hz, H-4β); ^{13}C NMR (ppm), *δ*: 158.6 (C), 129.2 (CH), 120.5 (CH), 116.9 (CH), 80.7 (CH), 56.4 (CH), 56.3 (CH), 47.7 (CH), 43.2 (C), 42.7 (C), 40.2 (CH_2), 39.5 (CH_2), 36.7 (C), 36.2 (CH_2), 35.8 (CH), 34.3 (CH_2), 33.3 (CH_2), 30.4 (CH), 28.2 (CH_2), 28.0 (CH), 25.1 (CH_2), 24.1 (CH_2), 23.9 (CH_2), 23.6 (CH), 22.81 (CH_3), 22.76 (CH_2), 22.6 (CH_3), 19.8 (CH_3), 18.7 (CH_3), 12.6 (CH_2), 12.2 (CH_3); EI MS, *m/z:* 462 (M^+, 1%), 369 [$(M\text{-}PhO)^+$, 100%].

Synthesis of 6β-*t*-butyldimethylsilyloxy-3α,5α-cyclocholestane (**6h**)

i-Cholesterol (1 g; 2.6 mmola), TBDMSCl (584 mg; 3.88 mmol, 1.5 equiv.), imidazole (530 mg; 7.8 mmol; 3 equiv.), and DMAP (64 mg; 0.52 mmol; 0.2 equiv.) were dissolved in 16 mL of anhydrous DMF. The reaction was carried out for 5 h (TLC control) at 80 °C under argon. The reaction was poured into water and extracted with benzene. The extract was dried with anhydrous Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was subjected to flash column chromatography with hexane as an eluent. Yield of 6β-*t*-butyldimethylsilyloxy-3α,5α-cyclocholestane (**6h**) - 688 mg (53%).

6h: White crystals, mp 70-71 °C (AcOEt-hexane); $[\alpha]_D^{20}$ +27.0 (*c* 1.0, $CHCl_3$); Rf = 0.84 (hexane); IR, ν_{max} (cm^{-1}): 1254, 1065; ^{1}H NMR (ppm), *δ*: 3.20 (m, 1H, H-6), 1.02 (s, 3H, H-19), 0.93 (d, 3H, *J* = 6.5 Hz, H-21), 0.89 (s, 9H, *t*-Bu), 0.881 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.877 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.72 (s, 3H, H-18), 0.48 (dd, 1H, *J* = 4.9 Hz, *J* = 3.8 Hz, H-4α), 0.18 (dd, 1H, *J* = 7.9 Hz, *J* = 4.9 Hz, H-4β), 0.01 (s, 3H, Si-CH_3), -0.01 (s, 3H, Si-CH_3); ^{13}C NMR (ppm), *δ*: 74.4 (CH), 56.4 (CH), 56.3 (CH), 47.9 (CH), 43.3 (C), 42.7 (C), 40.4 (CH_2), 39.6 (CH_2), 39.1 (CH_2), 38.3 (C), 36.3 (CH_2), 35.9 (CH), 33.4 (CH_2), 30.0 (CH), 28.4 (CH_2), 28.1 (CH), 25.8 (CH_3), 25.2 (CH_2), 24.3 (CH_2), 23.9 (CH_2), 23.6 (CH), 22.9 (CH_3), 22.8 (CH_2), 22.6 (CH_3), 20.2 (CH_3), 18.8 (CH_3), 18.0 (C), 12.8 (CH_2), 12.0 (CH_3), -4.5 (CH_3), -4.8 (CH_3); ESI MS, *m/z:* 523 [$(M+Na)^+$, 20%].

Typical electrochemical experiment. Anodic oxidation of 6β-phenyloxy-3α,5α-cyclocholestane (**6f**) in the presence of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**7**)

6β-Phenyloxy-3α,5α-cyclocholestane (138 mg; 0.30 mmol) and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (94 mg; 0.36 mmol) were dissolved in a 0.1 M solution of tetrabutylammonium-tetrafluoroborate in dichloromethane (3.5 mL) and introduced into the anodic compartment together with 0.5 g 3 Å molecular sieves to eliminate traces of water. The same supporting electrolyte was placed in the cathodic compartment with anionite (2 g, Dowex 2x8, 200–400 mesh,

perchlorate form) added. Preparative electrolysis was carried out in a divided H-cell in which the cathodic and anodic compartments (3.5 mL of electrolytes each) were separated by a glass frit under galvanostatic conditions. A direct current 7.5 mA was run for 4000 s. A platinum mesh was used as a cathode and a platinum plate (2 × 1.5 cm) was used as an anode. Ag/0.1 M $AgNO_3$ in acetonitrile electrode was used as a reference. When the electrolysis was completed, the solvent was removed from the reaction mixture and the products were separated by silica gel column chromatography. The hexane elution afforded diene **13** (1 mg; 1%) and cholesteryl chloride **14** (1 mg; 1%). With the hexane-ethyl acetate mixture (96:4), cholesteryl phenyl ether **12f** (31 mg; 22%) was eluted. Further elution with hexane-ethyl acetate (93:7) afforded 3β-*O*-(1',2':3',4'-di-*O*-isopropylidene-α-D-galactopyranos-6'-yl)-cholest-5-ene **11** (108 mg; 58%), followed by cholesterol **1** (5 mg, 4%) eluted with hexane/ethyl acetate (9:1).

Glycosylation product **11** was described in our previous report [5]. Also, other products of the electrochemical reactions (compounds **2**, **13**, **14**, and **15**) were described in our previous papers [6-9]. The isomerization products, i.e., 3β-cholesteryl ethers **12b** [10], **12c** [11], **12e** [12], **12f** [12], **12g** [9],and **12h** [13], are known compounds, except for **12d** which was obtained during electrochemical reaction of 3α,5α-cyclocholestan-6β-yl isopropyl ether (**6d**).

12d: White crystals, mp 122-124 °C (AcOEt-hexane); $[\alpha]_D^{20}$ -24.1 (*c* 1.0, $CHCl_3$); Rf = 0.44 (hexane-AcOEt 95:5); IR, ν_{max} (cm^{-1}): 1125, 1064; ^{1}H NMR (ppm), δ: 5.35 (m, 1H, H-6), 3.73 (h, 1H, *J* = 6.1 Hz, O-CH$(Me)_2$), 3.22 (m, 1H, H-6) 1.151 (d, 3H, *J* = 6.1 Hz, CH_3-isopropyl), 1.148 (d, 3H, *J* = 6.1 Hz, CH_3-isopropyl), 1.01 (s, 3H, H-19), 0.93 (d, 3H, *J* = 6.6 Hz, H-21), 0.877 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.873 (d, 3H, *J* = 6.6 Hz, H-26 or H-27), 0.67 (s, 3H, H-18); ^{13}C NMR (ppm), δ: 141.4 (C), 121.3 (CH), 76.3 (CH), 68.5 (CH), 56.8 (CH), 56.2 (CH), 50.3 (CH), 42.3 (C), 40.0 (CH_2), 39.8 (CH_2), 39.5 (CH_2), 37.5 (CH_2), 36.9 (C), 36.2 (CH_2), 35.8 (CH), 32.0 (CH_2), 31.9 (CH), 29.3 (CH_2), 28.2 (CH_2), 28.0 (CH), 24.3 (CH_2), 23.8 (CH_2), 23.03 (CH_3), 22.95 (CH_3), 22.8 (CH_3), 22.6 (CH_3), 21.1 (CH_2), 19.4 (CH_3), 18.7 (CH_3), 11.9 (CH_3); EI MS, *m/z:* 428 [M^+, 15%], 370 [(M-*i*-Pr-Me)$^+$, 63%], 329 (100%).

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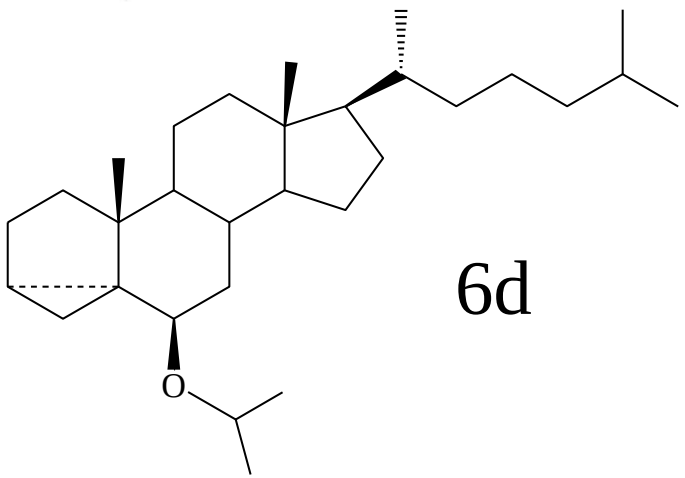

6d


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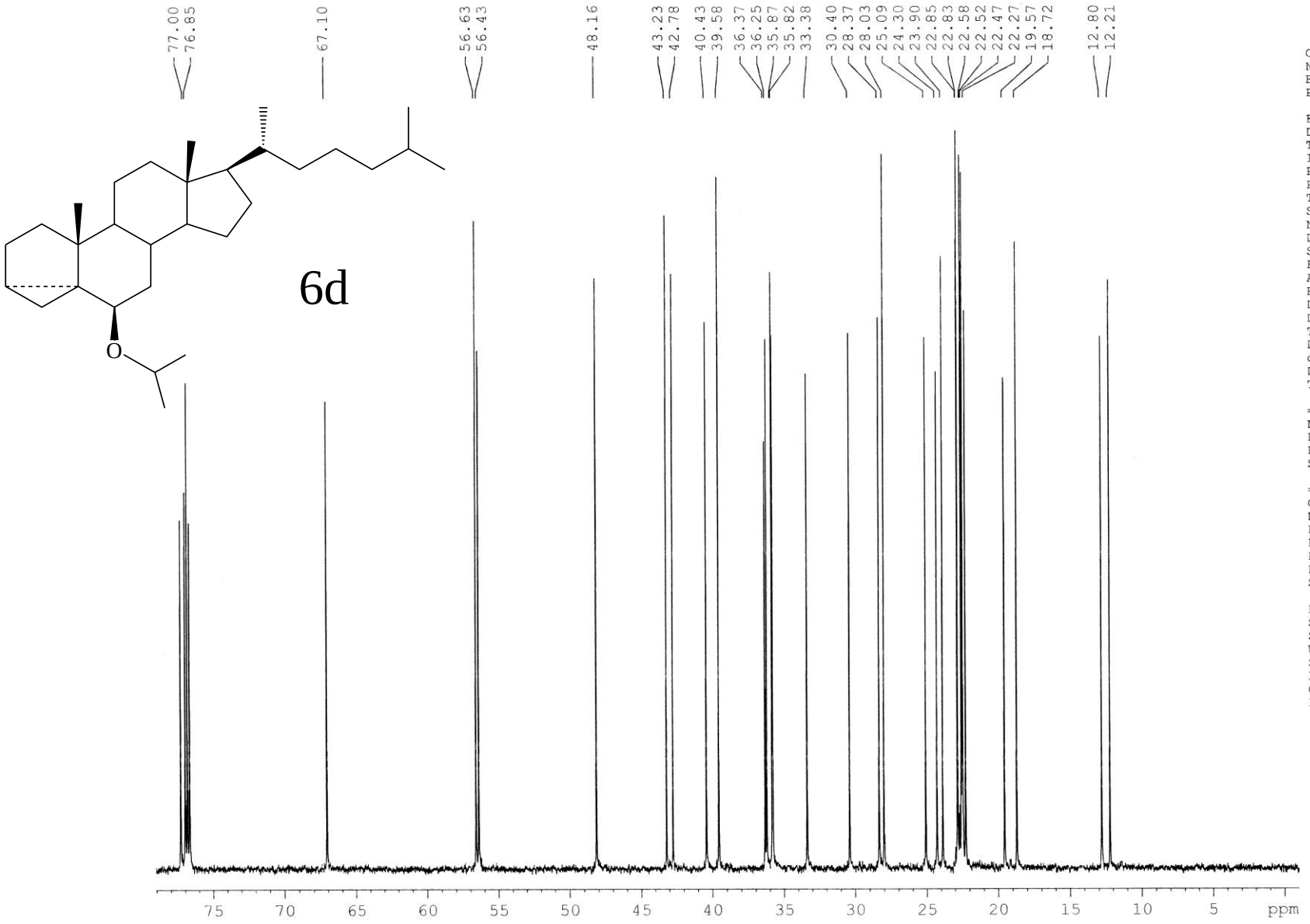


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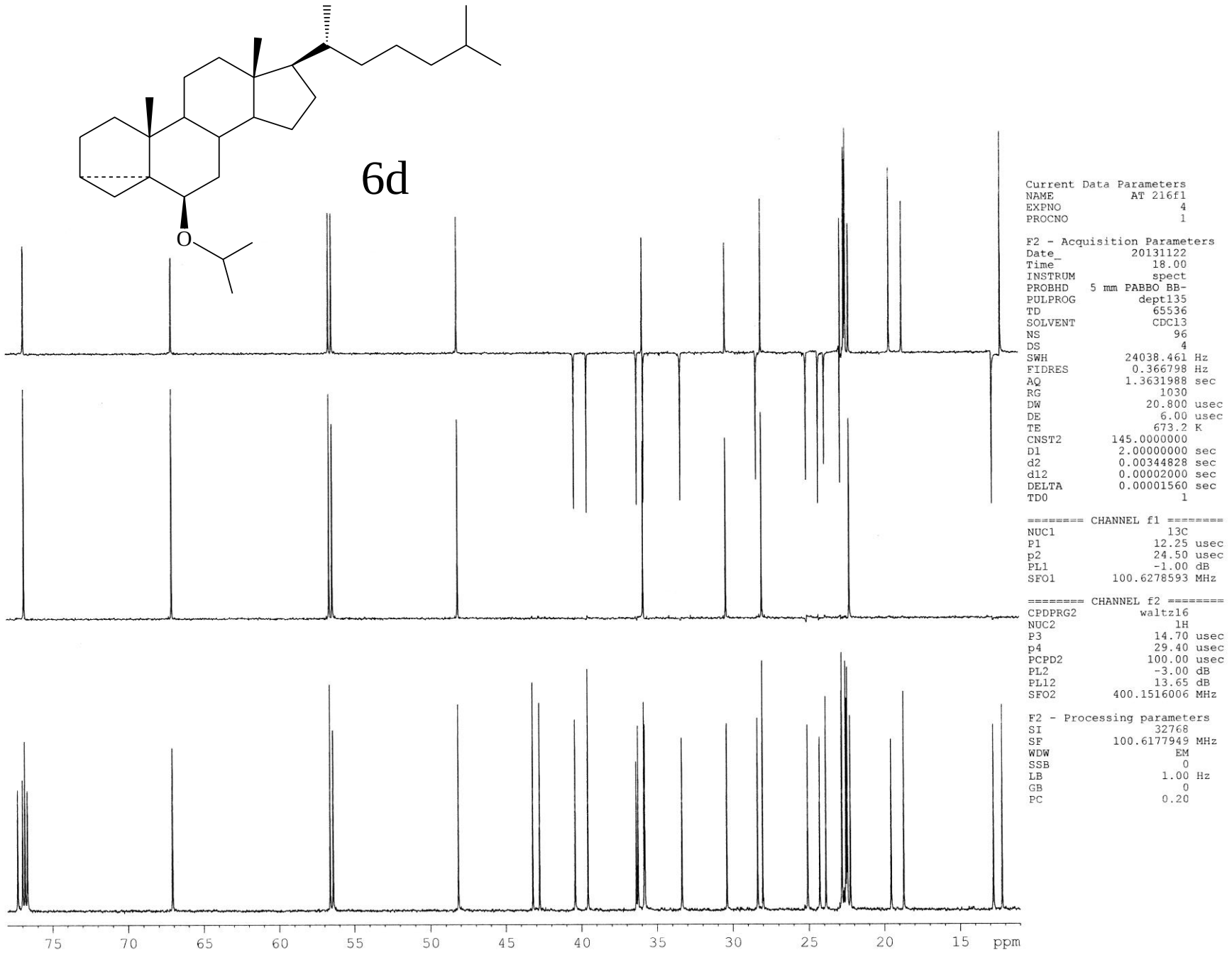


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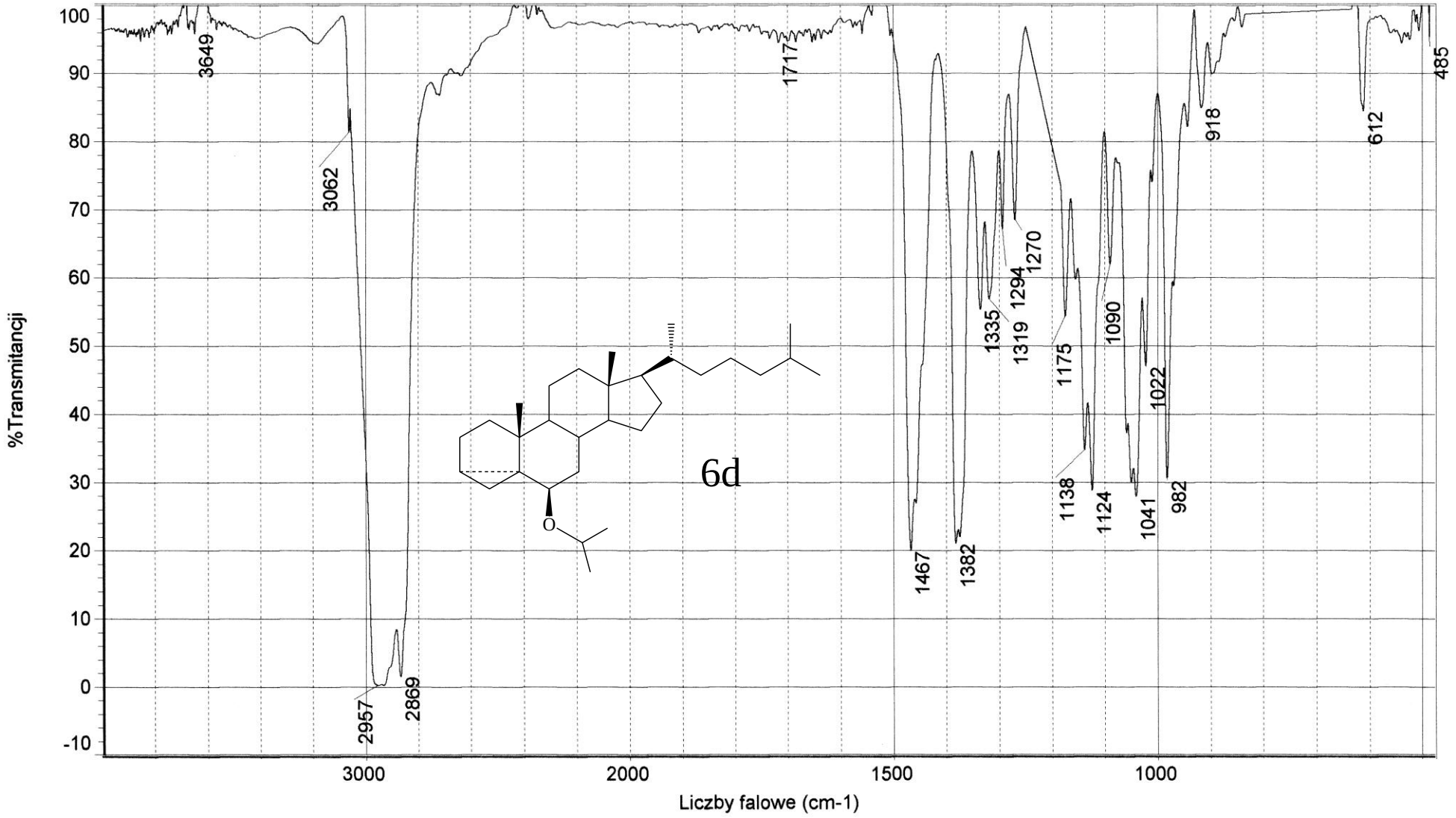
NUC2                        1H
P3                        14.70 usec
p4                        29.40 usec
PCPD2                    100.00 usec
PL2                       -3.00 dB
PL12                      13.65 dB
SFO2                400.1516006 MHz

F2 - Processing parameters
SI                          32768
SF                  100.6177949 MHz
WDW                            EM
SSB                             0
LB                         1.00 Hz
GB                              0
PC                           0.20
```


%Transmitancji
Liczby falowe (cm-1)
100
90
80
70
60
50
40
30
20
10
0
-10
3000
2000
1500
1000
3649
3062
2957
2869
1717
1467
1382
1335
1319
1294
1270
1175
1138
1124
1090
1041
1022
982
918
612
485
O
6d

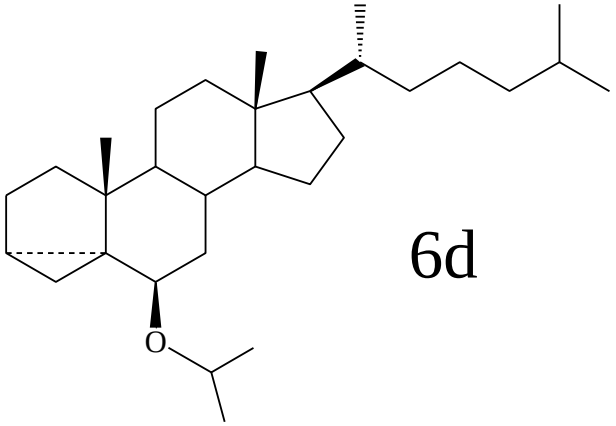
AUTOSPEC

22-Oct-2013 10:01:23

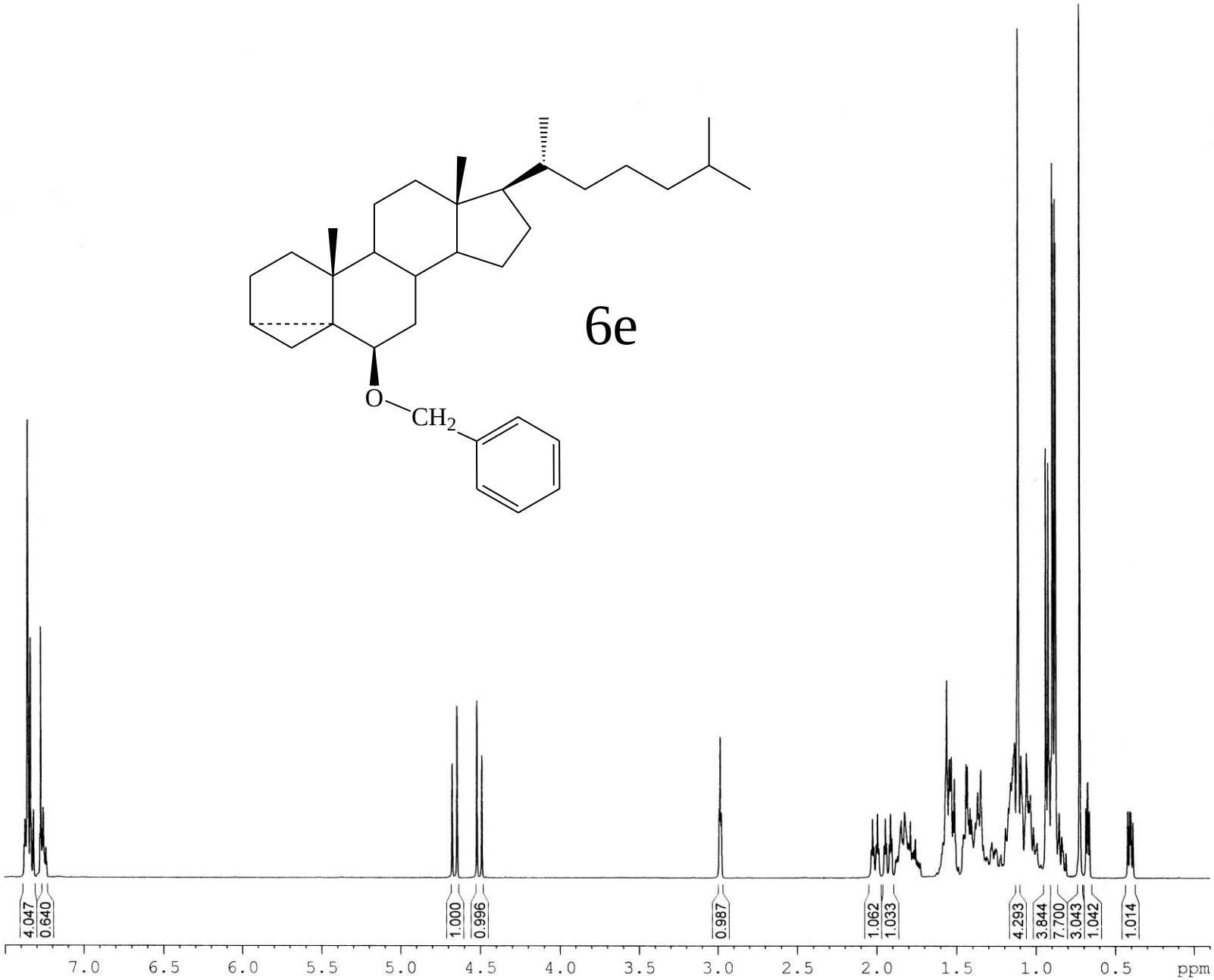
AT214

ub_jm3232 12 (0.952) Cm (9:17)

Magnet EI+
3.58e3



6d

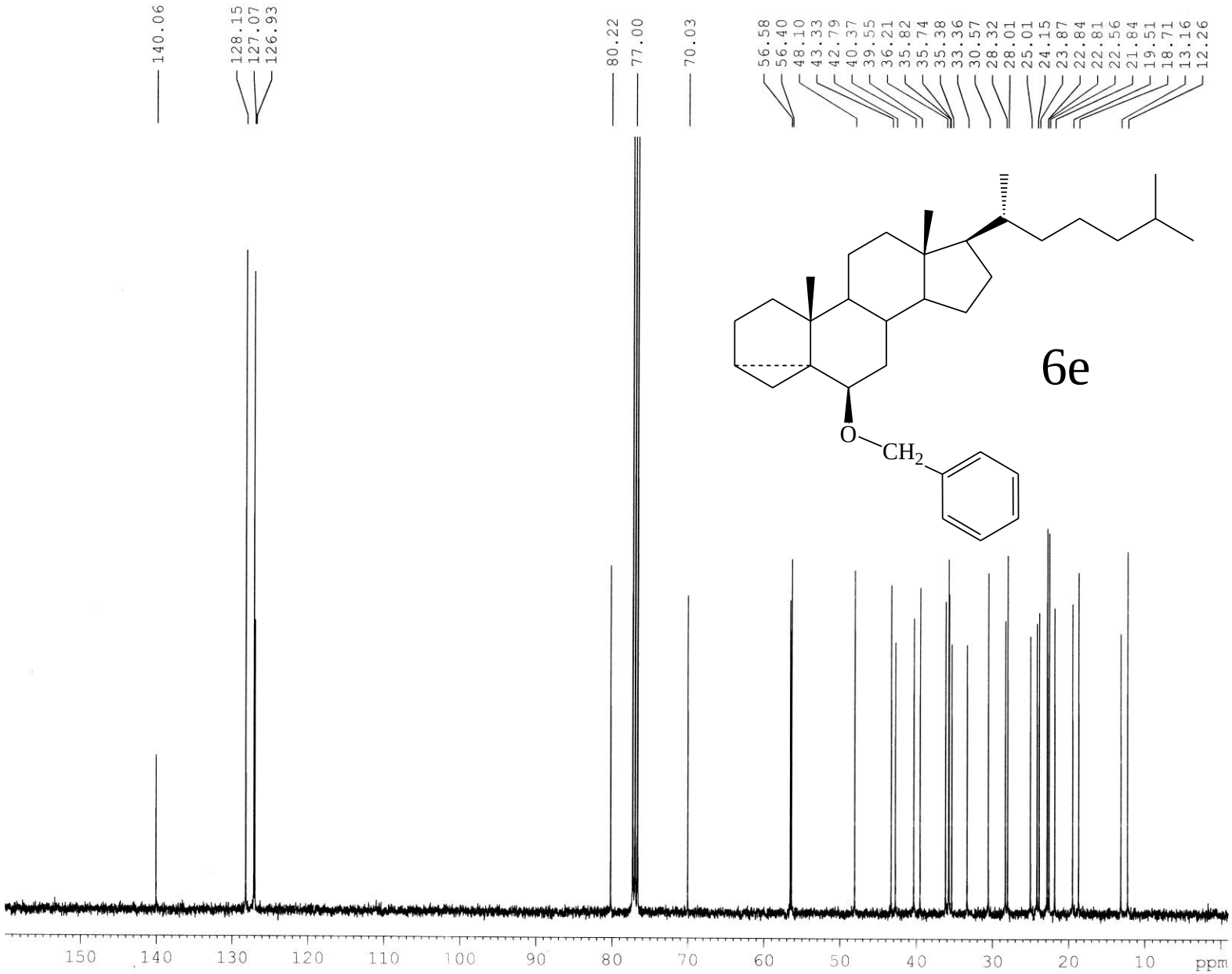



```
Current Data Parameters
NAME      AT benzylowy W6f1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131129
Time                 14.28
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       0
SWH               8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     114
DW                60.800 usec
DE                 8.00 usec
TE                 673.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.15 usec
PL1                 -3.00 dB
SFO1          400.1524711 MHz

F2 - Processing parameters
SI                   32768
SF            400.1500000 MHz
WDW                     GM
SSB                      0
LB                  -0.20 Hz
GB                     0.2
PC                    1.00
```



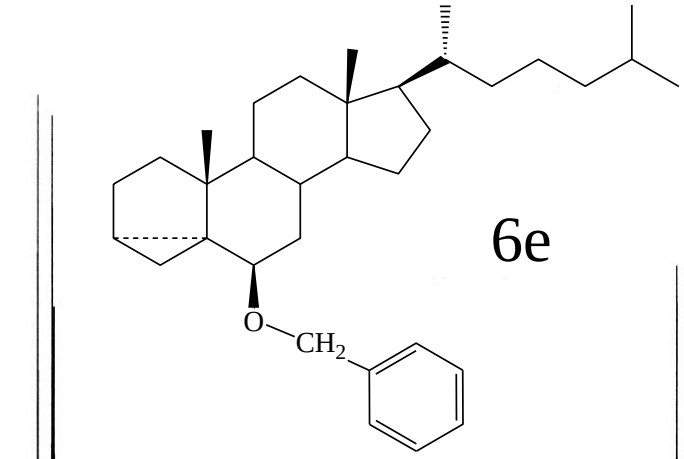

```
Current Data Parameters
NAME                  EM Eve18
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20130314
Time                     15.16
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         384
DS                           4
SWH                  27173.912 Hz
FIDRES                0.414641 Hz
AQ                    1.2059124 sec
RG                        2050
DW                      18.400 usec
DE                       6.00 usec
TE                      303.0 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       12.25 usec
PL1                      -1.00 dB
SFO1               100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -3.00 dB
PL12                     13.65 dB
PL13                     18.00 dB
SFO2               400.1516006 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6177986 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```



6e

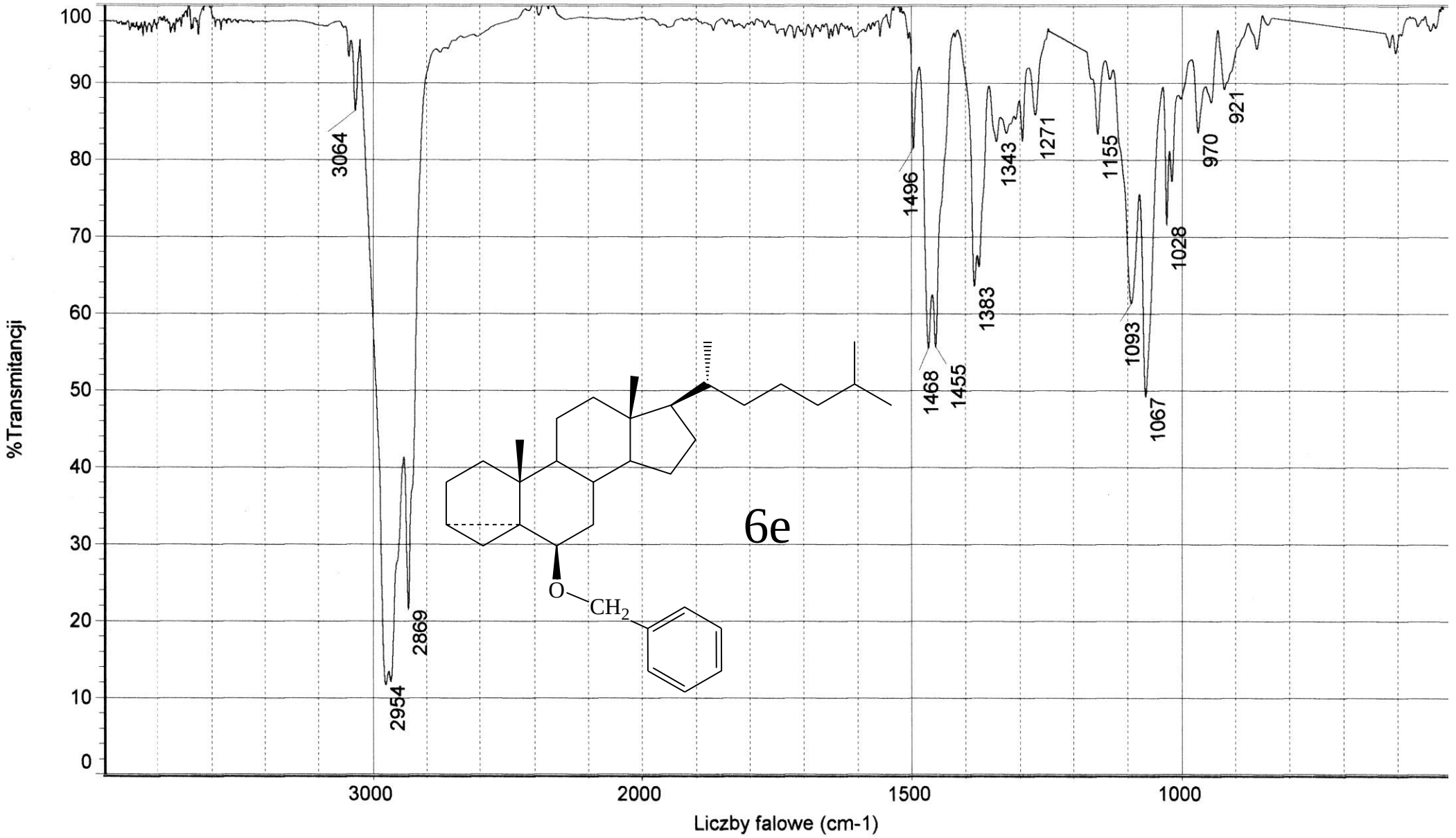

```
Current Data Parameters
NAME                  EM Eve18
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20130314
Time                     15.53
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                dept135
TD                       65536
SOLVENT                  CDCl3
NS                         192
DS                           4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        2050
DW                      20.800 usec
DE                       6.00 usec
TE                      303.0 K
CNST2              145.0000000
D1                   2.00000000 sec
d2                   0.00344828 sec
d12                  0.00002000 sec
DELTA                0.00001560 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       12.25 usec
p2                       24.50 usec
PL1                      -1.00 dB
SFO1               100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                       14.70 usec
p4                       29.40 usec
PCPD2                   100.00 usec
PL2                      -3.00 dB
PL12                     13.65 dB
SFO2               400.1516006 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6177985 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.40
```


%Transmitancji
100
90
80
70
60
50
40
30
20
10
0
3000
2000
1500
1000
Liczby falowe (cm-1)
3064
2954
2869
1496
1468
1455
1383
1343
1271
1155
1093
1067
1028
970
921
O
CH2
6e

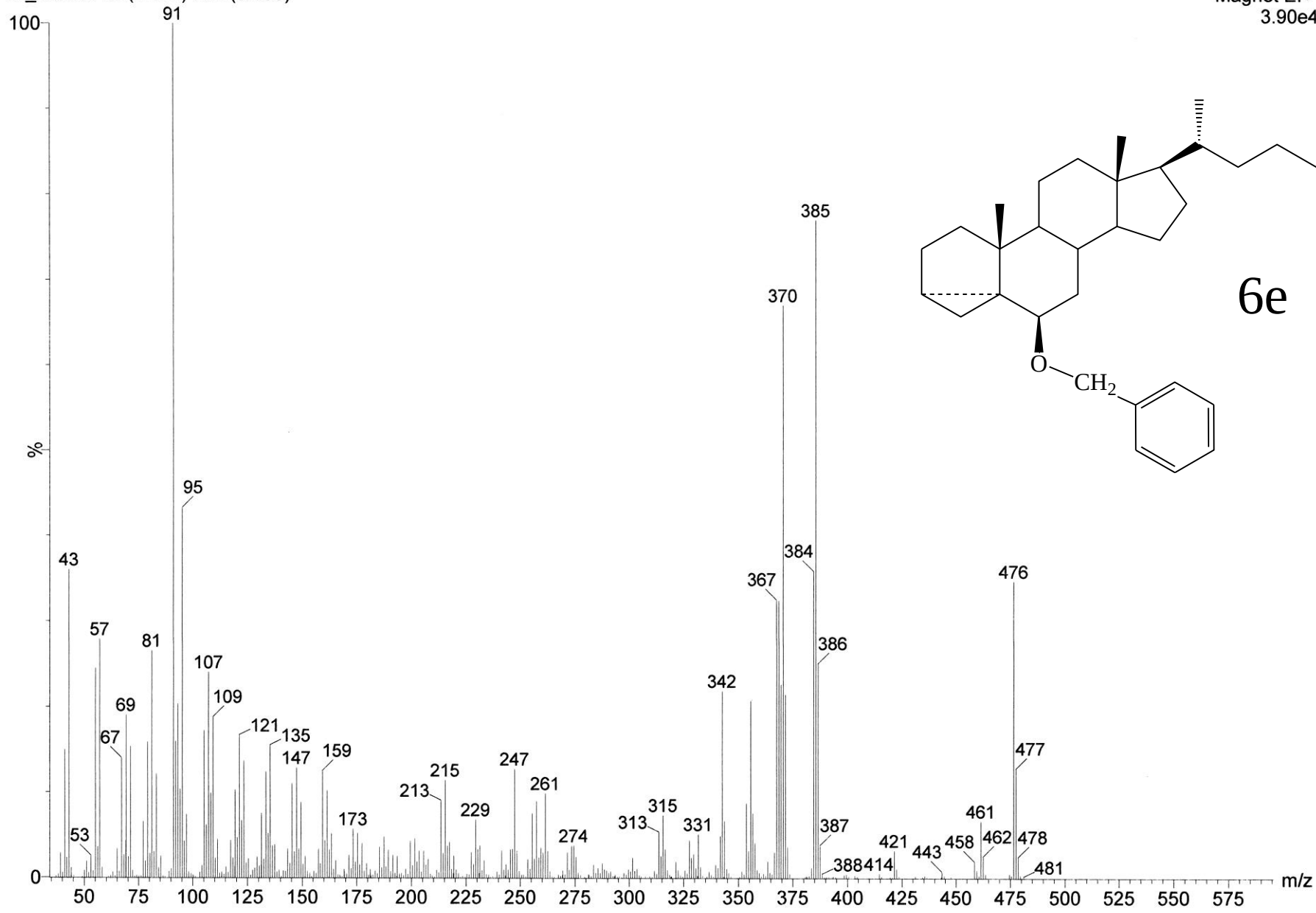
A. Tomkiel
Eve19

AUTOSPEC

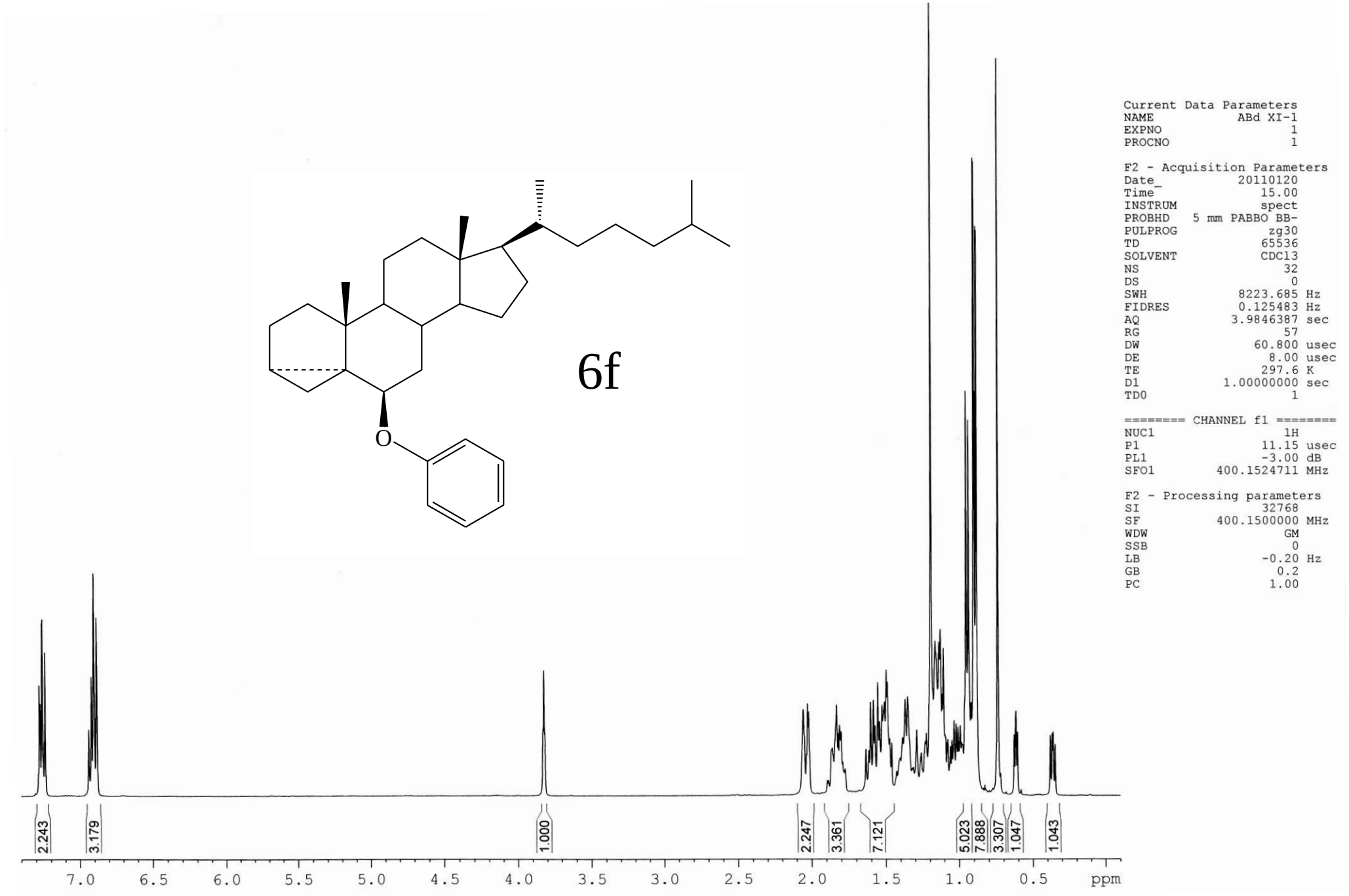
19-Mar-2013 08:51:05

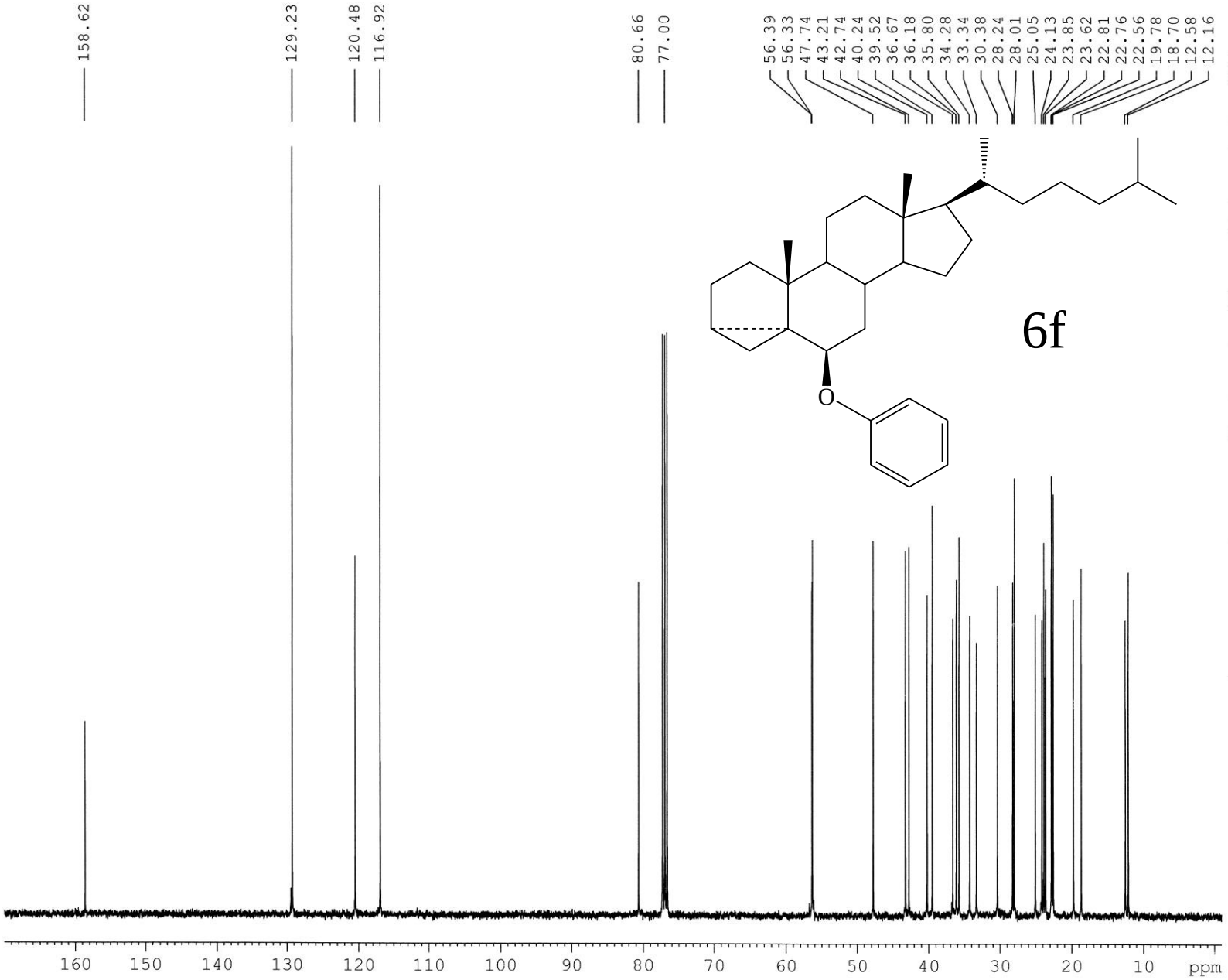
ub_at0865 35 (2.775) Cm (31:38)

Magnet EI+
3.90e4



6e


6f
O
Current Data Parameters
NAME ABd XI-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110120
Time 15.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 57
DW 60.800 usec
DE 8.00 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.15 usec
PL1 -3.00 dB
SFO1 400.1524711 MHz
F2 - Processing parameters
SI 32768
SF 400.1500000 MHz
WDW GM
SSB 0
LB -0.20 Hz
GB 0.2
PC 1.00
2.243
3.179
1.000
2.247
3.361
7.121
5.023
7.888
3.307
1.047
1.043
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



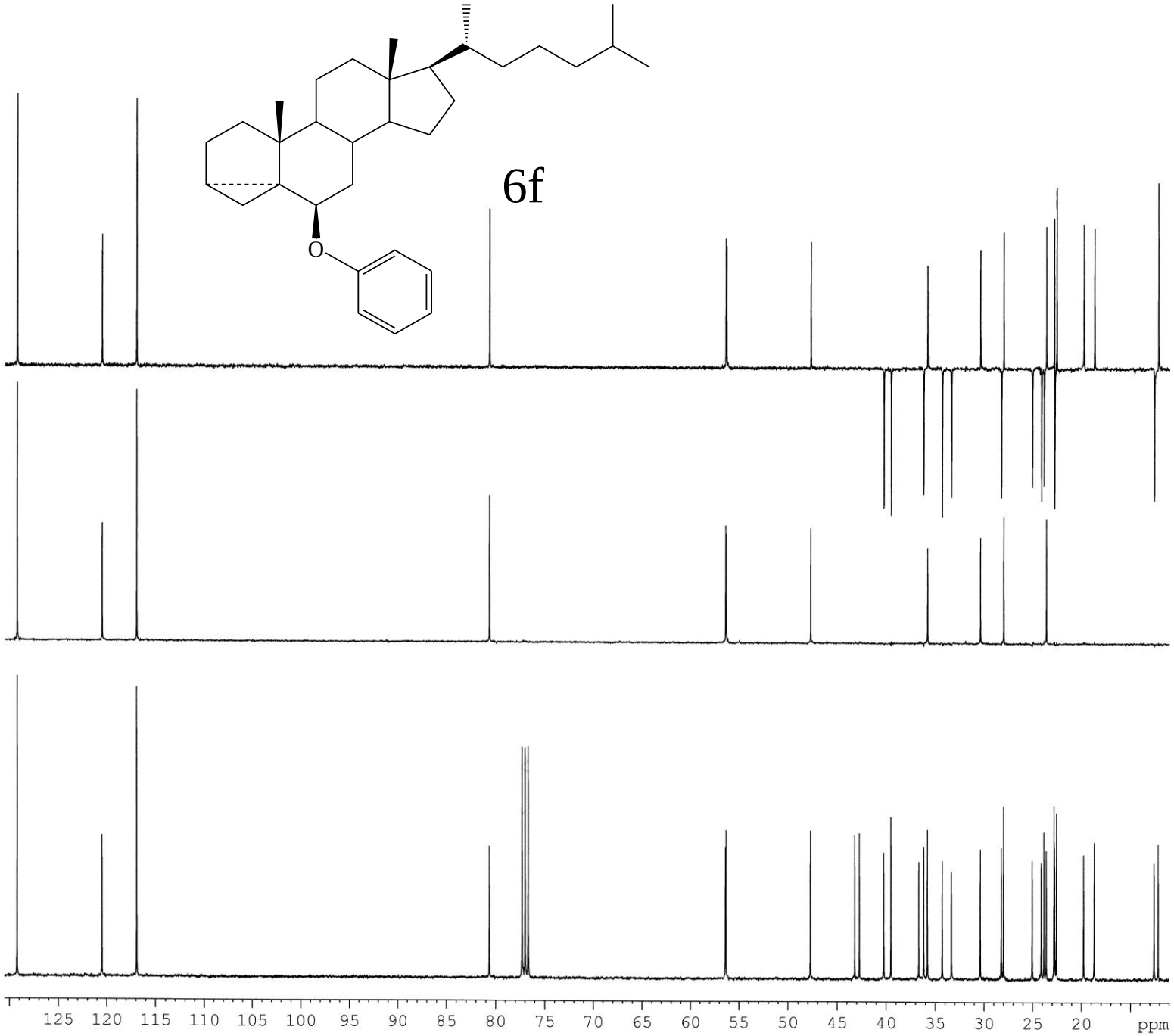

```
Current Data Parameters
NAME                  ABd XI-1
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20110329
Time                     12.56
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          576
DS                            4
SWH                 27173.912 Hz
FIDRES               0.414641 Hz
AQ                   1.2059124 sec
RG                         1030
DW                       18.400 usec
DE                        6.00 usec
TE                       299.1 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       11.00 usec
PL1                      -1.00 dB
SFO1              100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -3.00 dB
PL12                     13.65 dB
PL13                     18.00 dB
SFO2              400.1516006 MHz

F2 - Processing parameters
SI                         32768
SF                100.6178008 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                          0.10
```



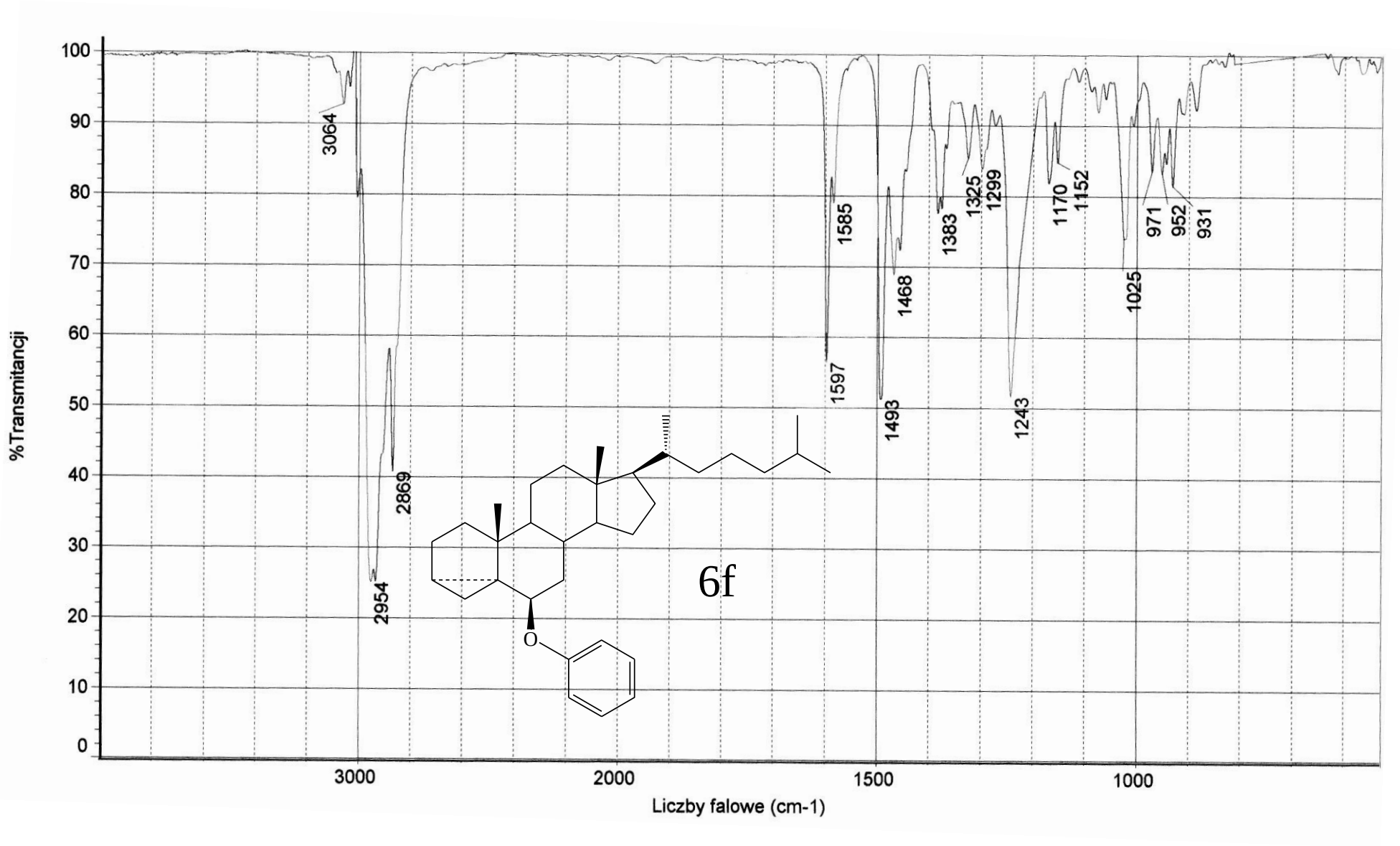

```
Current Data Parameters
NAME                  ABd XI-1
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20110329
Time                     13.41
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                dept135
TD                       65536
SOLVENT                  CDCl3
NS                         192
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                        2050
DW                      20.800 usec
DE                       6.00 usec
TE                      299.7 K
CNST2               145.0000000
D1                    2.00000000 sec
d2                    0.00344828 sec
d12                   0.00002000 sec
DELTA                 0.00001401 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                      11.00 usec
p2                      22.00 usec
PL1                     -1.00 dB
SFO1                100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                      14.70 usec
p4                      29.40 usec
PCPD2                  100.00 usec
PL2                     -3.00 dB
PL12                    13.65 dB
SFO2                400.1516006 MHz

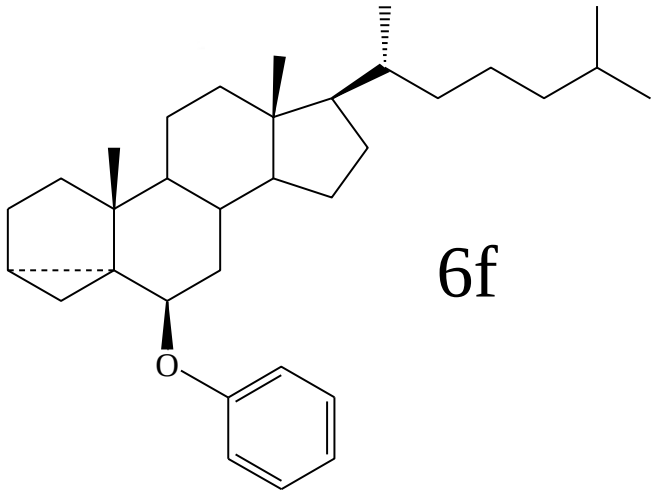
F2 - Processing parameters
SI                         32768
SF                  100.6178008 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          0.10
```


%Transmitancji
100
90
80
70
60
50
40
30
20
10
0
3000
2000
1500
1000
Liczby falowe (cm-1)
3064
2954
2869
1597
1585
1493
1468
1383
1325
1299
1243
1170
1152
1025
971
952
931
O
6f

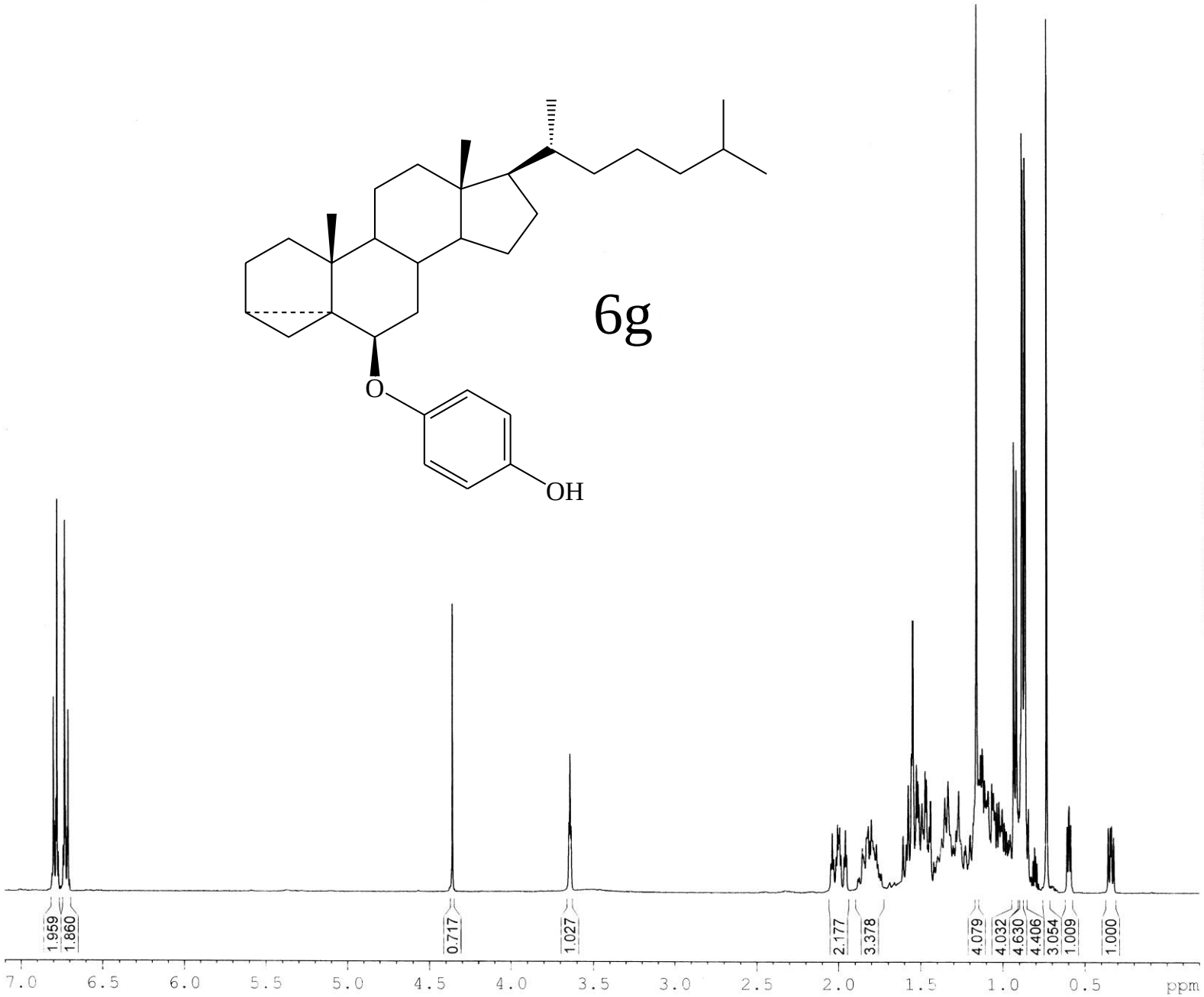
eter fenylowy w6

ub_jm1101 70 (5.698) Cm (70:77)

Magnet EI+
1.00e4



6f

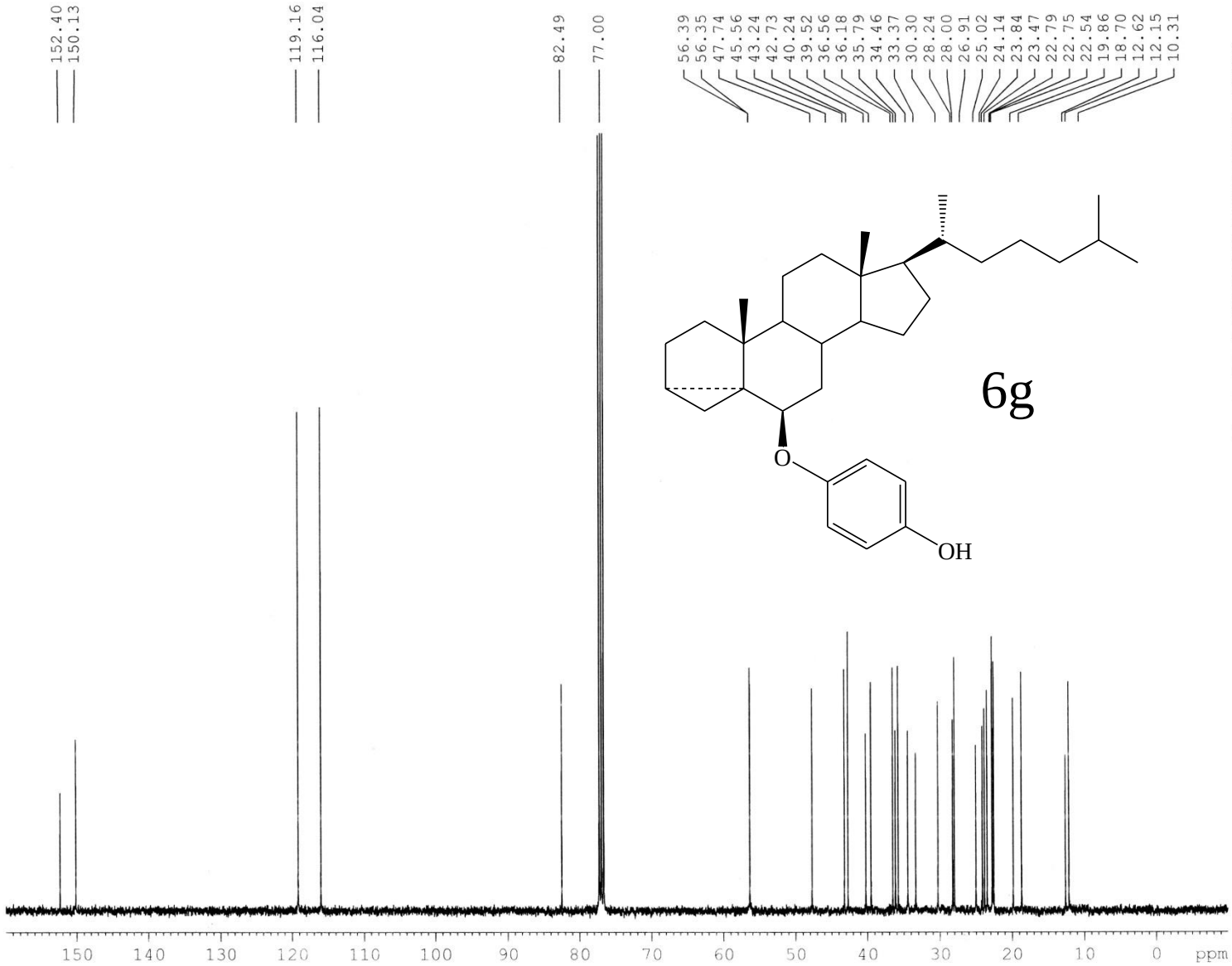



```
Current Data Parameters
NAME      EM 6-et.h.chinonowy cz.
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20130411
Time              11.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                 192
DS                   0
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 287
DW              60.800 usec
DE               8.00 usec
TE              673.2 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                30.00 usec
PL1               -3.00 dB
SFO1        400.1524711 MHz

F2 - Processing parameters
SI                32768
SF          400.1500000 MHz
WDW                  GM
SSB                  0
LB               -0.20 Hz
GB                 0.2
PC                1.00
```



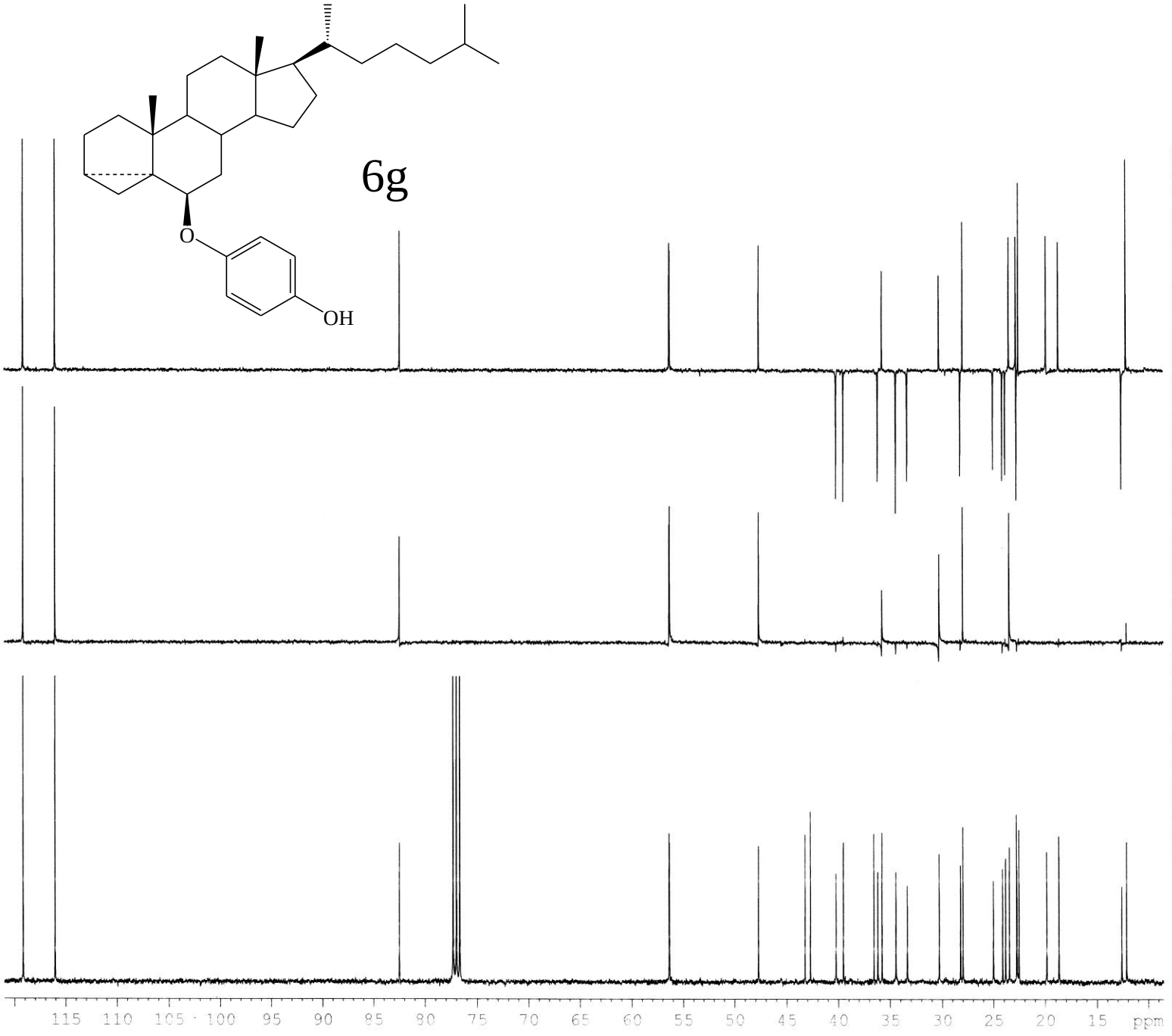

```
Current Data Parameters
NAME      EM Evel9czysty
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130315
Time              13.38
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  800
DS                    4
SWH           27173.912 Hz
FIDRES        0.414641 Hz
AQ            1.2059124 sec
RG                 2050
DW               18.400 usec
DE                6.00 usec
TE                303.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.25 usec
PL1               -1.00 dB
SFO1        100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              13.65 dB
PL13              18.00 dB
SFO2        400.1516006 MHz

F2 - Processing parameters
SI                32768
SF          100.6177986 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 0.10
```



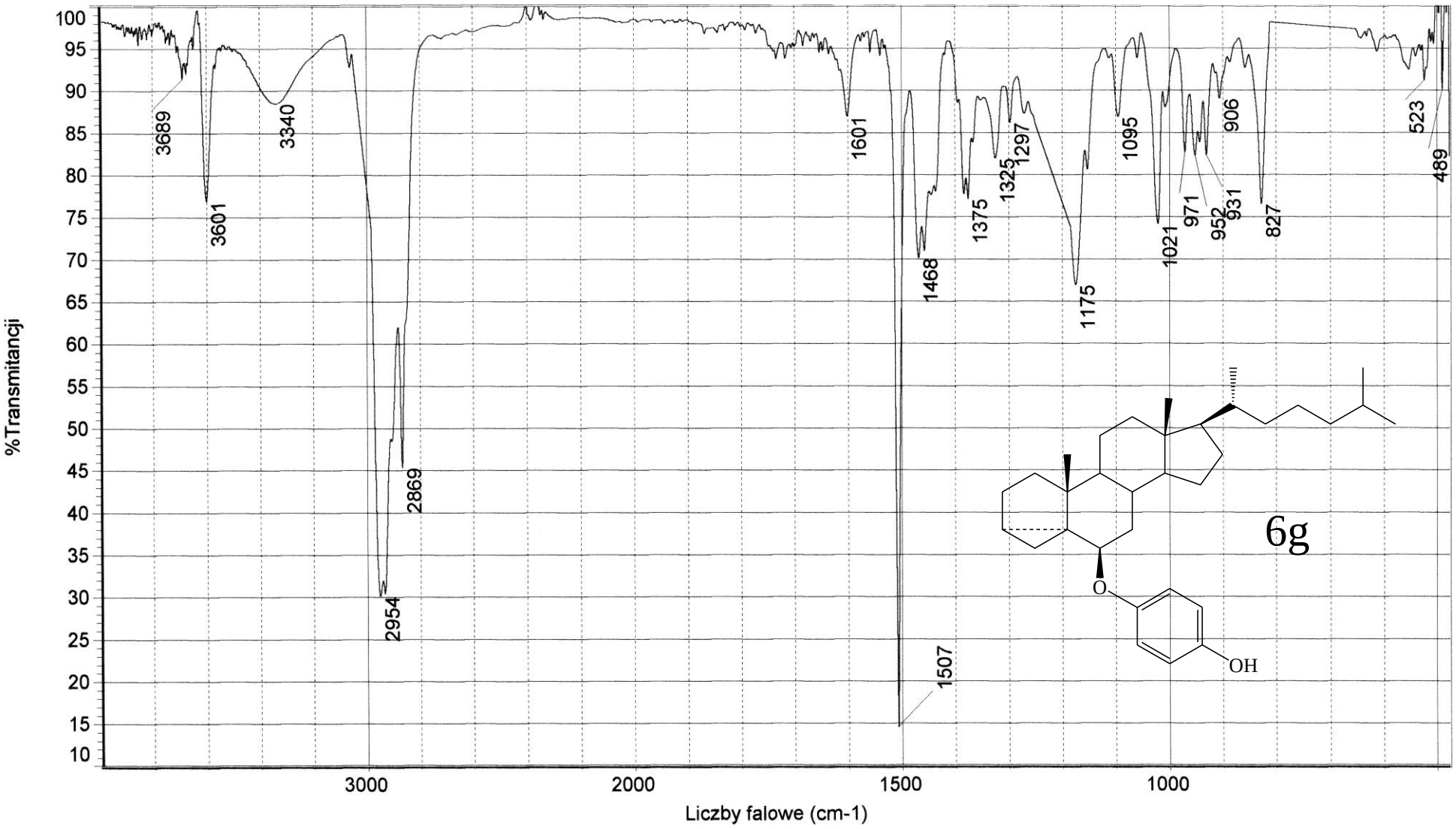

```
Current Data Parameters
NAME      EM Eve19czysty
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130315
Time_              15.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          dept135
TD                 65536
SOLVENT            CDCl3
NS                   320
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.00 usec
TE                303.0 K
CNST2         145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001560 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  12.25 usec
p2                  24.50 usec
PL1                 -1.00 dB
SFO1          100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
P3                  14.70 usec
p4                  29.40 usec
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                13.65 dB
SFO2          400.1516006 MHz

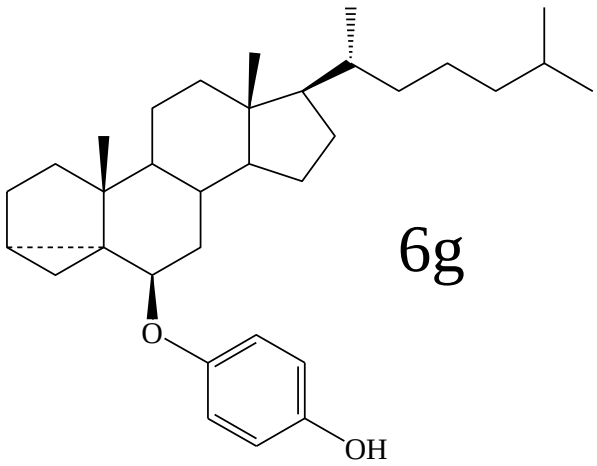
F2 - Processing parameters
SI                 32768
SF          100.6177987 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  0.10
```


%Transmitancji
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
3689
3601
3340
2954
2869
1601
1507
1468
1375
1325
1297
1175
1095
1021
971
952
931
906
827
523
489
3000
2000
1500
1000
Liczby falowe (cm-1)
O
OH
6g

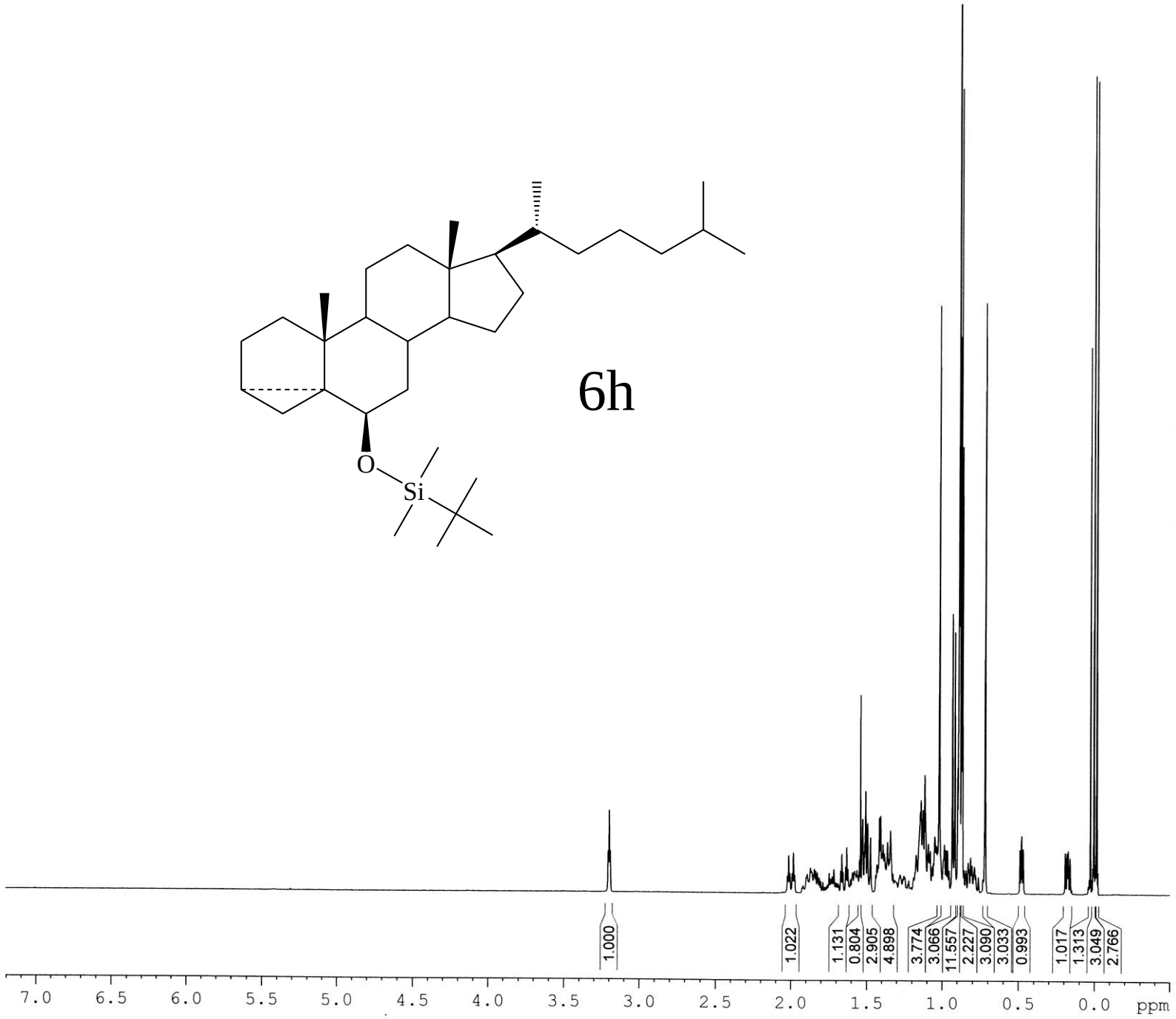
eter chinonowy w6

ub_jm1102 19 (1.546) Cm (19:27-3:6)

Magnet EI+
4.43e3



6g

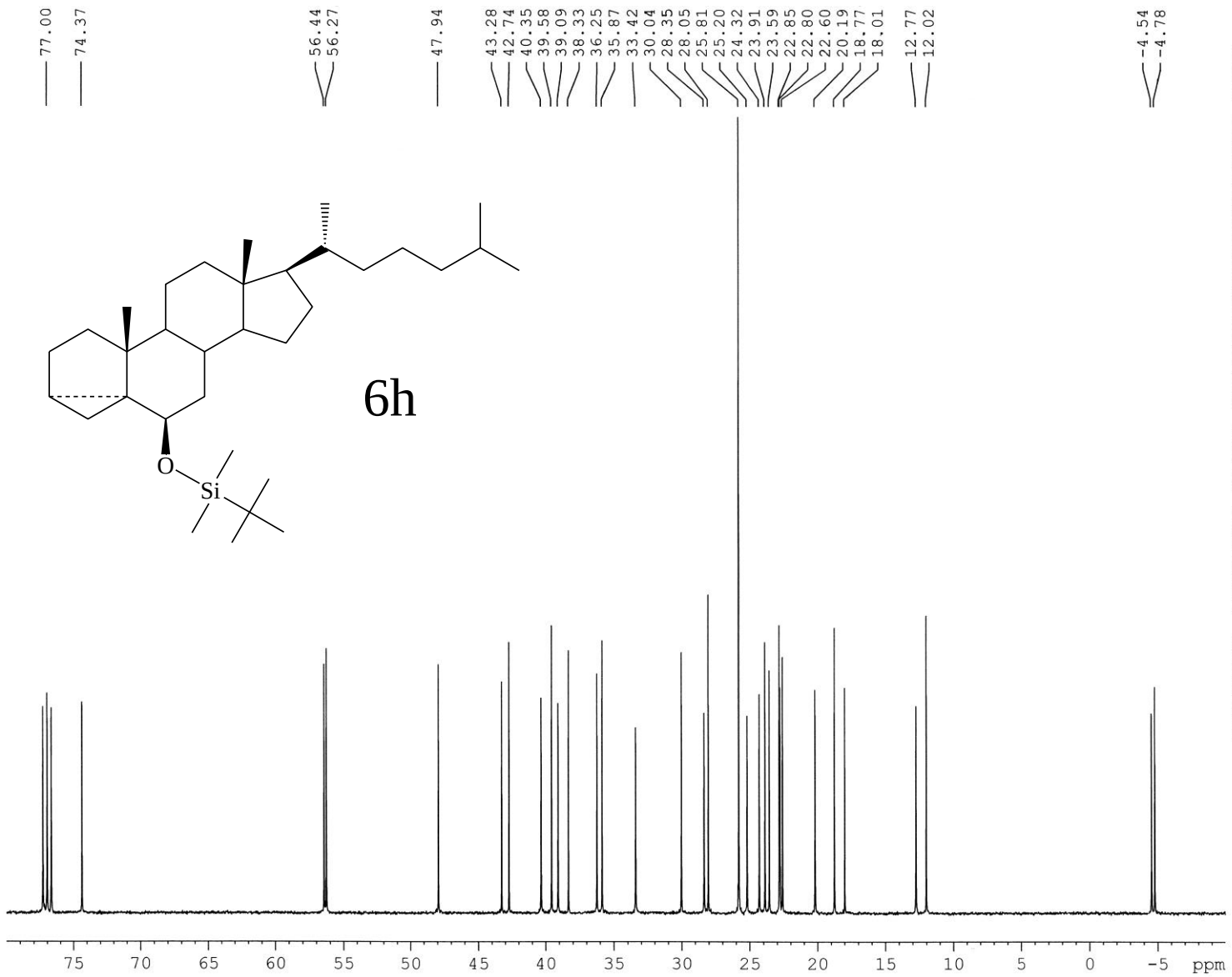



```
Current Data Parameters
NAME                  ABd VIII
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20101220
Time                     11.19
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                        128
DS                          0
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                        228
DW                     60.800 usec
DE                      8.00 usec
TE                     299.4 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.15 usec
PL1                    -3.00 dB
SFO1           400.1524711 MHz

F2 - Processing parameters
SI                      32768
SF             400.1500000 MHz
WDW                        GM
SSB                         0
LB                     -0.20 Hz
GB                        0.2
PC                       1.00
```



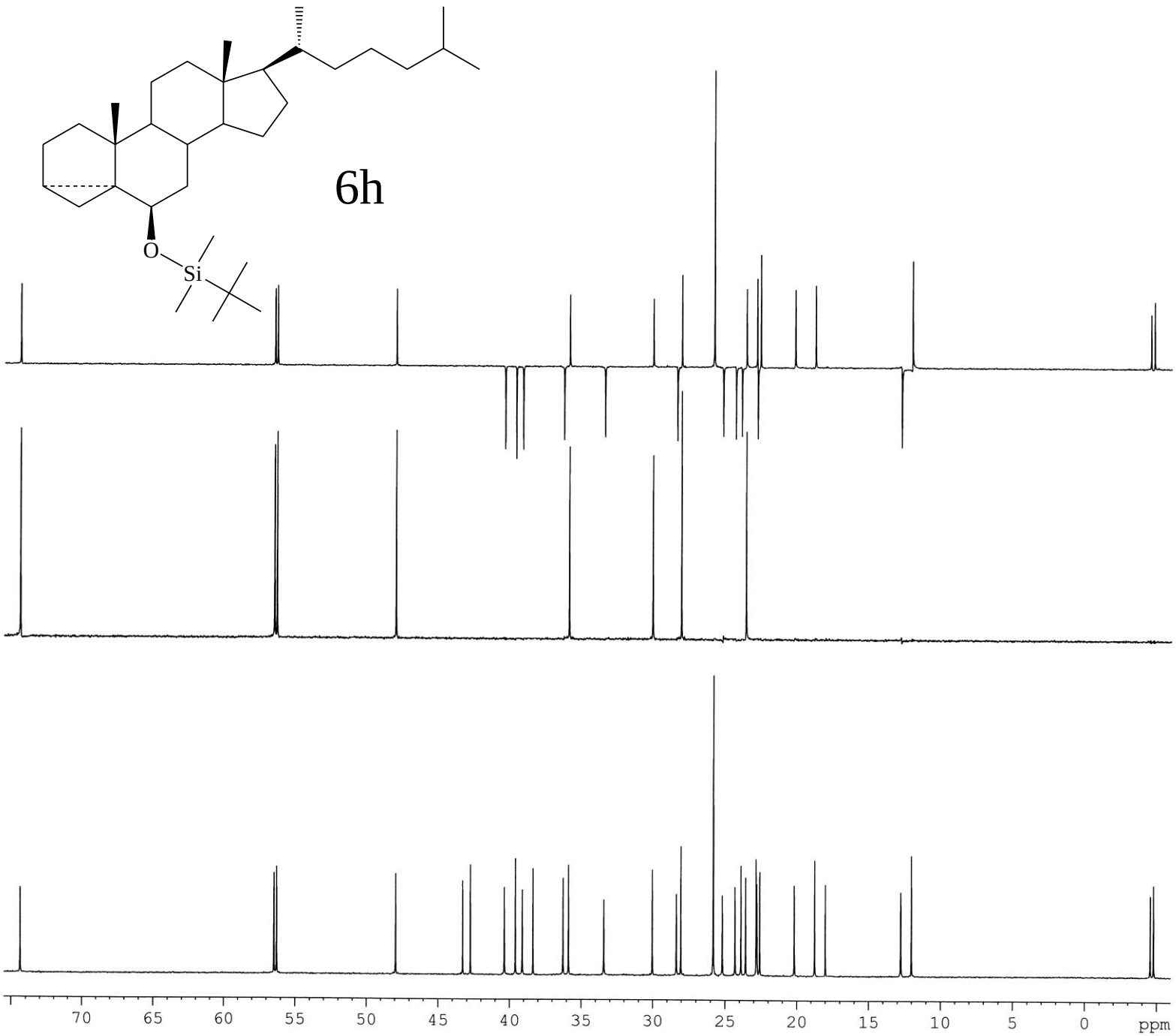

```
Current Data Parameters
NAME                  ABd VIII
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20110309
Time                     16.48
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         448
DS                           4
SWH                  27173.912 Hz
FIDRES                0.414641 Hz
AQ                    1.2059124 sec
RG                        1030
DW                      18.400 usec
DE                       6.00 usec
TE                      299.9 K
D1                   2.00000000 sec
d11                  0.03000000 sec
DELTA                1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                       11.00 usec
PL1                      -1.00 dB
SFO1               100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                   100.00 usec
PL2                      -3.00 dB
PL12                     13.65 dB
PL13                     18.00 dB
SFO2               400.1516006 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6177950 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                       1.40
```



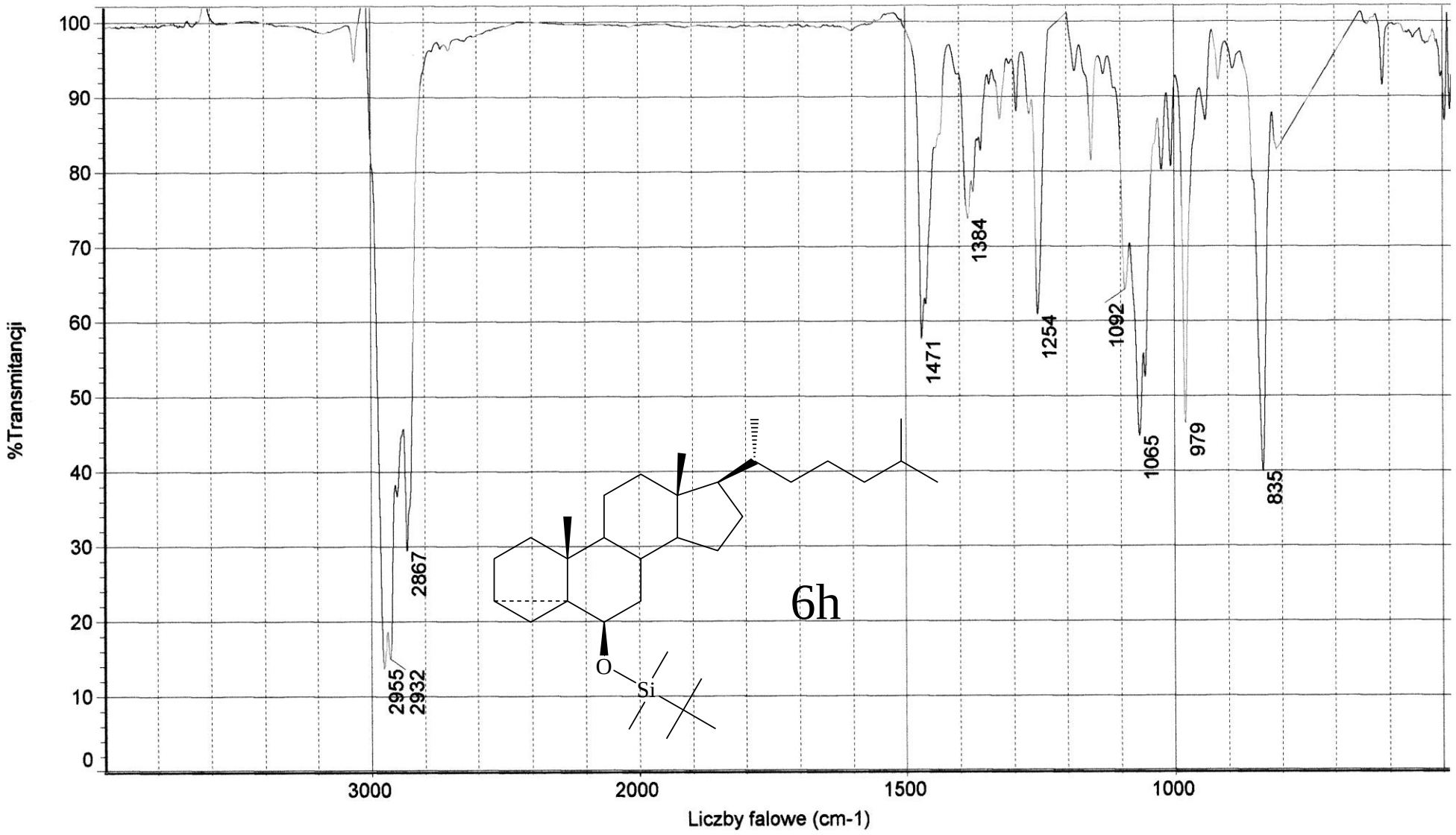

```
Current Data Parameters
NAME                  ABd VIII
EXPNO                        4
PROCNO                       1

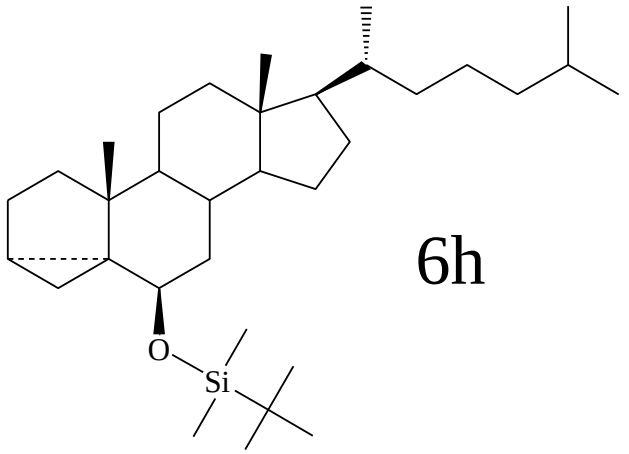
F2 - Acquisition Parameters
Date_                 20110309
Time                     17.25
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG               dept135
TD                       65536
SOLVENT                  CDCl3
NS                         128
DS                           4
SWH                 24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                        1030
DW                      20.800 usec
DE                       6.00 usec
TE                      299.8 K
CNST2               145.0000000
D1                    2.00000000 sec
d2                    0.00344828 sec
d12                   0.00002000 sec
DELTA                 0.00001401 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       11.00 usec
p2                       22.00 usec
PL1                      -1.00 dB
SFO1                100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                       14.70 usec
p4                       29.40 usec
PCPD2                   100.00 usec
PL2                      -3.00 dB
PL12                     13.65 dB
SFO2                400.1516006 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6177949 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                         0.50
```


%Transmitancji
100
90
80
70
60
50
40
30
20
10
0
3000
2000
1500
1000
Liczby falowe (cm-1)
2955
2932
2867
1471
1384
1254
1092
1065
979
835
O
Si
6h

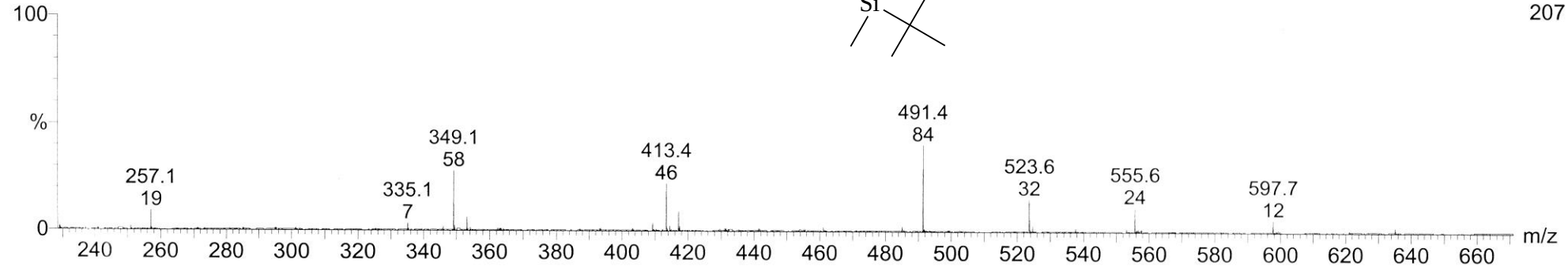


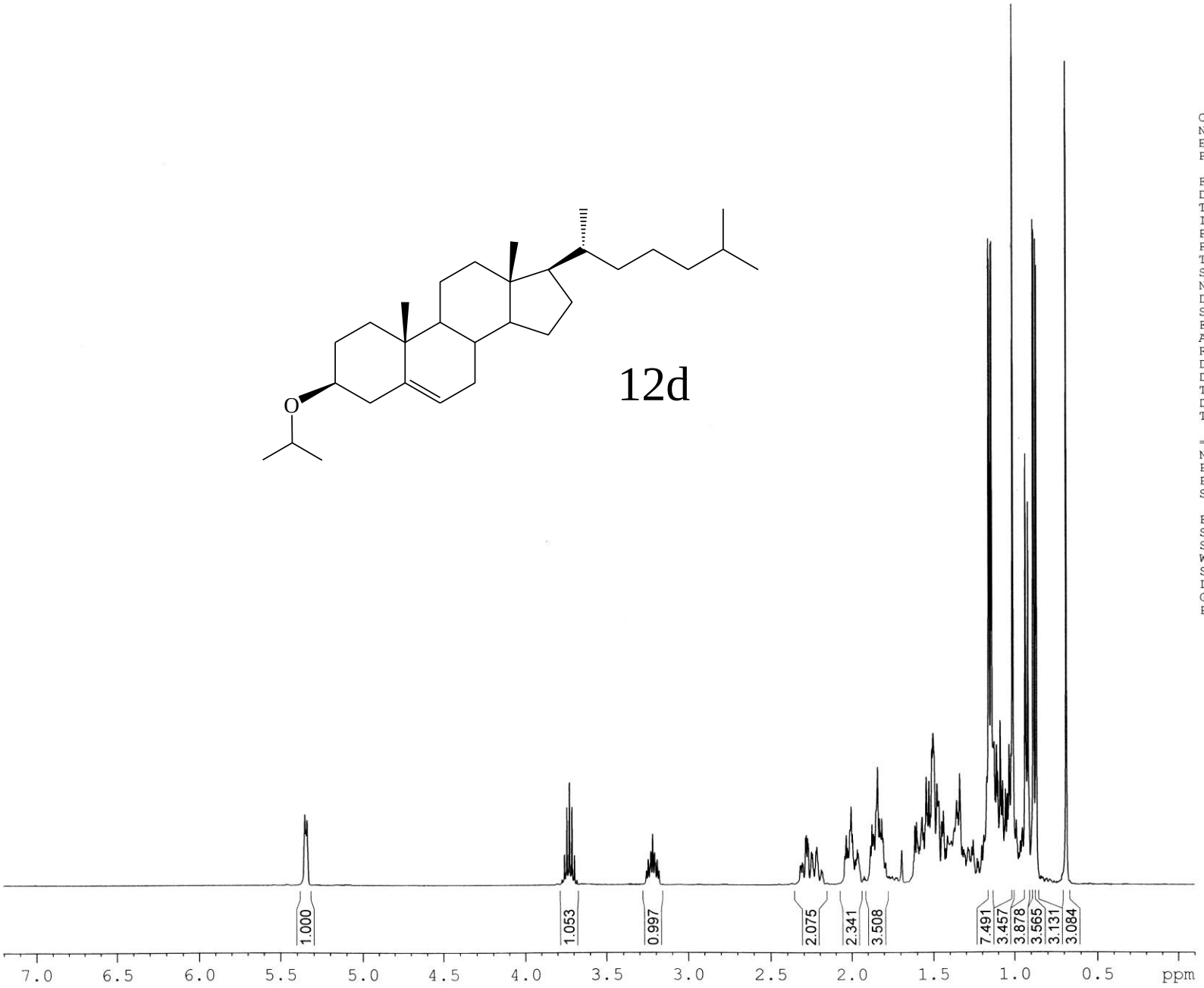
6h

A. Bd-VIII +HCOONa
LCT
9742_JWM_HCOONa 74 (1.233) Cm (1:94)

18-Jan-2011

TOF MS ES+
207



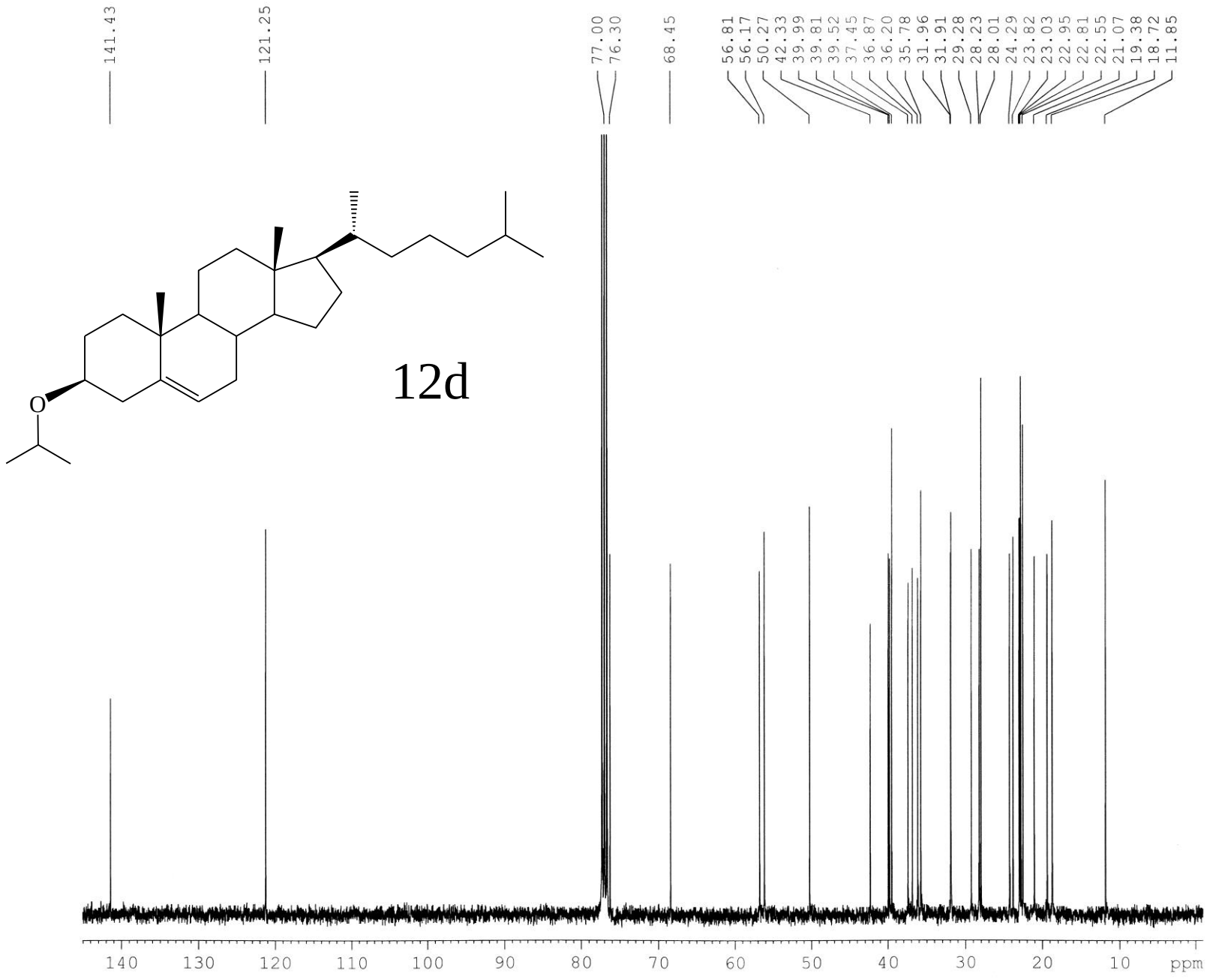



```
Current Data Parameters
NAME      AT eterizopropylowyw3
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20140425
Time               16.10
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG            zg30
TD                 65536
SOLVENT            CDCl3
NS                 64
DS                 0
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                 144
DW                 60.800 usec
DE                 8.00 usec
TE                 298.6 K
D1                 1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1               1H
P1                 11.15 usec
PL1                -3.00 dB
SFO1               400.1524711 MHz

F2 - Processing parameters
SI                 32768
SF                 400.1500000 MHz
WDW                GM
SSB                0
LB                 -0.20 Hz
GB                 0.2
PC                 1.00
```



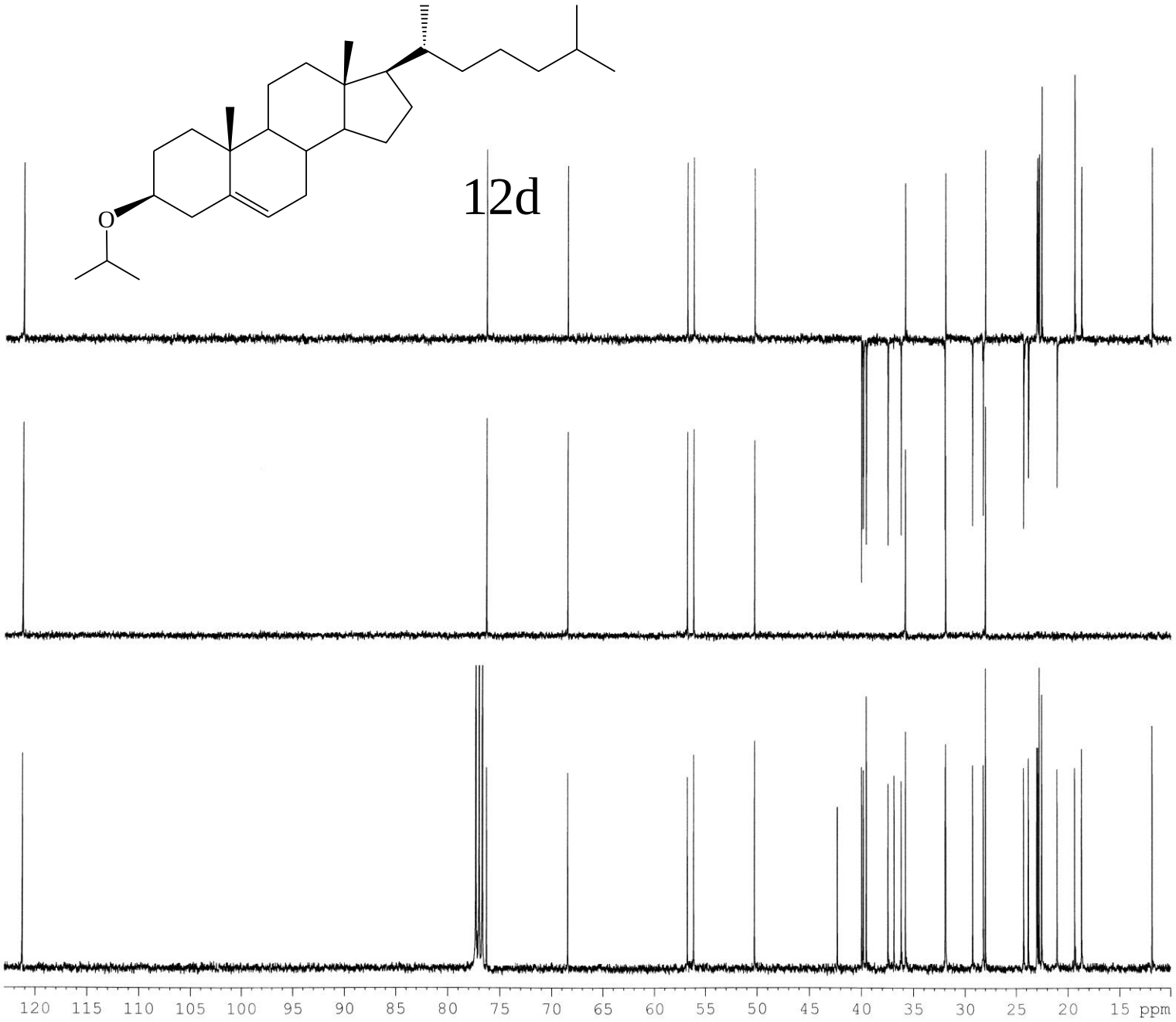

```
Current Data Parameters
NAME      AT eterizopropylowyw3
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_              20140425
Time                  16.16
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDC13
NS                      768
DS                        4
SWH               27173.912 Hz
FIDRES            0.414641 Hz
AQ                1.2059124 sec
RG                     2050
DW                   18.400 usec
DE                    6.00 usec
TE                   299.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   12.25 usec
PL1                  -1.00 dB
SFO1          100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -3.00 dB
PL12                 13.65 dB
PL13                 18.00 dB
SFO2          400.1516006 MHz

F2 - Processing parameters
SI                      32768
SF            100.6177982 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                     1.40
```



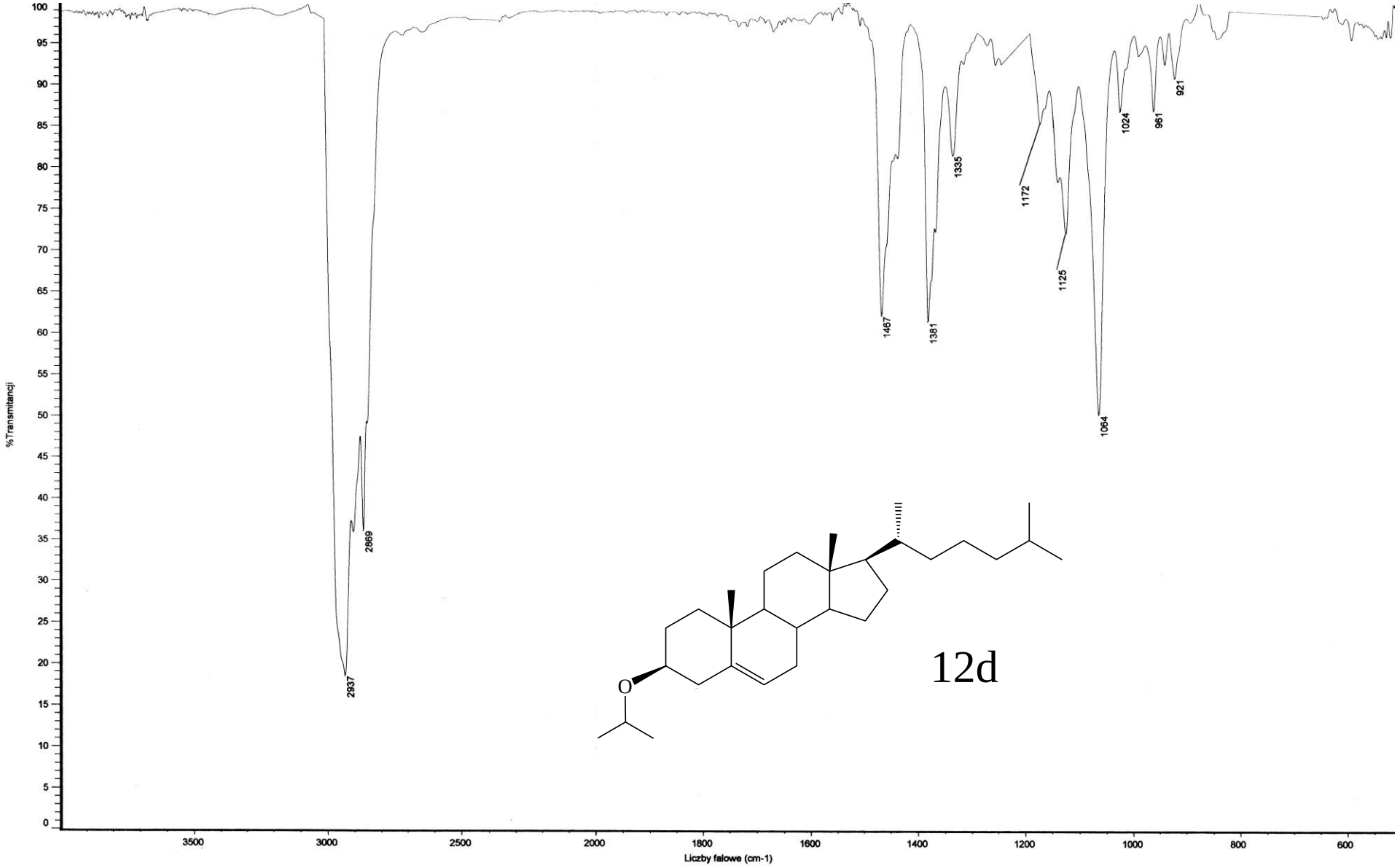

```
Current Data Parameters
NAME      AT eterizopropylowyw3
EXPNO                         4
PROCNO                        1

F2 - Acquisition Parameters
Date_              20140425
Time                 17.28
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                     320
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                   6.00 usec
TE                  299.4 K
CNST2          145.0000000
D1               2.00000000 sec
d2               0.00344828 sec
d12              0.00002000 sec
DELTA            0.00001560 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.25 usec
p2                   24.50 usec
PL1                  -1.00 dB
SFO1           100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
P3                   14.70 usec
p4                   29.40 usec
PCPD2               100.00 usec
PL2                  -3.00 dB
PL12                 13.65 dB
SFO2           400.1516006 MHz

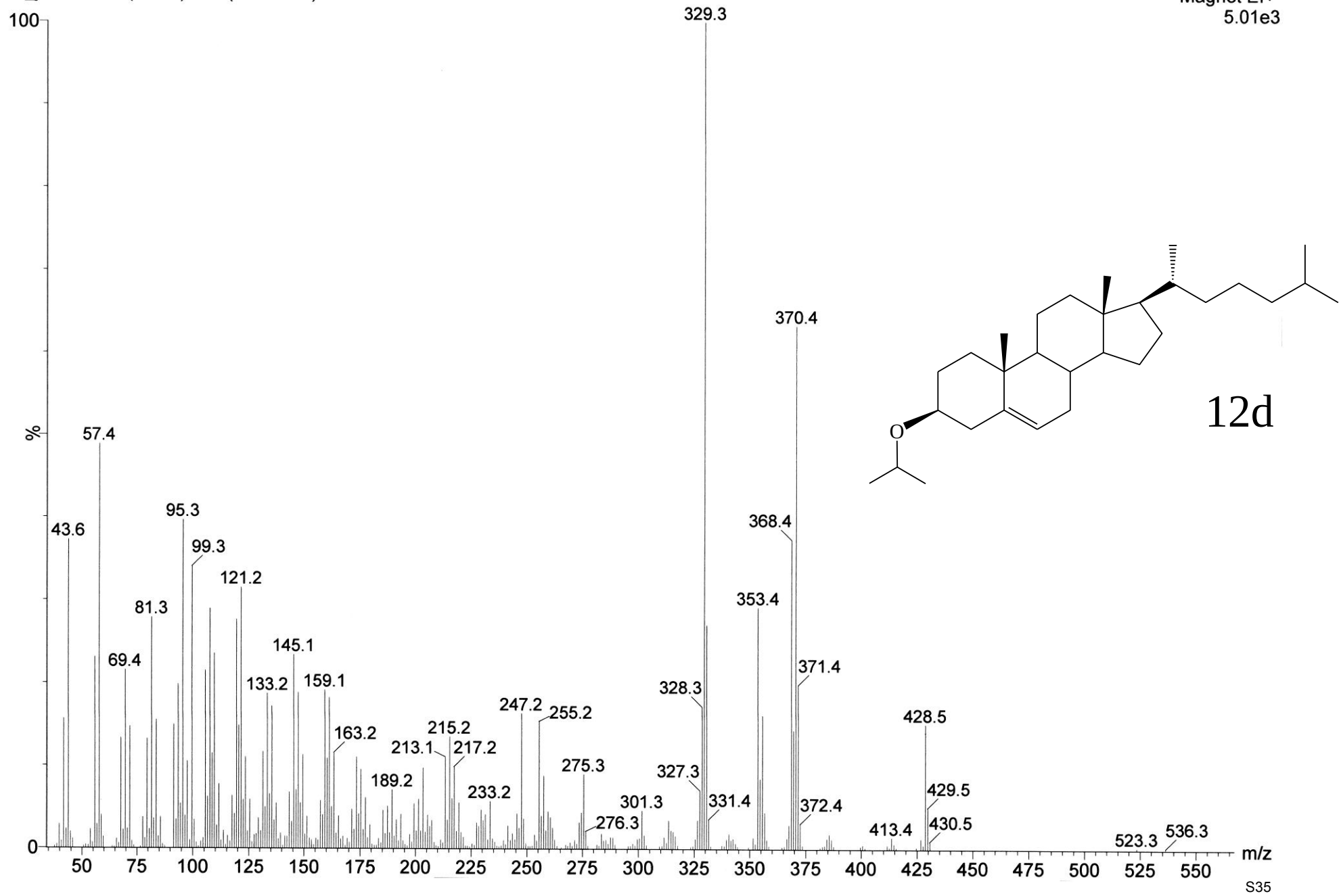
F2 - Processing parameters
SI                    32768
SF             100.6177983 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```


%Transmitancji
Liczby falowe (cm-1)
2937
2869
1467
1381
1335
1172
1125
1064
1024
961
921
O
12d

J. Morzycki
eter izopropylowy w3
ub_jm1100 54 (4.396) Cm (54:72-5:8)

AUTOSPEC

14-Apr-2014 10:30:58
operator: Malgorzata Grela
Magnet EI+
5.01e3



12d