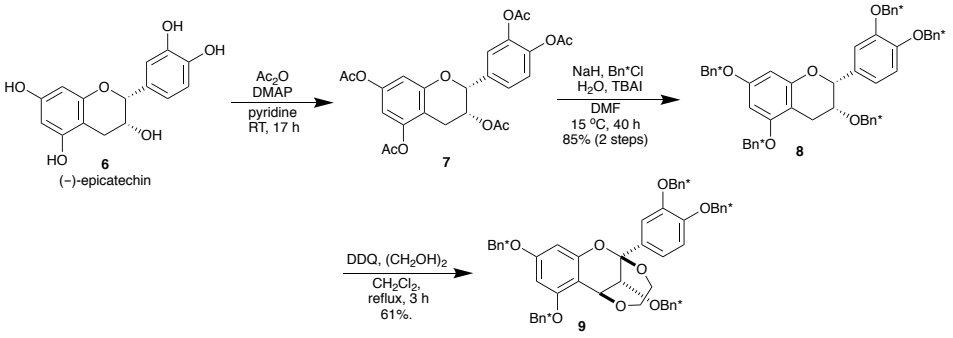
Supporting Information

General

All reactions utilizing air- or moisture-sensitive reagents were performed in flame-dried glasswares under an atmosphere of dry argon. Ethereal solvents and dichloromethane (anhydrous; Kanto Chemical Co., Inc.) were purified under argon, using an Organic Solvent Pure Unit (Wako Pure Chemical Industries, Ltd.). For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (TLC silica gel 60 F254, Art 5715, 0.25 mm) were used. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Silica gel 60 PF254 (Art 7747). For flash column chromatography, silica gel 60N (Spherical, neutral, 63–210 μm) from Kanto Chemical was used. Melting point (mp) determinations were performed by using a METTLER TOLEDO MP70 melting point system and are uncorrected. ^{1}H-, and ^{13}C-NMR were measured on a Bruker Avance III (600 MHz) spectrometer equipped with the cold probe (CryoProbe Prodigy^{TM}) and in the solvent indicated; Chemical shifts (d) are expressed in parts per million (ppm) downfield from internal standard (tetramethysilane 0.00 ppm) or referenced to residual undeuterated solvents as internal standard. All coupling constants (*J*) are reported as hertz (Hz). Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Thermo SCIENTIFIC NICOLET iS5 FT-IR spectrometer. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded by using Thermo SCIENTIFIC NICOLET iS5 FTIR spectrometer equipped iD5 ATR accessory. High-resolution mass spectra (HRMS) were obtained with Bruker Daltonics micrOTOF-Q II. Optical rotations ($[\alpha]_D$) were measured on a JASCO P-3000 polarimeter. High performance liquid chromatography (HPLC) analyses were performed on a LC-Net II/ADC controller (JASCO) equipped with a Jasco PU-2080 Plus Intelligent Pump, a Jasco MD-2010 Plus Multiwavelength Detector, a Jasco DG-2080-54 degasser and LG-2080-02 Ternary Gradient Unit. Preparative HPLC separation was performed on a LC-Net II/ADC controller (JASCO) equipped with a Jasco PU-2086 Plus Intelligent Prep Pump, a Jasco UV-1575 UV/Vis Detector and a Jasco DG-2080-54 degasser.

Preparation of acetal **9**



To a solution of (–)-epicatechin (**6**) (1.0 g, 3.4 mmol) in pyridine (3 mL) was added Ac_2O (1.95 mL, 20.7 mmol) and DMAP (12.6 mg, 0.103 mmol) at 0 °C and stirred for 17 h at room temperature. The reaction was quenched by adding water and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with 1 M HCl, brine, dried (Na_2SO_4), and concentrated in vacuo to give penta-acetate **7** as white solid which was used for the next reaction without further purification. To a solution of crude **7** in DMF (20 mL) at 0 °C was added NaH (1.8 g, 63% dispersion in mineral oil, 46 mmol) followed by tetrabutylammonium iodide (TBAI) (260 mg, 0.703 mmol). After stirring for 10 mins at 0 °C, $C_6D_5CD_2Cl$ (Bn*Cl) (2.1 mL, 18 mmol) was slowly added and the mixture was stirred at 15 °C for 40 h. The reaction was quenched at 0 °C by addition of water and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 4/1) to afford **8** (2.4 g, 85%) as a white amorphous foam.

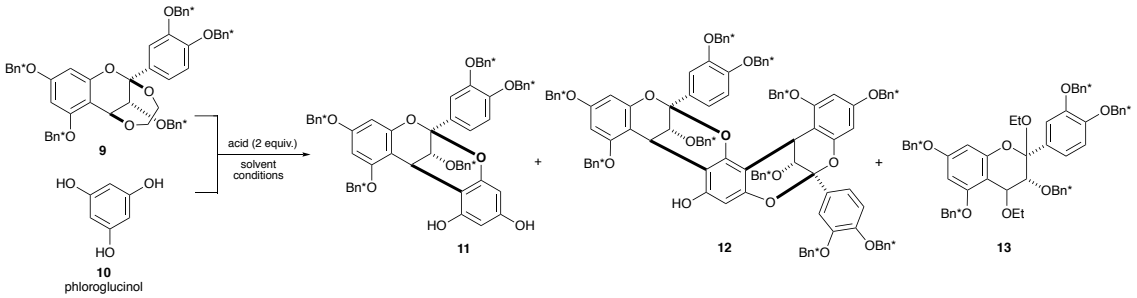
8: R_f = 0.78 (EtOAc/hexane = 1/2); $[\alpha]_D^{20}$ = –14 (*c* 0.80, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.80 (dd, *J* = 17.4, 4.2 Hz, 1H), 3.00 (dd, *J* = 17.4, 3.0 Hz, 1H), 3.94 (brs, 1H), 4.97 (s, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 6.93 (s, 1H), 6.94 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.7, 72.6, 78.3, 93.9, 94.9, 101.7, 114.1, 115.0, 120.0, 126.8–128.4, 132.4, 136.9, 137.0, 137.2, 137.3, 138.0, 148.6, 149.0, 155.8, 158.2, 158.8; IR (neat) 2894, 2272, 2179, 2074, 1616, 1590, 1513, 1492, 1356,1275, 1236, 1119, 1031, 1014, 1001, 815, 806, 771 cm^{-1}; HRMS (ESI) calcd for $C_{50}H_{10}D_{35}O_6$ [$(M+H)^+$] *m/z* 776.5407, found *m/z* 776.5437.

To a solution of **8** (1.0 g, 1.3 mmol) and ethylene glycol (120 mg, 1.93 mmol) in CH_2Cl_2 (50 mL) was added DDQ (1.2 g, 5.2 mmol) at room temperature, and then the mixture was refluxed for 3 h. Heating was stopped and reaction was quenched by addition of DMAP (1.27 g, 10.3 mmol) at

0 °C, and the stirring was continued for 30 min. The resulting precipitates were filtered off through a Celite® pad (washed with CH_2Cl_2). The filtrate was washed with saturated aqueous $NaHCO_3$ solution, H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 2/1) to afford **9** (0.66 g, 61%) as an ivory amorphous foam.

9: R_f = 0.52 (EtOAc/hexane = 1/2); $[\alpha]_D^{20}$ = –63 (*c* 0.89, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.36 (m, 2H), 3.97–3.99 (m, 1H), 4.01 (d, *J* = 1.8 Hz, 1H), 4.06–4.10 (m, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 6.30 (d, *J* = 1.8 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1 H), 7.09 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 65.8, 68.1, 70.5, 78.3, 95.3, 95.5, 100.4, 100.8, 114.3, 114.4, 119.6, 126.8–128.4, 135.1, 136.5, 136.8, 137.0, 137.2, 137.3, 148.8, 149.1, 155.1, 159.5, 161.2; IR (neat) 3008, 2920, 2280, 2196, 1616, 1590, 1183, 1162, 1141, 1054, 1032, 819, 754 cm^{-1}; HRMS (ESI) calcd for $C_{52}H_{12}D_{35}O_8$ [$(M+H)^+$] *m/z* 834.5462, found *m/z* 834.5496.

Model annulation study with phloroglucinol (**10**)



run	molar ratio of **9**/**10**	promotor	solvent (0.5 M)	conditions	**11**/%	**12**/%	**13**/%
1[a]	1/1	PPTS	EtOH	RT, 24 h	—	—	—
2[b]	1/1	PPTS	EtOH	reflux, 5 min	49	—	12
3	1/1	PPTS	EtOH	reflux, 0.5 h	50	24	—
4	1/1	CSA	EtOH	RT, 24 h	65	14	16
5	1/1	CSA	dioxane	RT, 24 h	66	8	—
6	1/1	CSA	EtOH, dioxane	RT, 24 h	84	7	—
7	1/1.5	CSA	EtOH, dioxane	RT, 24 h	98	1	—
8	1.5/1	CSA	EtOH, dioxane	RT, 24 h	52	44	—

a) Recovery of acetal **9**. b) 36% of **9** was recovered.

Procedure for entries 1, 4, 5 and 6

To a solution of acetal **9** (20 mg, 0.024 mmol) and phloroglucinol (**10)** (3.0 mg, 0.024 mmol) in solvent (as mentioned in table, 0.5 M) was added acid (as mentioned in table, 0.048 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford the products as mentioned in the table.

Procedure for entries 2, 3

To a solution of acetal **9** (20 mg, 0.024 mmol) and **10** (3.0 mg, 0.024 mmol) in ethanol (0.5 mL) was added PPTS (12 mg, 0.048 mmol) and stirred at refluxing temperature as per mentioned in table. It was allowed to cool to room temperature, diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford the product as mentioned in the table.

Procedure for the entry 7

To a solution of acetal **9** (20 mg, 0.024 mmol) and **10** (4.5 mg, 0.036 mmol) in mixture of ethanol and 1,4-dioxane (v/v = 1, 0.5 mL) was added CSA (11 mg, 0.048 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford **11** (21.0 mg, 98%) and **12** (0.4 mg, 1%).

Procedure for the entry 8

To a solution of acetal **9** (29.7 mg, 0.0356 mmol) and **10** (3.0 mg, 0.024 mmol) in mixed solvent ethanol and 1,4-dioxane (0.5 mL, v/v = 1) was added was added CSA (16.7 mg, 0.0719 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford to afford **11** (11.0 mg, 52%) and **12** (17.5 mg, 44%) as amorphous foam.

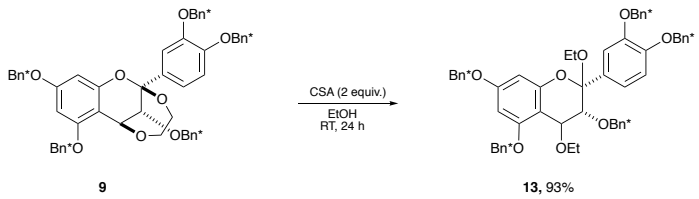
11: R_f = 0.32 (EtOAc/hexane = 3/7); $[\alpha]_D^{20}$ = –43 (*c* 0.41, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.82 (d, *J* = 3.0 Hz, 1H), 4.35 (d, *J* = 3.0 Hz, 1H), 4.68 (brs, 1H, OH), 6.01 (s, 1H), 6.02 (s, 2H), 6.34 (d, *J* = 3.6 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 6.96–6.98 (m, 2H), 7.24 (d, *J* = 1.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.6, 72.4, 95.1, 96.1, 96.3, 98.0, 98.7, 105.1, 106.1, 114.4, 114.7,

120.7, 127.0–128.8, 131.9, 135.0, 136.5, 137.0, 137.1, 137.1, 148.6, 149.6, 152.7, 153.5, 154.5, 155.4, 156.1, 159.1; IR (neat) 3416, 2310, 2180, 1604, 1505, 1419, 1274, 1181, 1136, 1084, 1038, 819, 542 cm^{-1}; HRMS (ESI) calcd for $C_{56}H_{12}D_{35}O_9$ [(M+H)$^+$] *m/z* 898.5415, found *m/z* 898.5382.

12: R_f = 0.55 (EtOAc/hexane = 3/7); $[\alpha]_D^{20}$ = –19 (*c* 0.82, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (d, *J* = 3.0 Hz, 1H), 3.84 (d, *J* = 3.6 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 4.98 (d, *J* = 3.0 Hz, 1H), 5.96 (d, *J* = 1.8 Hz, 1H), 6.15 (s, 1H), 6.23 (d, *J* = 2.4 Hz, 1H), 6.26 (d, *J* = 1.8 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 6.91 (s, 1H), 6.95 (d, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 7.19–7.22 (m, 2H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.5, 25.9, 72.4, 72.9, 94.5, 94.9, 95.3, 96.1, 98.2, 98.4, 98.6, 105.0, 105.1, 106.4, 106.7, 114.4.114.5, 114.5, 115.5, 1210.6, 120.6, 127.0-128.8, 132.5, 132.6, 135.0, 135.6, 136.8, 137.1, 137.2, 137.4, 138.1, 148.5, 141.6, 149.4, 149.6, 152.4, 152.8, 153.4, 143.7, 155.4, 157.6, 158.9, 159.1; IR (neat) 3419, 3011, 2359, 2341, 2275, 2188, 1617, 1508, 1490, 1418, 1273, 1183, 1140, 1085, 1052, 1036, 960, 819, 751, 541 cm^{-1}; HRMS (ESI) calcd for $C_{106}H_{17}D_{70}O_{15}$ [(M+H)$^+$] *m/z* 1670.0433, found *m/z* 1670.0453.

13: R_f = 0.83 (EtOAc/hexane = 3/7); $[\alpha]_D^{20}$ = –27.8 (*c* 1.45, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.96 (t, *J* = 4.8 Hz, 3H), 1.01 (t, *J* = 4.8 Hz, 3H), 3.20–3.23 (m, 1H), 3.35–3.42 (m, 2H), 3.50–3.52 (m, 1H), 3.69 (d, *J* = 1.2 Hz, 1H), 4.37 (d, *J* = 1.2 Hz, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1 H) 7.16 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.4, 15.7, 58.1, 64.5, 70.5, 94.7, 95.28, 101.2, 103.8, 114.4, 120.9, 127.3–128.3, 133.1, 136.8, 137.0, 137.2, 137.3, 148.6, 148.9, 153.0, 159.8, 160.6; IR (neat) 2912, 2848, 1666, 1650, 1643, 1580, 1538, 1503, 1462, 1454, 1159, 1089, 503 cm^{-1}; HRMS (ESI) calcd for $C_{54}H_{18}D_{35}O_8$ [(M+H)$^+$] *m/z* 864.5931, found *m/z* 864.5890.

Preparation of 2,4-diethoxy flavan **13** from **9**

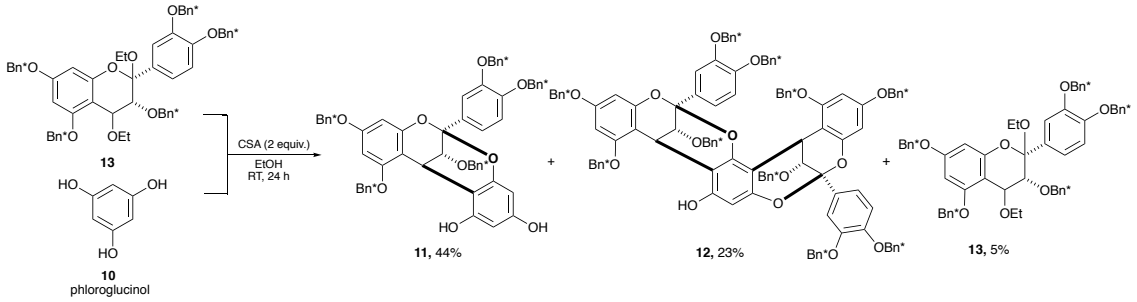


9 **13**, 93%

To a solution of acetal **9** (20 mg, 0.024 mmol) in mixture of ethanol and 1,4-dioxane (v/v = 1, 0.5 mL) was added CSA (11 mg, 0.048 mmol) at room temperature. After stirring for 16 h at the same

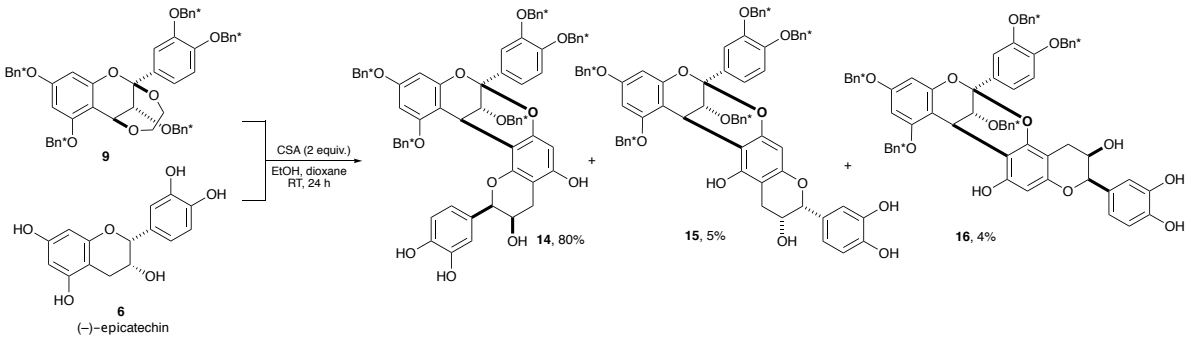
temperature, the reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 8/2) to afford **13** (19.3 mg, 93%).

Annulation of 2,4-diethoxy flavan **13** with phloroglucinol (**10**)



To a solution of 2,4-diethoxy flavan **13** (21.6 mg, 0.0248 mmol) and **10** (3.0 mg, 0.024 mmol) in ethanol (0.5 mL) was added CSA (11 mg, 0.048 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford to afford **11** (9.7 mg, 44%), **12** (4.5 mg, 23%), and recovered starting material **13** (1.2 mg, 5%).

Direct coupling of **9** with (–)-epicatechin (**6**)



To a solution of acetal **9** (50 mg, 0.059 mmol) and (–)-epicatechin (**6**) (26 mg, 0.090 mmol) in mixture of ethanol and 1,4-dioxane (v/v = 1, 1.25 mL) was added CSA (28 mg, 0.12 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (CH_2Cl_2/EtOAc = 7/3) to afford dimer **14** (50.8 mg,

80%) as a white amorphous form along with mixture of **15** and **16** which was separated by PTLC (CH_2Cl_2/EtOAc = 7/3, two runs) giving **15** (3.2 mg, 5%) and **16** (2.7 mg, 4%).

14: R_f = 0.20 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –59 (*c* 0.74, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 2.45 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.90 (dd, *J* =16.2, 5.4 Hz, 1H), 3.87 (d, *J* = 6.6 Hz, 1H), 4.18 (brs, 1H), 4.84 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 3.6 Hz, 1H), 6.08 (s, 1H), 6.16 (d, *J* = 1.8 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 27.5, 28.4, 67.9, 75.8, 80.9, 96.5, 96.7, 96.8, 100.8, 103.4, 106.9, 108.0, 116.1, 116.8, 116.8, 121.0, 122.5, 128.2–129.9, 132.2, 134.8, 139.2, 139.2, 139.3, 139.5, 139.9, 146.5, 146.5, 150.2, 151.3, 153.2, 154.3, 156.2, 157.1, 159.5, 160.8; IR (neat) 3400, 2276, 2116, 1615, 1509, 1494, 1470, 1327, 1183, 1144, 1115, 1095, 1052, 959, 833, 819, 754, 542 cm^{-1}; HRMS (ESI) calcd for $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5862.

15: R_f = 0.28 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –33 (*c* 0.82, $CHCl_3$); ^{1}H NMR (600 MHz, D_2O in $CDCl_3$) δ 2.80–2.89 (m, 2H), 3.81 (d, *J* = 3.6 Hz, 1H), 4.15 (brs, 1H), 4.35 (d, *J* = 3.6 Hz, 1H), 4.80 (s, 1H), 6.19 (s, 1H), 6.34 (d, *J* = 1.8 Hz, 1H), 6.42 (d, *J* = 1.8 Hz, 1H), 6.81 (s, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.26 (2H, overlapped with CH of $CHCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.9, 28.2, 66.8, 72.4, 78.2, 95.2, 96.2, 96.8, 98.7, 101.3, 105.2, 106.3, 113.7, 114.5, 115.5, 119.0, 120.8, 123.0–128.8, 131.1, 132.0, 135.1, 136.5, 137.0, 137.1, 137.1, 143.77, 143.80, 148.6, 149.6, 150.6, 151.9, 153.6, 154.2, 155.4, 159.1; IR (neat) 3411 (br), 2922, 1619, 1600, 1510, 1419, 1275, 1194, 1052, 1124, 1038, 960, 838, 819, 752, 543 cm^{-1}; HRMS (ESI) calcd for $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5857.

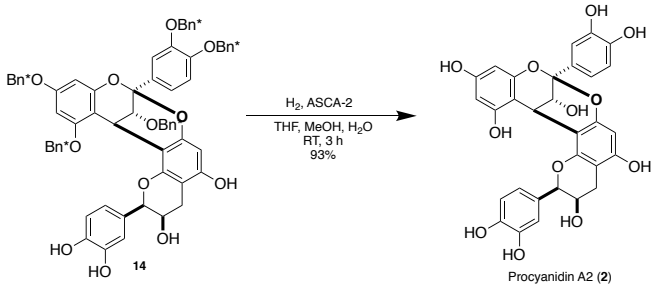
16: R_f = 0.33 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –51 (*c* 0.90, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 2.67 (dd, *J* = 16.8, 2.4 Hz 1H), 2.73 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.86 (d, *J* = 3.6 Hz, 1H), 4.06–4.08 (m, 1H), 4.73 (d, *J* = 3.6 Hz, 1H), 4.76 (s, 1H), 6.09 (s, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.77 (s, 1H), 6.78 (s, 1H), 6.96 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5, 30.2, 67.8, 72.3, 75.2, 80.3, 80.8, 96.7, 97.5, 99.2, 100.5, 101.6, 107.7, 108.1, 116.0, 116.1, 116.8, 116.9, 120.3, 122.8, 128.9-130.2, 132.9, 134.6, 138.5, 139.2, 139.3, 139.4, 139.4, 146.7, 146.8, 150.3, 151.45, 152.5, 154.7, 155.7, 156.7, 158.4, 161.0; IR (neat) 3412 (br), 2920, 1601, 1508, 1419, 1327, 1274,

1184, 1152, 1084, 1051, 819, 542 cm^{-1}; HRMS (ESI) calcd for $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5843.

General procedure for hydrogenolysis of dimers **14**, **15** and **16**:

To a solution of dimer (1.0 equiv.) in the presence of ASCA-2 (0.75 equiv.) in a mixture of THF, MeOH and H_2O (v/v/v = 2/2/1, 0.005M) was stirred under H_2 atmosphere at room temperature. After stirring for 3.0 h, the mixture was carefully filtered through a glass fiber filter (MeOH) under argon atmosphere and the filtrate was evaporated to remove organic solvents and lyophilized to give a crude material, which was further purified by preparative HPLC [Mightysil RP-18GP II, (20 mm f × 250 mm), l = 280 nm, 25 °C, MeOH, H_2O = 35/65 containing 0.1% TFA, flow rate 10 mL/min, 20 x 250 mm] and lyophilization to give debenzylated products.

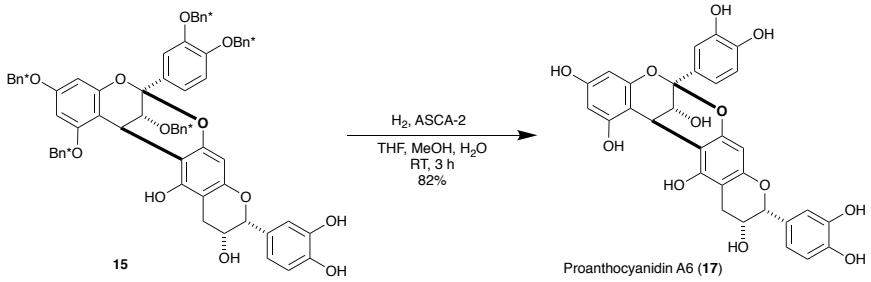
Synthesis of procyanidin A2 (**2**)



Starting from dimer **14** (23 mg, 0.021 mmol) in the presence of ASCA-2 (47 mg, 0.017 mmol), procyanidin A2 (**2**) (11.2 mg, 89%) was obtained as a white amorphous foam.

2: $[\alpha]_D^{20}$ = +70 (*c* 0.10, acetone), [lit.[1] $[\alpha]_D^{20}$ = +55.63 (*c* 1.08, acetone)]; ^{1}H NMR (600 MHz, CD_3OD) δ 2.79 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.98 (dd, *J* = 16.8, 4.8 Hz, 1H), 4.08 (d, *J* = 3.6 Hz, 1H), 4.27 (brs, 1H), 4.44 (d, *J* = 3.6 Hz, 1H), 4.96 (s, 1H), 6.04 (d, *J* = 1.8 Hz, 1H), 6.10 (d, *J* = 1.8 Hz, 1H), 6.12 (s, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 29.9, 30.1, 68.7, 69.0, 85.4, 97.4, 97.4, 99.0, 101.2, 104.0, 104.9, 107.7, 116.5, 116.6, 116.6, 117.2, 120.7, 121.5, 131.4, 133.2, 146.5, 147.2, 147.6, 147.7, 152.3, 153.1, 155.1, 157.0, 157.6, 159.0; IR (ATR) 3400 (br), 2276, 2116 1615, 1509, 1494, 1476, 1327, 1183, 1144, 1115, 1052, 959, 838, 819, 754, 542 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}O_{12}$ ([$M+H]^+$) *m/z* 577.1340, found *m/z* 577.1231.

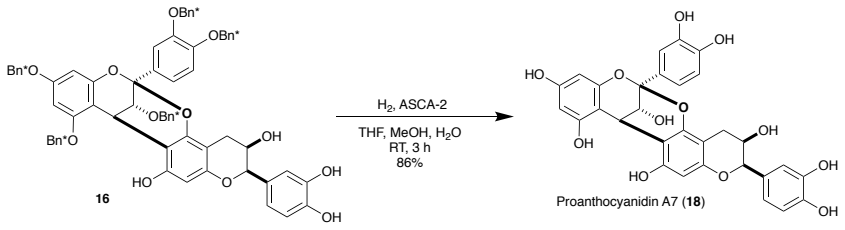
Synthesis of proanthocyanidin A6 (**17**)



Starting from dimer **15** (20 mg, 0.018 mmol) in the presence of ASCA-2 (41 mg, 0.015 mmol), **17** (9.0 mg, 82%) was obtained as a white amorphous foam.

17: $[\alpha]_D^{20}$ = +32 (c 0.14, acetone), [lit.[2] $[\alpha]_D^{21}$ = +22.4 (c 1.2, acetone)]; ^{1}H NMR (600 MHz, CD_3OD) δ 2.81 (dd, *J* = 16.8, 3.0 Hz, 1H), 2.96 (dd, *J* = 16.8, 5.4 Hz, 1H), 4.11–4.14 (m, 1H), 4.21 (brs, 1H), 4.31 (d, *J* = 3.6 Hz, 1H), 4.84 (s, 1H), 6.06 (d, *J* = 2.4 Hz, 1H), 6.11 (d, *J* = 2.4 Hz, 1H), 6.14 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.81 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 30.4, 30.6, 62.4, 68.3, 68.5, 80.8, 97.8, 97.8, 101.4, 103.9, 105.1, 109.7, 116.1, 116.5, 116.7, 116.7, 120.2, 120.8, 132.9, 133.1, 146.5, 146.7 146.8, 147.7, 152.6, 153.7, 155.3, 156.2, 156.6, 159.0; IR (ATR) 3224 (br), 1606, 1519, 1449, 1352, 1284, 1210, 1106, 969, 867, 820, 793, 714, 654 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{24}O_{12}$ ($[M–H]^-$) m/z 575.1195, found *m/z* 575.1181.

Synthesis of proanthocyanidin A7 (**18**)

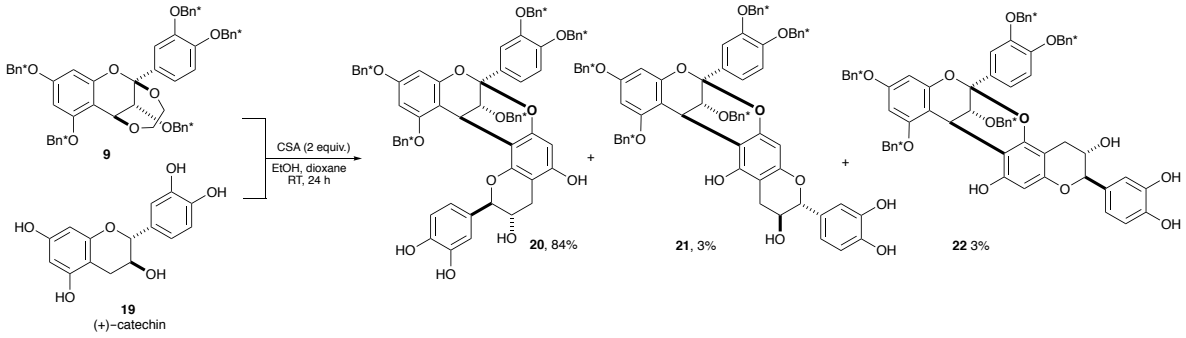


Starting from dimer **16** (19.3 mg, 0.0181 mmol) in the presence of ASCA-2 (39 mg, 0.014 mmol), **18** (8.9 mg, 86%) was obtained as a white amorphous foam.

18: $[\alpha]_D^{20}$ = +36 (*c* 0.15, acetone), [lit.[2] $[\alpha]_D^{21}$ = +35.9 (c 1.2, acetone)]; ^{1}H NMR (600 MHz, CD_3OD) δ 2.80 (dd, *J* = 16.8, 3.0 Hz, 1H), 3.01 (dd, *J* = 16.8, 4.2 Hz, 1H), 4.14 (d, *J* = 3.6 Hz, 1H), 4.21 (brs, 1H), 4.32 (d, *J* = 3.6 Hz, 1H), 4.87 (1H, overlapped with HOD), 6.03 (d, *J* = 2.4

Hz, 1H), 6.09 (d, *J* = 2.4 Hz, 1H), 6.14 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 1.8 Hz, 1H), 7.11 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 27.9, 28.2, 65.6, 66.3, 78.6, 95.2, 96.3, 96.5, 99.1, 99.6, 103.0, 107.3, 113.8, 114.3, 114.5, 118.0, 118.6, 130.6, 130.9, 144.3, 144.4, 144.6, 145.4, 150.4, 151.1, 152.8, 154.2, 154.7, 156.8; IR (ATR) 3291 (br), 2565, 2187, 1608, 1519, 1443, 1281, 1197, 1078, 1027, 1010, 972, 880, 821, 784, 621 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}O_{12}$ ([M+H]$^+$) *m/z* 577.1340, found *m/z* 577.1327.

Direct coupling of **9** with (+)-catechin (**19**)



To a solution of acetal **9** (50 mg, 0.059 mmol) and (+)-catechin (**19**) (26 mg, 0.090 mmol) in mixture of ethanol and 1,4-dioxane (v/v = 1, 1.25 mL) was added CSA (28 mg, 0.12 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction mixture was diluted with ethyl acetate, washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (CH_2Cl_2/EtOAc = 7/3) to afford dimer **20** (53.0 mg, 84%) as a white amorphous foam along with mixture of **21** and **22**, which was further separated by PTLC (CH_2Cl_2/EtOAc = 7/3, two runs), giving **21** (1.8 mg, 3%) and **22** (1.8 mg, 3%).

20: R_f = 0.22 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –74 (*c* 0.60, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 2.50 (dd, *J* = 16.8, 4.2 Hz, 1H), 2.64 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.90 (brs, 1H), 4.07 (d, *J* = 4.2 Hz, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 5.15 (d, *J* = 2.4 Hz, 1H), 6.06 (s, 1H), 6.20 (s, 1H), 6.32 (s, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.60 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H) 7.23 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 26.6, 27.4, 68.6, 75.7, 82.7, 96.1, 96.6, 100.8, 103.0, 106.8, 108.0, 115.3, 116.1, 116.8, 116.9, 119.9, 112.5, 128.2–130.0, 133.4, 134.9, 139.26, 139.28, 139.3, 139.6, 139.6, 146.6, 146.9, 150.2, 151.3, 152.9, 153.0, 153.7,

153.7, 156.3, 157.1, 157.1, 159.4, 160.9; IR (neat) 3412(br), 2310, 1610, 1508, 1447, 1420, 1274, 1182, 1149, 1116, 1052, 1039, 819, 754 cm^{-1}; HRMS (ESI) calcd for $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5845.

21: R_f = 0.25 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –34 (*c* 1.4, $CHCl_3$); ^1H NMR (600 MHz, CD_3OD) δ 2.55 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.80 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.86 (d, *J* = 3.6 Hz, 1H), 4.00 (brs, 1H), 4.50 (d, *J* = 3.0 Hz, 1H), 4.59 (d, *J* = 7.20 Hz, 1H), 6.06 (s, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 27.8, 29.1, 69.2, 72.4, 75.0, 83.5, 96.8, 97.7, 97.9, 100.7, 104.6, 107.4, 107.8, 116.0, 116.1, 116.8, 117.0, 120.6, 122.6, 128.9–130.3, 132.9, 134.4, 137.8, 139.0, 139.2, 139.3, 139.3, 147.1, 147.1, 140.2, 151.4, 152.6, 153.6, 155.6, 156.6, 156.4, 157.7, 161.1; IR (neat) 3402 (br), 2310, 1618, 1596, 1488, 1404, 1273, 1184, 1120, 1052, 1039, 819, 747 cm^{-1}; HRMS (ESI) calcd $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5852.

22: R_f = 0.38 (EtOAc/CH_2Cl_2 = 3/7); $[\alpha]_D^{20}$ = –46 (*c* 1.1, $CHCl_3$); ^1H NMR (600 MHz, CD_3OD) δ 2.59 (dd, *J* = 16.8, 7.8 Hz, 1H), 2.74 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.85 (d, *J* = 3.6 Hz, 1H), 3.93 (brs, 1H), 4.66 (d, *J* = 7.2 Hz, 1H), 4.71 (d, *J* = 3.6 Hz, 1H), 6.05 (s, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 27.5, 28.6, 69.1, 72.2, 72.3, 75.2, 83.6, 96.8, 97.6, 98.9, 100.6, 102.3, 107.6, 108.0, 115.8, 116.1, 116.9, 117.0, 120.6, 122.7, 128.9–130.2, 132.9, 134.6, 138.4, 139.1, 139.2, 139.3, 139.4, 147.1, 150.3, 151.4, 152.1, 154.8, 155.7, 156.2, 158.5, 161.0; IR (neat) 3419 (br), 2315, 1601, 1508, 1419, 1328, 1270, 1184, 1152, 1038, 819, 542 cm^{-1}; HRMS (ESI) calcd for $C_{65}H_{20}D_{35}O_{12}$ [$(M+H)^+$] *m/z* 1062.5884, found *m/z* 1062.5876.

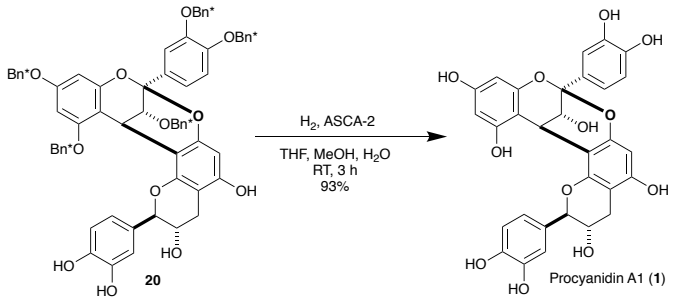
General procedure for hydrogenolysis of annulation products **20**, **21** and **22**

To a solution of dimers (1.0 equiv.) in the presence of ASCA-2 (0.75 equiv.) in a mixture of THF, MeOH and H_2O (v/v/v = 2/2/1, 0.005 M) was stirred under H_2 atmosphere at room temperature. After stirring for 3.0 h, the mixture was carefully filtered through a glass fiber filter (MeOH) under argon atmosphere and the filtrate was evaporated to remove organic solvents and lyophilized to give a crude material, which was further purified by preparative HPLC [Mightysil RP-18GP II, (20 mm f × 250 mm), l = 280 nm, 25 °C, MeOH, H_2O = 35/65 containing 0.1% TFA,

flow rate 10 mL/min, 20 x 250 mm] and lyophilization to give products a white amorphous compounds.

*Procyanidin A1 (**1**)*

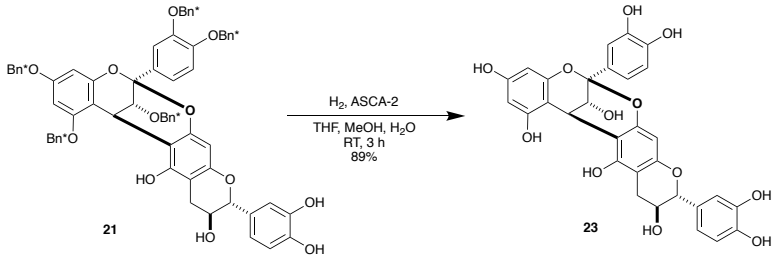
Starting from dimer **20** (20 mg, 0.018 mmol) in the presence of ASCA-2 (41 mg, 0.015 mmol), procyanidin A_1 (**1**) (10.1 mg, 93%) was obtained as a white amorphous foam.



1: $[\alpha]_D^{20}$ = +78 (*c* 0.57, acetone) [lit.[3] $[\alpha]_D^{26}$ = +62.9 (c 1.4, acetone)]; ^{1}H NMR (600 MHz, CD_3OD) δ 2.60 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.97 (dd, *J* = 16.8, 6.6 Hz, 1H), 4.10 (d, *J* = 3.6 Hz, 1H), 4.16–4.19 (m, 1H), 4.26 (d, *J* = 3.6 Hz, 1H), 4.76 (d, *J* = 7.8 Hz, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 6.09 (d, *J* = 2.4 Hz, 1H), 6.11 (s, 1H), 6.83–6.84 (m, 3H), 6.94 (s, 1H), 7.04 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 29.9, 30.1, 68.7, 67.0, 85.4, 97.4, 97.4, 99.0, 101.2, 104.0, 104.9, 107.7, 116.5, 116.6, 116.6, 117.2, 120.7, 121.5, 131.4, 133.2, 146.5, 147.2, 147.6, 147.7, 152.3, 153.1, 155.1, 157.0, 157.6, 159.0; IR (ATR) 3412 (br), 2232, 1610, 1508, 1508, 1447, 1420, 1327, 1274, 1182, 1149, 1116, 1052, 1039, 960, 819, 754, 543 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}O_{12}$ ($[M+H]^+$) *m/z* 577.1340, found *m/z* 577.1318.

*Doubly-linked dimeric proanthocyanidin **23***

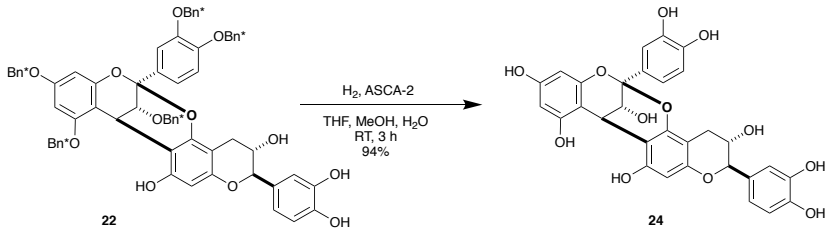
Starting from regioisomeric annulation product **21** (24 mg, 0.023 mmol) in the presence of ASCA-2 (50 mg, 0.018 mmol), **23** (11.7 mg, 89%) was obtained as a white amorphous foam.



23: $[\alpha]_D^{20}$ = +9 (*c* 0.1, acetone), [lit.[1] $[\alpha]_D^{20}$ +10.128 (c 1.05, acetone)]; ^{1}H NMR (600 MHz, CD_3OD) δ 2.65 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.84 (dd, *J* = 16.2, 5.4 Hz, 1H), 4.05–4.09 (m, 1H), 4.14 (d, *J* = 2.4 Hz, 1H), 4.31 (d, *J* = 2.4 Hz, 1H), 4.70 (d, *J* = 6.6 Hz, 1H), 6.05 (s, 1H), 6.06 (s, 1H), 6.11 (s, 1H), 6.71 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 1.8 Hz, 1H), 6,85 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.19 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 28.7, 30.6, 68.5, 69.3, 83.4, 97.5, 97.8, 101.4, 104.4, 105.1, 109.6, 115.8, 116.5, 116.7, 117.0, 120.4, 120.8, 133.0, 133.1, 146.5, 147.0, 147.1, 152.9, 153.4, 155.3, 156.0, 156.2, 159.1; IR (ATR) 3280 (br), 1606, 1519, 1441, 1342, 1280, 1170, 1103, 1081, 1003, 970, 867, 818, 780, 626 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{23}O_{12}$ ([M–H]$^-$) *m/z* 575.1195, found *m/z* 575.1173.

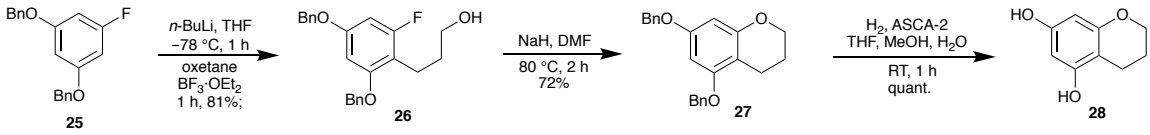
*Doubly-linked dimeric proanthocyanidin **24***

Starting from regioisomeric annulation product **22** (28 mg, 0.027 mmol) in the presence of ASCA-2 (58 mg, 0.021 mmol), **24** (14.5 mg, 94%) was obtained as a white amorphous foam.



24: $[\alpha]_D^{20}$ = +33 (*c* 0.15, acetone); ^{1}H NMR (600 MHz, CD_3OD) δ 2.68 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.80 (dd, *J* = 16.2, 5.4 Hz, 1H), 4.03–4.06 (m, 1H), 4.13 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 3.0 Hz, 1H), 4.73 (d, *J* = 6.6 Hz, 1H), 6.06 (s, 1H), 6.11 (s, 1H), 6.12 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.78 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 28.3, 30.3, 68.5, 69.1, 83.6, 97.5, 98.3, 98.6, 101.4, 102.5, 105.2, 109.4, 115.6, 116.5, 116.7, 117.0, 120.5, 120.9, 133.0, 133.1, 146.5, 147.0, 147.07, 147.70, 152.2, 153.4, 155.0, 156.1, 156.9, 159.1; IR (ATR) 3299 (br), 1608, 1517, 1441, 1283, 1177, 1120, 1082, 1008, 971, 872, 818, 781 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{23}O_{12}$ ([M–H]$^-$) *m/z* 575.1195, found *m/z* 575.1163.

Synthesis of model substrate **28**



To a solution of fluorobenzene **25** (1.0 g, 3.2 mmol) in THF (8 mL) was added *n*-BuLi (2.2 mL, 1.58 M hexane solution, 3.5 mmol) at –78 °C. After stirring for 1 h, a solution of oxetane (0.25 mL, 3.84 mmol) and $BF{\cdot}OEt_2$ (0.48 mL, 3.88 mmol) in THF (10 mL) were successively added at –78 °C. The stirring was continued for 30 min and the reaction was stopped by adding saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc (x3), and the combined extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 5:1) to afford alcohol **26** (961 mg, 81%) as a white solid.

26: R_f = 0.51 (EtOAc/hexane = 2/3); mp 73–75 °C (hexane/EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.68 (brs, 1H), 1.77–1.82 (m, 2H), 2.73 (t, *J* = 6.6 Hz, 2H), 3.56 (t, *J* = 5.4 Hz, 2H), 5.00 (s, 2H), 5.03 (s, 2H), 7.33–7.36 (m, 2H), 7.38-7.42 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.3, 18.3, 32.4, 61.9, 70.5, 70.8, 94.6, 94.8, 96.5, 96.6, 110.1, 110.3, 127.5, 127.7, 128.3, 128.4, 128.8, 128.9, 136.5, 136.6, 158.3, 158.4, 158.4, 158.5, 161.5, 163.1; IR (neat) 3358 (br), 2925, 2862, 1498, 1586, 1452, 1374, 1357, 1164, 1101, 1064, 1036, 1003, 984, 818, 802, 692 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}FO_3$ [(M+H)$^+$] *m/z* 367.1704, found *m/z* 367.1592.

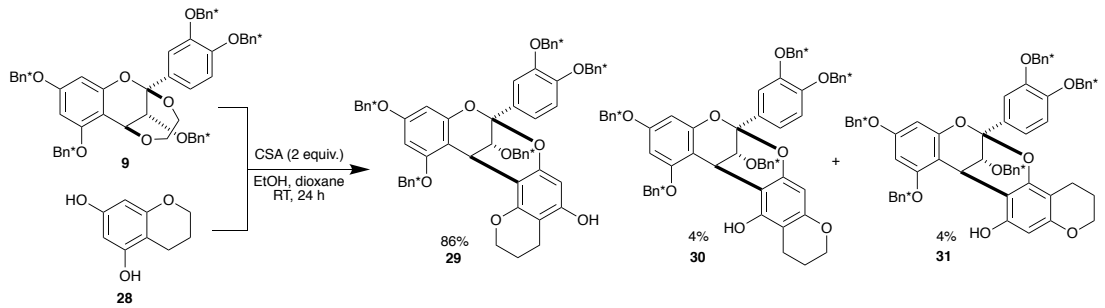
To a suspension of NaH (63% dispersion in mineral oil, 75 mg, 2.0 mmol) in DMF (13 mL) was added alcohol **26** (480 mg, 1.31 mmol) in DMF (13 mL) at 0 °C. After stirring at 80 °C for 2 h, the reaction was quenched with slow addition of water at 0 °C and extracted with EtOAc (x3). The combined extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford pyran **27** (326 mg, 72%) as off-white solid.

27: R_f = 0.76 (EtOAc/hexane = 2/3); mp 84–85 °C (hexane/EtOAc), ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.95–1.99 (m, 2H), 2.67 (t, *J* = 6.6 Hz, 2H), 4.15 (t, *J* = 5.4 Hz, 2H), 5.00 (s, 2H), 5.02 (s, 2H), 6.14 (d, *J* = 2.4 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 7.32–7.35 (m, 2H), 7.38–7.44 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.2, 22.1, 70.0, 70.3, 93.2, 94.9, 104.6, 127.3, 127.7, 127.9, 128.1, 128.7, 128.7, 137.2, 137.4, 156.3, 157.9, 158.5; IR (neat) 3064, 2954, 2883, 1613, 1594, 1583, 1498, 1468, 1436, 1376, 1228, 1127, 1065, 1035, 910, 808, 765, 744 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}O_3$ [(M+H)$^+$] *m/z* 347.1641, found *m/z* 347.1636.

To a solution of pyran **27** (321 mg, 0.926 mmol) in the presence of ASCA-2 (624 mg, 0.223 mmol) in a mixture of THF, MeOH and H_2O (v/v/v = 2/2/1, 50 mL) was stirred under H_2 atmosphere at room temperature. After stirring for 1 h, the mixture was carefully filtered through a glass fiber filter (MeOH) under argon atmosphere. The filtrate was evaporated, and the residue was purified by recrystallization (EtOAc) to give phenol **28** (152 mg, quant.) as ivory solid.

28: R_f = 0.18 (EtOAc/hexane = 2/3); mp 178–179 °C (lit.[4] 176 °C), ^{1}H NMR (600 MHz, CD_3OD) δ 1.89–1.93 (m, 2H), 2.54 (t, *J* = 6.2 Hz, 2H), 4.09 (t, *J* = 5.4 Hz, 2H), 5.78 (d, *J* = 2.4 Hz, 1H), 5.90 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (150 MHz, CD_3OD) δ 20.7, 24.2, 68.1, 96.7, 96.7, 103.6, 158.1, 158.1, 158.2, 158.2, 158.38, 158.40; IR (ATR) 3352, 3217, 1618, 1518, 1472, 1442, 1385, 1275, 1189, 1046, 1011, 948, 875, 802 cm^{-1}; HRMS (ESI) calcd for $C_9H_{11}O_3$ [(M+H)$^+$] *m/z* 167.0702, found *m/z* 167.0707.

Annulation of **9** with model substrate **28**



To a solution of acetal **9** (50 mg, 0.059 mmol) and **28** (15 mg, 0.090 mmol) in mixture of ethanol and 1,4-dioxane (v/v=1, 1.25 mL) was added CSA (28 mg, 0.12 mmol) at room temperature. After stirring for 24 h at the same temperature, the reaction mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 3/2) to afford dimer **29** (48.2 mg, 86%) as a white amorphous foam along with mixture of **30** and **31** which was separated by PTLC (hexane/CH_2Cl_2/EtOAc = 65/30/5, three runs) giving **30** (2.3 mg, 4%) and **31** (2.0 mg, 4%) as a gummy solid.

29: R_f = 0.65 (EtOAc/hexane = 1/1); $[\alpha]_D^{20}$ = –36 (*c* 0.84, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.77–1.83 (m, 2H), 2.47–2.54 (m, 2H), 3.65–3.74 (m, 2H), 3.85 (d, *J* = 3.0 Hz, 1H), 4.71 (s, 1H), 4.98 (d, *J* = 3.0 Hz, 1H), 5.97 (s, 1H), 6.25 (s, 1H), 6.35 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.0, 21.6, 21.7, 25.1, 65.9,

73.2, 94.7, 94.9, 98.6, 103.0, 105.6, 106.6, 114.4, 114.5, 120.6, 125.5–128.4, 129.2, 132.6, 136.8, 137.2, 137.2, 137.5, 137.5, 138.1, 148.5, 149.3, 151.0, 152.8, 153.2, 153.9, 157.6, 158.9; IR (neat) 3419 (br), 2938, 2276, 1615, 1490, 1453, 1490, 1441, 1419, 1327, 1273, 1201, 1123, 1098, 1051, 960, 909, 818, 730, 542 cm^{-1}; HRMS (ESI) calcd for $C_{59}H_{16}D_{35}O_9$ [$(M+H)^+$] *m/z* 938.5724, found *m/z* 938.5742.

30: R_f = 0.68 (EtOAc/hexane = 1/1); $[\alpha]_D^{20}$ = –24 (*c* 0.53, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.89–1.91 (m, 2H), 2.51–2.61 (m, 2H), 3.82 (d, *J* = 3.6 Hz, 1H), 4.03–4.09 (m, 2H), 4.37 (d, *J* = 3.6 Hz, 1H), 6.06 (s, 1H), 6.33 (s, 1H), 6.42 (s, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 7.03 (s, 1H), 7.24–7.26 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.3, 22.1, 25.9, 66.6, 72.4, 95.2, 96.1, 96.6, 98.6, 104.9, 105.2, 105.3, 114.4, 114.5, 120.7, 127.1–128.7, 132.1, 135.1, 136.5, 137.0, 137.1, 137.1, 148.6, 149.5, 150.1, 151.3, 153.6, 155.2, 155.4, 159.1; IR (neat) 3418 (br), 3010, 2355, 1619, 1597, 1507, 1490, 1450, 1273, 1201, 1120, 1083, 1052, 1038, 959, 909, 819, 731, 541 cm^{-1}; HRMS (ESI) calcd for $C_{59}H_{16}D_{35}O_9$ [$(M+H)^+$] *m/z* 938.5724 found *m/z* 938.5700.

31: R_f = 0.68 (EtOAc/hexane = 1/1); $[\alpha]_D^{20}$ = –59 (*c* 0.74, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 1.85–1.86 (m, 2H), 2.43–2.54 (m, 2H), 3.81 (d, *J* = 3.6 Hz, 1H), 4.00–4.08 (m, 2H), 4.39 (d, *J* = 3.6 Hz, 1H), 6.04 (s, 1H), 6.34 (s, 1H), 6.43 (s, 1H), 6.80 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 22.0, 25.6, 66.5, 72.3, 95.1, 96.0, 98.4, 98.5, 103.3, 105.2, 105.5, 114.3, 114.7, 120.9, 126.9, 127.1–129.2, 132.2, 135.0, 136.5, 137.1, 137.09, 137.13, 148.5, 149.4, 149.5, 151.8, 153.5, 155.1, 155.5, 159.1; IR (neat) 3424 (br), 2936, 2228, 1618, 1597, 1508, 1491, 1419, 1328, 1274, 1194, 1153, 1130, 1052, 976, 909, 731, 543 cm^{-1}; HRMS (ESI) calcd for $C_{59}H_{16}D_{35}O_9$ [$(M+H)^+$] *m/z* 938.5724, found *m/z* 938.5755.

References:

1. H. Lou, Y. Yamazaki, T. Sasaki, M. Uchida, H. Tanaka and S. Oka, *Phytochemistry*, 1999, **51**, 297.
2. S. Morimoto, G. -I. Nonaka and I. Nishioka, *Chem. Pharm. Bull.,* 1987, **35**, 4717.
3. G.-I. Nonaka, S. Morimoto, J.-I. Kinjo, T. Nohara and I. Nishioka, *Chem. Pharm. Bull.,* 1987, **35**, 149.
4. S. Belapure, Z. G. Beamer, J. E. Bartmess and Shawn R. Campagna, *Tetrahedron,* 2011, **67**, 9265.

Computational studies

Initial conformer search for **32** and **33** were carried out with Spartan'18 program (Wavefunction, Inc. Irvine, CA) using the MMFF molecular mechanics model, respectively. Structures of each conformers, keeping only those that are within 15 kJ/mol of the lowest energy conformer, were optimized by the DFT method at the ωB97X-D/6-31G(d) level of theory. Further accurate calculations were carried out with Gaussian16 program.[5] The structures of **32**, **33** were optimized by the DFT method at the ωB97X-D/6-311G(d, p) level of theory. The frequency analyses gave thermodynamic parameters with/without an imaginary wavenumber. The calculations were carried out by the IEFPCM (ethanol) method.

Reference

5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, 2016.

Cartesian coordinates of optimized **32**

C	-2.093630	-0.070093	-0.213986	H	2.803562	-0.354996	1.464336
C	-1.061662	-1.145845	-0.217478	H	4.023538	0.174724	0.305344
C	-1.775494	1.243065	-0.070772	C	2.094437	1.141666	0.072290
H	-2.540952	2.009530	-0.041596	H	2.172950	1.908215	0.844699
C	0.339818	-0.626166	-0.225827	H	2.428892	1.597734	-0.864618
C	0.661554	0.692973	-0.051514	C	-0.411657	1.608130	0.026673
O	-3.320390	-0.535352	-0.333385	O	-0.069240	2.865457	0.184747
H	-3.976103	0.170258	-0.296848	H	-0.836190	3.447323	0.236489
O	1.222930	-1.584971	-0.374738	C	-1.268974	-2.081169	1.000080
C	2.624487	-1.224744	-0.482336	H	-2.273105	-2.500974	0.971225
H	2.807893	-0.984876	-1.532502	H	-1.137978	-1.524696	1.929944
H	3.159748	-2.134166	-0.221668	H	-0.540356	-2.889048	0.960434
C	2.965142	-0.061895	0.423137	H	-1.202408	-1.735651	-1.129820

Summary of the frequency analysis for **32**

Calculation Type = FREQ
Calculation Method = RwB97XD
Basis Set = 6-311G(d,p)
Charge = 1
Spin = Singlet
Solvation = scrf=(iefpcm,solvent=ethanol)

E(RwB97XD) = -614.36585 Hartree
RMS Gradient Norm = 1.4978e-05 Hartree/Bohr
Imaginary Freq = 0
Dipole Moment = 4.6155345 Debye
Polarizability (?) = 151.22033 a.u.
Point Group = C1
Job cpu time: 0 days 1 hours 26 minutes 5.3 seconds.
Thermo Tab Data Section:
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Temperature = 298.15 Kelvin
Pressure = 1 atm
Frequencies scaled by = 1
Electronic Energy (EE) = -614.36585 Hartree
Zero-point Energy Correction = 0.221483 Hartree
Thermal Correction to Energy = 0.232946 Hartree
Thermal Correction to Enthalpy = 0.23389 Hartree
Thermal Correction to Free Energy = 0.18442 Hartree
EE + Zero-point Energy = -614.14437 Hartree
EE + Thermal Energy Correction = -614.13291 Hartree
EE + Thermal Enthalpy Correction = -614.13196 Hartree
EE + Thermal Free Energy Correction = -614.18143 Hartree
E (Thermal) = 146.176 kcal/mol
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Entropy (S) = 104.119 cal/mol-kelvin

Opt Tab Data Section:
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Maximum force = 4.1e-05 Converged
RMS force = 6e-06 Converged
Maximum displacement = 0.001944 Not converged
RMS displacement = 0.000456 Converged
Predicted energy change = -3.480319e-08 Hartree

Cartesian coordinates of optimized **33**

C	1.740369	-1.014863	-0.253705	H	-3.091003	0.094471	-1.423158
C	1.866015	0.470482	-0.233087	H	-4.074240	0.811351	-0.145033
C	0.550220	-1.643192	-0.098750	C	-1.966202	1.295234	-0.015983
H	0.460480	-2.721039	-0.069472	H	-1.956488	2.116404	-0.738583
C	0.550421	1.175405	-0.196366	H	-2.126294	1.731416	0.975486
C	-0.654288	0.549370	-0.051073	C	-0.630067	-0.869408	0.033593
O	2.901634	-1.626538	-0.397016	C	2.745603	0.914571	0.961869
H	2.802702	-2.584879	-0.368530	H	3.720255	0.434754	0.891855
O	-1.712033	-1.572593	0.219303	H	2.273422	0.631353	1.904138
C	-2.985027	-0.913431	0.460854	H	2.875254	1.995065	0.936337
H	-3.034291	-0.709617	1.532746	H	2.369971	0.774168	-1.158148
H	-3.726536	-1.664192	0.201618	O	0.688675	2.484088	-0.297156
C	-3.111133	0.346909	-0.359649	H	-0.154902	2.944627	-0.226515

Summary of the frequency analysis for **33**
Calculation Type = FREQ
Calculation Method = RwB97XD

Basis Set = 6-311G(d,p)
Charge = 1
Spin = Singlet
Solvation = scrf=(iefpcm,solvent=ethanol)
E(RwB97XD) = -614.36427 Hartree
RMS Gradient Norm = 9.608e-06 Hartree/Bohr
Imaginary Freq = 0
Dipole Moment = 1.7212947 Debye
Polarizability (?) = 151.787 a.u.
Point Group = C1
Job cpu time: 0 days 1 hours 23 minutes 41.3 seconds.

Thermo Tab Data Section:
Imaginary Freq = 0
Temperature = 298.15 Kelvin
Pressure = 1 atm
Frequencies scaled by = 1
Electronic Energy (EE) = -614.36427 Hartree
Zero-point Energy Correction = 0.221317 Hartree
Thermal Correction to Energy = 0.232853 Hartree
Thermal Correction to Enthalpy = 0.233797 Hartree
Thermal Correction to Free Energy = 0.18423 Hartree
EE + Zero-point Energy = -614.14296 Hartree
EE + Thermal Energy Correction = -614.13142 Hartree
EE + Thermal Enthalpy Correction = -614.13048 Hartree
EE + Thermal Free Energy Correction = -614.18004 Hartree
E (Thermal) = 146.117 kcal/mol
Heat Capacity (Cv) = 45.828 cal/mol-kelvin
Entropy (S) = 104.323 cal/mol-kelvin

Opt Tab Data Section:
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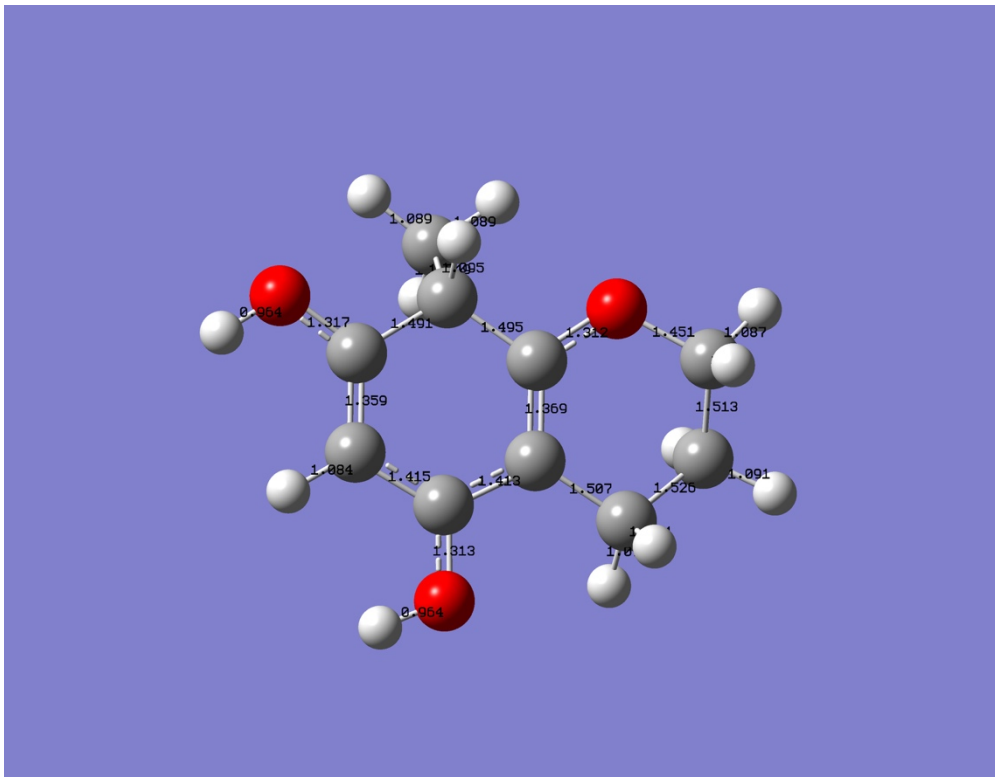
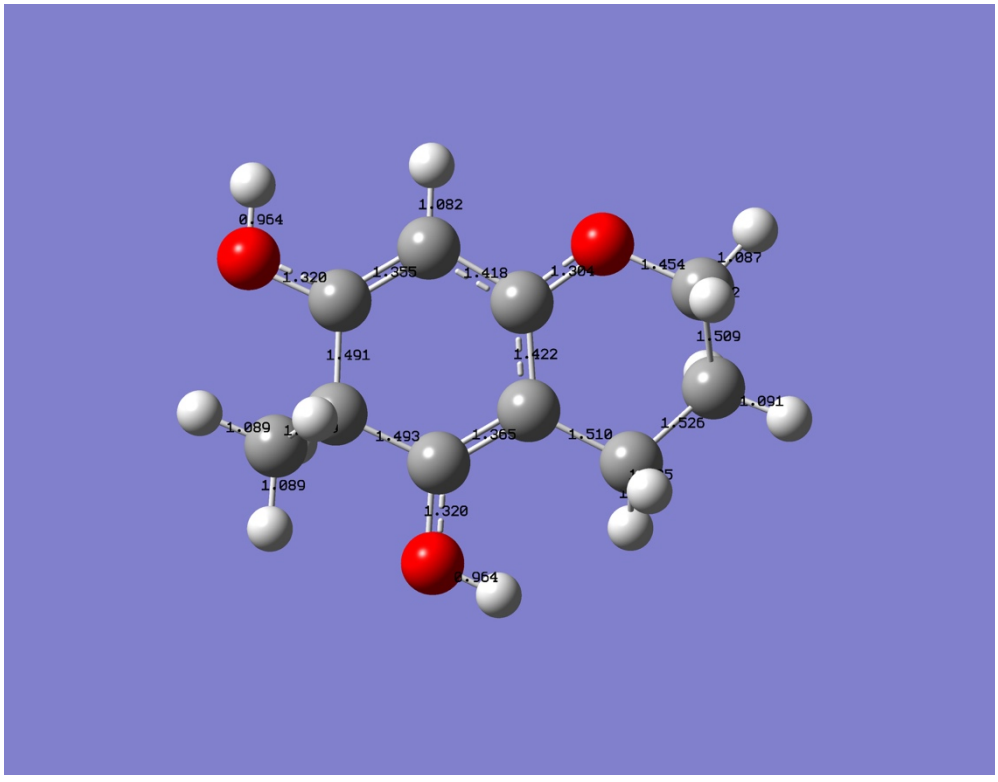
RMS displacement = 0.000374 Converged
Predicted energy change = -2.50007e-08 Hartree

Optimized structures of **32** and **33**

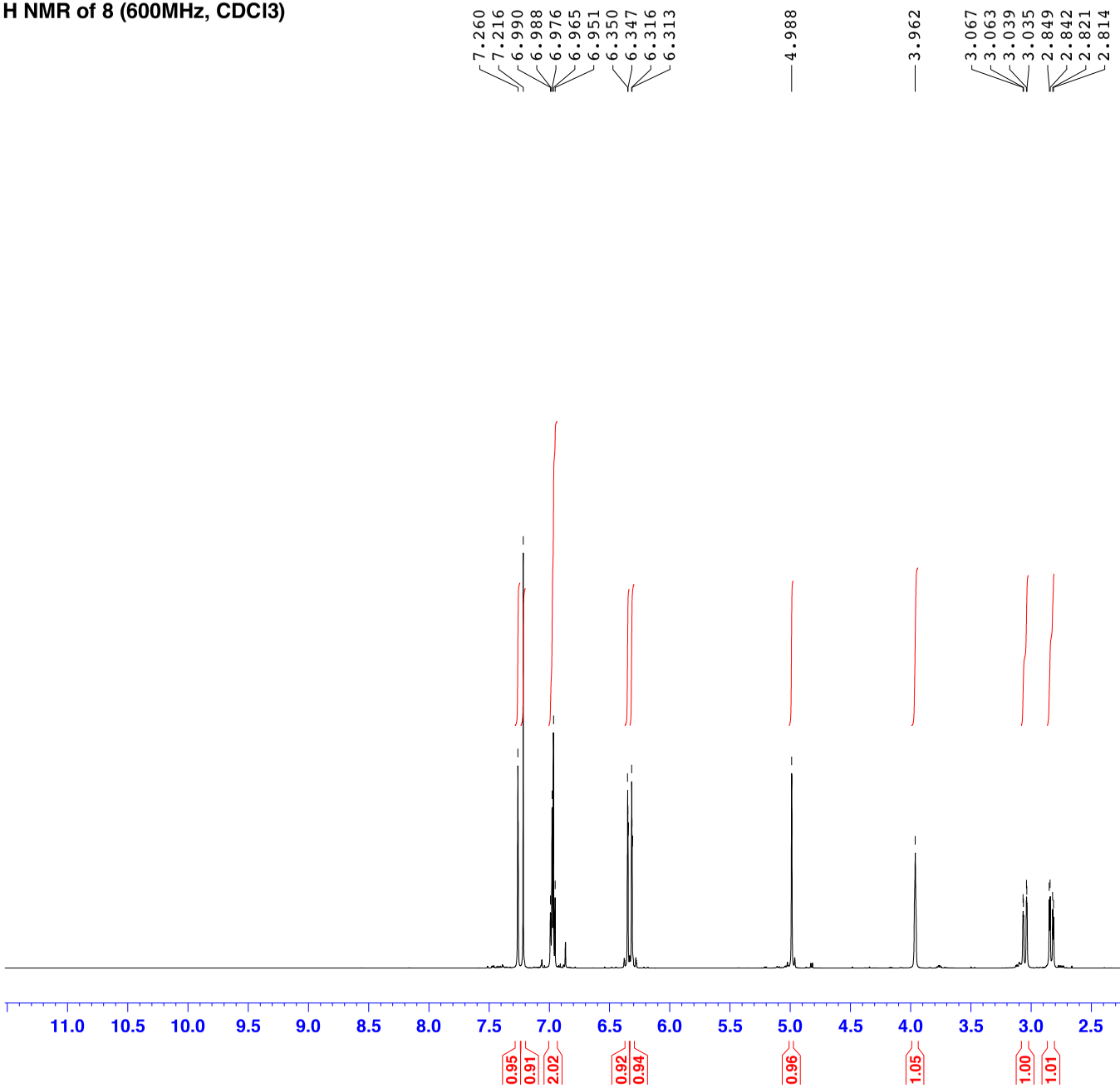
Intermediate **32**



Intermediate **33**



1H NMR of 8 (600MHz, CDCl3)

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DS                      2
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TE                298.1 K
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TD0                     1

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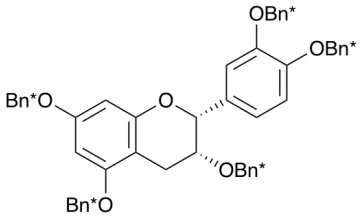
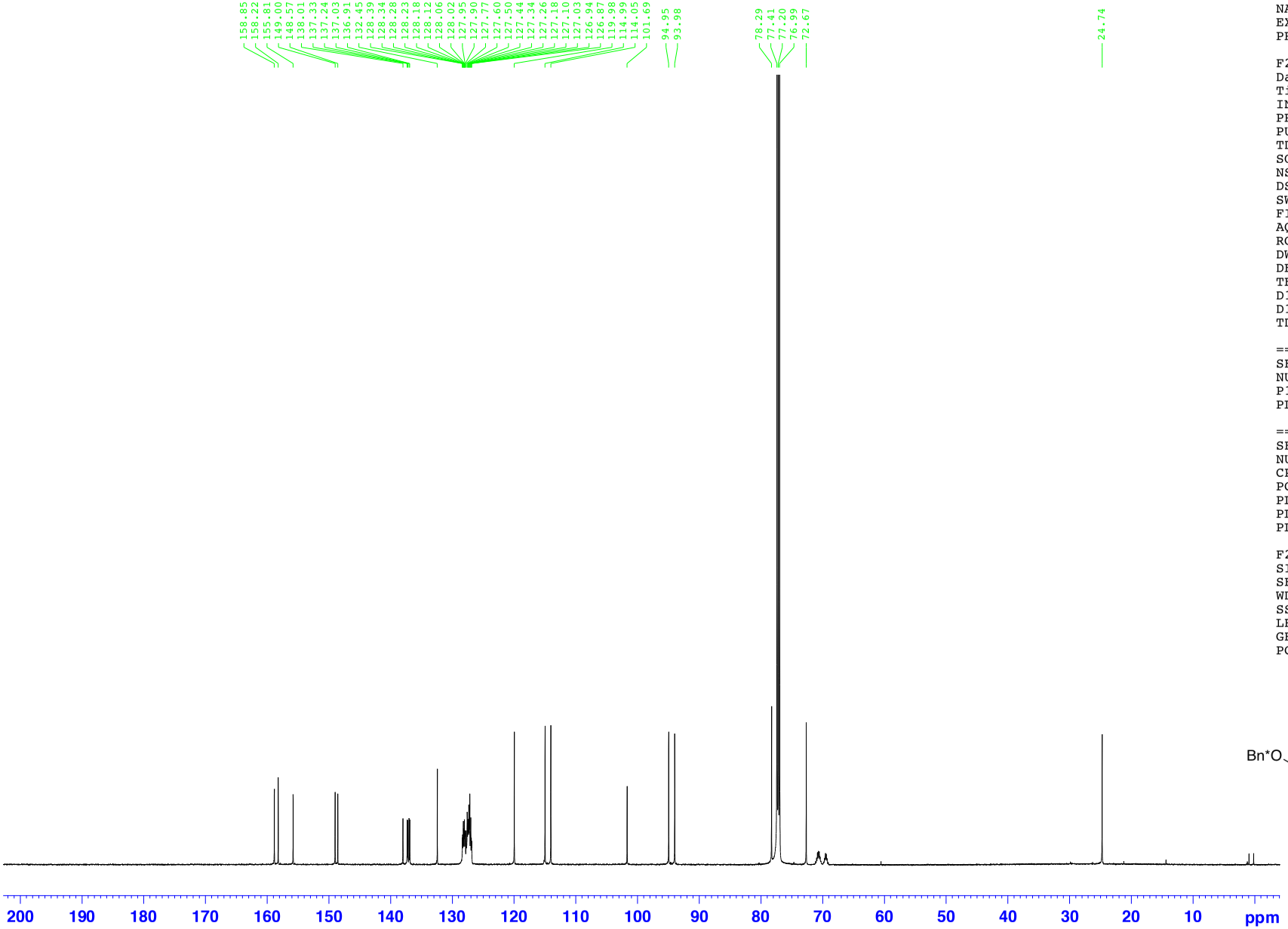


^{13}C NMR of 8 (600MHz, $CDCl_3$)

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TE                    299.9 K
D1               2.00000000 sec
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NUC2                    1H
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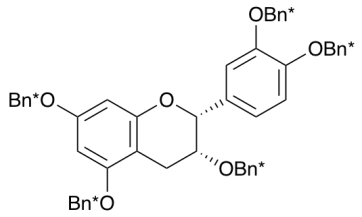
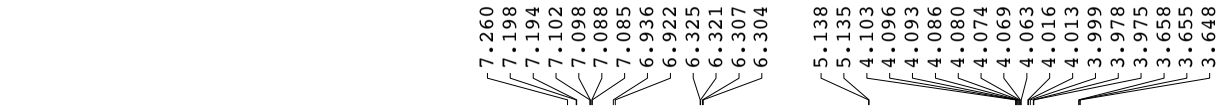
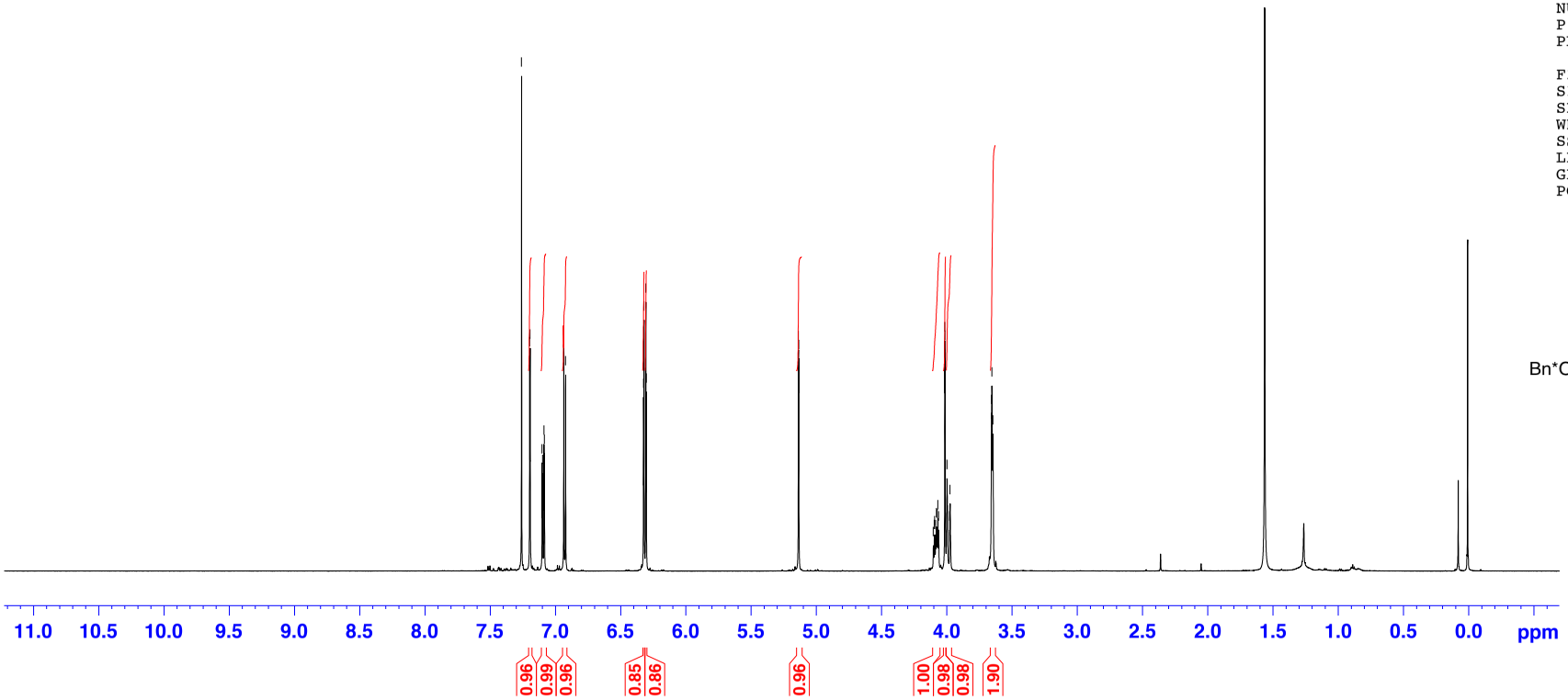


^{1}H NMR of 9 (600MHz, $CDCl_3$)



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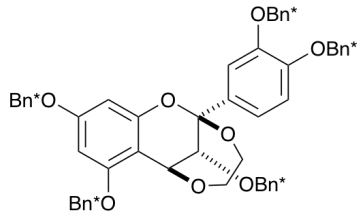
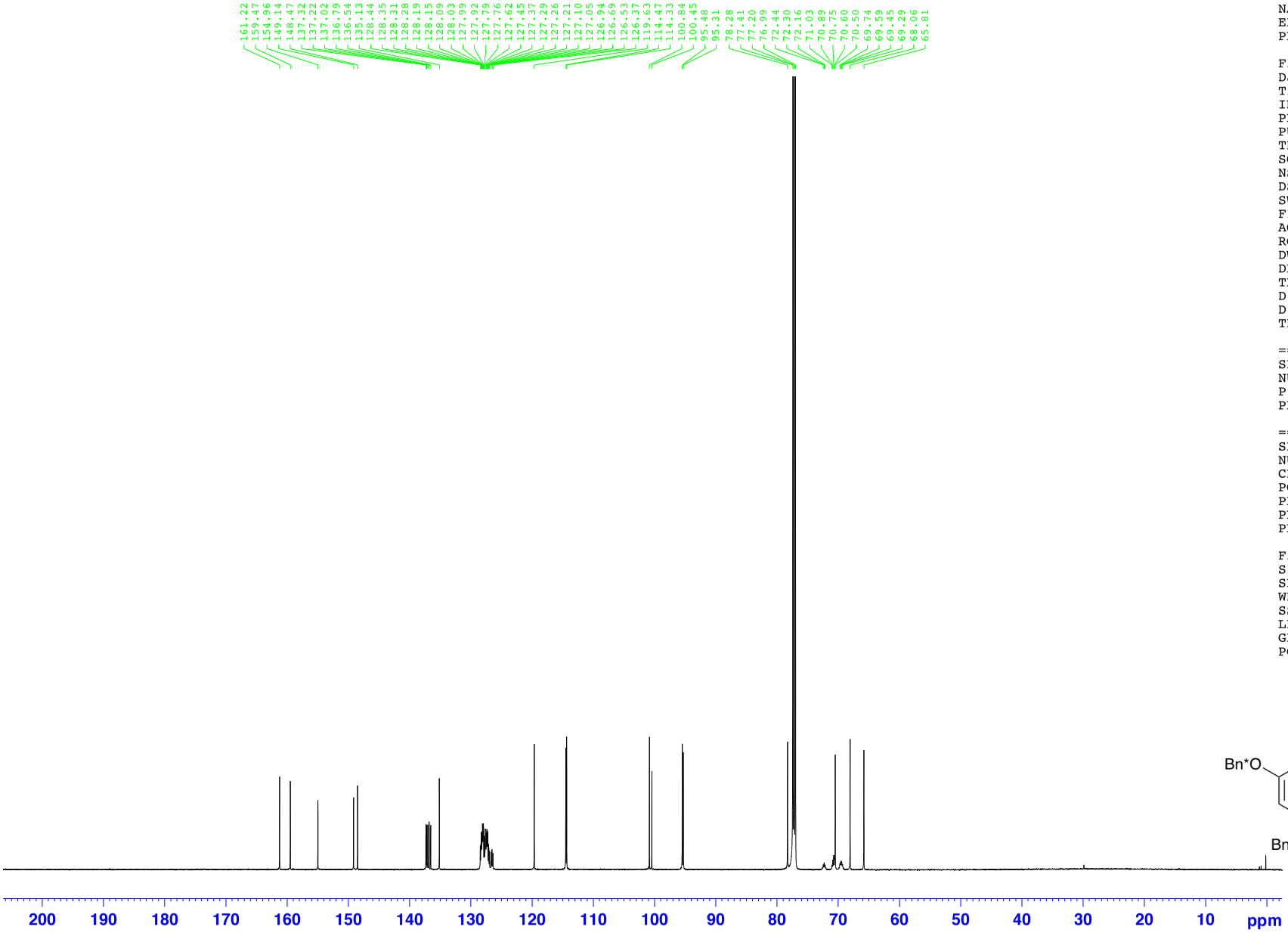


^{13}C NMR of 9 (600MHz, $CDCl_3$)

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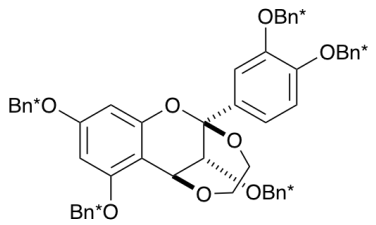
Time                   6.53
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8192
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9087659 sec
RG                   175.56
DW                   13.867 usec
DE                    18.00 usec
TE                    300.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

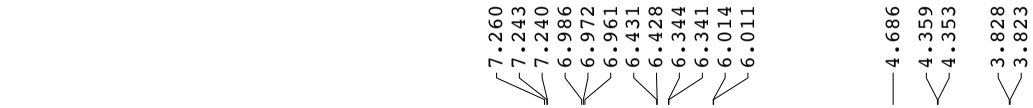
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

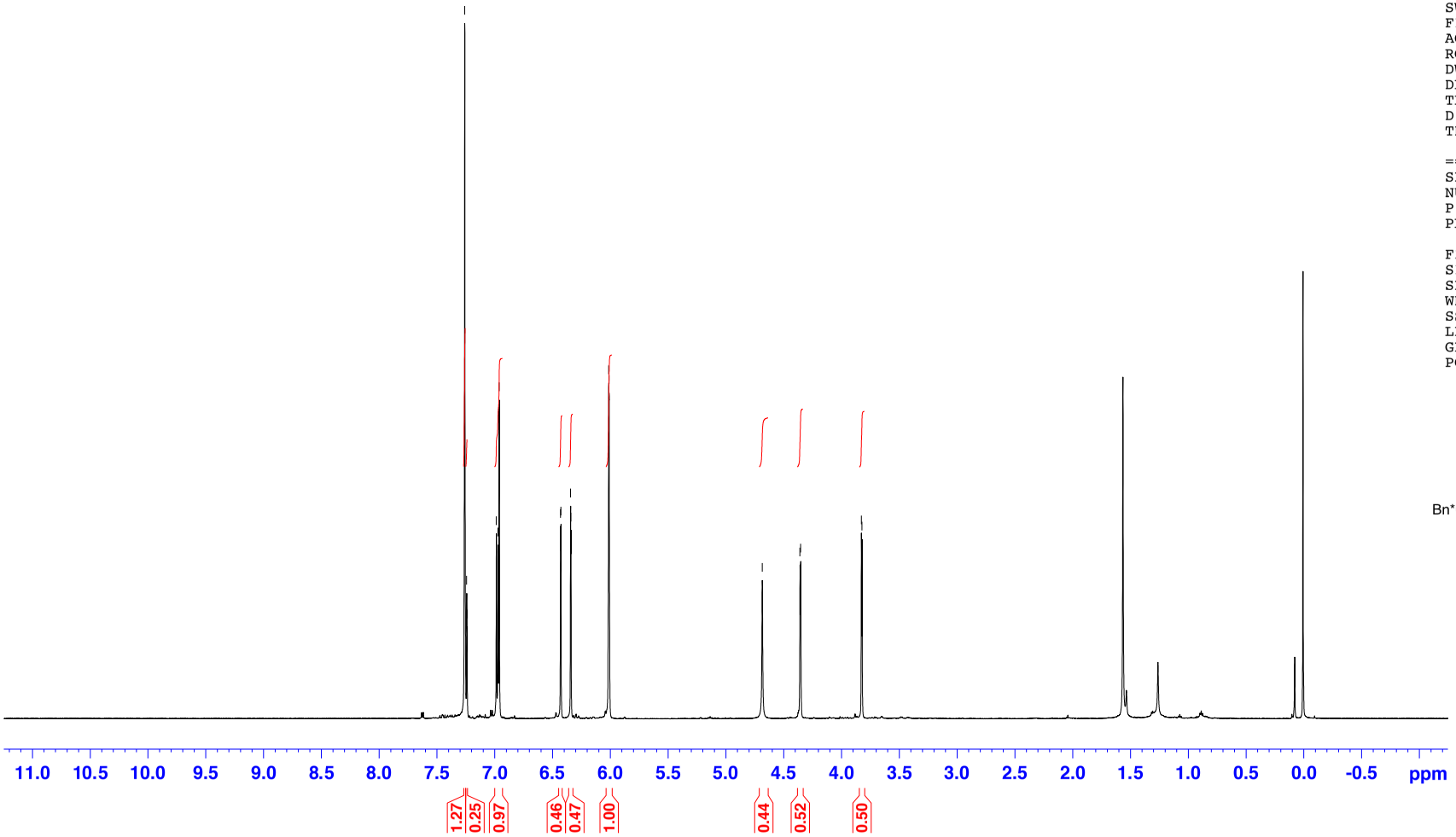
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                    32768
SF             150.9027859 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```



^{1}H NMR of 11 (600MHz, $CDCl_3$)



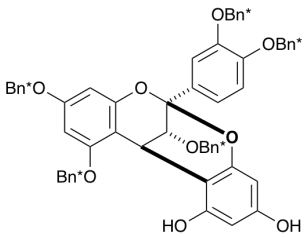



```
Current Data Parameters
NAME                  VB-117-2
EXPNO                       10
PROCNO                       1

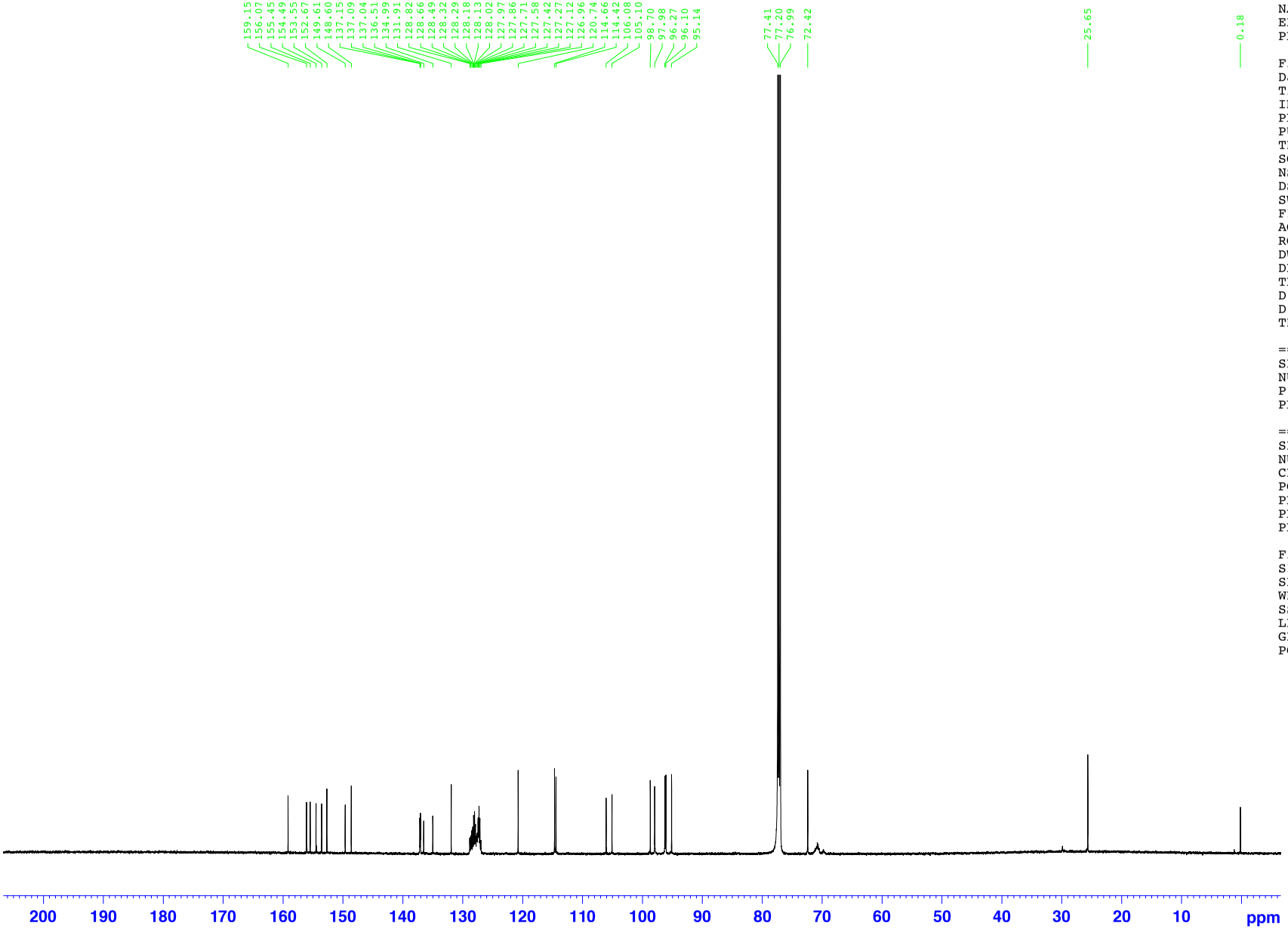
F2 - Acquisition Parameters
Date_                 20180326
Time                     17.19
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                       18.96
DW                      41.600 usec
DE                      10.00 usec
TE                      299.9 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               23.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1300150 MHz
WDW                        EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```



^{13}C NMR of 11 (150MHz, $CDCl_3$)



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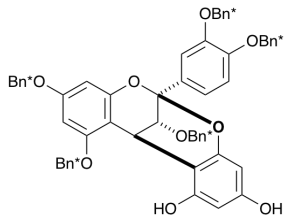
```
Current Data Parameters
NAME              VB-117-2
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_              20180327
Time                   6.50
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8192
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9087659 sec
RG                   175.56
DW                   13.867 usec
DE                    18.00 usec
TE                    299.9 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

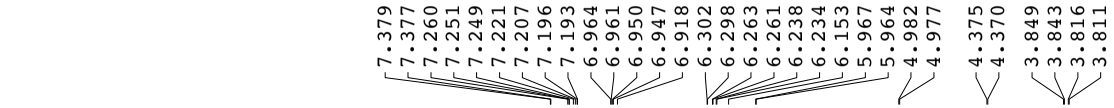
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

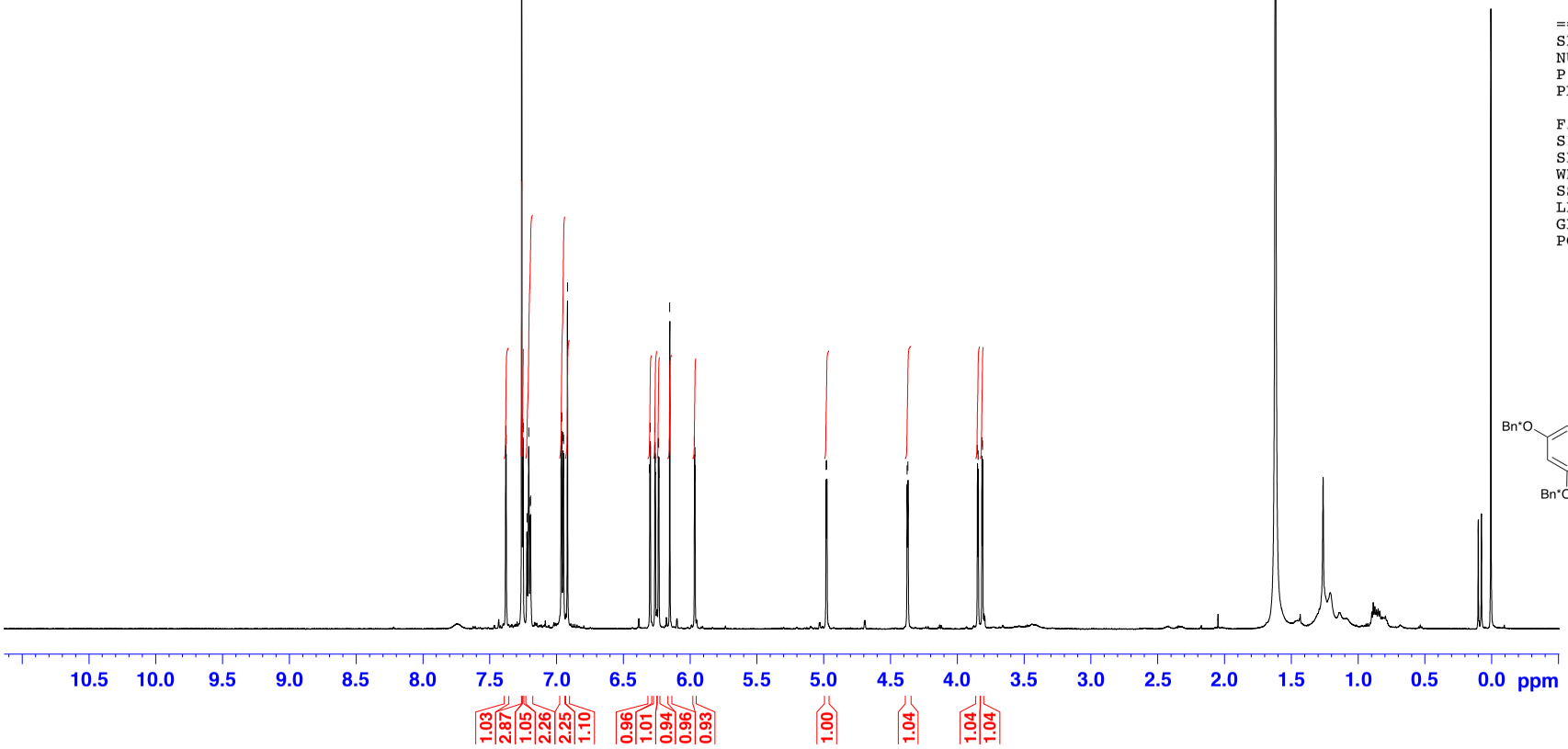
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                    32768
SF             150.9027827 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



^{1}H NMR of 12 (600MHz, $CDCl_3$)



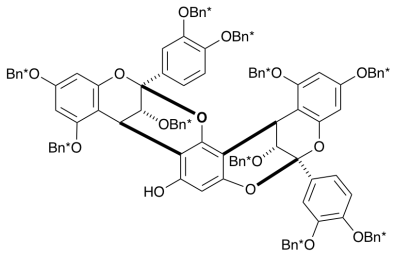



```
Current Data Parameters
NAME                  VB-141-1
EXPNO                       10
PROCNO                       1

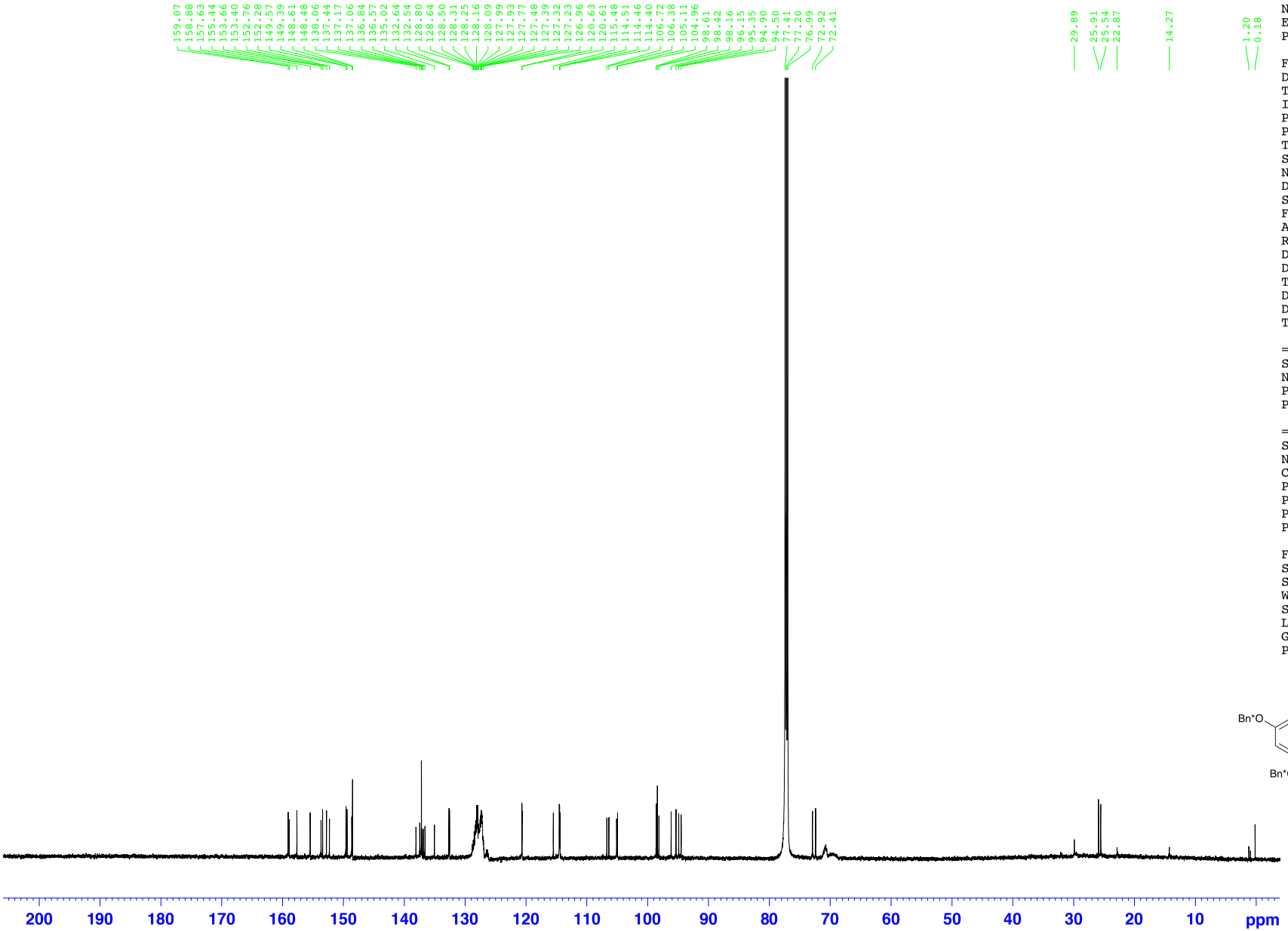
F2 - Acquisition Parameters
Date_                 20180529
Time                     13.31
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       300.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               23.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1300146 MHz
WDW                        EM
SSB             0
LB                        0.30 Hz
GB              0
PC                        1.00
```



^{13}C NMR of 12 (150MHz $CDCl_3$)



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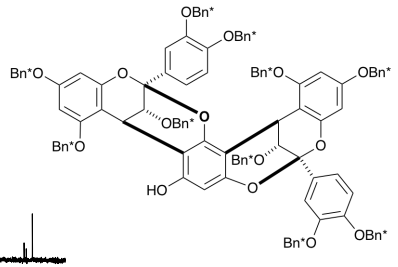
```
Current Data Parameters
NAME              VB-141-1
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_              20180601
Time                   7.03
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8192
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

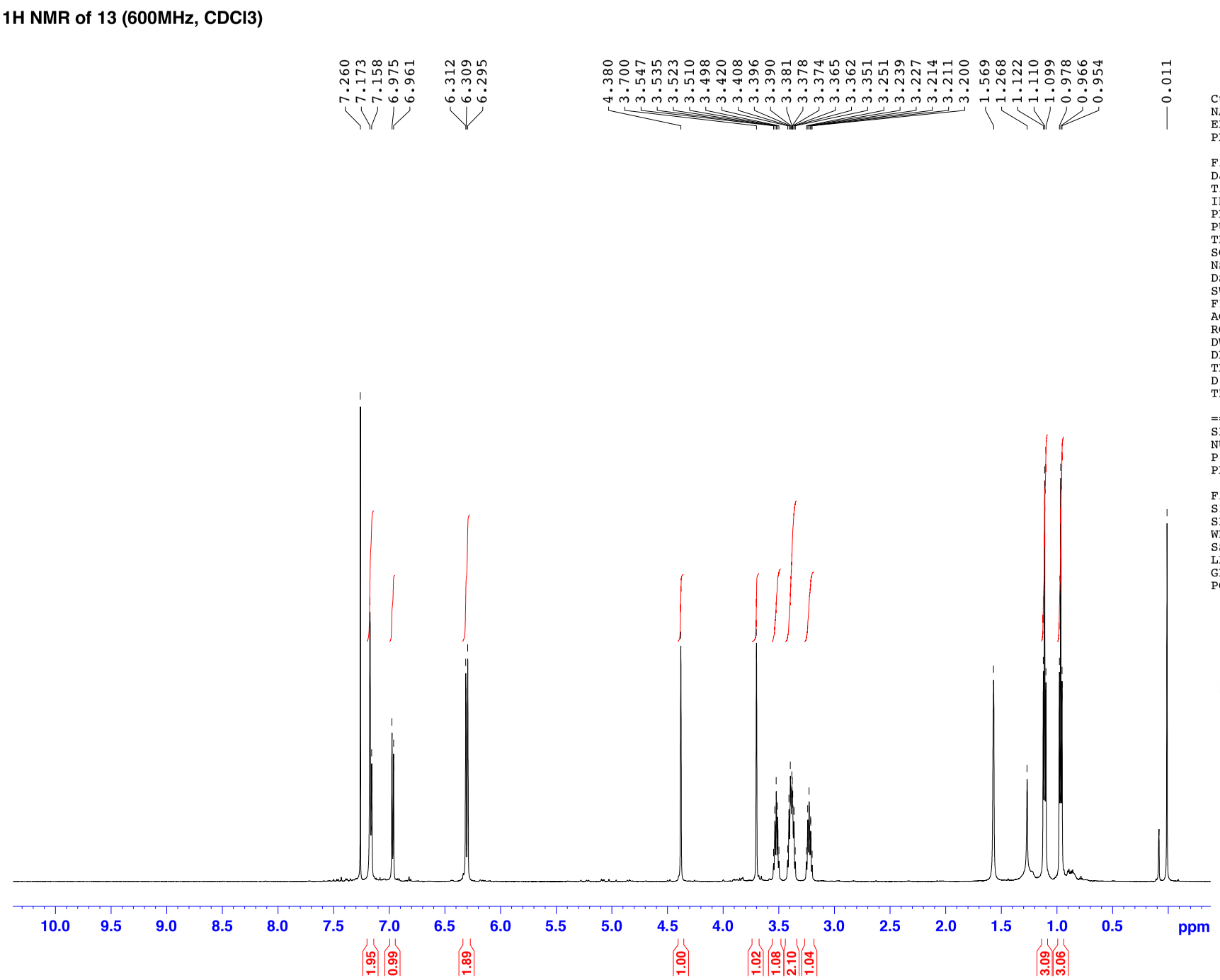
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                    32768
SF             150.9027824 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```



1H NMR of 13 (600MHz, CDCl3)



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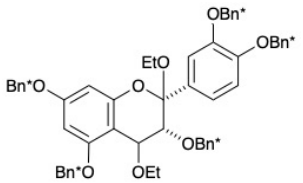
```
Current Data Parameters
NAME              VB-OBC-13
EXPNO                    30
PROCNO                    1

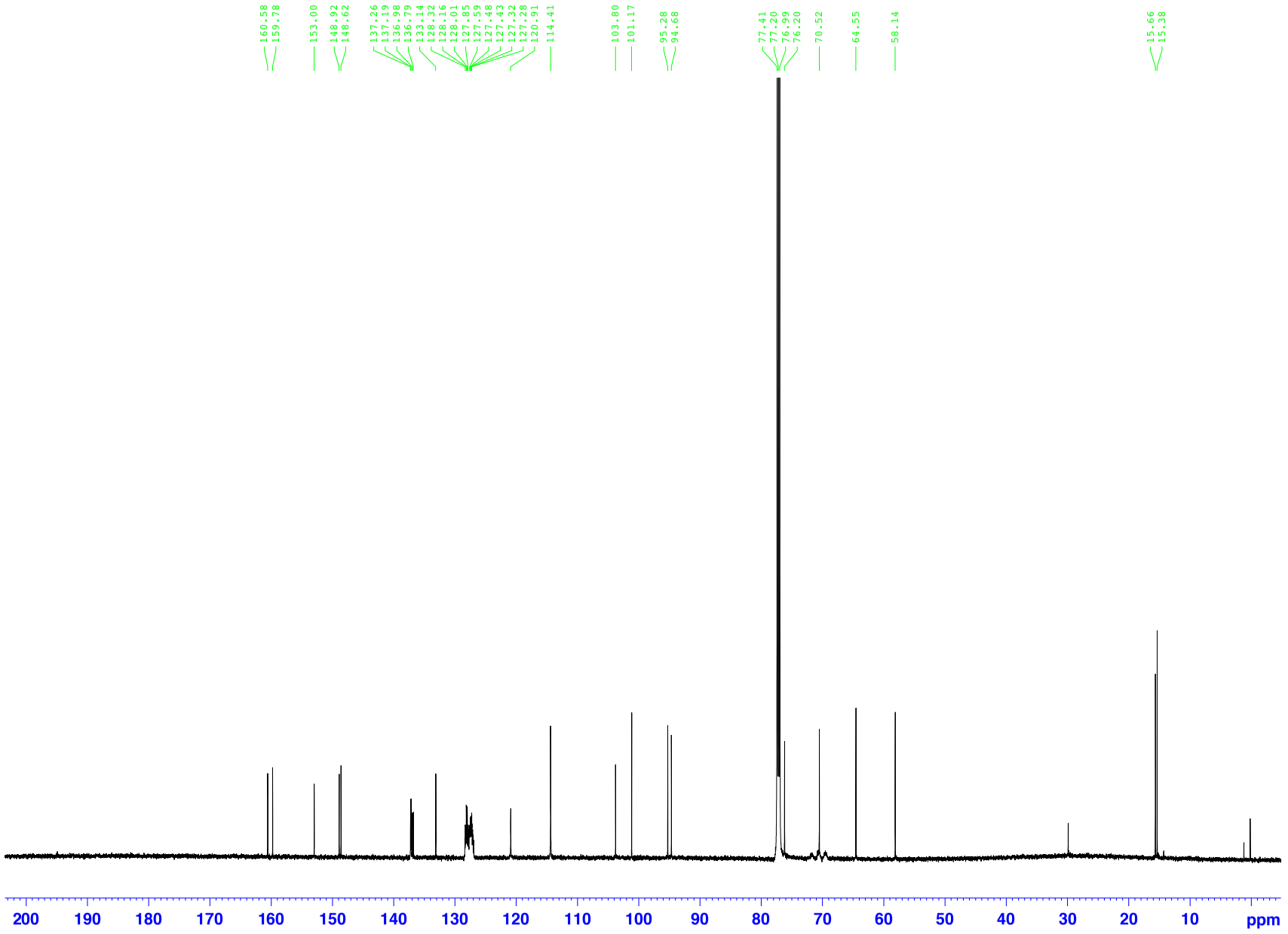
F2 - Acquisition Parameters
Date_              20190917
Time                 15.36
INSTRUM              spect
PROBHD   5 mm CPPBBO BB
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ                2.7262976 sec
RG                   31.94
DW                  41.600 usec
DE                  10.00 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          600.1337060 MHz
NUC1                    1H
P1                   12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                   65536
SF            600.1300143 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



^{13}C NMR of 13 (150MHZ, $CDCl_3$)



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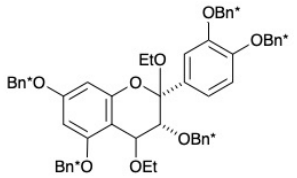
```
Current Data Parameters
NAME                  VB-312
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190531
Time                   3.25
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     4000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

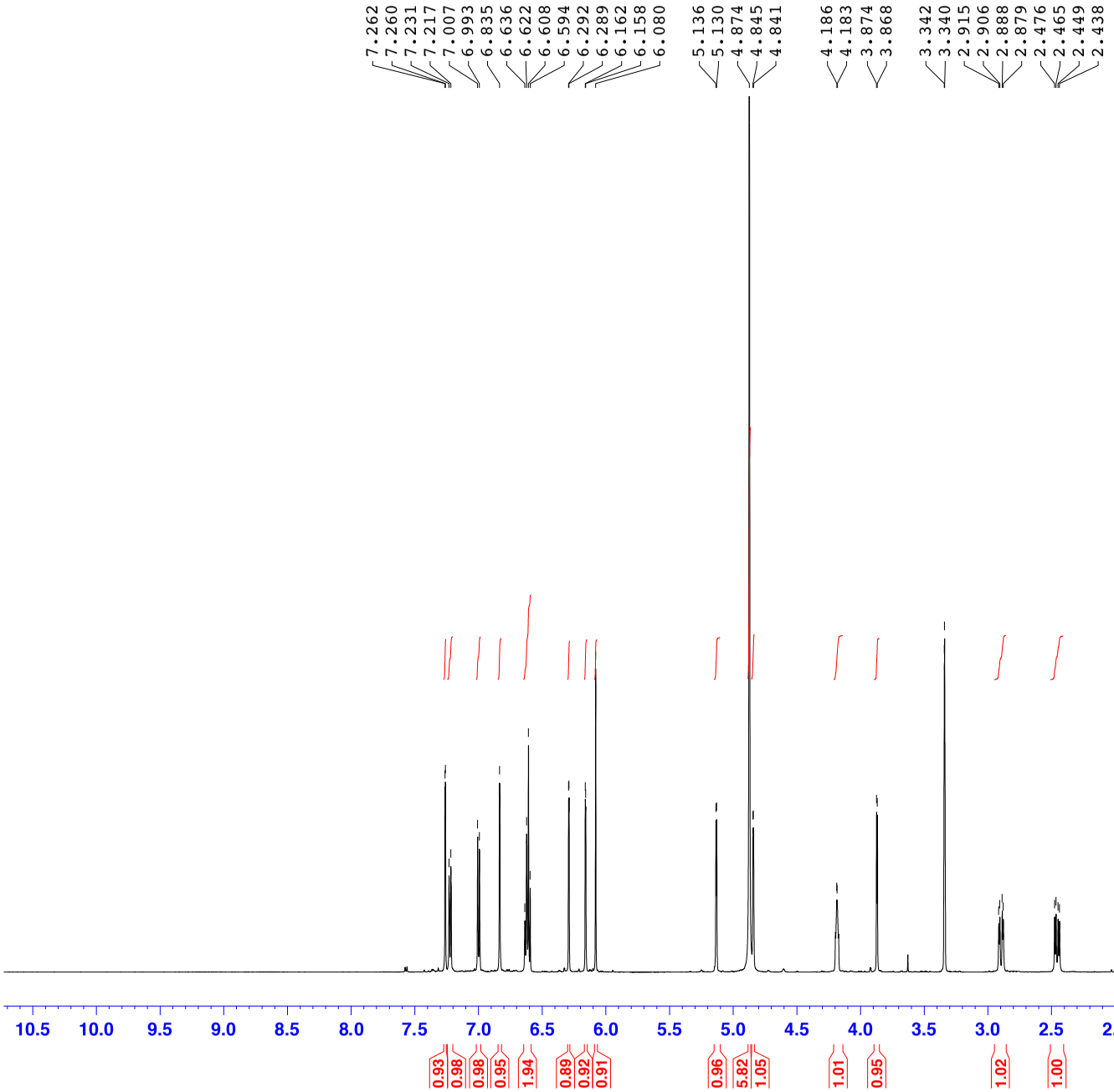
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           80.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                     32768
SF             150.9027830 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 14 (600MHz, CD_3OD)

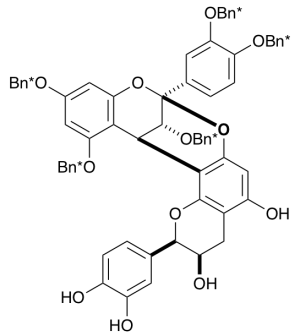



```
Current Data Parameters
NAME                  VB-119-03
EXPNO                        10
PROCNO                        1

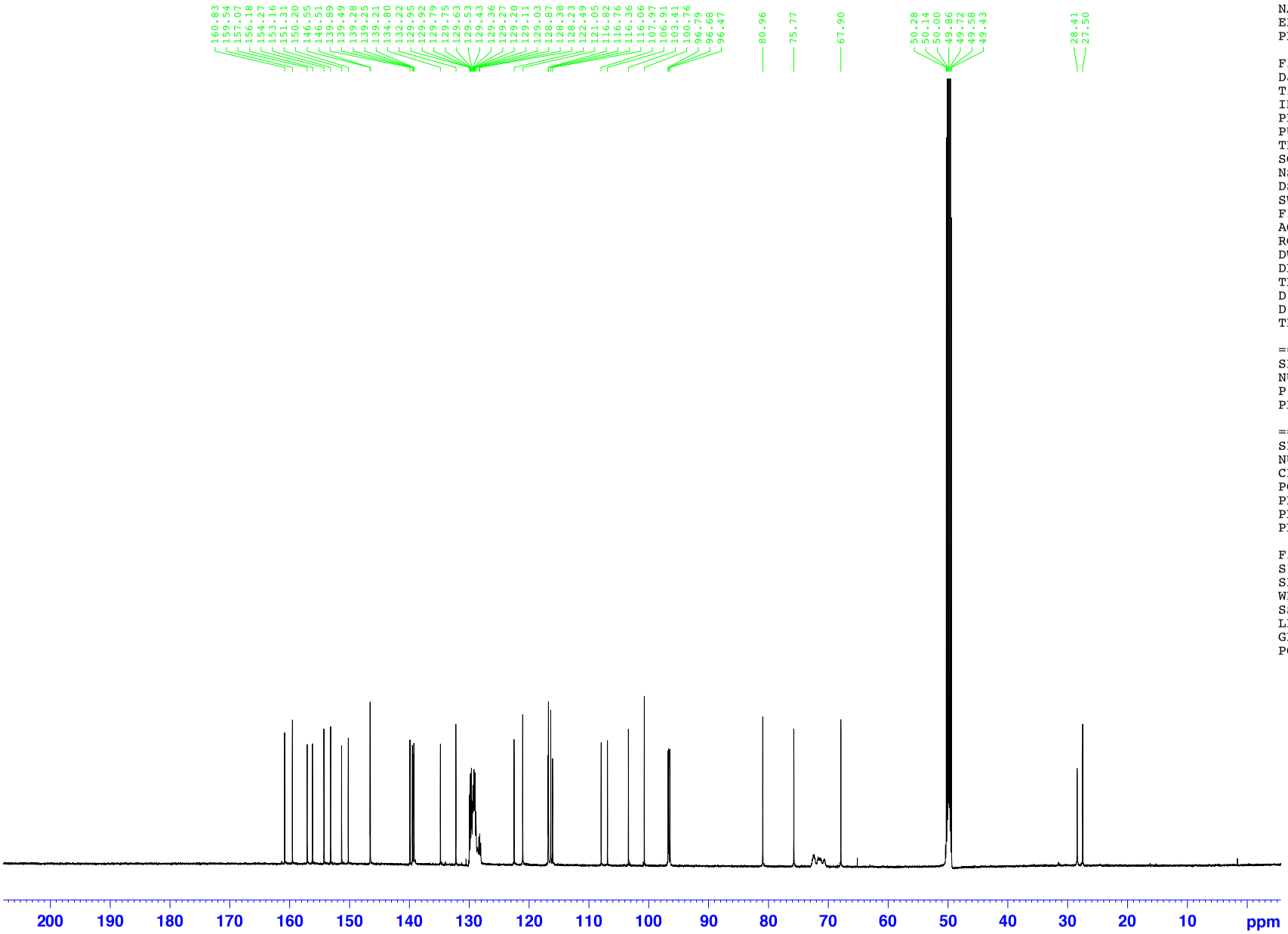
F2 - Acquisition Parameters
Date_                  20180330
Time                      17.09
INSTRUM                   spect
PROBHD    5 mm CPPBBO BB
PULPROG                   zg30
TD                       65536
SOLVENT                   MeOD
NS                          16
DS                           2
SWH                  12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       300.0 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                23.00000000 W

F2 - Processing parameters
SI                       65536
SF                  600.1299925 MHz
WDW                         EM
SSB                0
LB                        0.30 Hz
GB                 0
PC                        1.00
```



^{13}C NMR of 14 (150MHz, CD_3OD)



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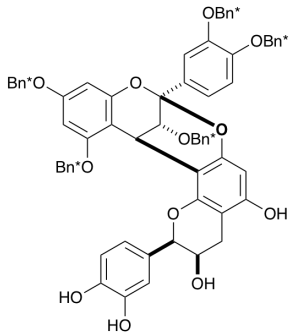
```
Current Data Parameters
NAME              VB-119-03
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20180401
Time                   6.50
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                     8192
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   299.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

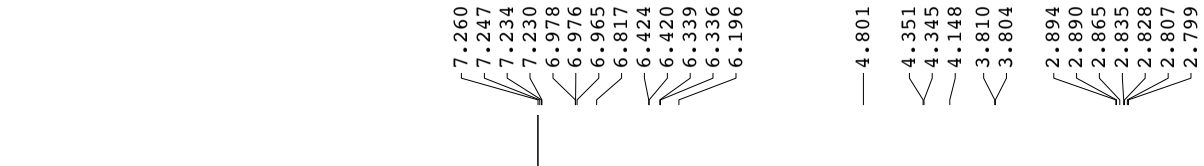
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

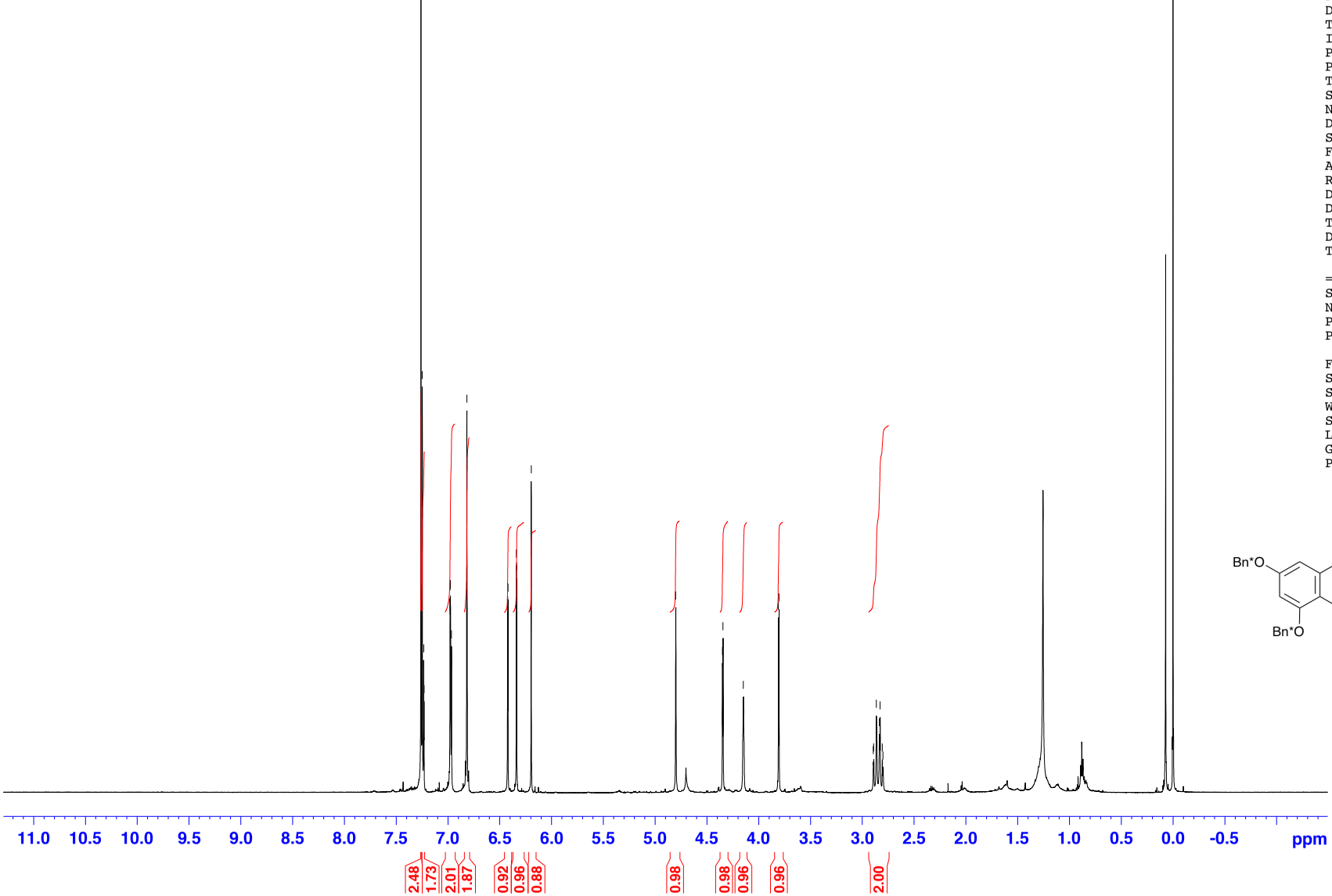
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9024717 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 15 (600MHz, 5%D_2O in $CDCl_3$)



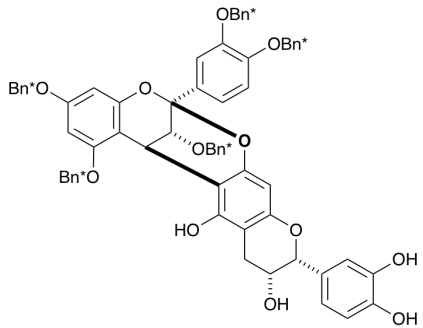



```
Current Data Parameters
NAME         VB-186-2D2O
EXPNO                 20
PROCNO                 1

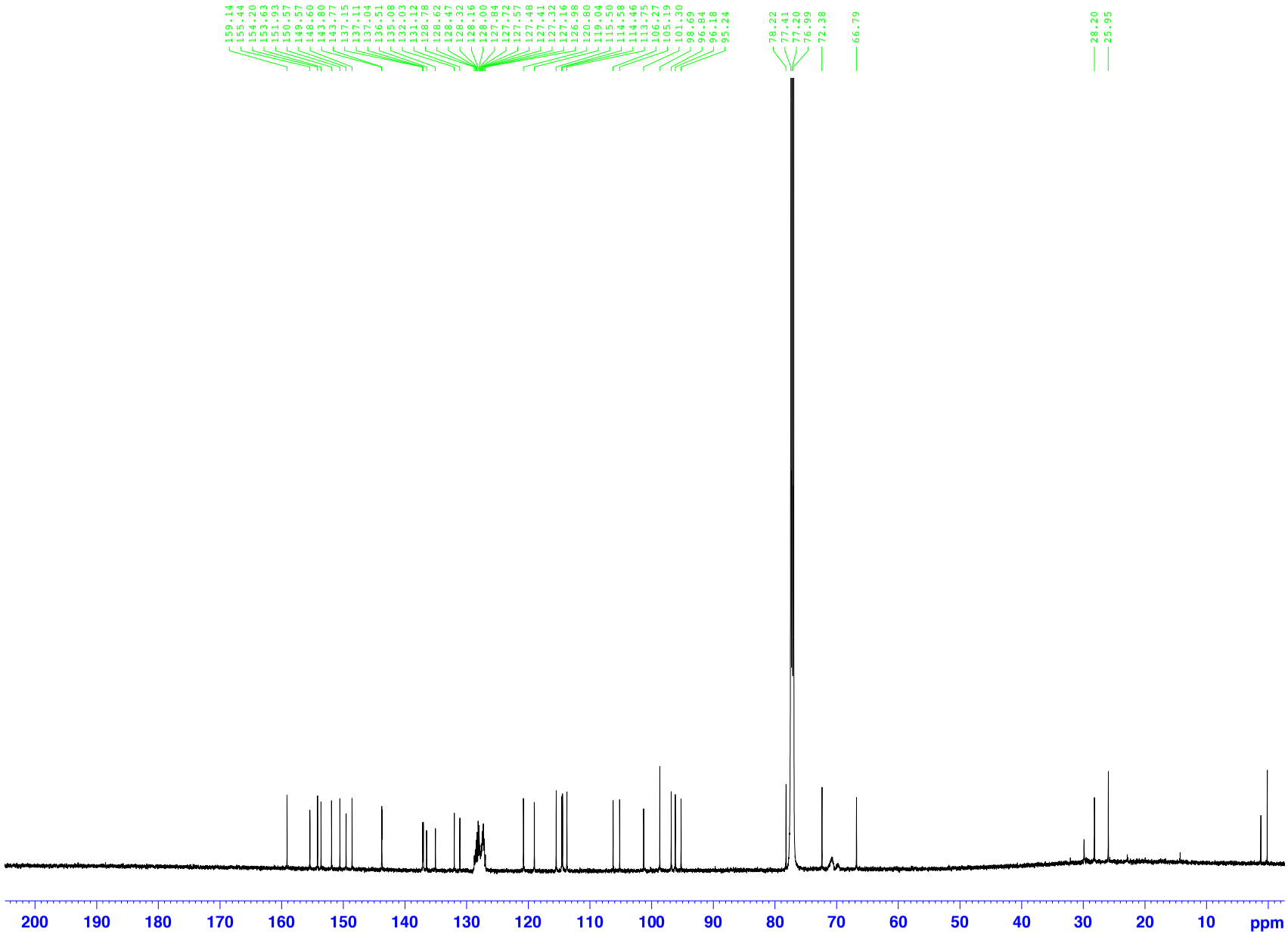
F2 - Acquisition Parameters
Date_           20181130
Time              20.04
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   50
DS                    2
SWH           12019.230 Hz
FIDRES         0.183399 Hz
AQ            2.7262976 sec
RG                31.94
DW               41.600 usec
DE               10.00 usec
TE                300.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                12.00 usec
PLW1         23.00000000 W

F2 - Processing parameters
SI                65536
SF           600.1300144 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



^{13}C NMR of 15 (150MHz, $CDCl_3$)



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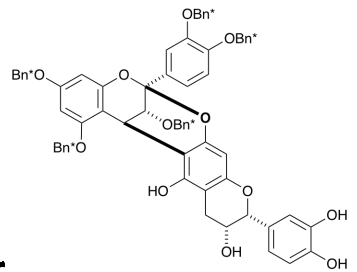
```
Current Data Parameters
NAME              VB-186-2
EXPNO                   31
PROCNO                   1

F2 - Acquisition Parameters
Date_              20181123
Time                  12.06
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                   14500
DS                       4
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                  18.00 usec
TE                  300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

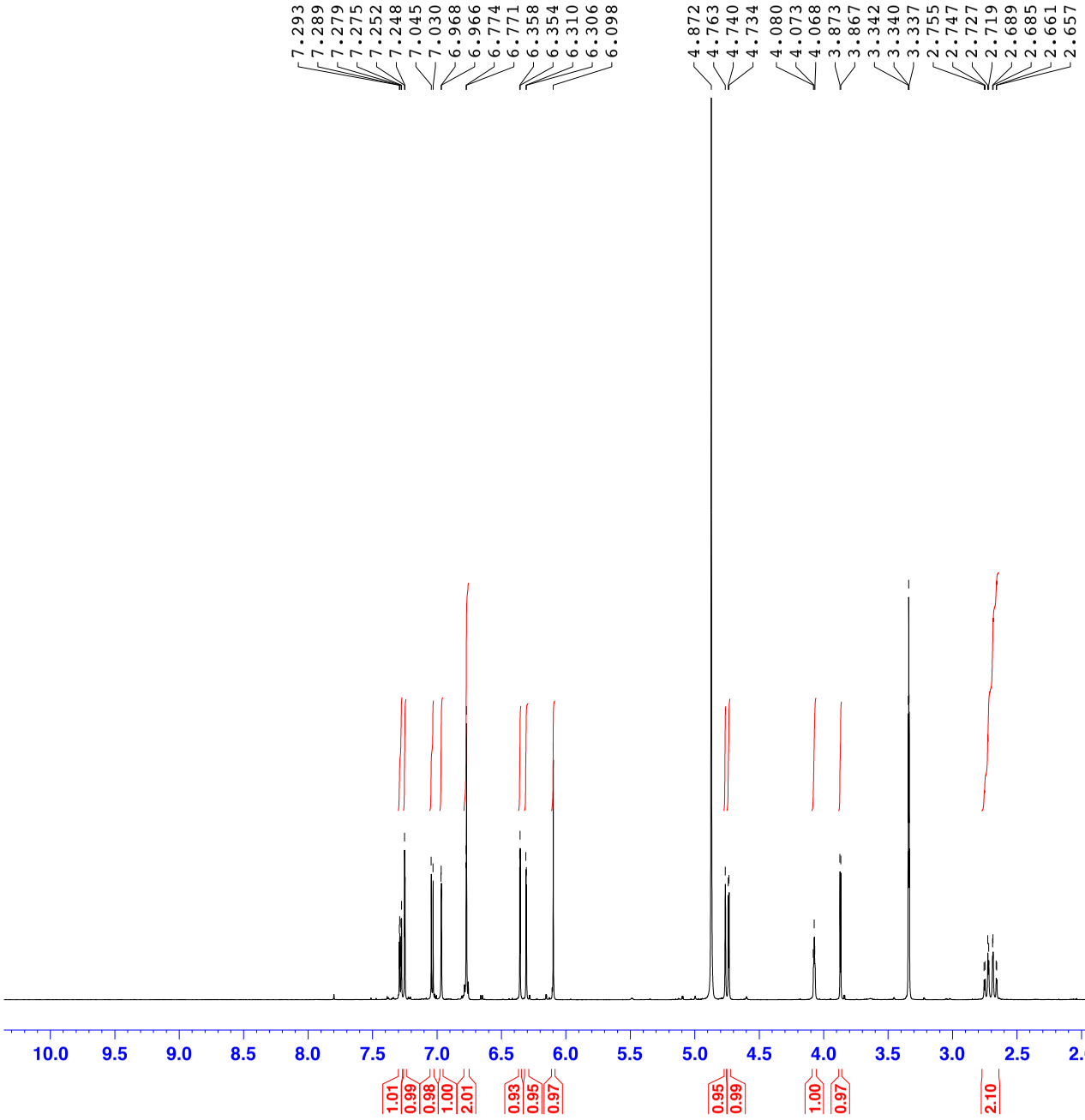
======== CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                   13C
P1                  10.00 usec
PLW1          70.00000000 W

======== CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          14.00000000 W
PLW12          0.64286000 W
PLW13          0.32335001 W

F2 - Processing parameters
SI                    32768
SF            150.9027818 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



^{1}H NMR of 16 (600MHz, CD_3OD)

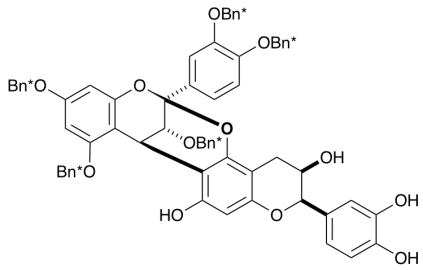



```
Current Data Parameters
NAME                  VB-186-1
EXPNO                       40
PROCNO                       1

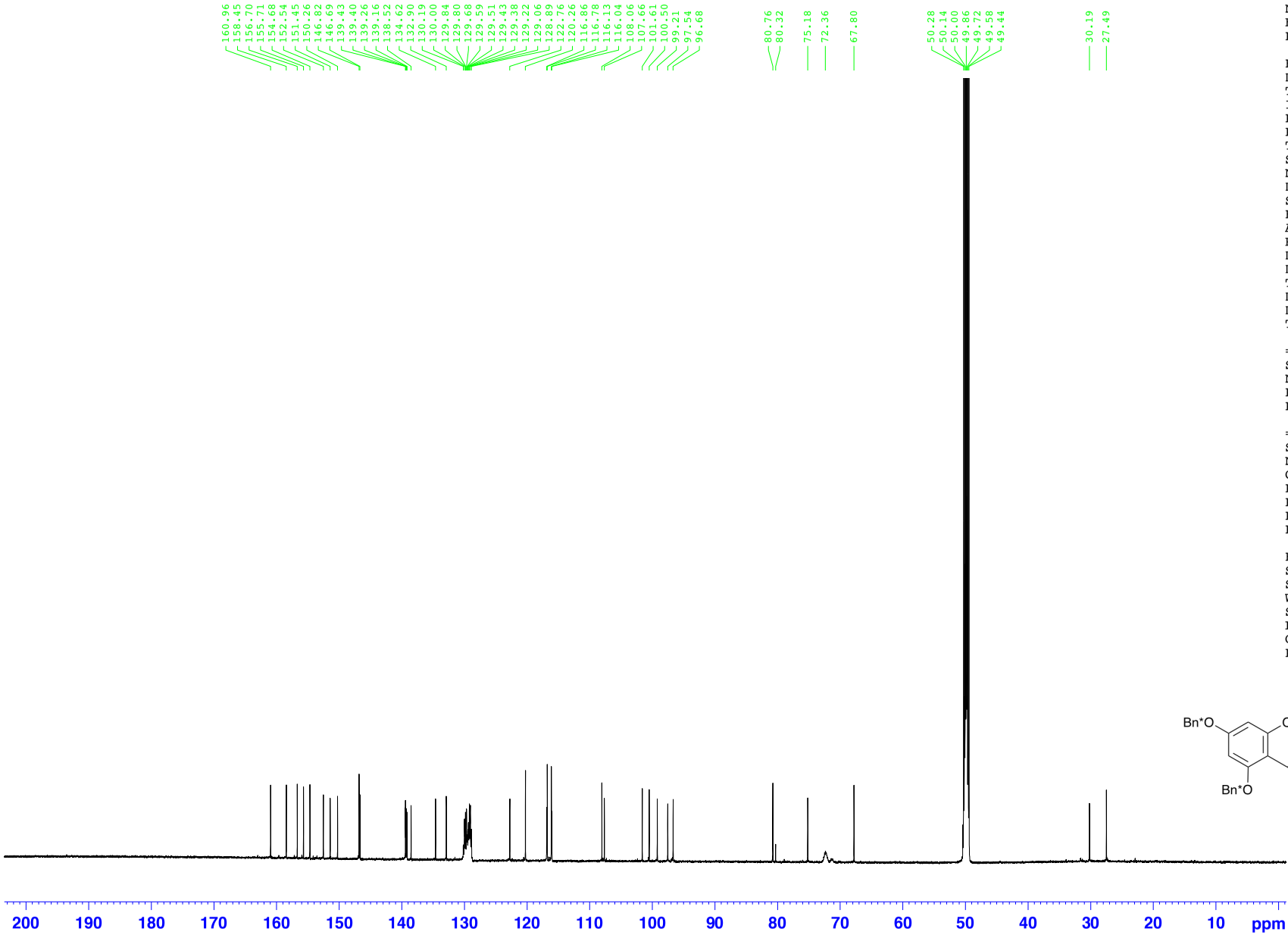
F2 - Acquisition Parameters
Date_                 20181121
Time                     20.25
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                  MeOD
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       300.1 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                23.00000000 W

F2 - Processing parameters
SI                      65536
SF                  600.1299934 MHz
WDW                        EM
SSB                 0
LB                       0.30 Hz
GB                  0
PC                       1.00
```



^{13}C NMR of 16 (150MHz, CD_3OD)



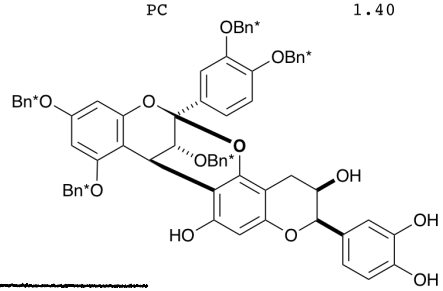

```
Current Data Parameters
NAME                  VB-186-1
EXPNO                       41
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20181122
Time                      7.36
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zgpg30
TD                       65536
SOLVENT                   MeOD
NS                        9000
DS                           4
SWH                 36057.691 Hz
FIDRES               0.550197 Hz
AQ                  0.9087659 sec
RG                     175.56
DW                     13.867 usec
DE                      18.00 usec
TE                      300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

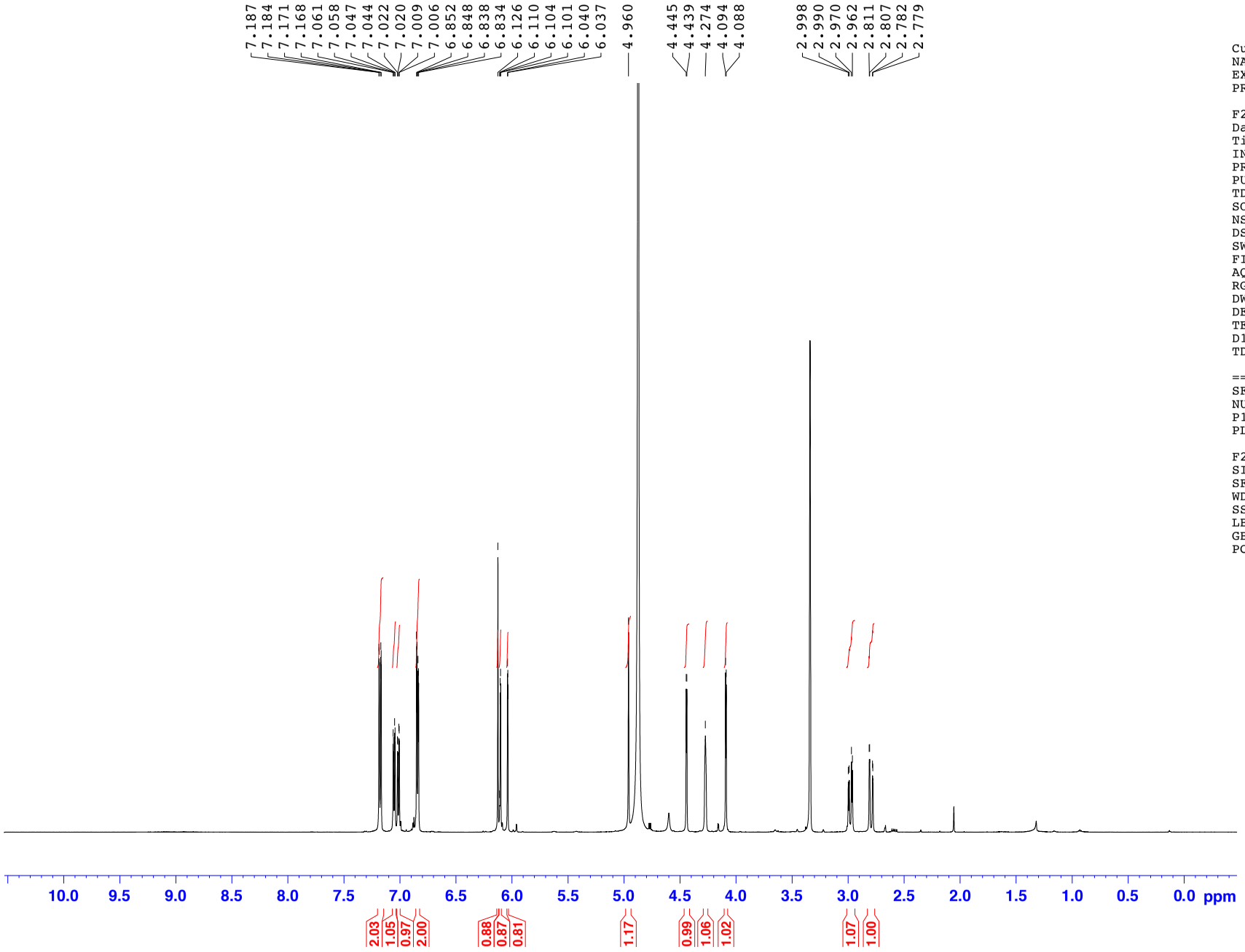
======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                       10.00 usec
PLW1               70.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                    70.00 usec
PLW2               14.00000000 W
PLW12               0.64286000 W
PLW13               0.32335001 W

F2 - Processing parameters
SI                       32768
SF                 150.9024684 MHz
WDW                         EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```



^{1}H NMR of 2 (600MHz, CD_3OD)

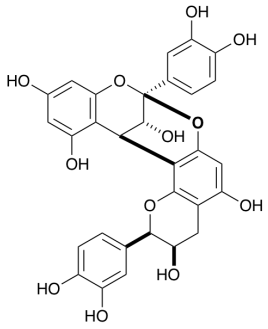



```
Current Data Parameters
NAME                  VB-178
EXPNO                     30
PROCNO                     1

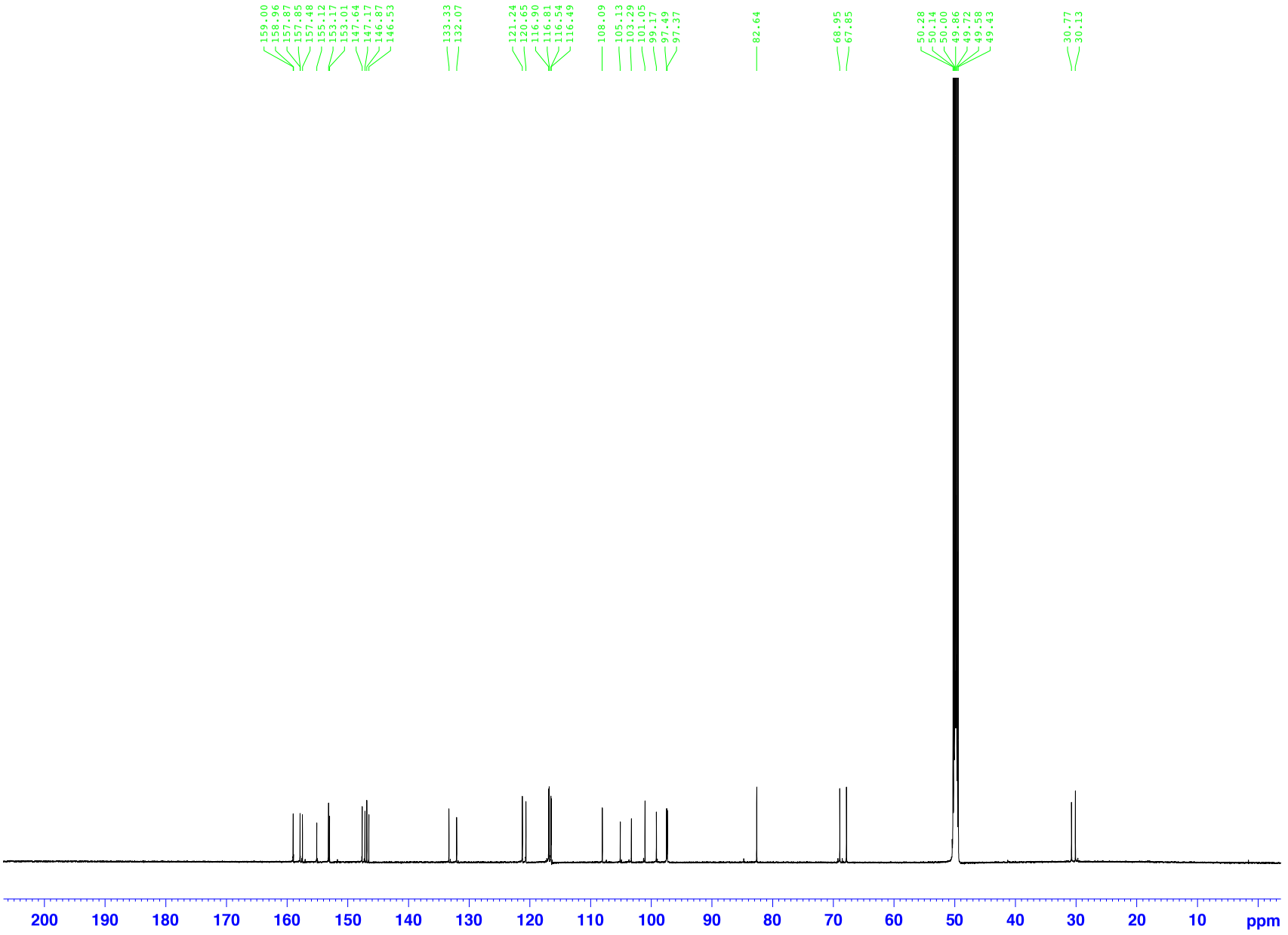
F2 - Acquisition Parameters
Date_              20181108
Time                  10.16
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       50
DS                        2
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ                2.7262976 sec
RG                    31.94
DW                  41.600 usec
DE                  10.00 usec
TE                  300.1 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           600.1337060 MHz
NUC1                     1H
P1                    12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                    65536
SF               600.1299940 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



^{1}H NMR of 2 (150MHz, CD_3OD)



Current Data Parameters

NAME	VB-178
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20181109
Time	9.21
INSTRUM	spect
PROBHD	5 mm CPPBBO BB
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	9000
DS	4
SWH	36057.691 Hz
FIDRES	0.550197 Hz
AQ	0.9087659 sec
RG	175.56
DW	13.867 usec
DE	18.00 usec
TE	300.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

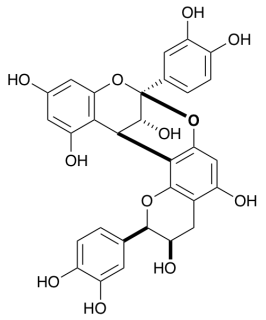
SFO1	150.9178981 MHz
NUC1	13C
P1	10.00 usec
PLW1	70.00000000 W

======== CHANNEL f2 ========

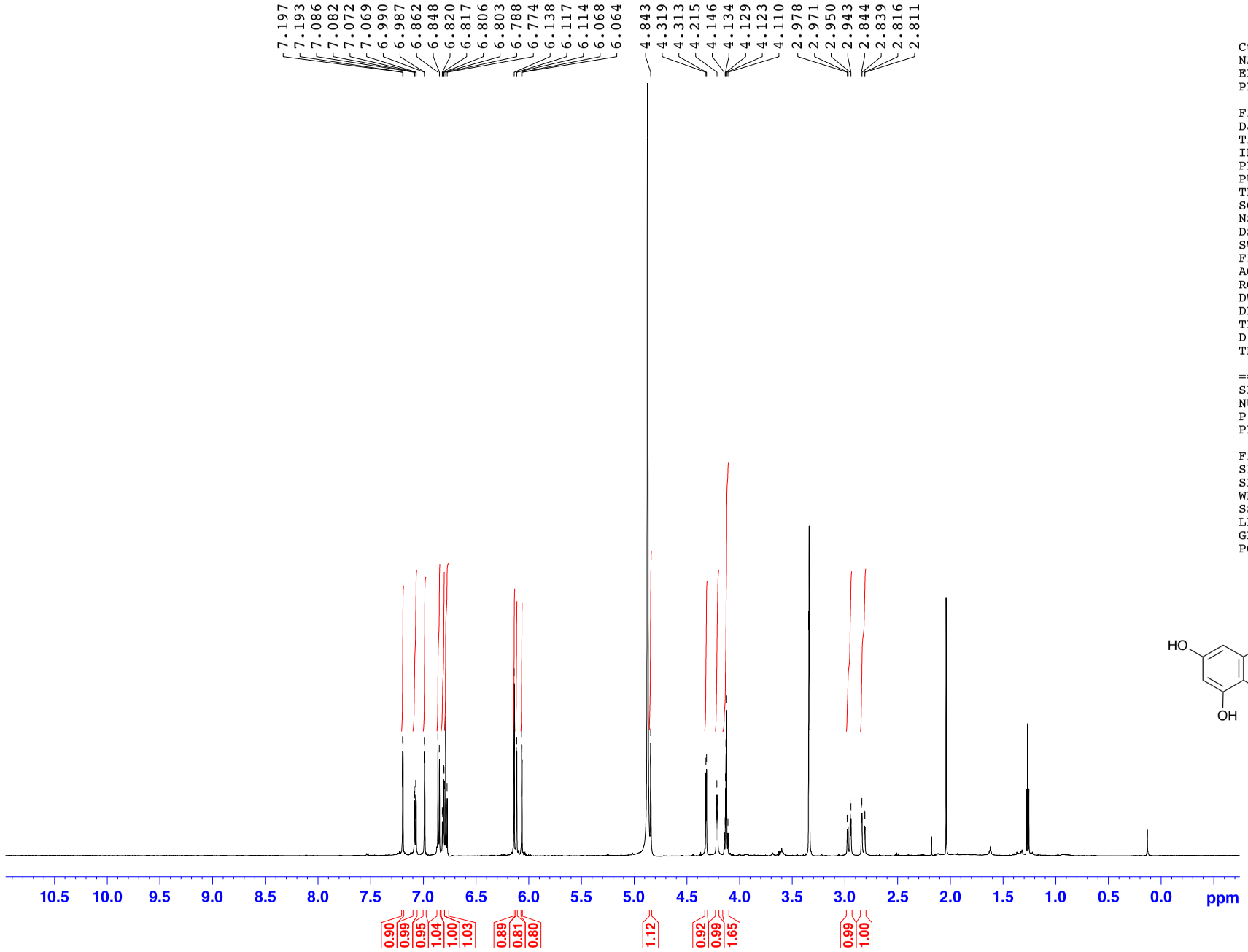
SFO2	600.1324005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	70.00 usec
PLW2	14.00000000 W
PLW12	0.64286000 W
PLW13	0.32335001 W

F2 - Processing parameters

SI	32768
SF	150.9024683 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



^{1}H NMR of 17 (600MHz, CD_3OD)

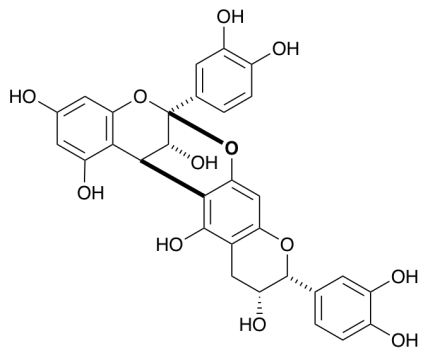



```
Current Data Parameters
NAME                  VB-295
EXPNO                     11
PROCNO                     1

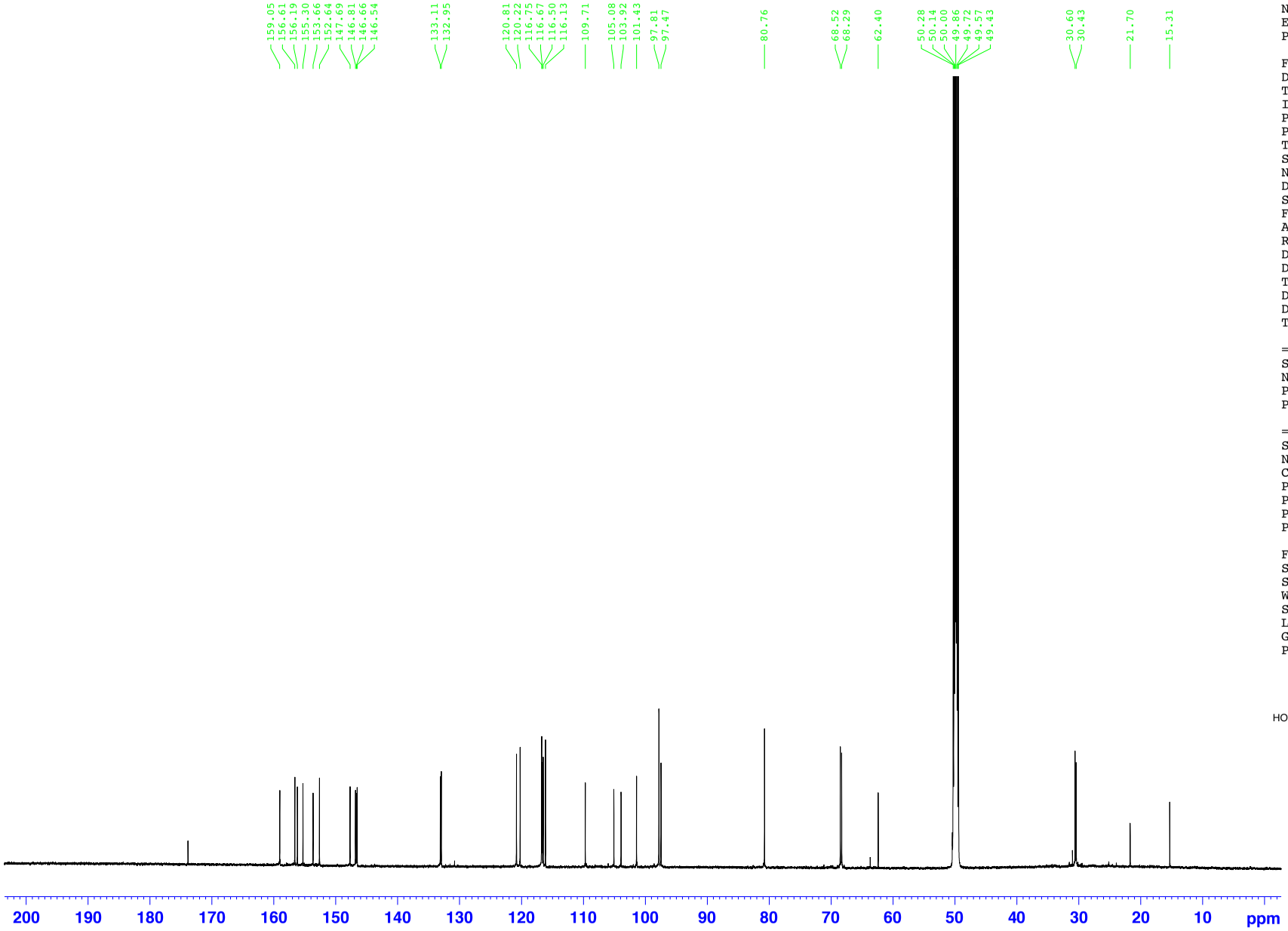
F2 - Acquisition Parameters
Date_              20190220
Time                   0.09
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       50
DS                        2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                2.7262976 sec
RG                    31.94
DW                   41.600 usec
DE                   10.00 usec
TE                   300.1 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                      1H
P1                     12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                        65536
SF              600.1299933 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 17 (150MHz, CD_3OD)



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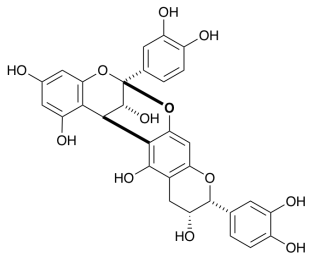
```
Current Data Parameters
NAME                  VB-295
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190220
Time                   8.28
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                    10000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9087659 sec
RG                   175.56
DW                  13.867 usec
DE                  18.00 usec
TE                  300.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

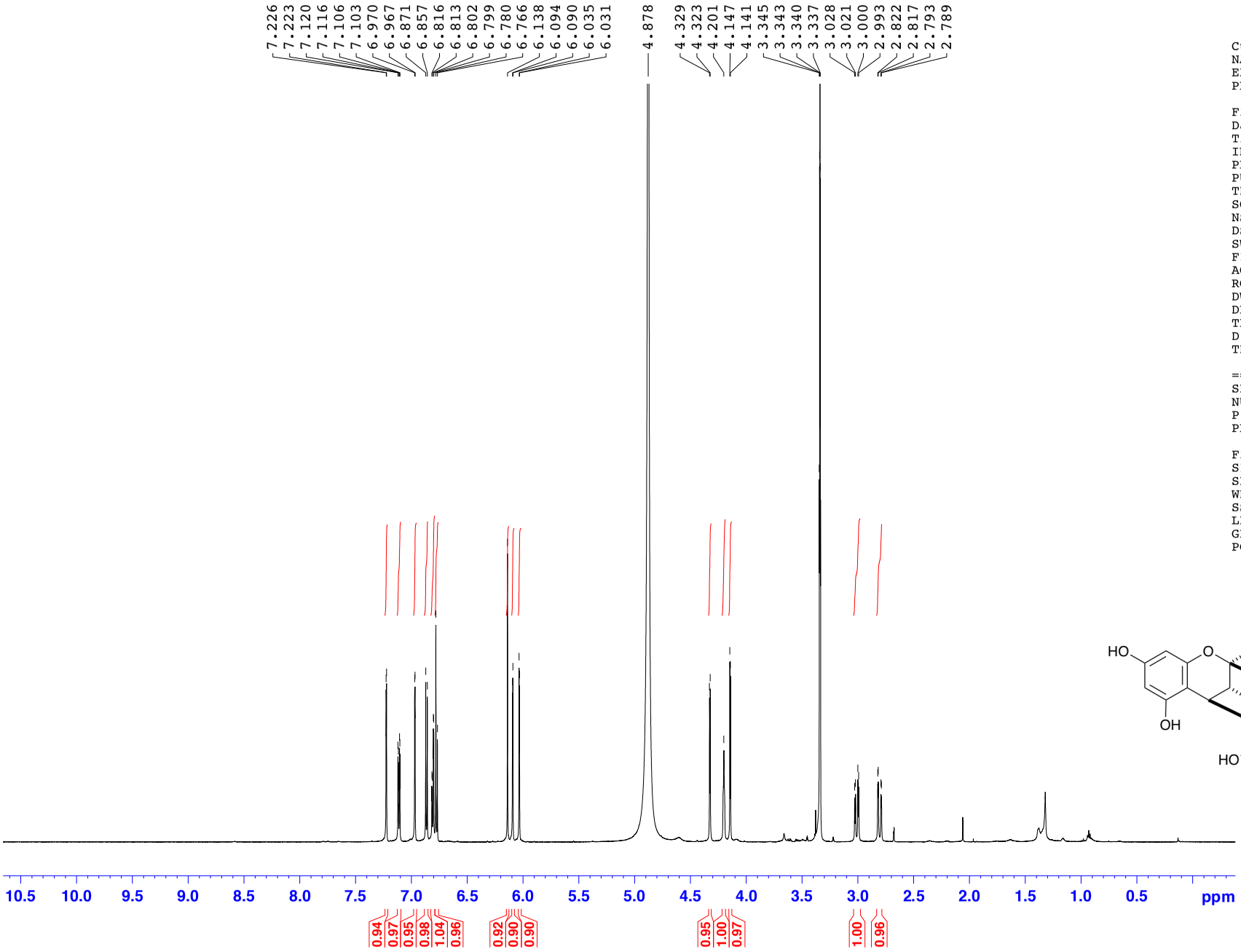
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                   10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9024682 MHz
WDW                       EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```



^{1}H NMR of 18 (600MHz, CD_3OD)

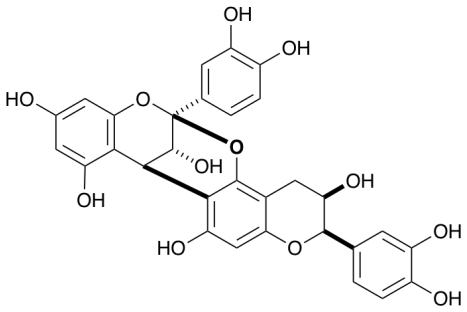



```
Current Data Parameters
NAME                  VB-236-2
EXPNO                       10
PROCNO                       1

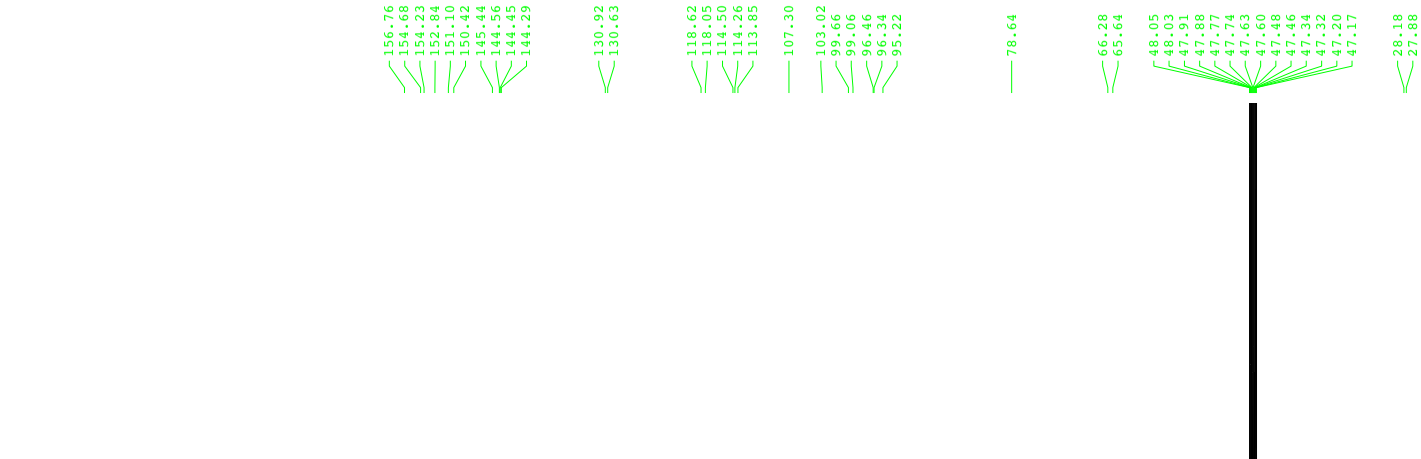
F2 - Acquisition Parameters
Date_                 20181206
Time                     10.51
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                  MeOD
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       299.9 K
D1                  1.00000000 sec
TD0                          1

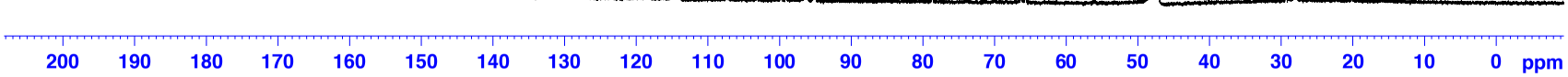
======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               23.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1299936 MHz
WDW                        EM
SSB                 0
LB                       0.30 Hz
GB                  0
PC                       1.00
```



^{13}C NMR of 18 (150MHz, CD_3OD)





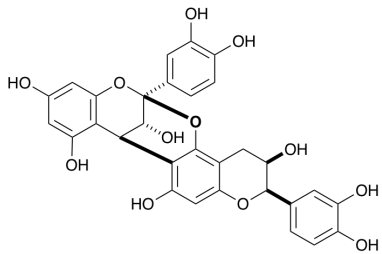

```
Current Data Parameters
NAME                  VB-236
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20181209
Time                  10.05
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                    12000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                   175.56
DW                 13.867 usec
DE                 18.00 usec
TE                 300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

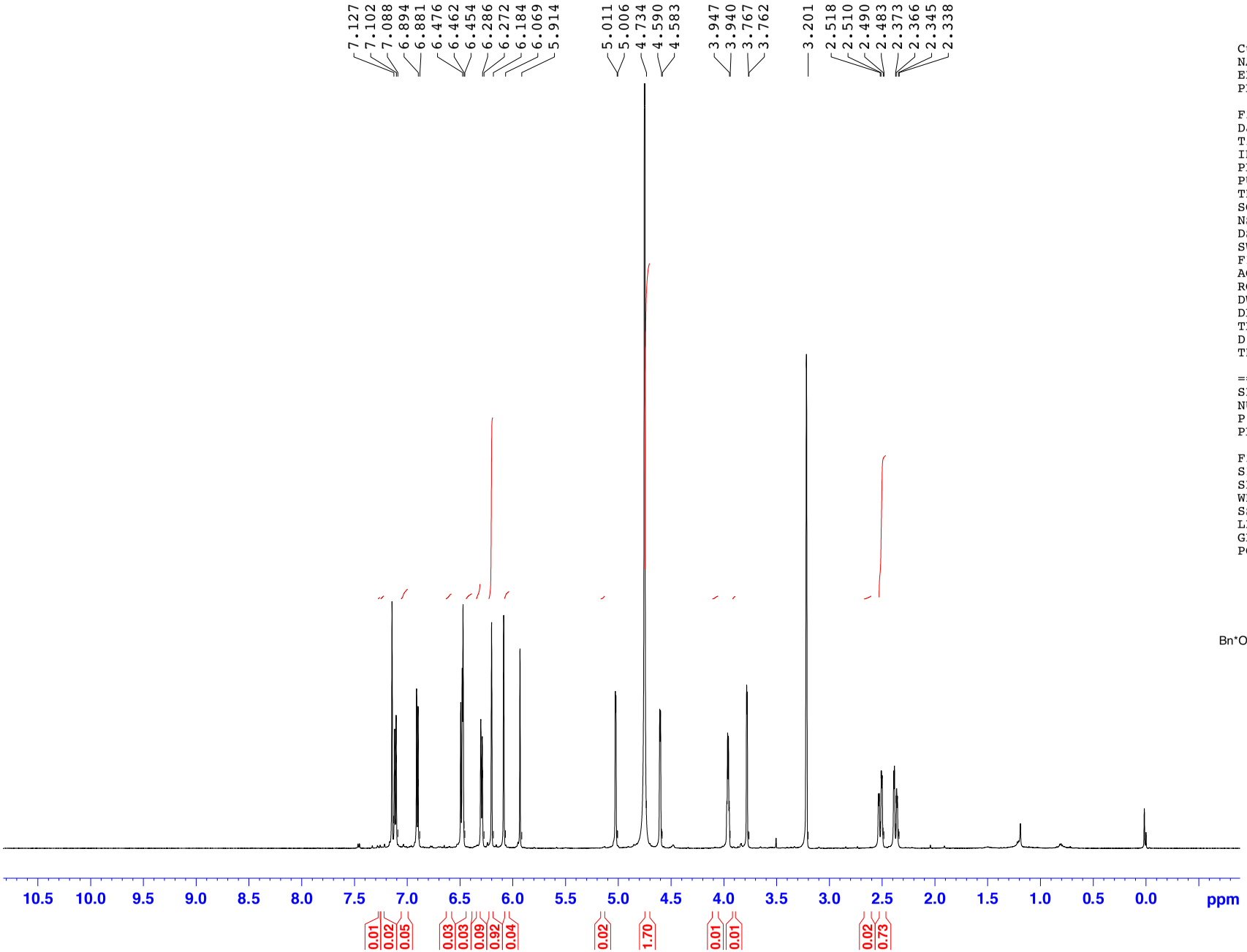
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                  10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2               70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9028090 MHz
WDW                       EM
SSB          0
LB                   1.00 Hz
GB           0
PC                   1.40
```



^{1}H NMR of 20 (600MHz, CD_3OD)



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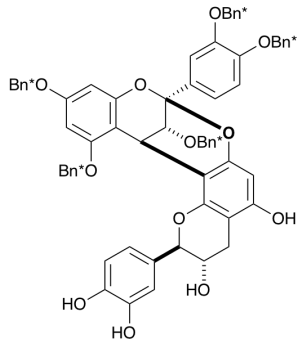
```
Current Data Parameters
NAME                  VB-118
EXPNO                     10
PROCNO                     1

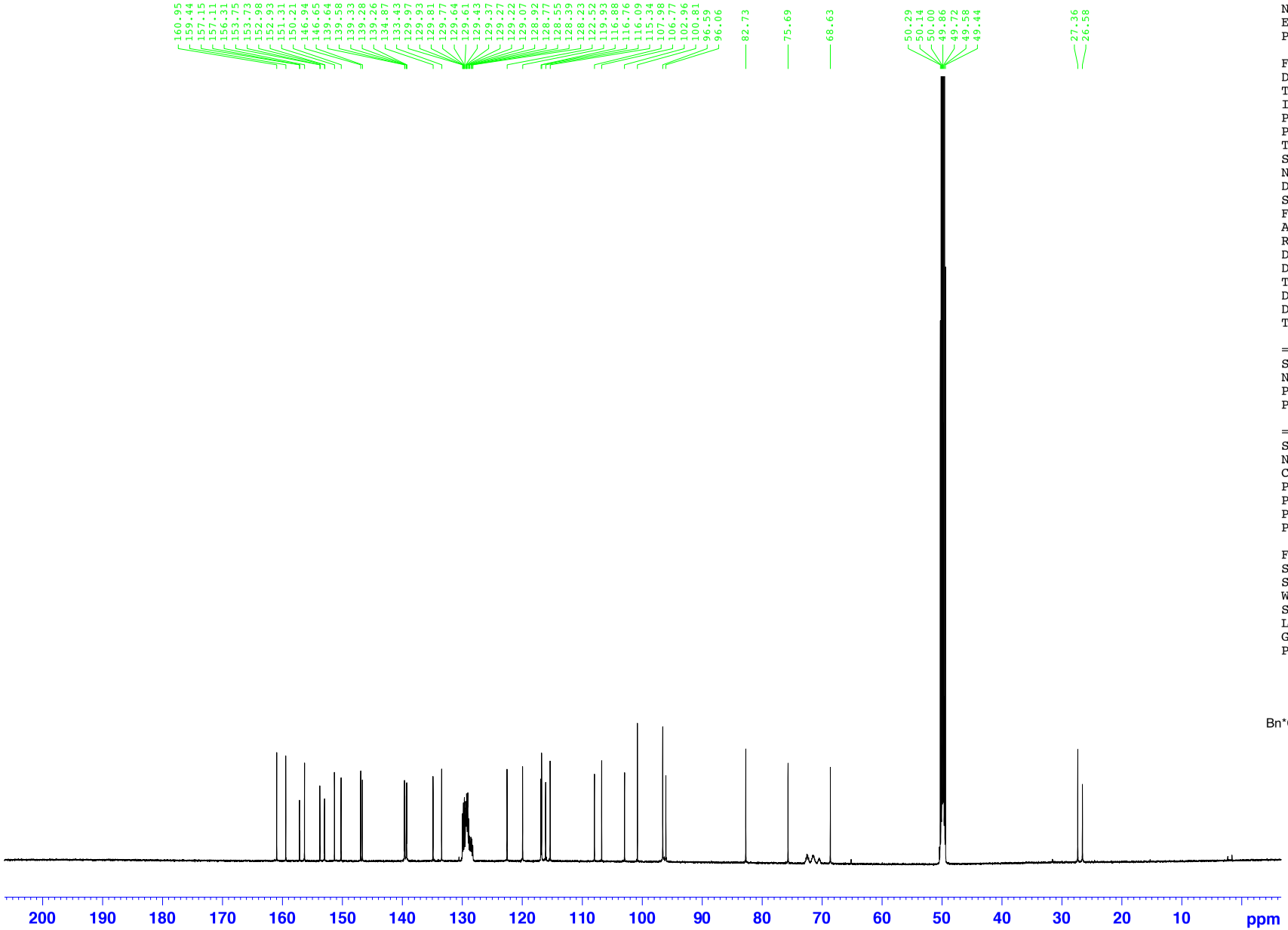
F2 - Acquisition Parameters
Date_              20180407
Time                  15.59
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       16
DS                        2
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ                2.7262976 sec
RG                    31.94
DW                   41.600 usec
DE                   10.00 usec
TE                   300.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           600.1337060 MHz
NUC1                     1H
P1                    12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                    65536
SF               600.1300672 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



^{13}C NMR of 20 (600MHz, CD_3OD)



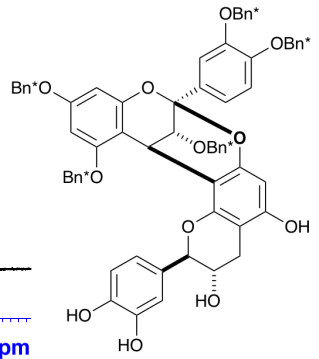

```
Current Data Parameters
NAME                  VB-118
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180408
Time                   6.04
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG               zgpg30
TD                     65536
SOLVENT                MeOD
NS                      7186
DS                         4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                   175.56
DW                   13.867 usec
DE                    18.00 usec
TE                    299.9 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                        1

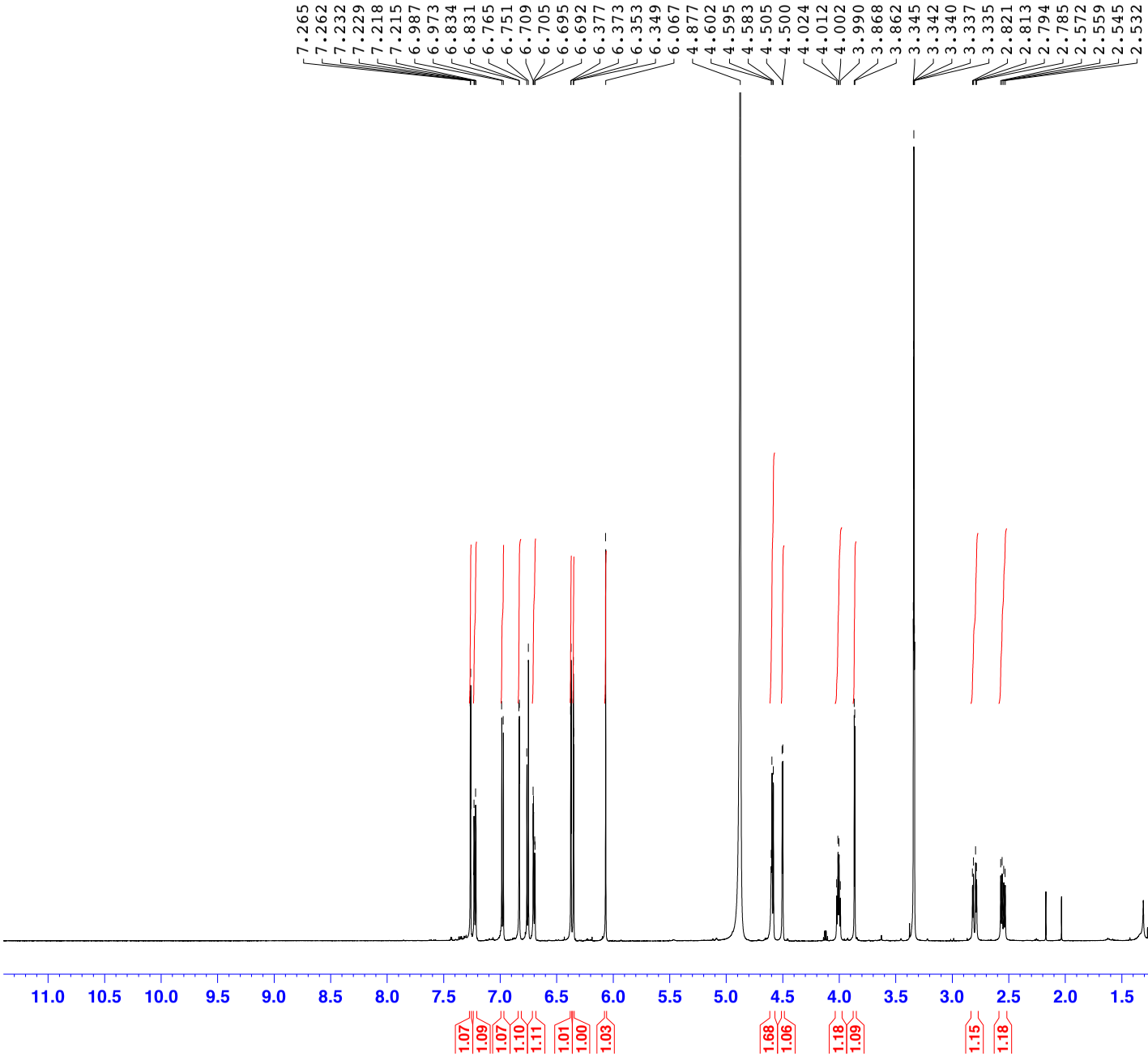
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF               150.9024705 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 21 (600MHz, CD_3OD)



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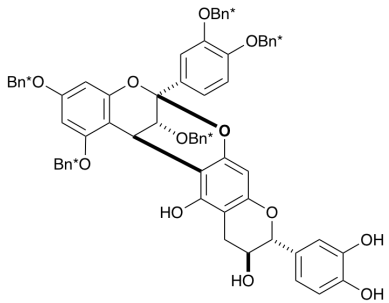
```
Current Data Parameters
NAME                  VB-182-3
EXPNO                       31
PROCNO                       1

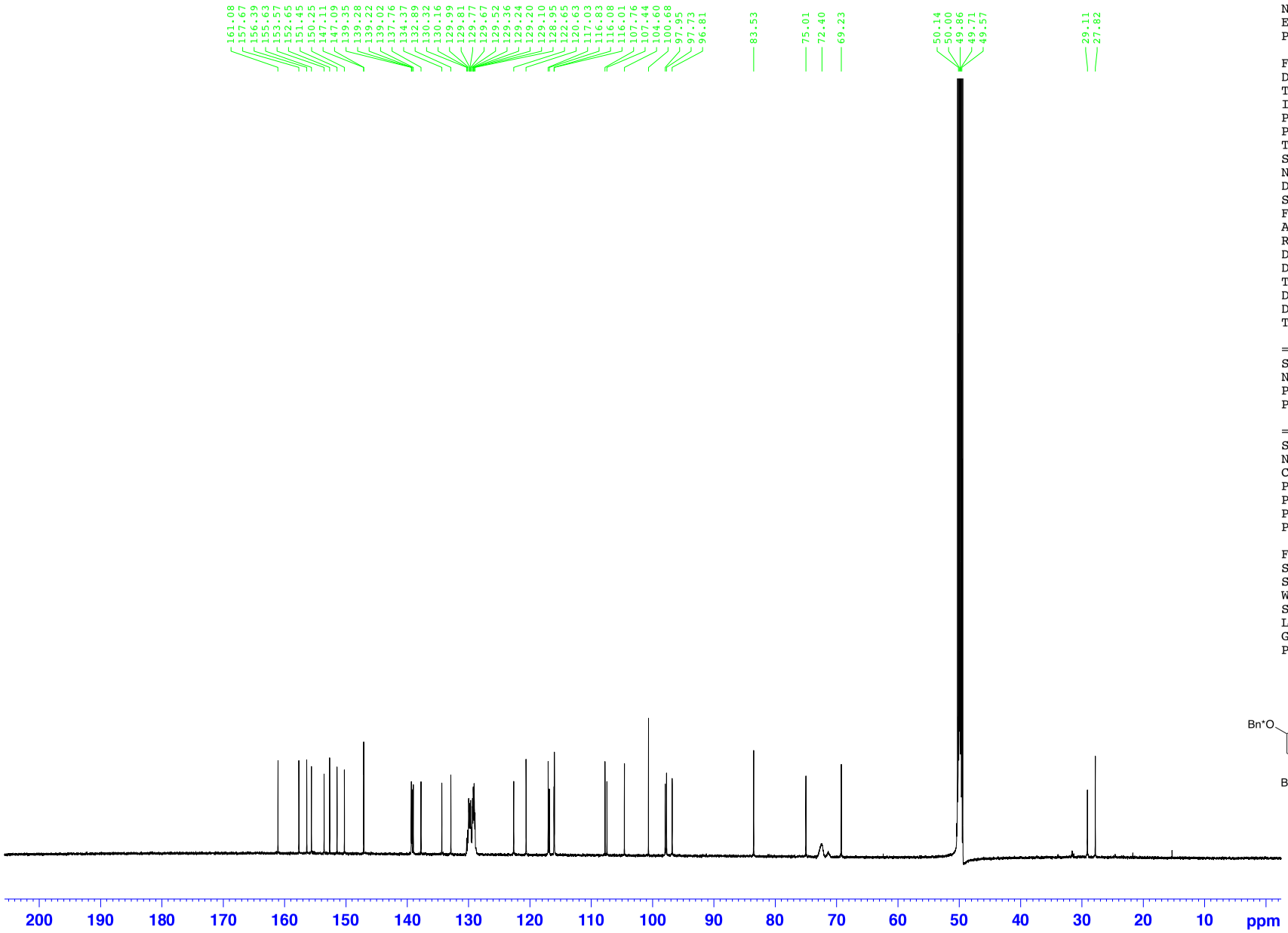
F2 - Acquisition Parameters
Date_                 20180717
Time                     13.52
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                  MeOD
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       300.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               23.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1299939 MHz
WDW                        EM
SSB             0
LB                        0.30 Hz
GB              0
PC                        1.00
```



^{13}C NMR of 21 (150MHz, CD_3OD)



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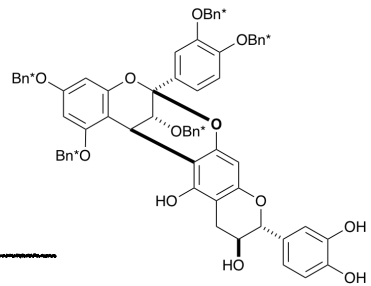
```
Current Data Parameters
NAME              VB-182-3
EXPNO                   30
PROCNO                   1

F2 - Acquisition Parameters
Date_              20180715
Time                 23.51
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG             zgpg30
TD                   65536
SOLVENT                MeOD
NS                      8192
DS                         4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

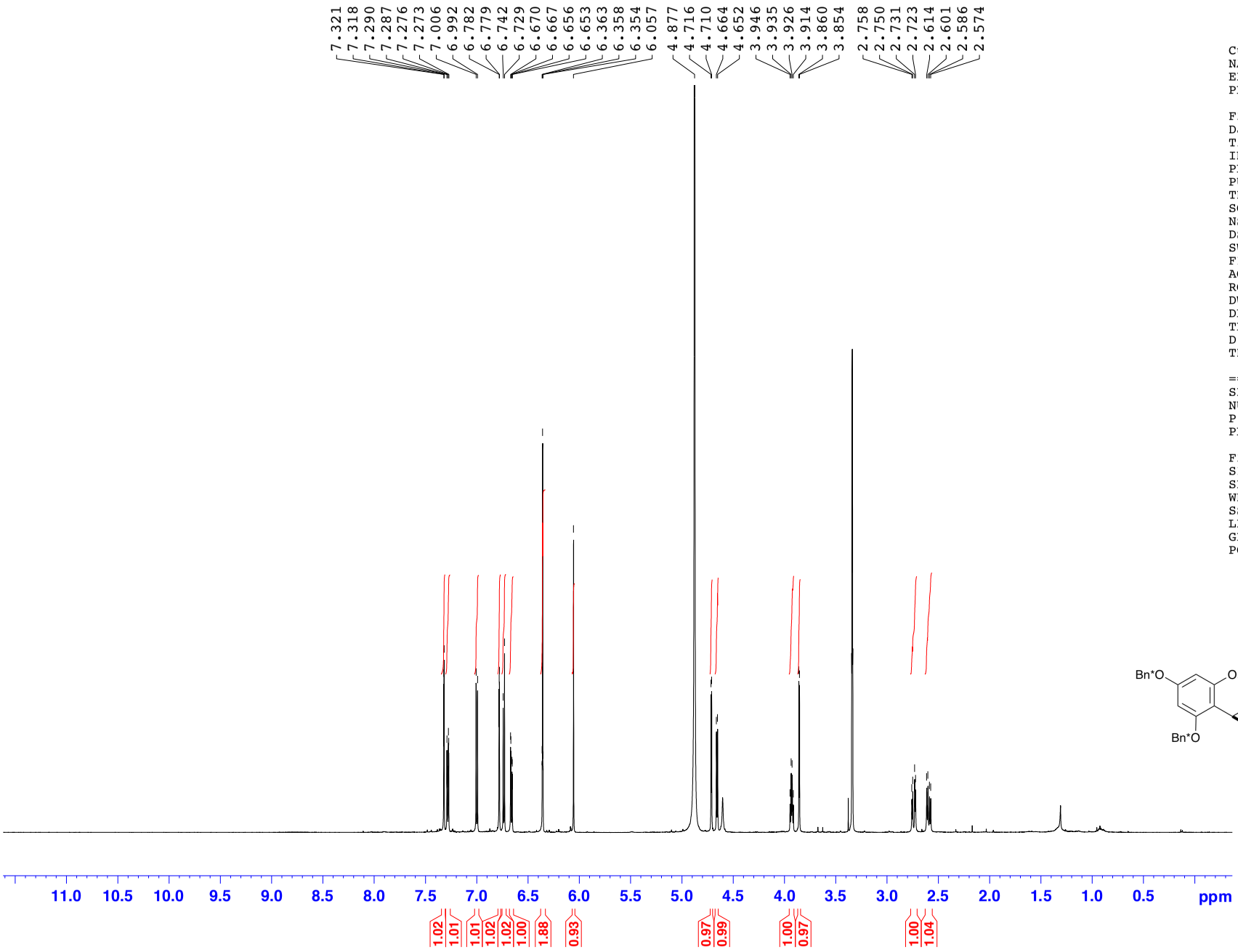
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                      32768
SF           150.9024696 MHz
WDW                        EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



^{1}H NMR of 22 (600MHz, CD_3OD)

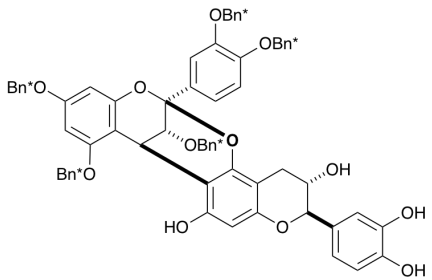



```
Current Data Parameters
NAME                  VB-182-2
EXPNO                       31
PROCNO                       1

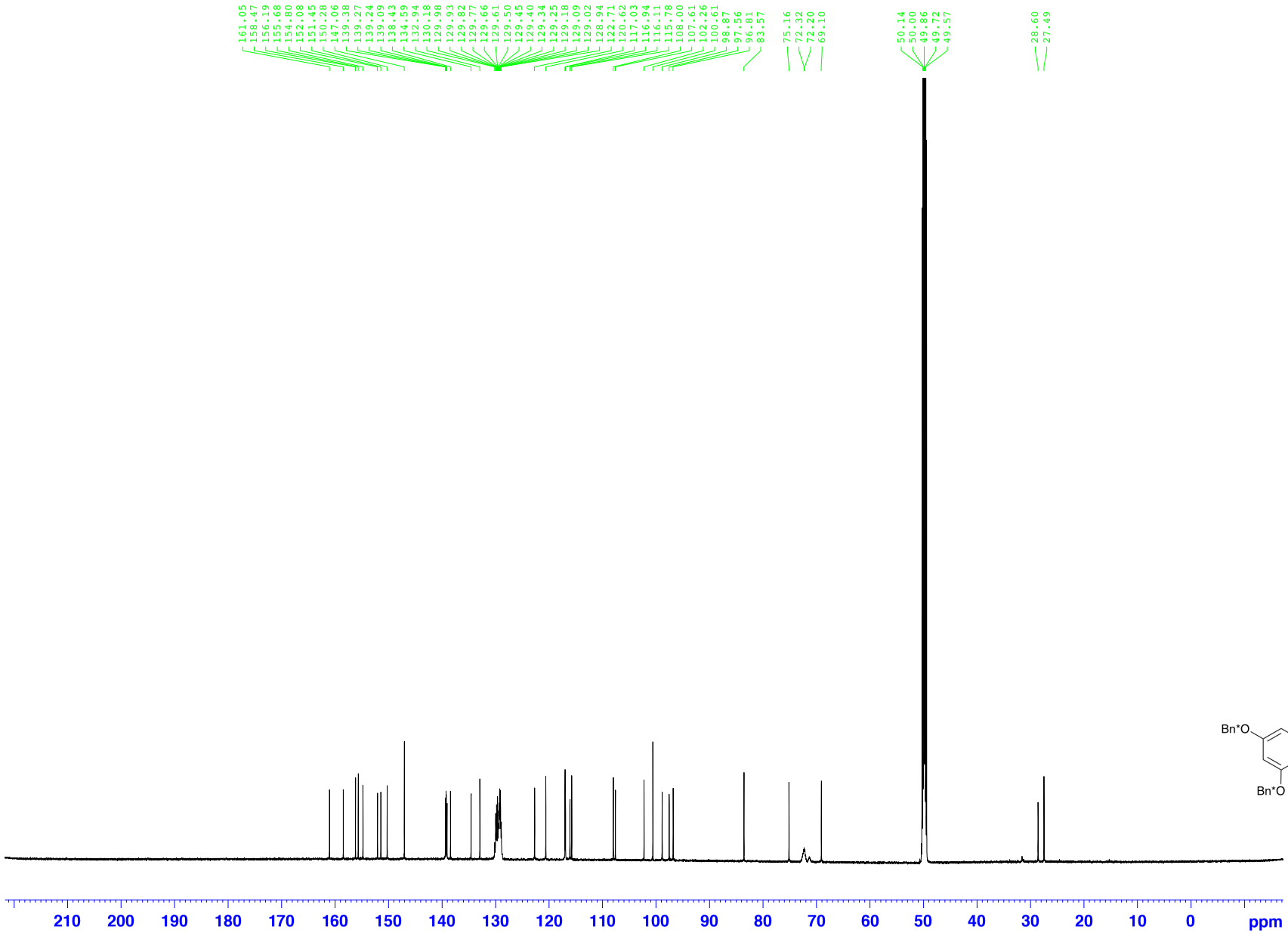
F2 - Acquisition Parameters
Date_                 20180717
Time                     13.47
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                  MeOD
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       300.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               23.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1299938 MHz
WDW                        EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```



^{13}C NMR of 22 (150MHz, CD_3OD)



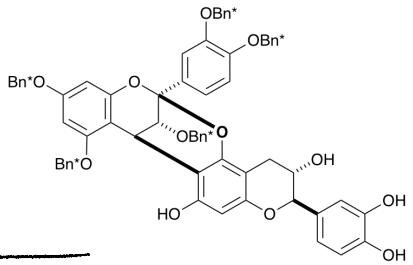

```
Current Data Parameters
NAME                  VB-182-2
EXPNO                       30
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20180715
Time                     16.56
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zgpg30
TD                       65536
SOLVENT                   MeOD
NS                        8192
DS                           4
SWH                  36057.691 Hz
FIDRES                0.550197 Hz
AQ                    0.9087659 sec
RG                       175.56
DW                       13.867 usec
DE                       18.00 usec
TE                       300.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

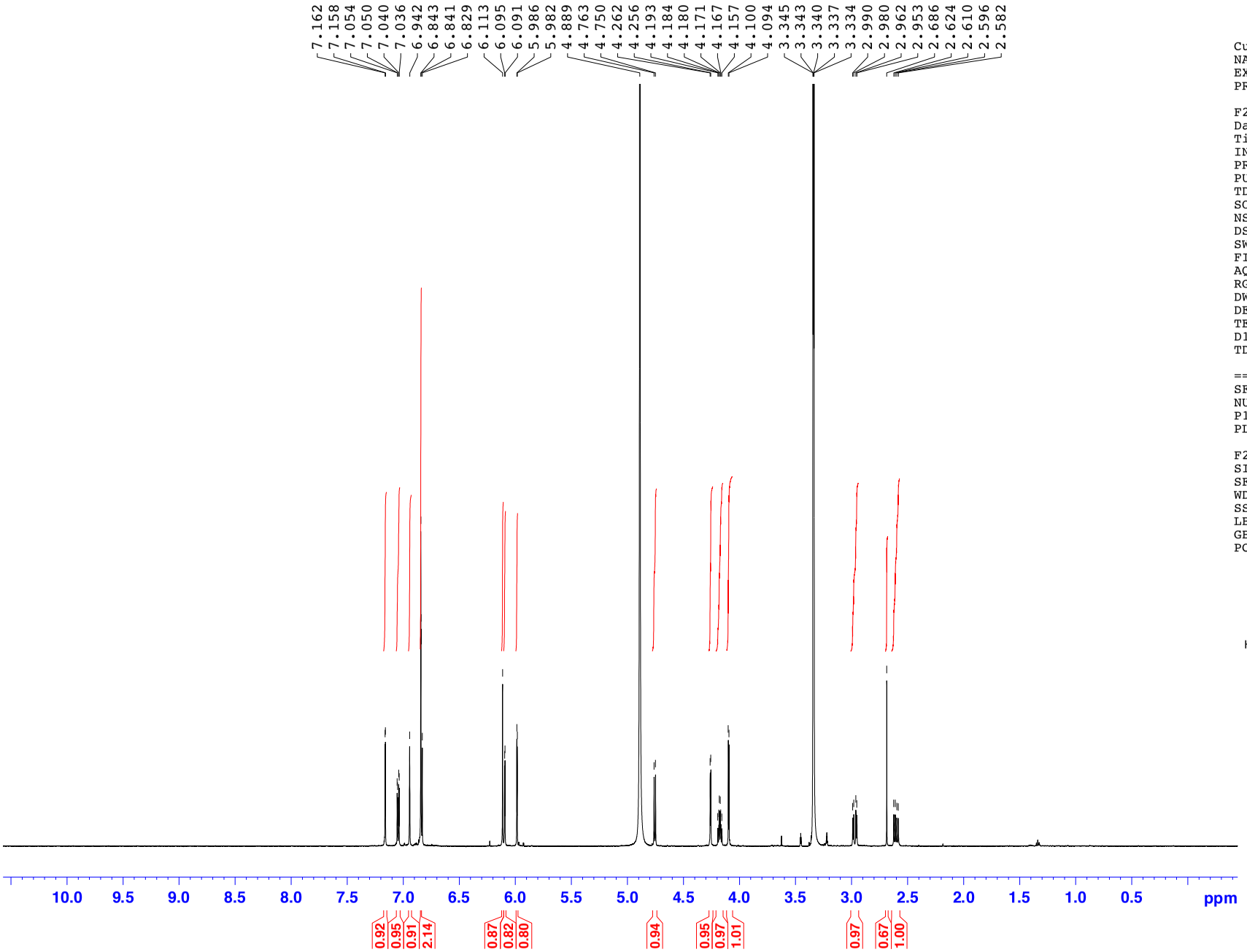
======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                        13C
P1                       10.00 usec
PLW1                70.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                    70.00 usec
PLW2                14.00000000 W
PLW12                0.64286000 W
PLW13                0.32335001 W

F2 - Processing parameters
SI                        32768
SF                 150.9024698 MHz
WDW                          EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```



^{1}H NMR of 1 (600MHz, CD_3OD)



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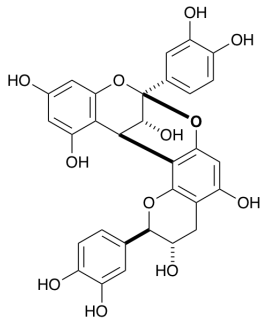
```
Current Data Parameters
NAME                  VB-81
EXPNO                    20
PROCNO                    1

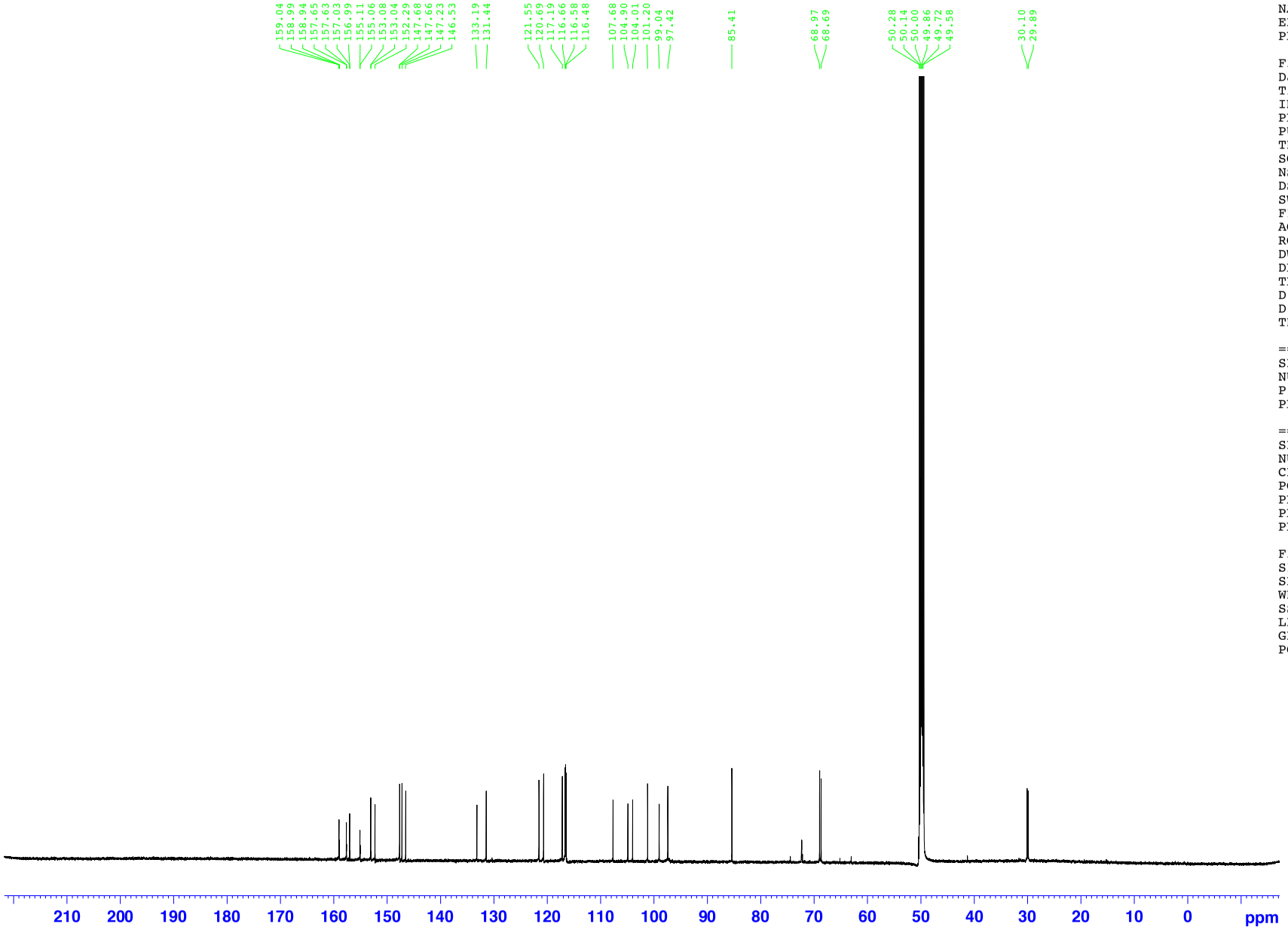
F2 - Acquisition Parameters
Date_              20190712
Time                  23.13
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                 2.7262976 sec
RG                    31.94
DW                   41.600 usec
DE                   10.00 usec
TE                   298.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                      1H
P1                     12.00 usec
PLW1           21.00000000 W

F2 - Processing parameters
SI                    65536
SF              600.1299934 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 1 (150MHz, CD_3OD)



Current Data Parameters

NAME	VB-81
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20180408
Time	12.52
INSTRUM	spect
PROBHD	5 mm CPPBBO BB
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	8192
DS	4
SWH	36057.691 Hz
FIDRES	0.550197 Hz
AQ	0.9087659 sec
RG	175.56
DW	13.867 usec
DE	18.00 usec
TE	300.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

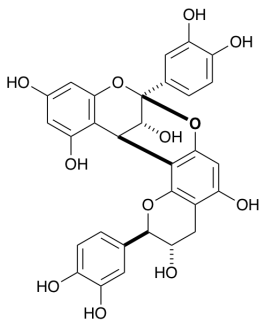
SFO1	150.9178981 MHz
NUC1	13C
P1	10.00 usec
PLW1	70.00000000 W

======== CHANNEL f2 ========

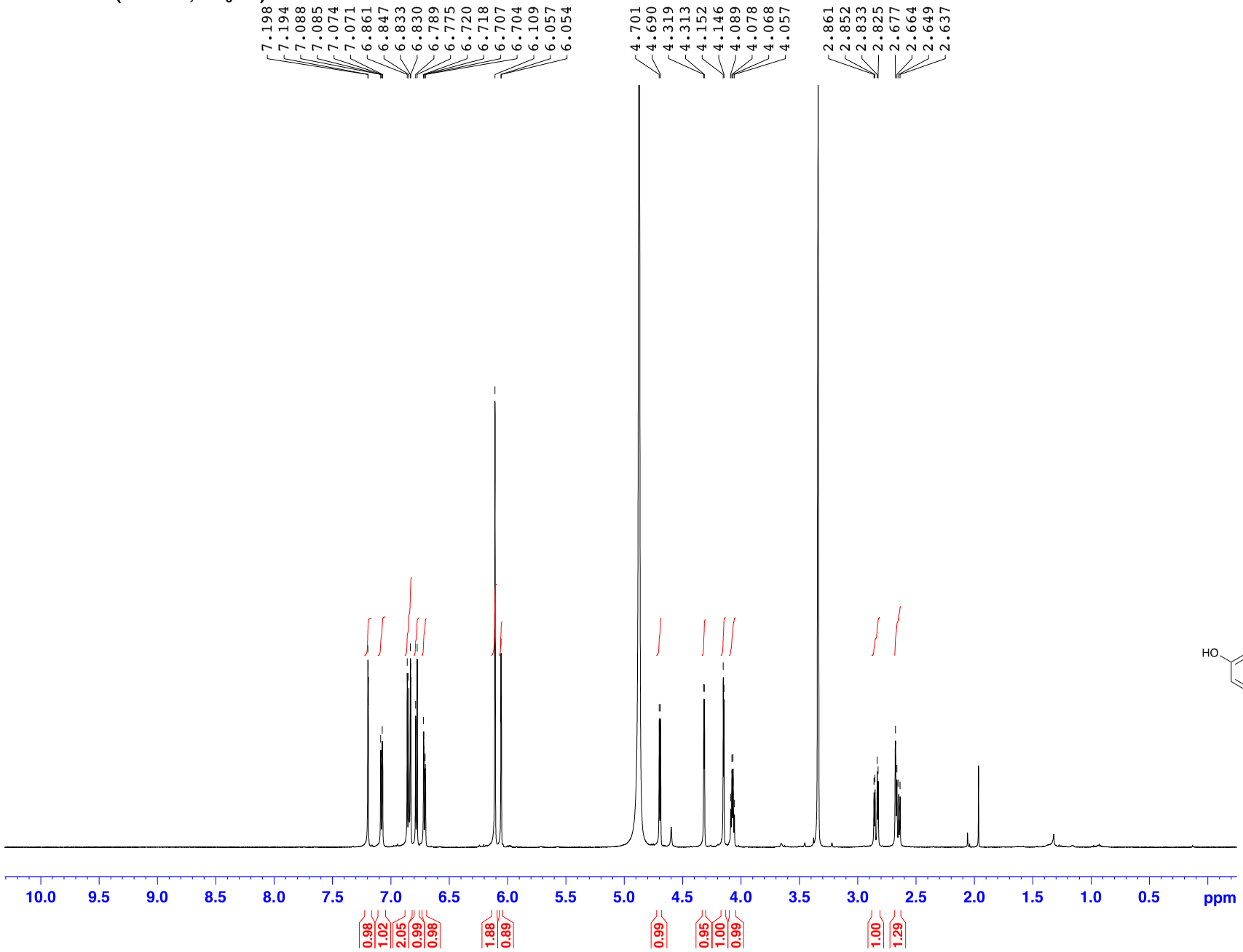
SFO2	600.1324005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	70.00 usec
PLW2	14.00000000 W
PLW12	0.64286000 W
PLW13	0.32335001 W

F2 - Processing parameters

SI	32768
SF	150.9024672 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



^{1}H NMR of 23 (600MHz, CD_3OD)



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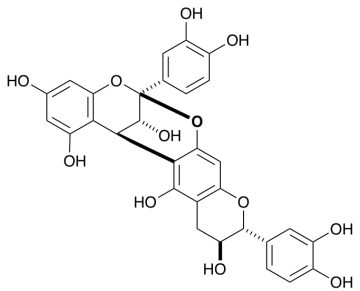
```
Current Data Parameters
NAME                  VB-217
EXPNO                     10
PROCNO                     1

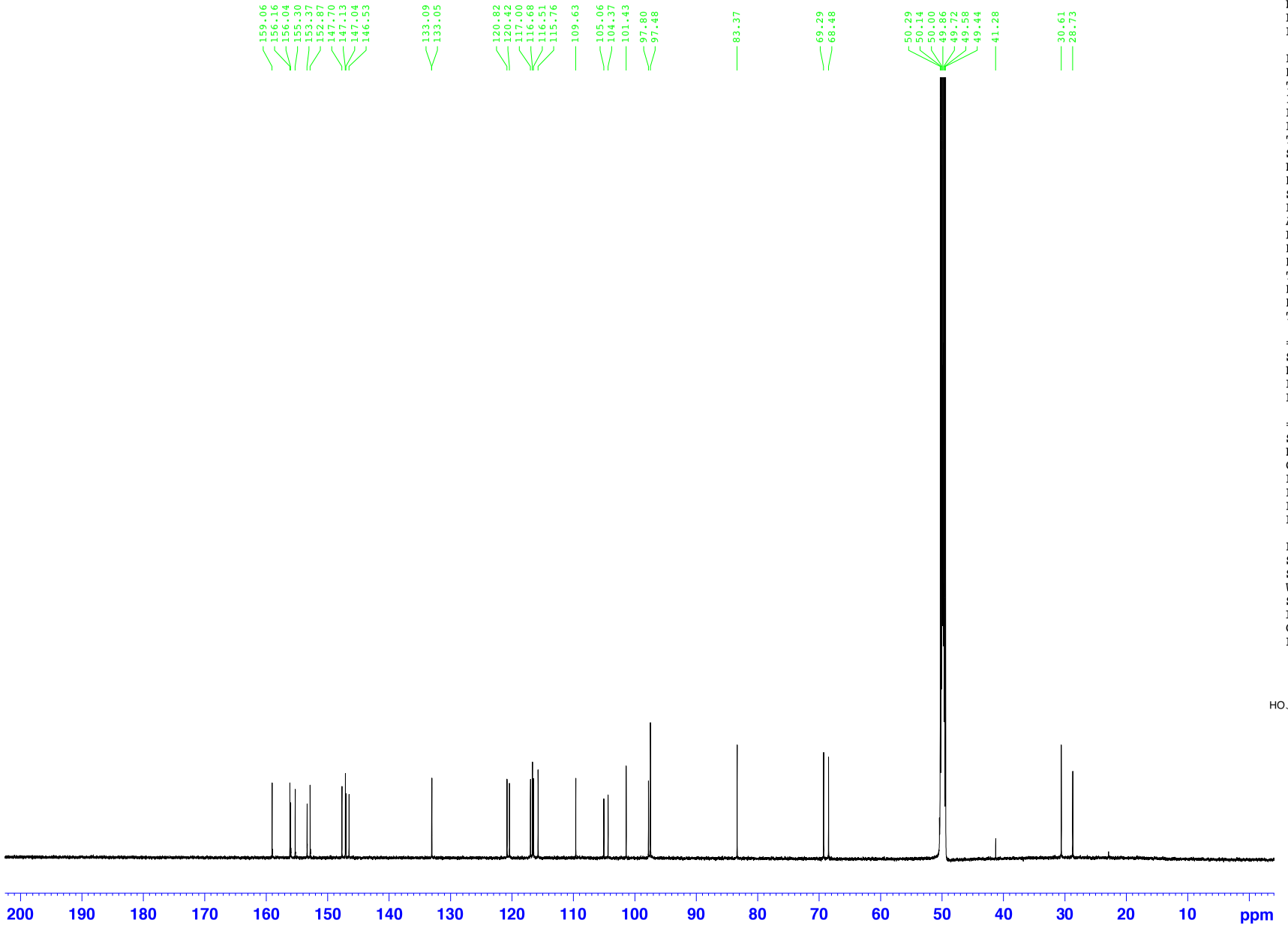
F2 - Acquisition Parameters
Date_              20181114
Time                  15.37
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                        30
DS                         2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                 2.7262976 sec
RG                    31.94
DW                   41.600 usec
DE                   10.00 usec
TE                   300.1 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                      1H
P1                     12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                        65536
SF              600.1299938 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 23 (150MHz, CD_3OD)



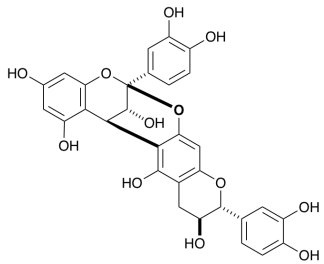

```
Current Data Parameters
NAME                  VB-217
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20181115
Time                   8.05
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                     5500
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

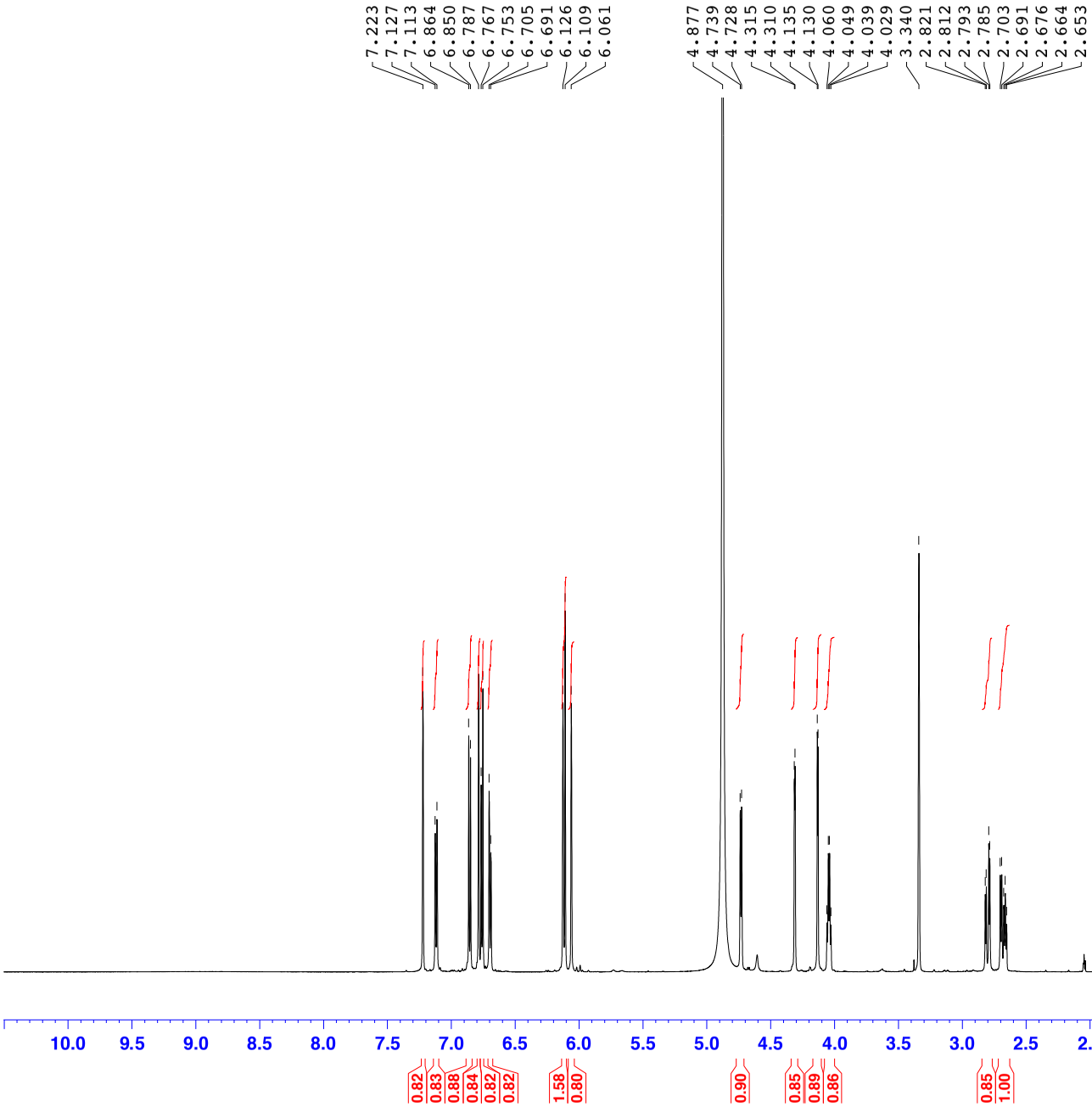
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9024674 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 24 (600MHz, CD_3OD)



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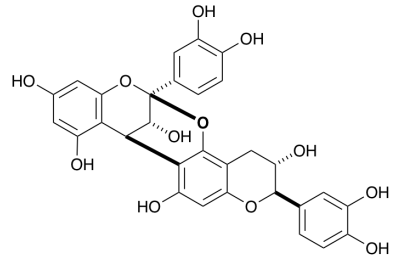
```
Current Data Parameters
NAME                  VB-216
EXPNO                     10
PROCNO                     1

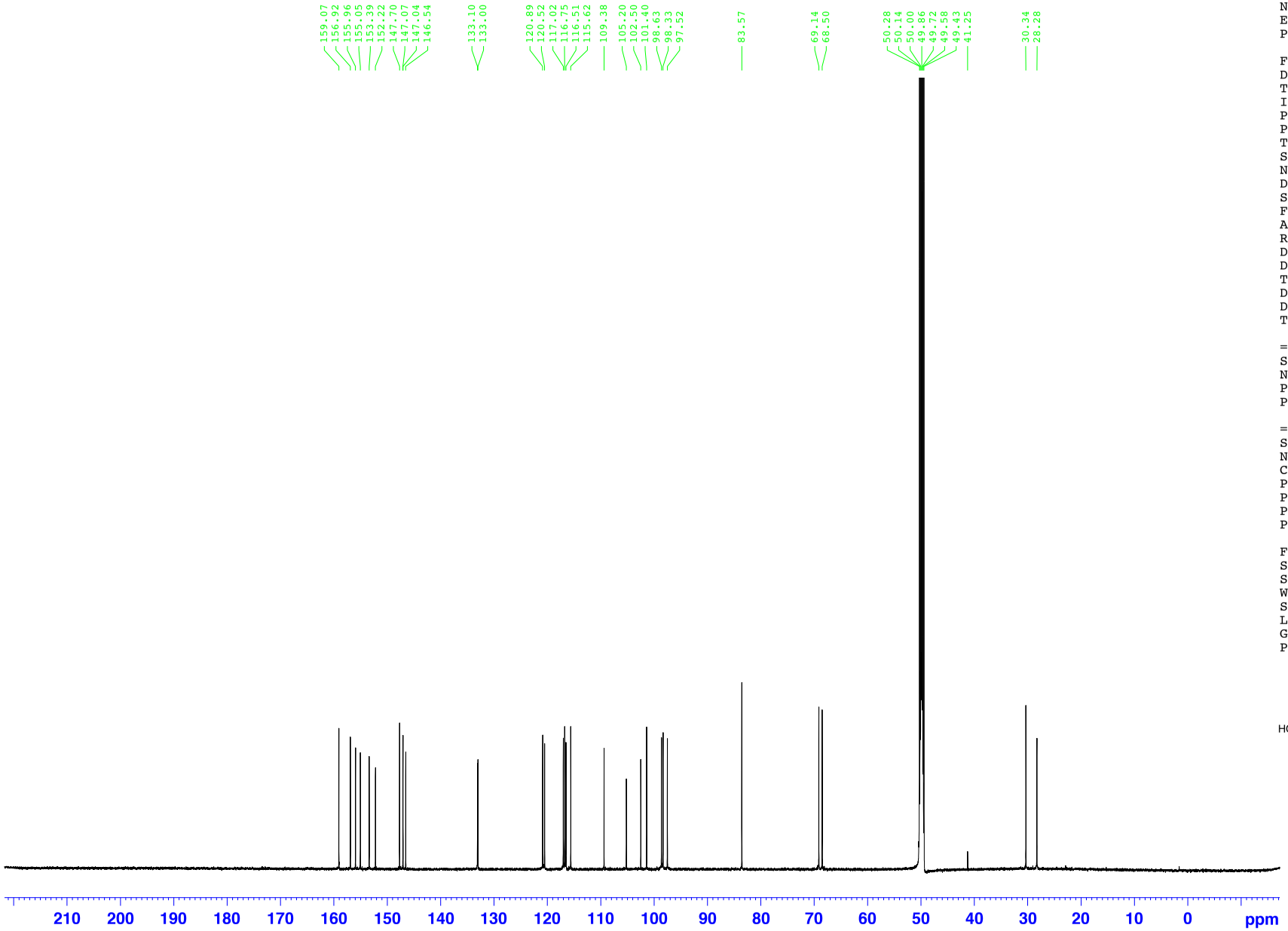
F2 - Acquisition Parameters
Date_              20181114
Time                  15.30
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                        30
DS                         2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                2.7262976 sec
RG                    31.94
DW                   41.600 usec
DE                   10.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                      1H
P1                     12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                        65536
SF              600.1299942 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 24 (150MHz, CD_3OD)



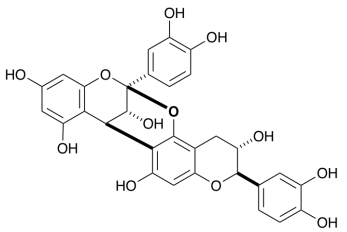

```
Current Data Parameters
NAME                  VB-216
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20181115
Time                   3.24
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                     4000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

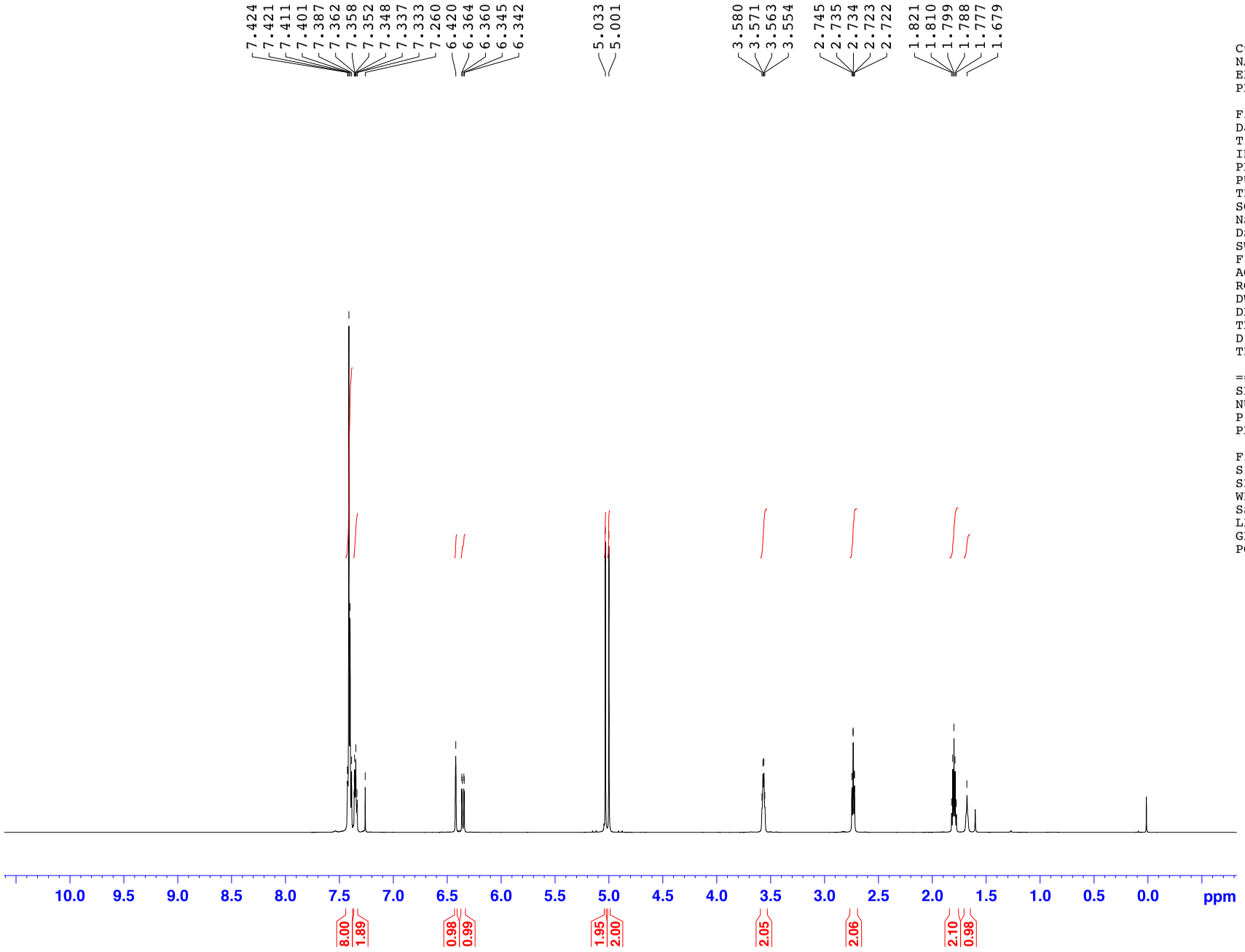
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9024703 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 26 (600MHz, $CDCl_3$)



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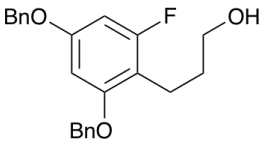
```
Current Data Parameters
NAME                  VB-297
EXPNO                     10
PROCNO                     1

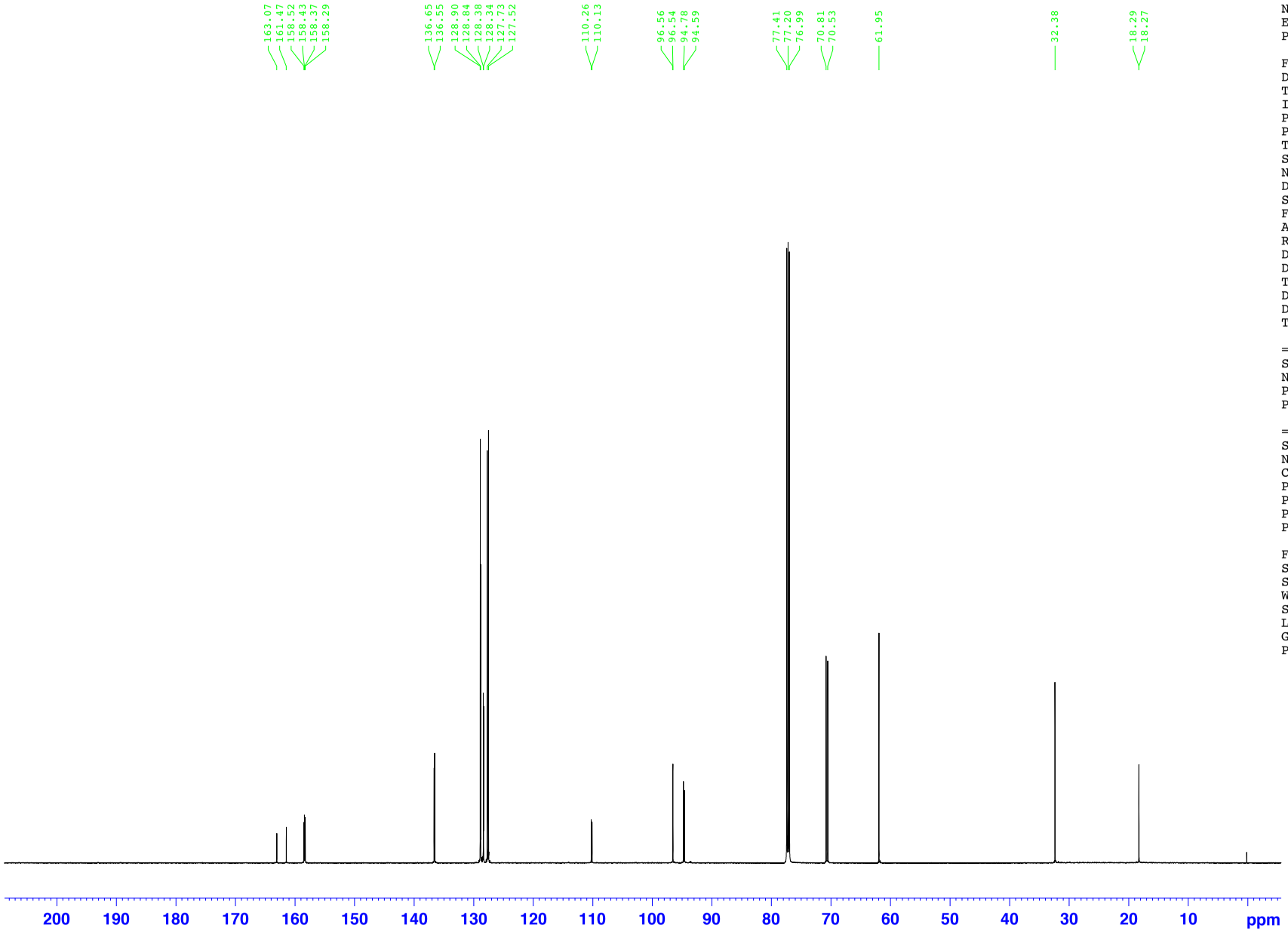
F2 - Acquisition Parameters
Date_              20190227
Time                  12.09
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                 2.7262976 sec
RG                      17.5
DW                    41.600 usec
DE                    10.00 usec
TE                    300.1 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           600.1337060 MHz
NUC1                     1H
P1                    12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                    65536
SF               600.1300146 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 26 (150MHz, $CDCl_3$)



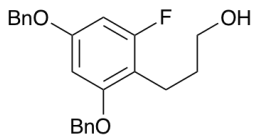

```
Current Data Parameters
NAME                  VB-297
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190228
Time                   2.48
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     3300
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                  18.00 usec
TE                  300.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

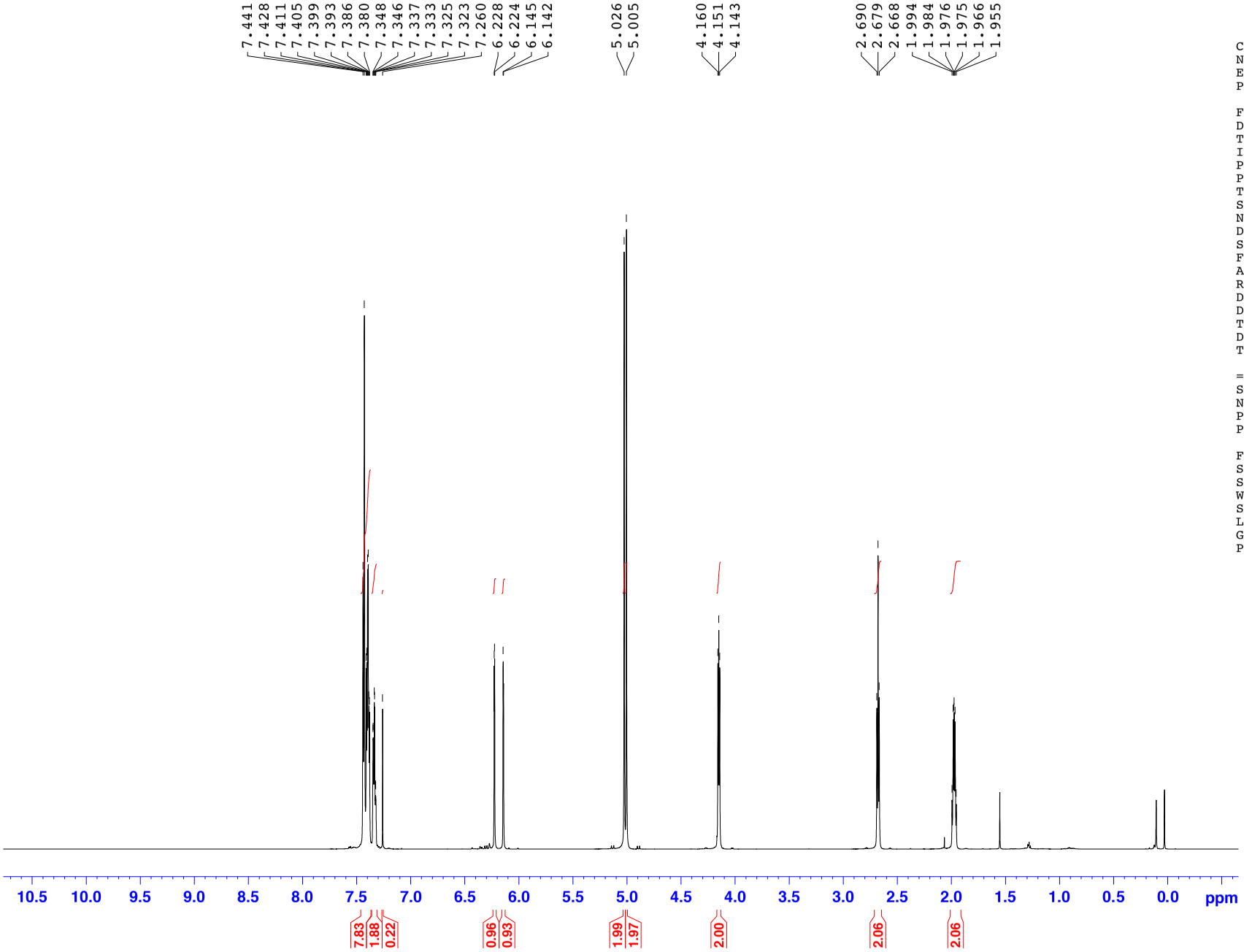
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                   13C
P1                  10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                    32768
SF             150.9027849 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



^{1}H NMR of 27 (600MHz, $CDCl_3$)

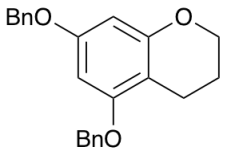


Current Data Parameters
NAME VB-300
EXPNO 10
PROCNO 1

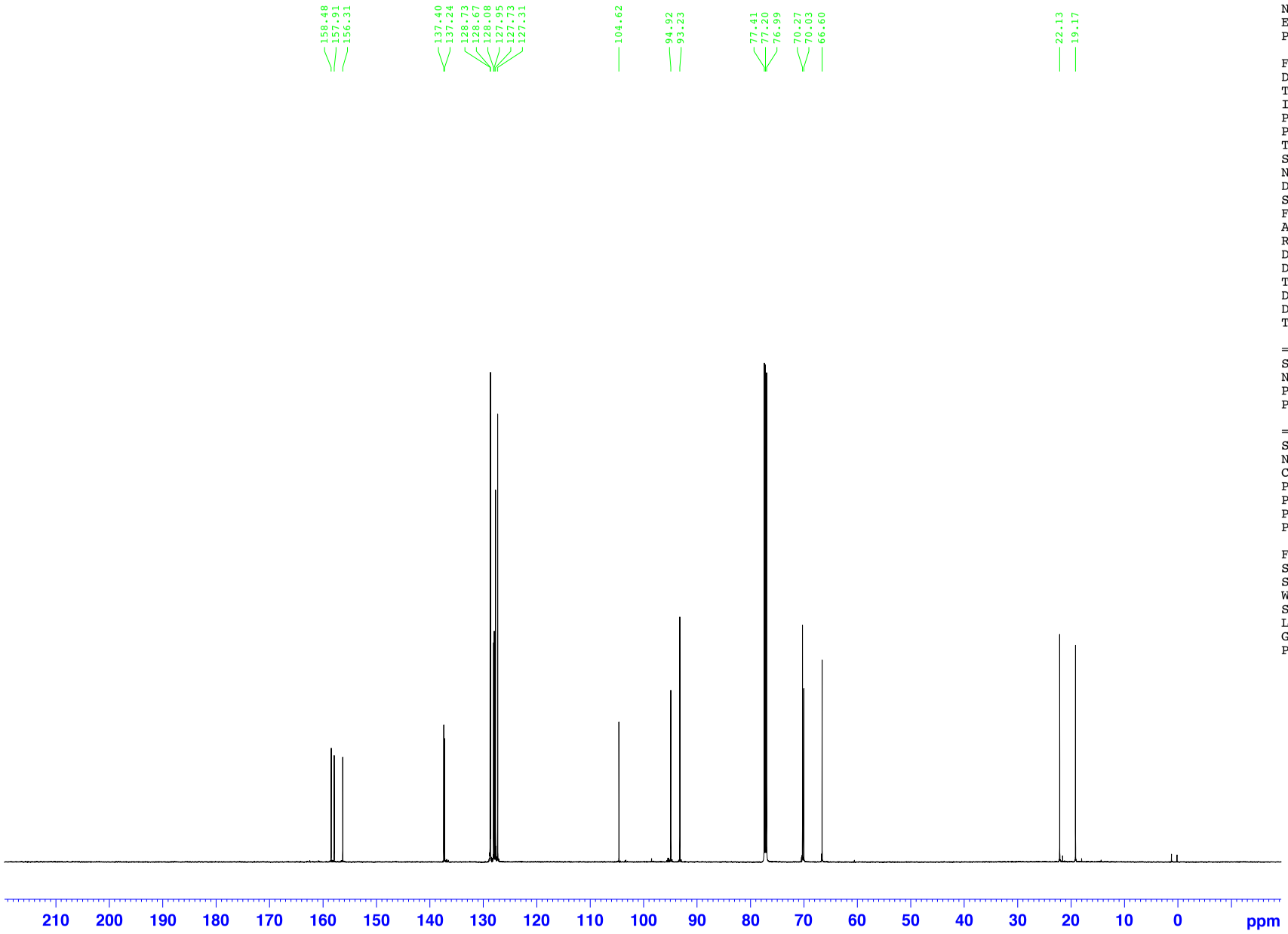
F2 - Acquisition Parameters
Date_ 20190228
Time 18.40
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 15.79
DW 41.600 usec
DE 10.00 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1337060 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.00000000 W

F2 - Processing parameters
SI 65536
SF 600.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^{13}C NMR of 27 (150MHz, $CDCl_3$)



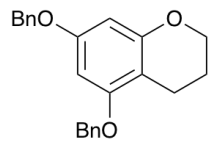

```
Current Data Parameters
NAME                  VB-300
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_               20190303
Time                    2.48
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      3300
DS                         4
SWH               36057.691 Hz
FIDRES             0.550197 Hz
AQ                 0.9087659 sec
RG                    175.56
DW                    13.867 usec
DE                    18.00 usec
TE                    300.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

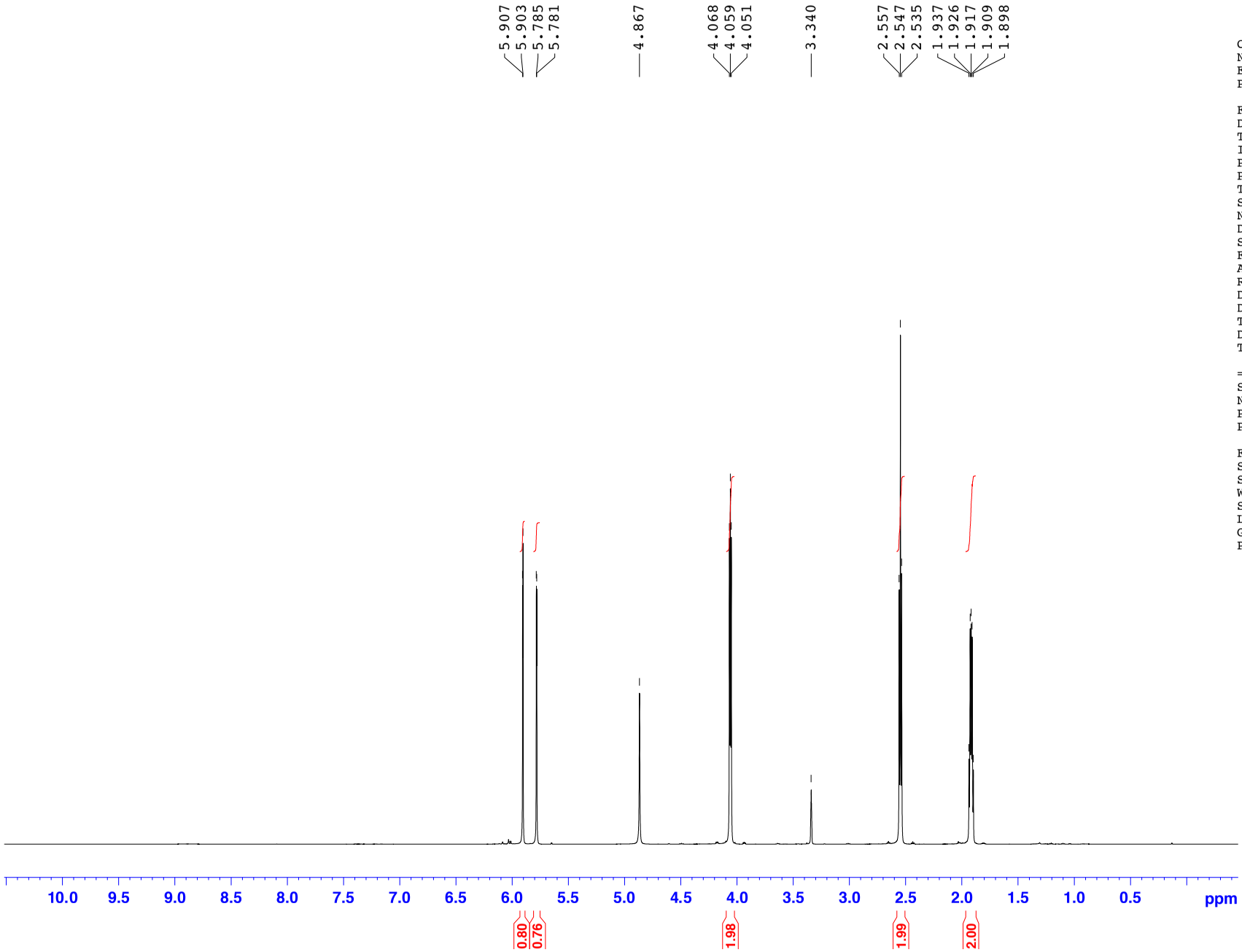
======== CHANNEL f1 ========
SFO1            150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2            600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF              150.9027882 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



^{1}H NMR of 28 (600MHz, CD_3OD)

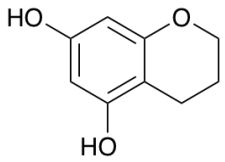



```
Current Data Parameters
NAME                  VB-306
EXPNO                     20
PROCNO                     1

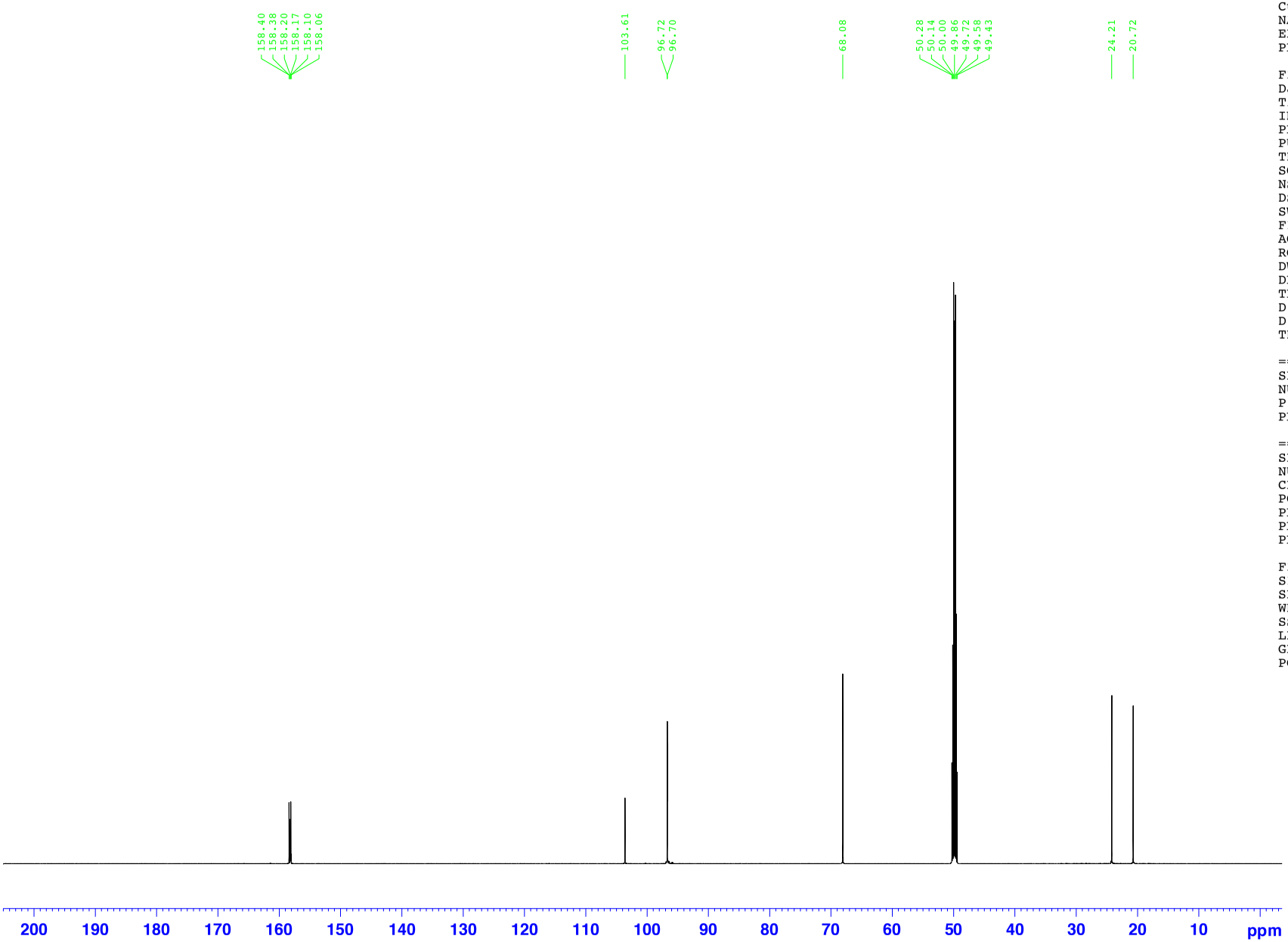
F2 - Acquisition Parameters
Date_              20190320
Time                  17.41
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                2.7262976 sec
RG                    24.73
DW                   41.600 usec
DE                   10.00 usec
TE                   300.1 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           600.1337060 MHz
NUC1                     1H
P1                    12.00 usec
PLW1           23.00000000 W

F2 - Processing parameters
SI                    65536
SF               600.1299938 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



^{13}C NMR of 28 (150MHz, CD_3OD)



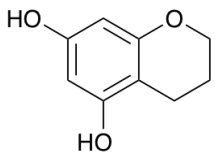

```
Current Data Parameters
NAME                  VB-306
EXPNO                     21
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190321
Time                  17.02
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG               zgpg30
TD                     65536
SOLVENT                MeOD
NS                      2200
DS                         4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                   175.56
DW                   13.867 usec
DE                    18.00 usec
TE                    300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                        1

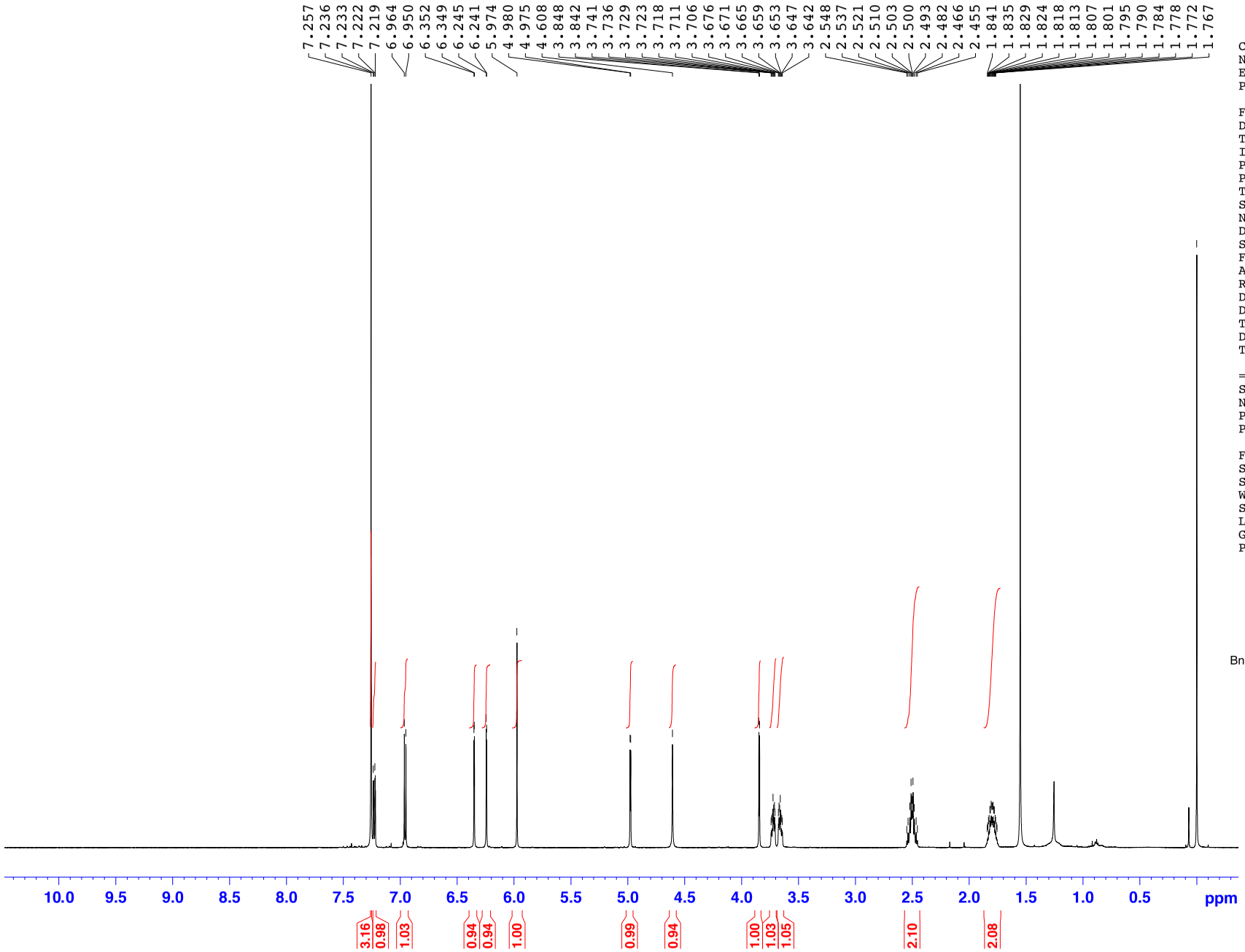
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           70.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           14.00000000 W
PLW12           0.64286000 W
PLW13           0.32335001 W

F2 - Processing parameters
SI                     32768
SF             150.9024737 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



^{1}H NMR of 29 (600MHz, $CDCl_3$)

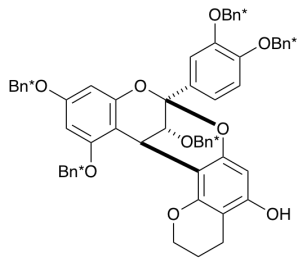



```
Current Data Parameters
NAME                  VB-343-3
EXPNO                       30
PROCNO                       1

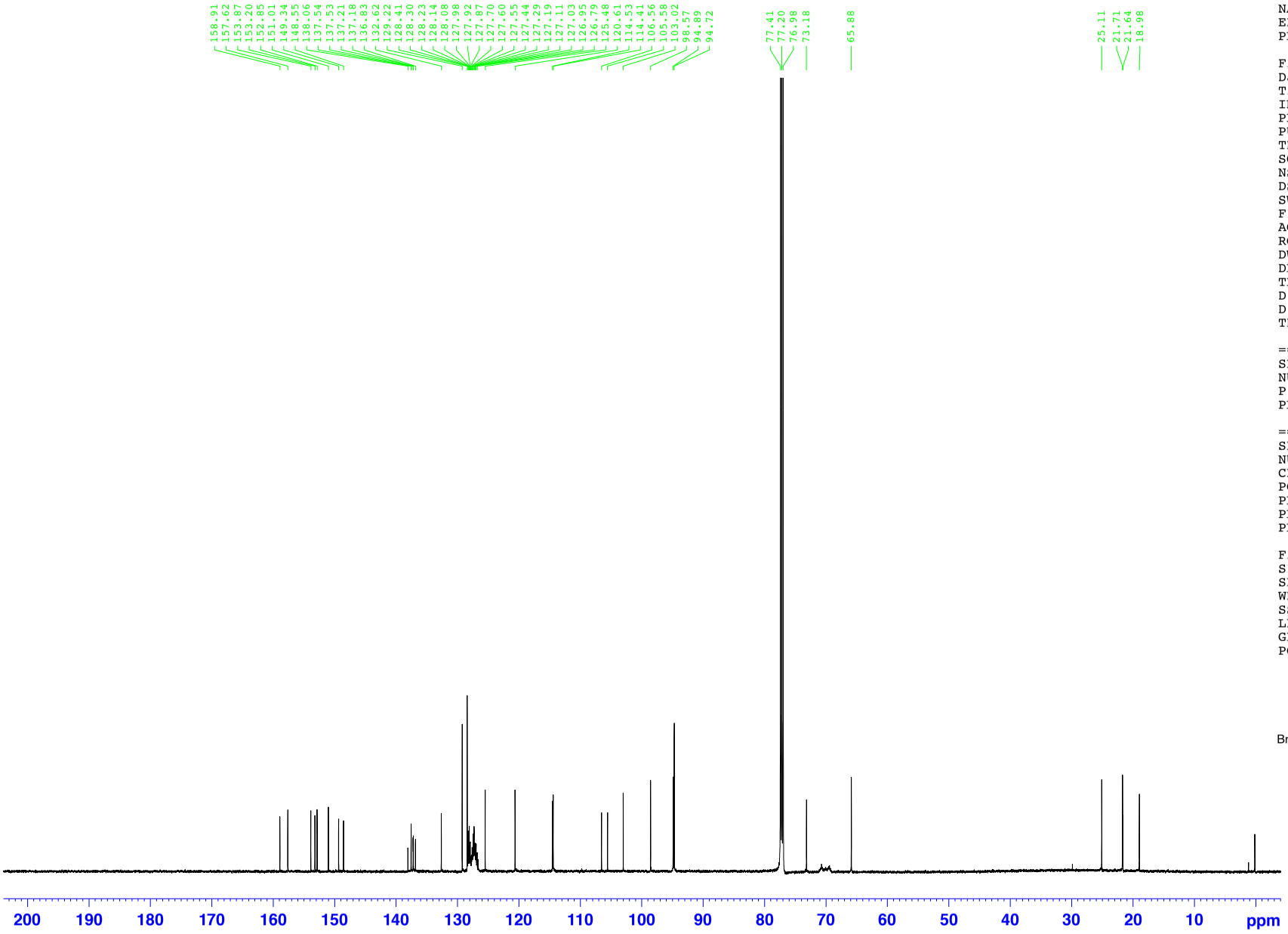
F2 - Acquisition Parameters
Date_                 20190530
Time                     23.41
INSTRUM                  spect
PROBHD    5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       298.2 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
SI                      65536
SF                 600.1300163 MHz
WDW                        EM
SSB           0
LB                        0.30 Hz
GB            0
PC                        1.00
```



^{13}C NMR of 29 (150MHz, $CDCl_3$)



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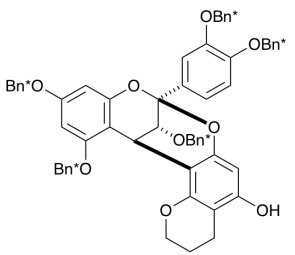
```
Current Data Parameters
NAME              VB-310-2
EXPNO                   13
PROCNO                   1

F2 - Acquisition Parameters
Date_              20190711
Time                  3.00
INSTRUM              spect
PROBHD   5 mm CPPBBO BB
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    3500
DS                       4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

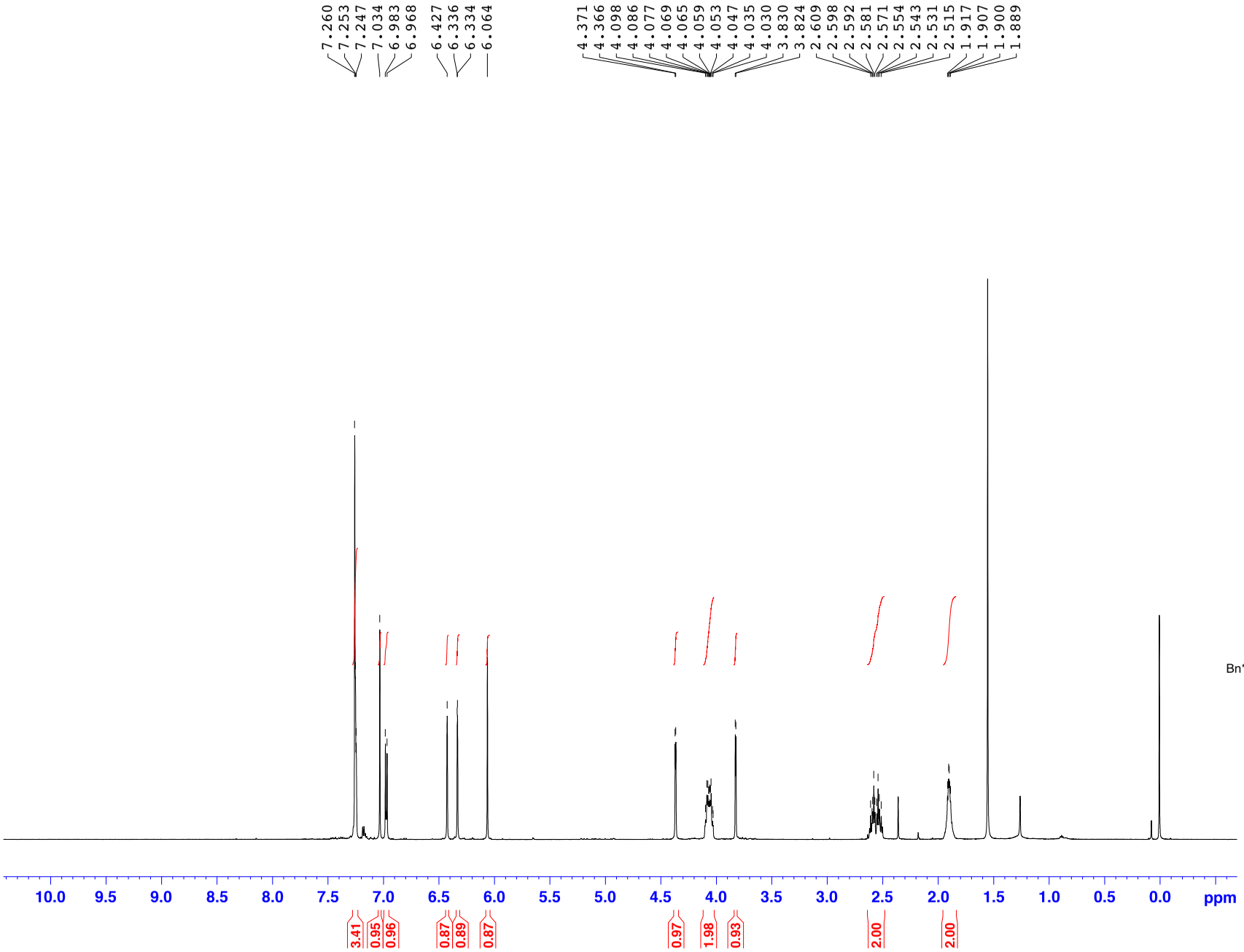
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           80.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                    32768
SF             150.9027849 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



^{1}H NMR of 30 (600MHz, $CDCl_3$)



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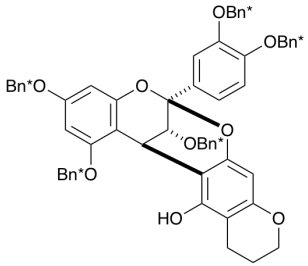
```
Current Data Parameters
NAME                  VB-310-1A
EXPNO                        30
PROCNO                        1

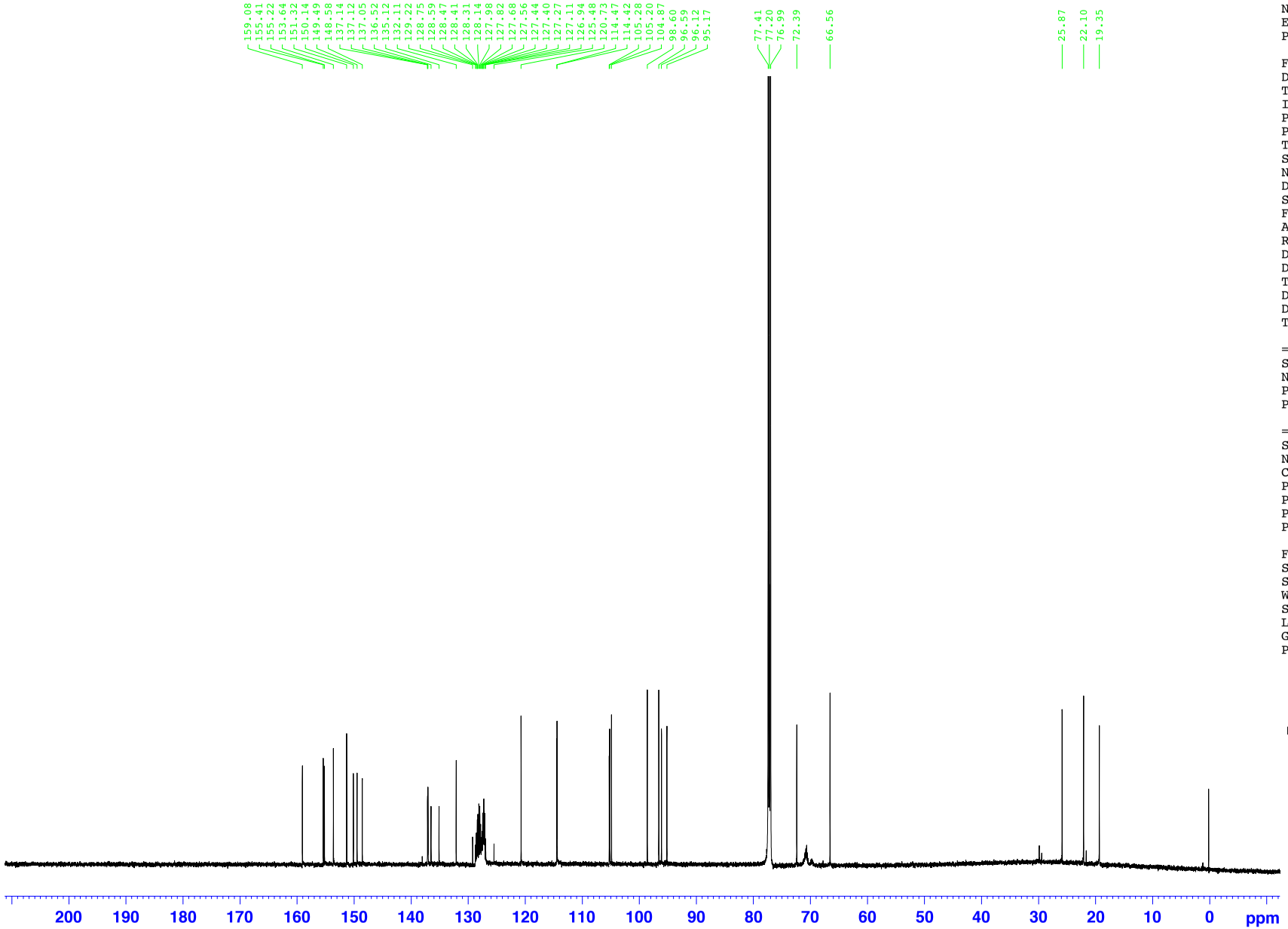
F2 - Acquisition Parameters
Date_                  20190709
Time                      12.20
INSTRUM                   spect
PROBHD    5 mm CPPBBO BB
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       298.2 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                21.00000000 W

F2 - Processing parameters
SI                       65536
SF                  600.1300145 MHz
WDW                         EM
SSB                0
LB                        0.30 Hz
GB                 0
PC                        1.00
```



^{13}C NMR of 30 (150MHz, $CDCl_3$)



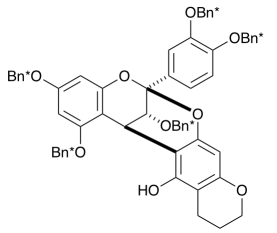

```
Current Data Parameters
NAME              VB-310-1A
EXPNO                    31
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190710
Time                   7.05
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     4000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

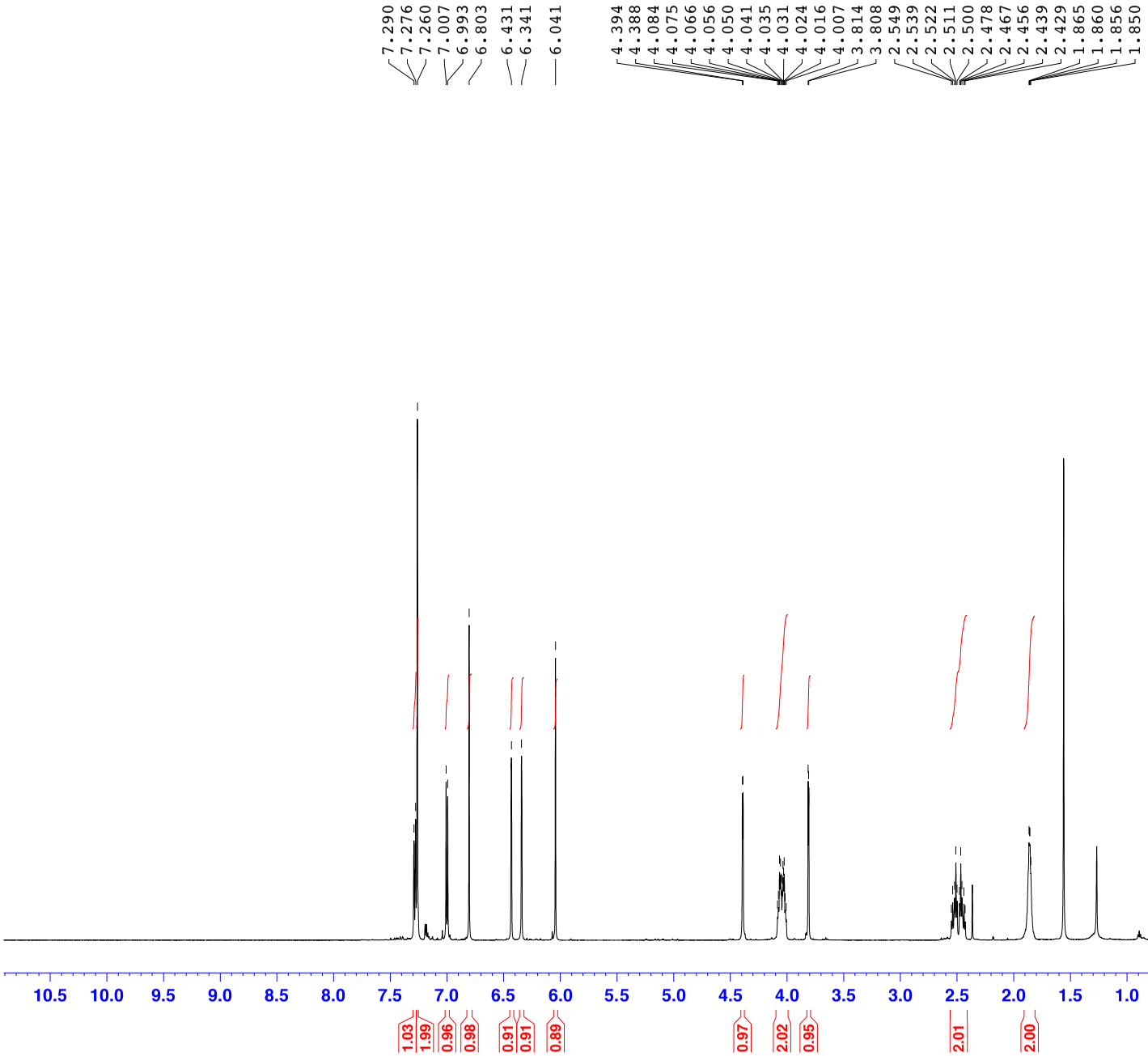
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           80.00000000 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                 70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                    32768
SF             150.9027838 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```



^{1}H NMR of 31 (600MHz, $CDCl_3$)

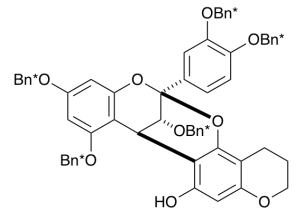



```
Current Data Parameters
NAME            VB-310-1B
EXPNO                  30
PROCNO                  1

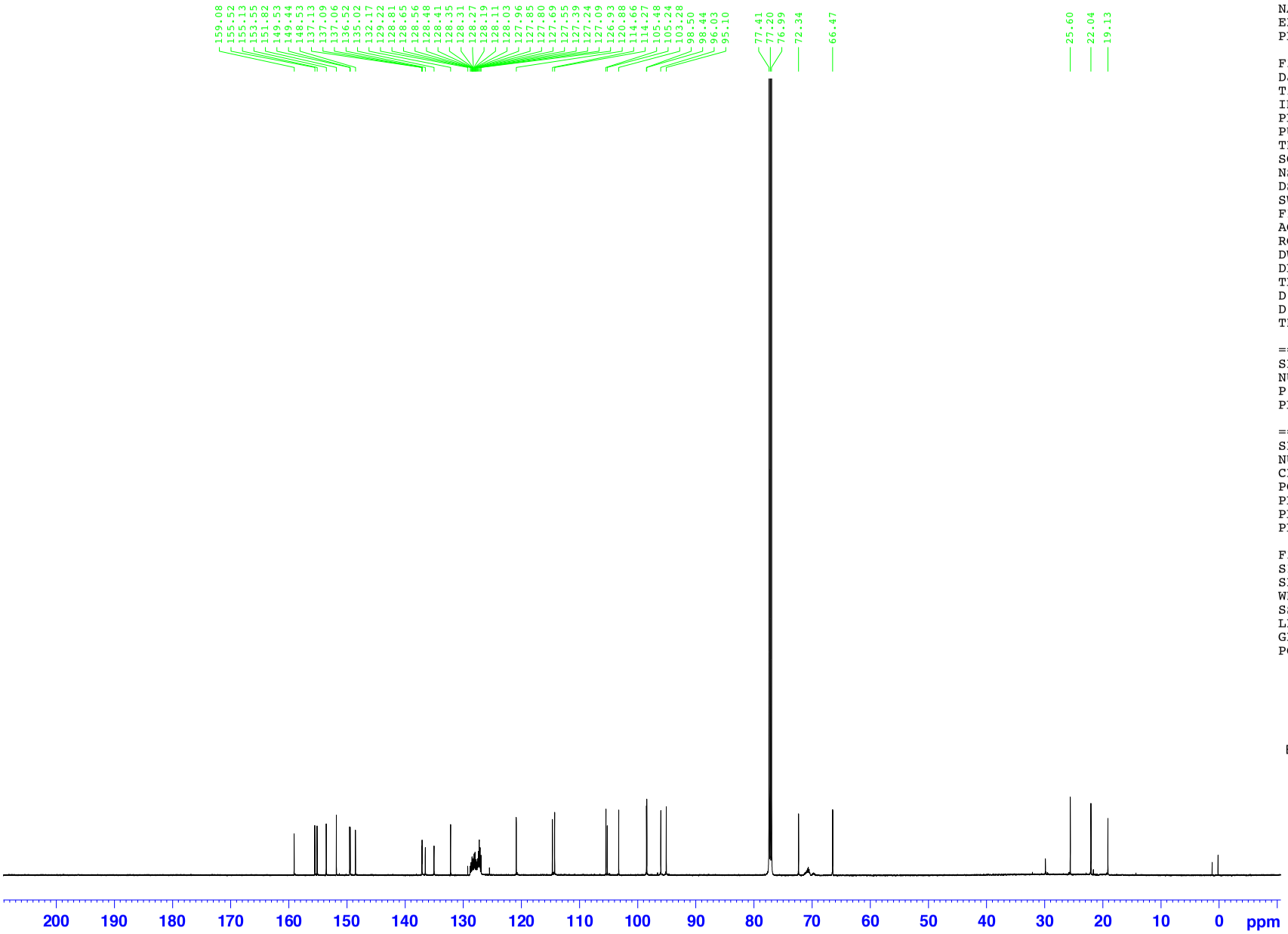
F2 - Acquisition Parameters
Date_            20190709
Time                12.15
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH           12019.230 Hz
FIDRES         0.183399 Hz
AQ             2.7262976 sec
RG                 31.94
DW                41.600 usec
DE                10.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 12.00 usec
PLW1         21.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300148 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



^{13}C NMR of 31 (150MHz, $CDCl_3$)



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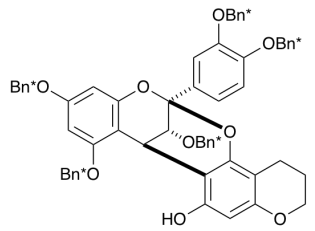
```
Current Data Parameters
NAME              VB-310-1B
EXPNO                    31
PROCNO                    1

F2 - Acquisition Parameters
Date_              20190710
Time                   3.25
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     4000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

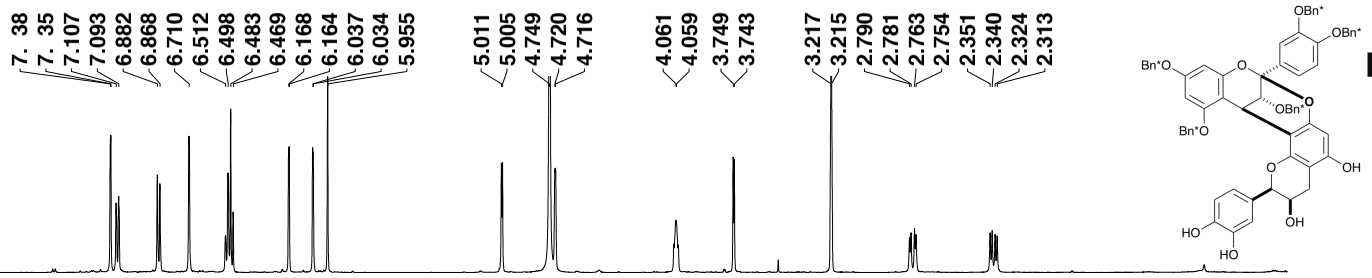
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           80.00000000 W

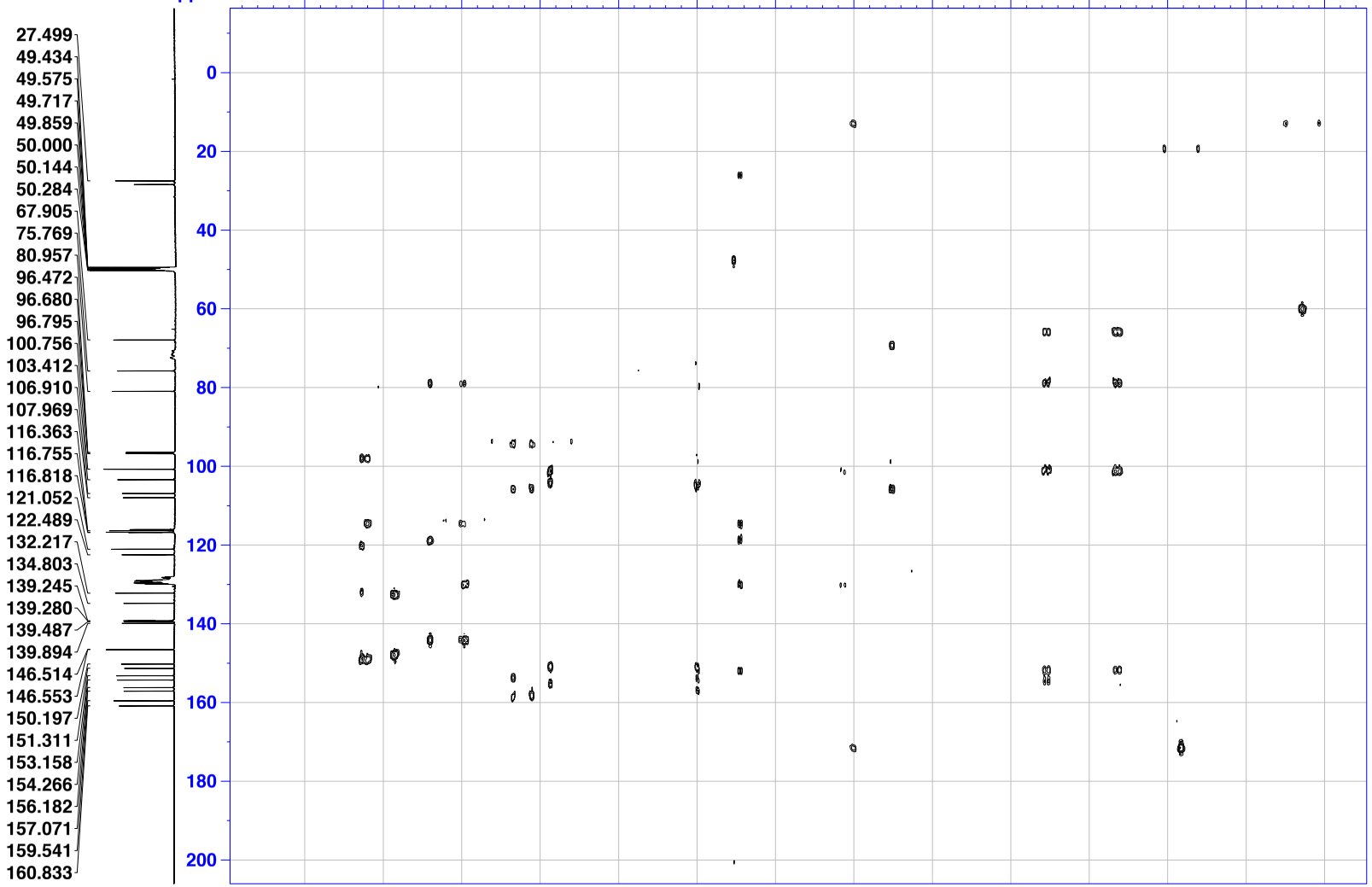
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                     32768
SF             150.9027851 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



HMBC of 14 (CD_3OD)





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```
Current Data Parameters
NAME                  VB-119
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_               20190715
Time                   18.40
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG     hmbcgplpndqf
TD                      2048
SOLVENT                 MeOD
NS                        16
DS                        16
SWH                4347.826 Hz
FIDRES             2.122962 Hz
AQ                 0.2355200 sec
RG                    175.56
DW                   115.000 usec
DE                    10.00 usec
TE                   298.1 K
CNST2              145.0000000
CNST13              10.0000000
D0                  0.00000300 sec
D1                  1.39555204 sec
D2                  0.00344828 sec
D6                  0.05000000 sec
D16                 0.00020000 sec
IN0                 0.00001490 sec

======== CHANNEL f1 ========
SFO1               600.1325918 MHz
NUC1                       1H
P1                      12.00 usec
P2                      24.00 usec
PLW1               21.00000000 W

======== CHANNEL f2 ========
SFO2               150.9178741 MHz
NUC2                       13C
P3                      10.00 usec
PLW2               80.00000000 W

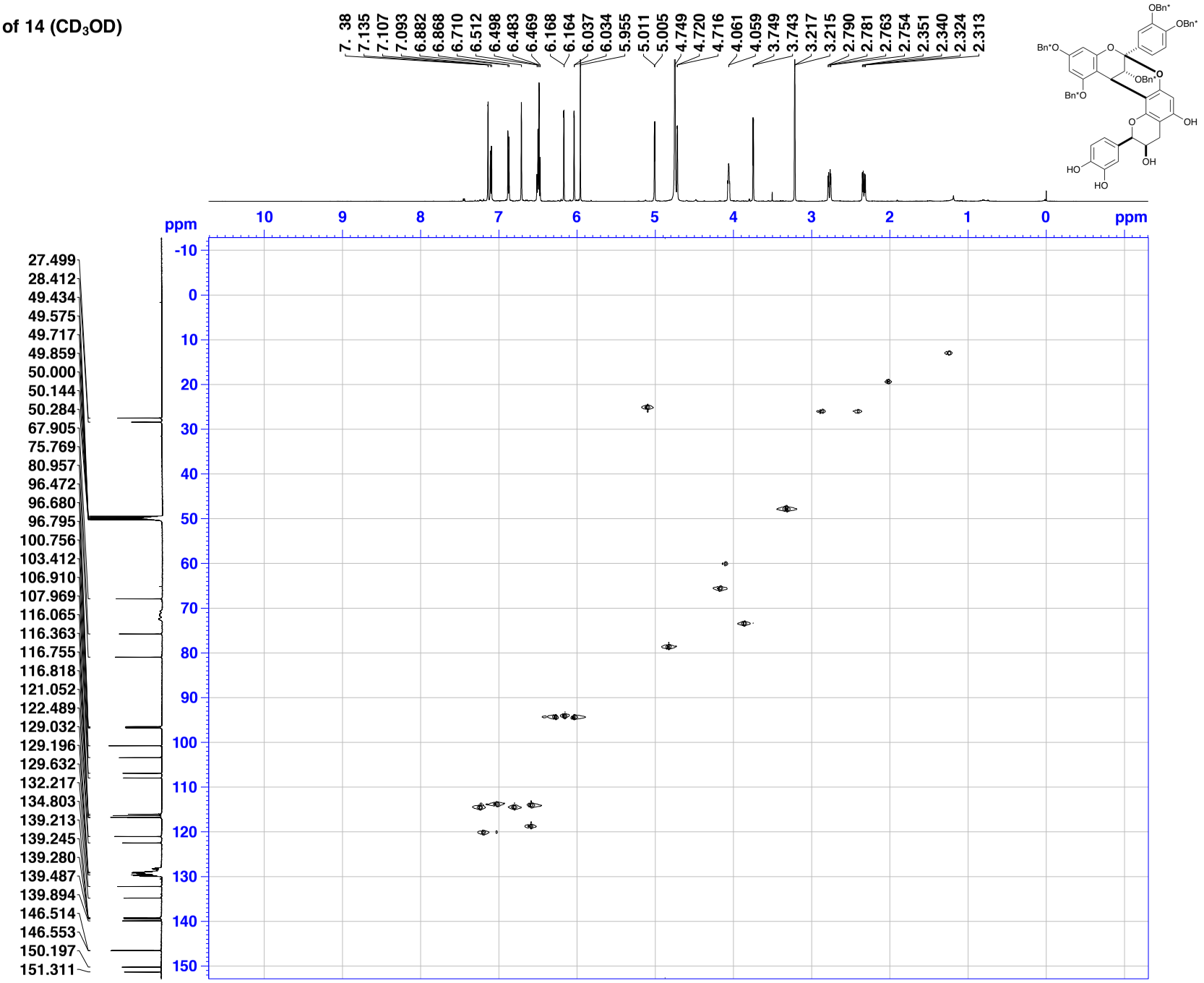
====== GRADIENT CHANNEL =====
GPNAM[1]          SMSQ10.100
GPNAM[2]          SMSQ10.100
GPNAM[3]          SMSQ10.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         32
SFO1               150.9179 MHz
FIDRES          1048.657715 Hz
SW                  222.353 ppm
FnMODE                   QF

F2 - Processing parameters
SI                       2048
SF                 600.1300654 MHz
WDW                      SINE
SSB          0
LB           0 Hz
GB           0
PC                       1.40

F1 - Processing parameters
SI                       1024
MC2                      QF
SF                 150.9028090 MHz
WDW                      SINE
SSB          0
LB           0 Hz
GB           0
```

HSQC of 14 (CD_3OD)



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```
Current Data Parameters
NAME                  VB-119
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190715
Time                  18.56
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG   hsqcedetgpsisp2.3
TD                      2048
SOLVENT                 MeOD
NS                        16
DS                        32
SWH                 7211.539 Hz
FIDRES              3.521259 Hz
AQ                  0.1419947 sec
RG                     175.56
DW                    69.333 usec
DE                    10.00 usec
TE                    298.2 K
CNST2              145.0000000
CNST17              -0.5000000
D0                  0.00000300 sec
D1                  2.00000000 sec
D4                  0.00172414 sec
D11                 0.03000000 sec
D16                 0.00020000 sec
D21                 0.00360000 sec
D24                 0.00089000 sec
IN0                 0.00002000 sec

======== CHANNEL f1 ========
SFO1               600.1328224 MHz
NUC1                       1H
P1                      12.00 usec
P2                      24.00 usec
P28            0 usec
PLW1               21.00000000 W

======== CHANNEL f2 ========
SFO2               150.9133710 MHz
NUC2                       13C
CPDPRG[2                 garp
P3                      10.00 usec
P14                    500.00 usec
P24                   2000.00 usec
P31                   1730.00 usec
PCPD2                   60.00 usec
PLW0           0 W
PLW2                80.00000000 W
PLW12                2.22219992 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3                    0.500
SPOFFS3   0 Hz
SPW3                12.22299957 W
SPNAM[7]    Crp60comp.4
SPOAL7                    0.500
SPOFFS7   0 Hz
SPW7                12.22299957 W
SPNAM[18  Crp60_xfilt.2
SPOAL18                   0.500
SPOFFS18  0 Hz
SPW18                3.53270006 W

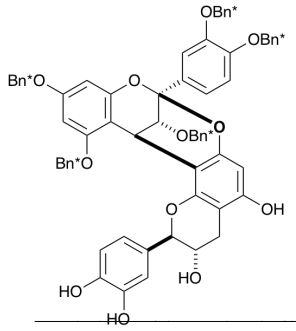
====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPNAM[4]      SMSQ10.100
GPZ1                 80.00 %
GPZ2                 20.10 %
GPZ3                 11.00 %
GPZ4                 -5.00 %
P16                1000.00 usec
P19                 600.00 usec

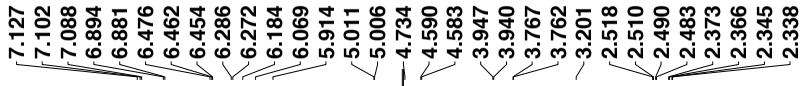
F1 - Acquisition parameters
TD                        64
SFO1               150.9134 MHz
FIDRES          390.625000 Hz
SW                 165.658 ppm
FnMODE     Echo-Antiecho

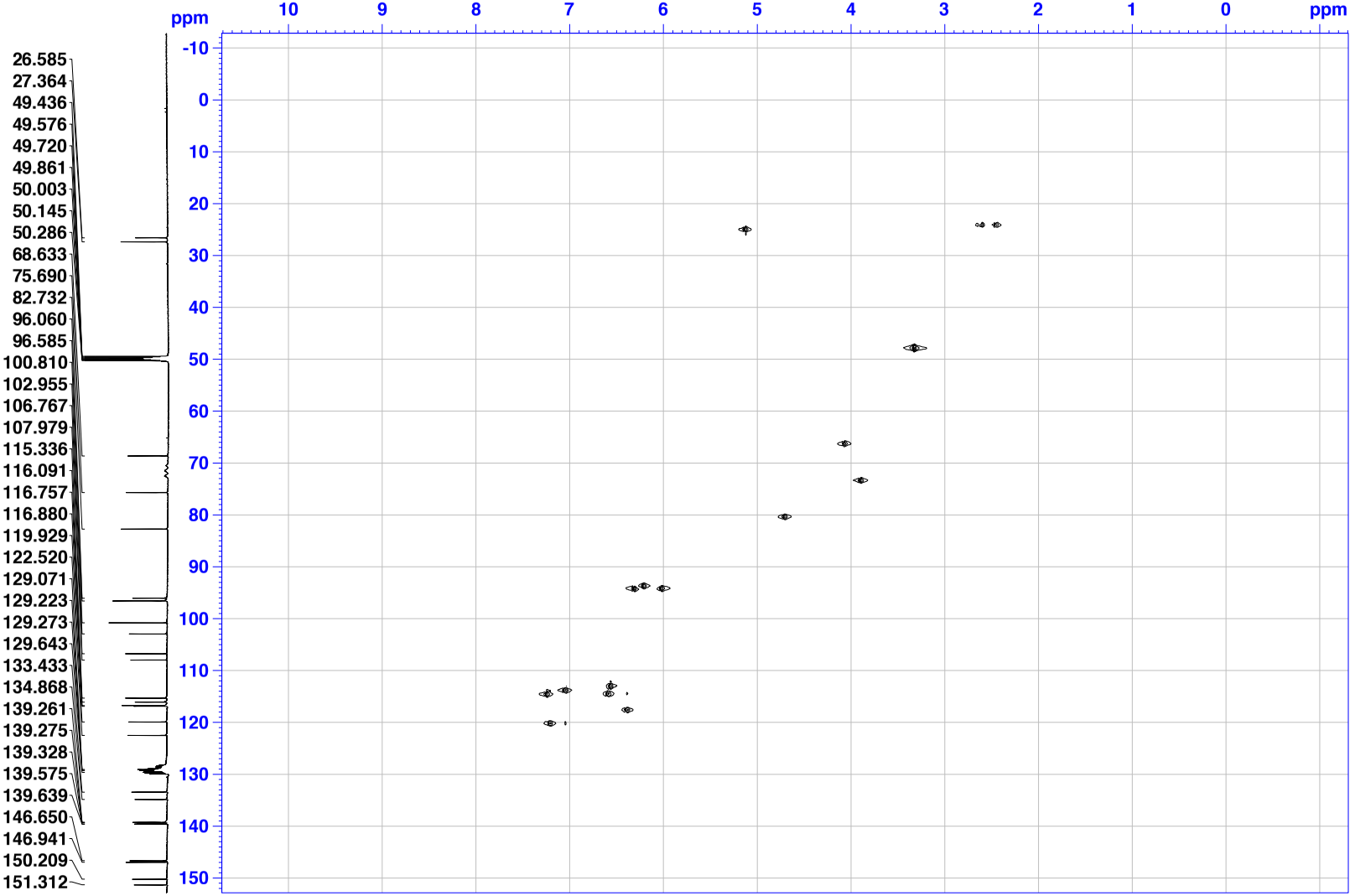
F2 - Processing parameters
SI                      1024
SF                600.1300000 MHz
WDW                     QSINE
SSB                        2
LB             0 Hz
GB             0
PC                      1.40

F1 - Processing parameters
SI                      1024
MC2          echo-antiecho
SF                150.9028090 MHz
WDW                     QSINE
SSB                        2
LB             0 Hz
GB             0
```

HSQC of 20 (CD_3OD)







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```
Current Data Parameters
NAME                  VB-118
EXPNO                     33
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190715
Time                  17.49
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG   hsqcedetgpsisp2.3
TD                      2048
SOLVENT                 MeOD
NS                        16
DS                        32
SWH                 7211.539 Hz
FIDRES              3.521259 Hz
AQ                  0.1419947 sec
RG                     175.56
DW                    69.333 usec
DE                    10.00 usec
TE                    298.2 K
CNST2              145.0000000
CNST17              -0.5000000
D0                  0.00000300 sec
D1                  2.00000000 sec
D4                  0.00172414 sec
D11                 0.0300000 sec
D16                 0.00020000 sec
D21                 0.00360000 sec
D24                 0.00089000 sec
IN0                 0.00002000 sec

======== CHANNEL f1 ========
SFO1               600.1328224 MHz
NUC1                       1H
P1                      12.00 usec
P2                      24.00 usec
P28          0 usec
PLW1               21.00000000 W

======== CHANNEL f2 ========
SFO2               150.9133710 MHz
NUC2                       13C
CPDPRG[2                 garp
P3                      10.00 usec
P14                    500.00 usec
P24                   2000.00 usec
P31                   1730.00 usec
PCPD2                   60.00 usec
PLW0         0 W
PLW2                80.00000000 W
PLW12                2.22219992 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3                   0.500
SPOFFS3   0 Hz
SPW3                12.22299957 W
SPNAM[7]    Crp60comp.4
SPOAL7                   0.500
SPOFFS7   0 Hz
SPW7                12.22299957 W
SPNAM[18  Crp60_xfilt.2
SPOAL18                  0.500
SPOFFS18  0 Hz
SPW18                3.53270006 W

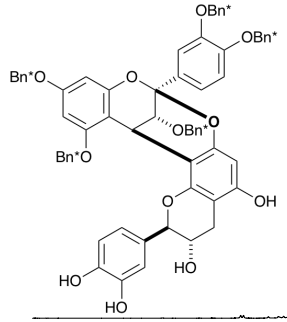
====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPNAM[4]      SMSQ10.100
GPZ1                    80.00 %
GPZ2                    20.10 %
GPZ3                    11.00 %
GPZ4                    -5.00 %
P16                   1000.00 usec
P19                    600.00 usec

F1 - Acquisition parameters
TD                         64
SFO1                150.9134 MHz
FIDRES             390.625000 Hz
SW                    165.658 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                       1024
SF                600.1300000 MHz
WDW                      QSINE
SSB                         2
LB           0 Hz
GB           0
PC                       1.40

F1 - Processing parameters
SI                       1024
MC2           echo-antiecho
SF                150.9028090 MHz
WDW                      QSINE
SSB                         2
LB           0 Hz
GB           0
```

HMBC of 20 (CD_3OD)




```
Current Data Parameters
NAME                  VB-118
EXPNO                     32
PROCNO                     1

F2 - Acquisition Parameters
Date_               20190715
Time                   17.33
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG    hmbcgplpndqf
TD                      2048
SOLVENT                 MeOD
NS                        16
DS                        16
SWH               4000.000 Hz
FIDRES               1.953125 Hz
AQ                0.2560000 sec
RG                   175.56
DW                  125.000 usec
DE                   10.00 usec
TE                   298.2 K
CNST2             145.0000000
CNST13             10.0000000
D0                 0.00000300 sec
D1                 1.37507200 sec
D2                 0.00344828 sec
D6                 0.05000000 sec
D16                0.00020000 sec
IN0                0.00001490 sec

======== CHANNEL f1 ========
SFO1              600.1331444 MHz
NUC1                      1H
P1                     12.00 usec
P2                     24.00 usec
PLW1              21.00000000 W

======== CHANNEL f2 ========
SFO2              150.9178741 MHz
NUC2                      13C
P3                     10.00 usec
PLW2              80.00000000 W

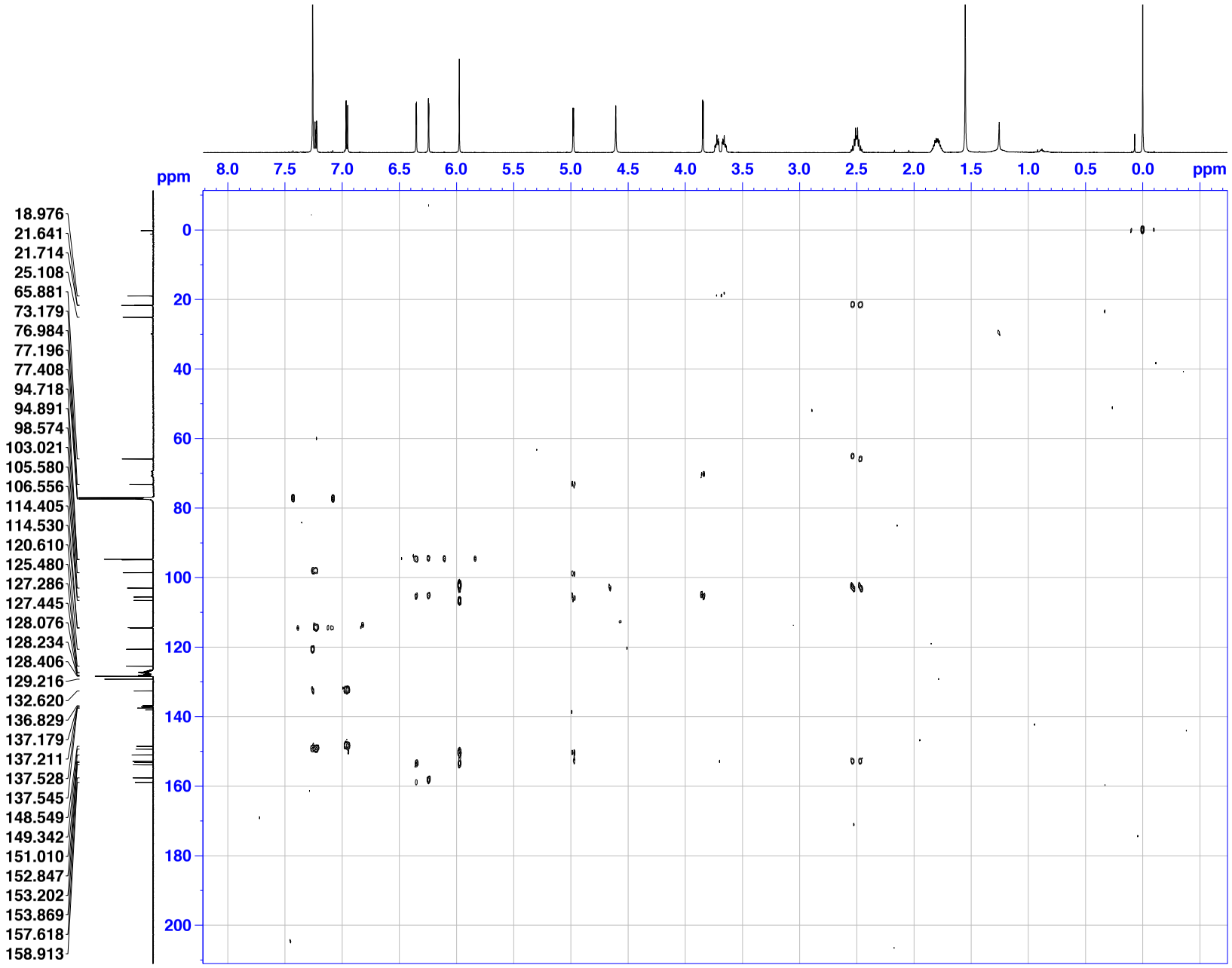
====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[2]       SMSQ10.100
GPNAM[3]       SMSQ10.100
GPZ1                50.00 %
GPZ2                30.00 %
GPZ3                40.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                        32
SFO1               150.9179 MHz
FIDRES            1048.657715 Hz
SW                 222.353 ppm
FnMODE                    QF

F2 - Processing parameters
SI                      2048
SF                600.1300652 MHz
WDW                     SINE
SSB       0
LB        0 Hz
GB        0
PC                     1.40

F1 - Processing parameters
SI                      1024
MC2                       QF
SF                150.9028090 MHz
WDW                     SINE
SSB       0
LB        0 Hz
GB        0
```

HMBC of 29 ($CDCl_3$)



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```
Current Data Parameters
NAME                  VB-343
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190606
Time                  17.02
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG     hmbcgplpndqf
TD                     2048
SOLVENT             CDCl3
NS                       16
DS                       16
SWH               5376.344 Hz
FIDRES            2.625168 Hz
AQ                0.1904640 sec
RG                   175.56
DW                   93.000 usec
DE                   10.00 usec
TE                   298.2 K
CNST2            145.0000000
CNST13            10.0000000
D0                0.00000300 sec
D1                1.44060802 sec
D2                0.00344828 sec
D6                0.05000000 sec
D16               0.00020000 sec
IN0               0.00001490 sec

======== CHANNEL f1 ========
SFO1            600.1322613 MHz
NUC1                    1H
P1                   12.00 usec
P2                   24.00 usec
PLW1            21.00000000 W

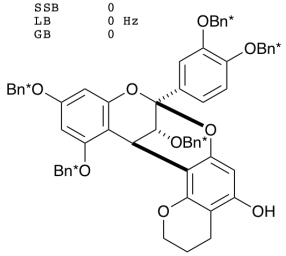
======== CHANNEL f2 ========
SFO2            150.9178741 MHz
NUC2                   13C
P3                   10.00 usec
PLW2            80.00000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[2]       SMSQ10.100
GPNAM[3]       SMSQ10.100
GPZ1                 50.00 %
GPZ2                 30.00 %
GPZ3                 40.10 %
P16                1000.00 usec

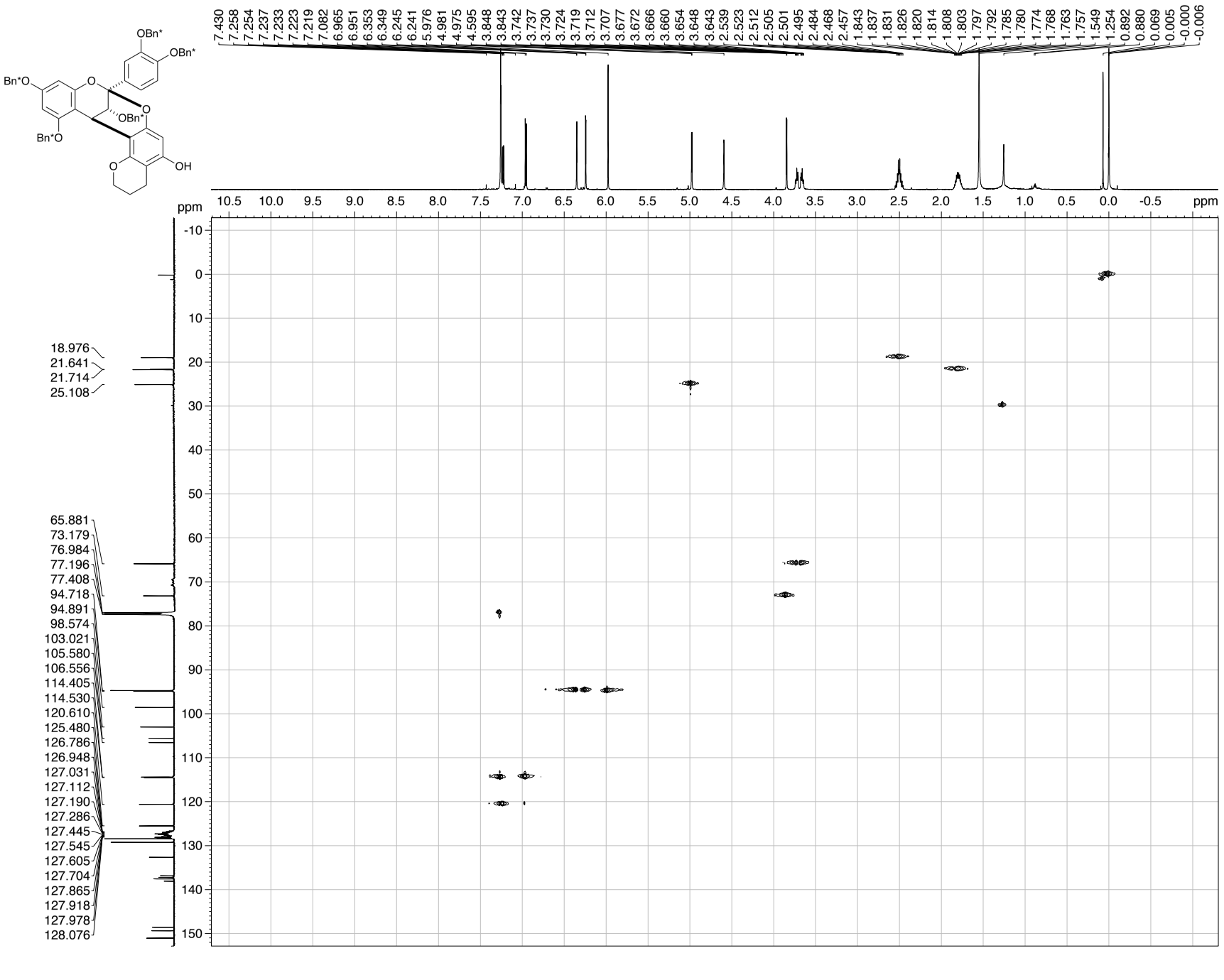
F1 - Acquisition parameters
TD                       32
SFO1              150.9179 MHz
FIDRES         1048.657715 Hz
SW                222.353 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     2048
SF              600.1300176 MHz
WDW                    SINE
SSB       0
LB        0 Hz
GB        0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              150.9028090 MHz
WDW                    SINE
SSB       0
LB        0 Hz
GB        0
```



HSQC of 29 (CDCl3)



BRUKER

```
Current Data Parameters
NAME                  VB-343
EXPNO                     21
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190718
Time                   5.59
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG   hsqcedetgpsisp2.3
TD                      2048
SOLVENT                CDCl3
NS                        16
DS                        32
SWH                7211.539 Hz
FIDRES             3.521259 Hz
AQ                 0.1419947 sec
RG                    175.56
DW                   69.333 usec
DE                   10.00 usec
TE                   298.1 K
CNST2             145.0000000
CNST17             -0.5000000
D0                 0.00000300 sec
D1                 2.00000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D16                0.00020000 sec
D21                0.00360000 sec
D24                0.00089000 sec
IN0                0.00002000 sec

======== CHANNEL f1 ========
SFO1              600.1328224 MHz
NUC1                      1H
P1                     12.00 usec
P2                     24.00 usec
P28           0 usec
PLW1              21.00000000 W

======== CHANNEL f2 ========
SFO2              150.9133710 MHz
NUC2                      13C
CPDPRG[2                  garp
P3                     10.00 usec
P14                   500.00 usec
P24                  2000.00 usec
P31                  1730.00 usec
PCPD2                  60.00 usec
PLW0          0 W
PLW2               80.00000000 W
PLW12               2.22219992 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3                    0.500
SPOFFS3   0 Hz
SPW3               12.22299957 W
SPNAM[7]     Crp60comp.4
SPOAL7                    0.500
SPOFFS7   0 Hz
SPW7               12.22299957 W
SPNAM[18  Crp60_xfilt.2
SPOAL18                   0.500
SPOFFS18  0 Hz
SPW18               3.53270006 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPNAM[4]      SMSQ10.100
GPZ1                  80.00 %
GPZ2                  20.10 %
GPZ3                  11.00 %
GPZ4                  -5.00 %
P16                 1000.00 usec
P19                  600.00 usec

F1 - Acquisition parameters
TD                        64
SFO1               150.9134 MHz
FIDRES          390.625000 Hz
SW                 165.658 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                      1024
SF              600.1300000 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                      1024
MC2          echo-antiecho
SF              150.9028090 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```

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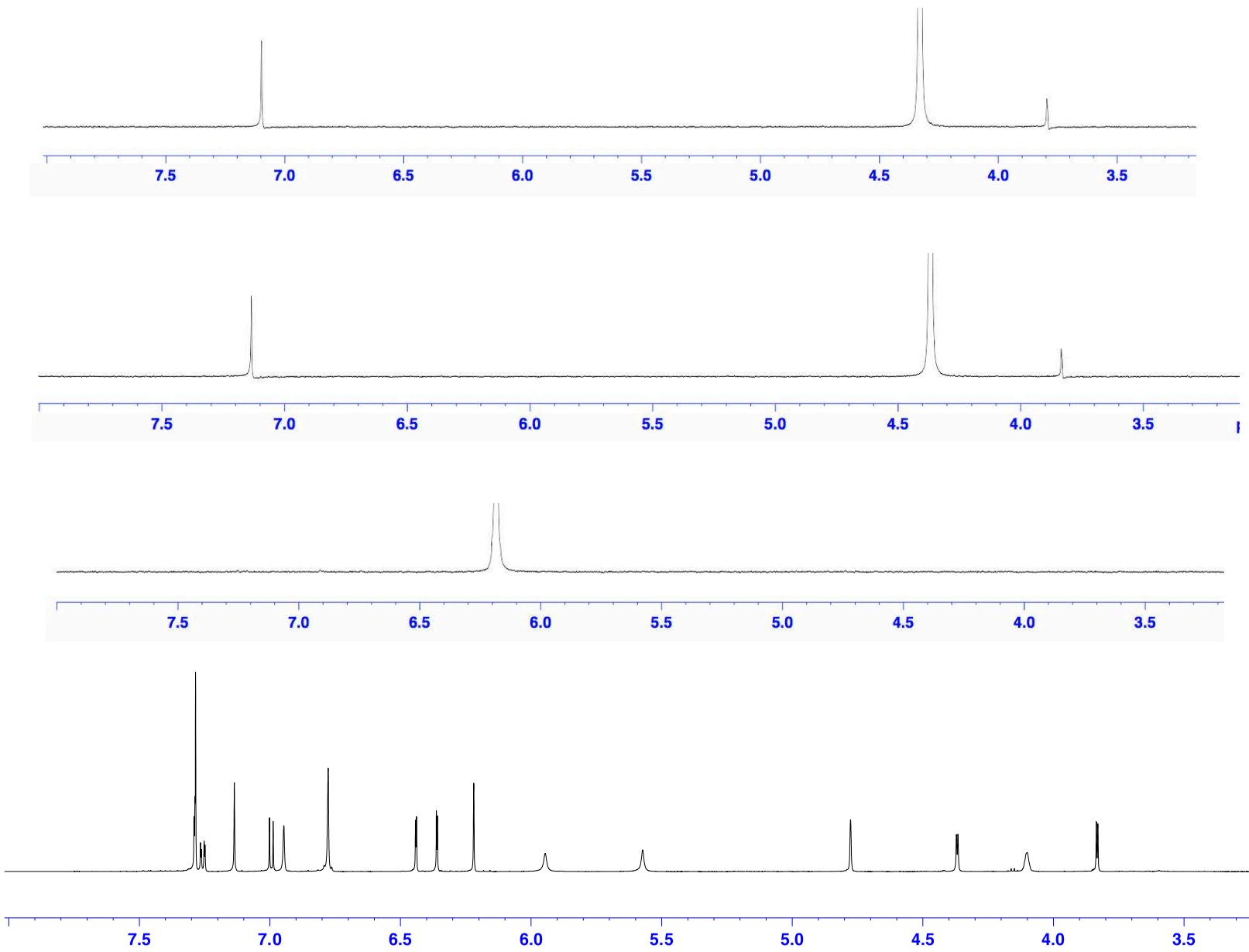
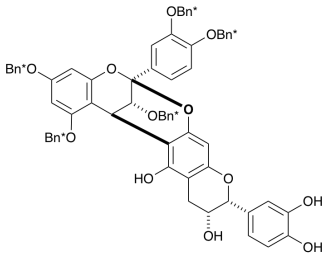



```
Current Data Parameters
NAME            VB-186-2C
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180730
Time                12.45
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH           12019.230 Hz
FIDRES         0.183399 Hz
AQ             2.7262976 sec
RG                 31.94
DW                41.600 usec
DE                10.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                  12.00 usec
PLW1         23.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300000 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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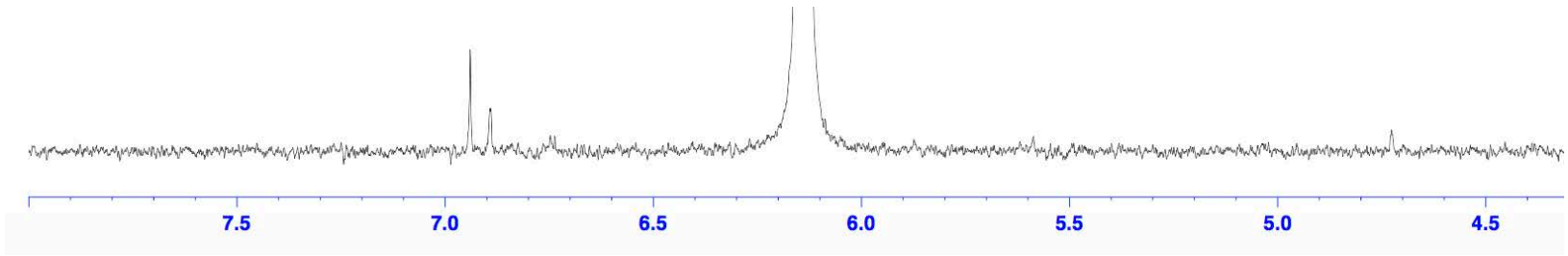
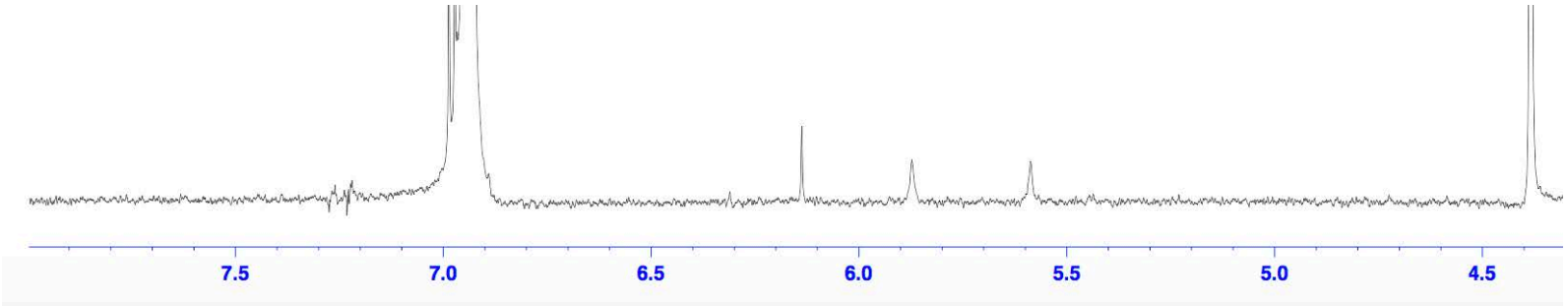
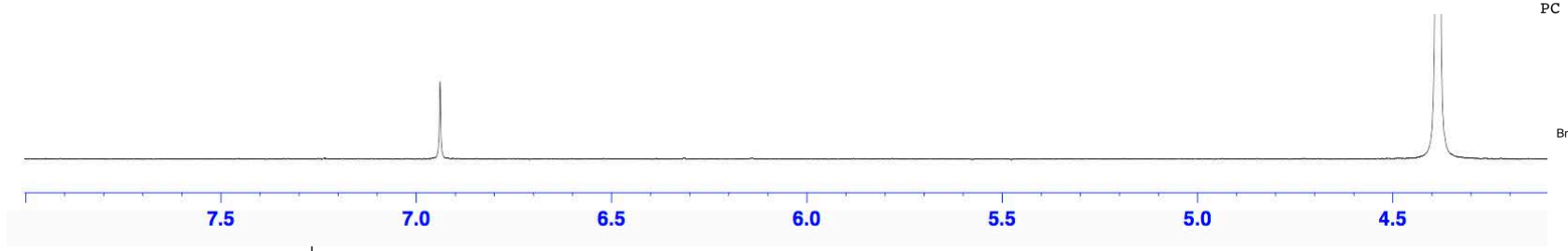
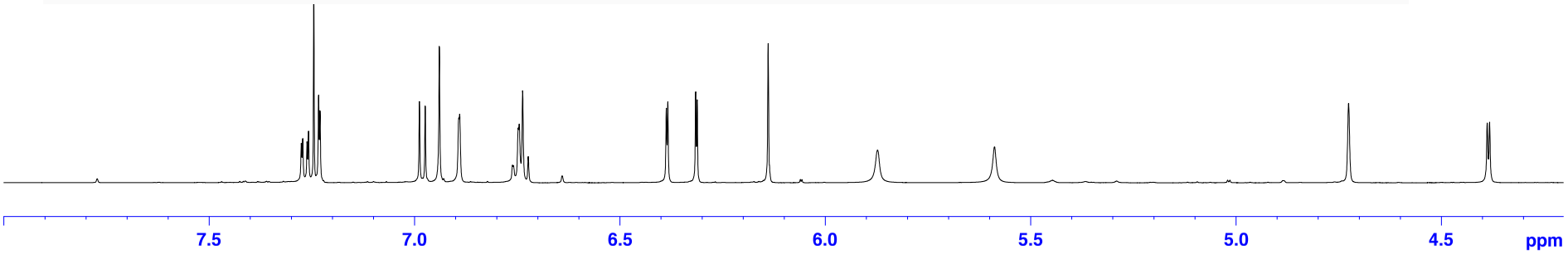






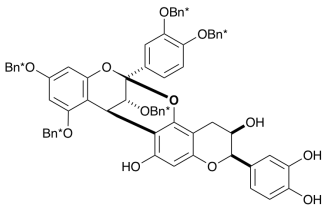



```
Current Data Parameters
NAME            VB-186-1C
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180730
Time                12.33
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ               2.7262976 sec
RG                  31.94
DW                 41.600 usec
DE                 10.00 usec
TE                 300.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1337060 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          23.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300233 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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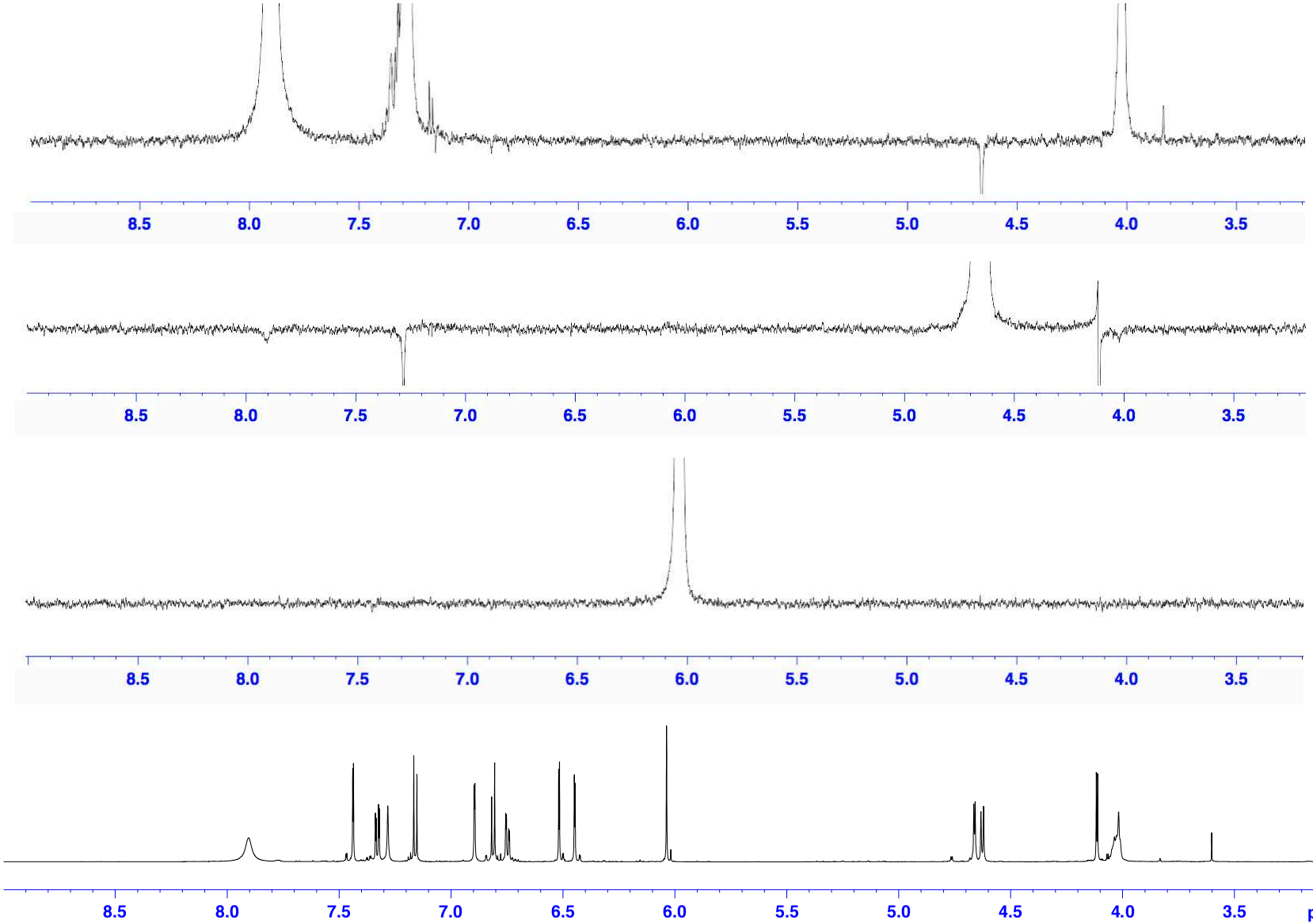
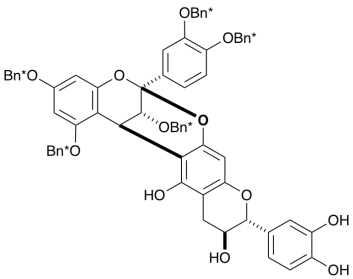



```
Current Data Parameters
NAME            VB-313-1B
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190515
Time                22.38
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                     16
DS                      2
SWH           12019.230 Hz
FIDRES         0.183399 Hz
AQ             2.7262976 sec
RG                 31.94
DW                41.600 usec
DE                10.00 usec
TE                298.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                  12.00 usec
PLW1         21.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300000 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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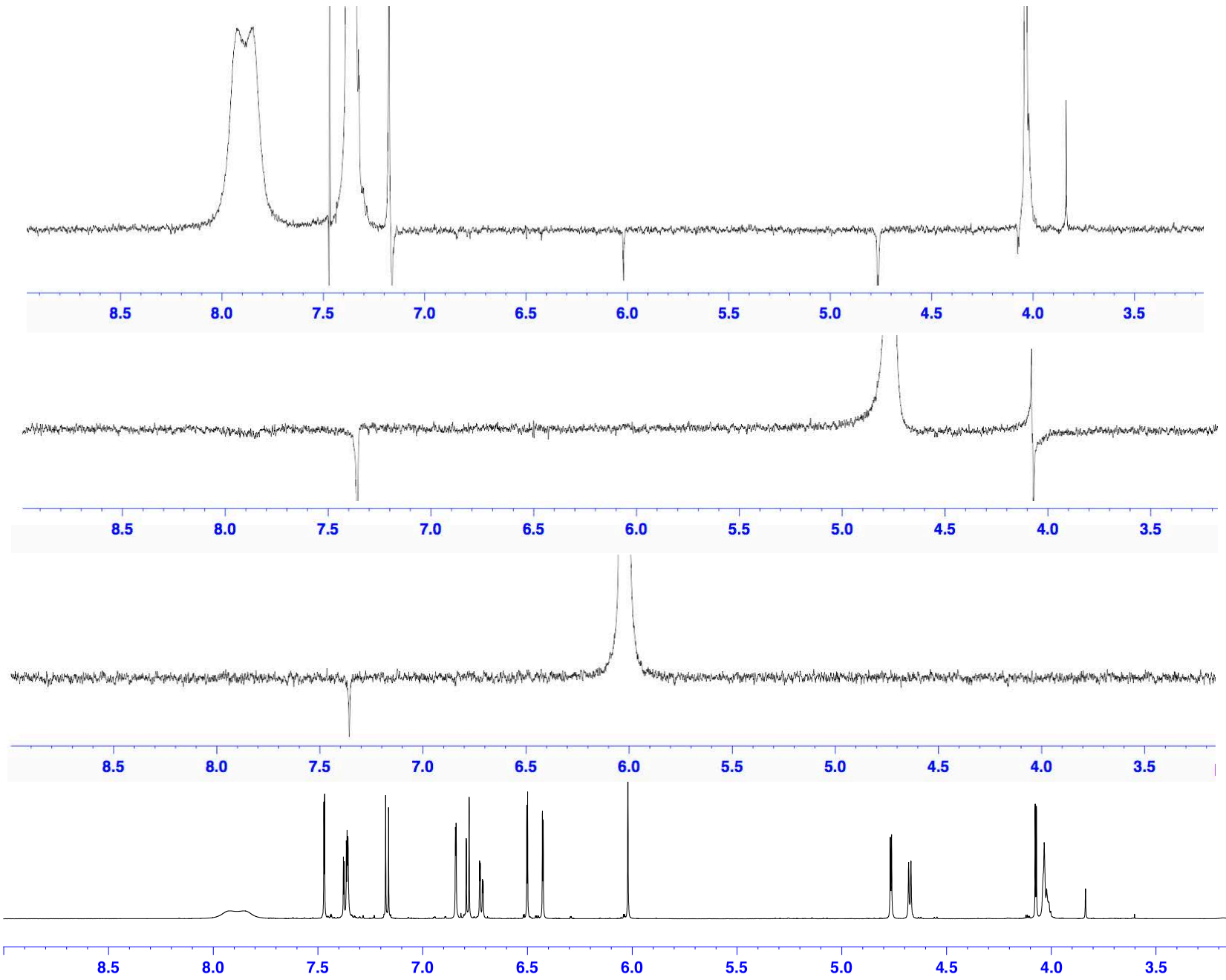
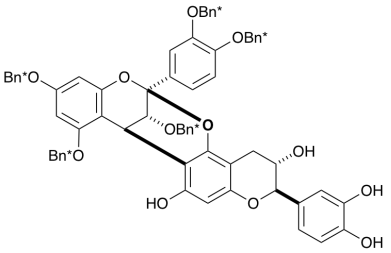



```
Current Data Parameters
NAME            VB-313-1A
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190517
Time                19.22
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                     16
DS                      2
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ               2.7262976 sec
RG                  18.96
DW                 41.600 usec
DE                 10.00 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1337060 MHz
NUC1                    1H
P1                  12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300000 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



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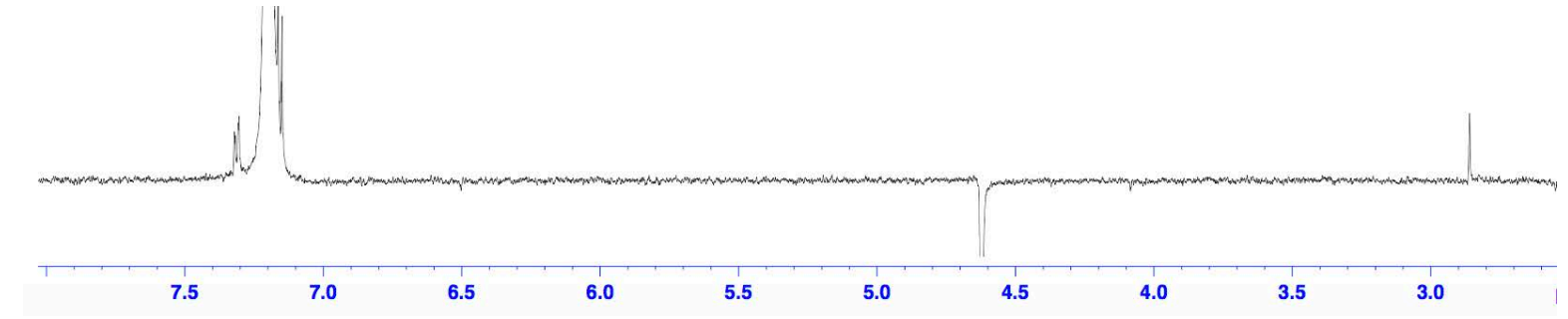
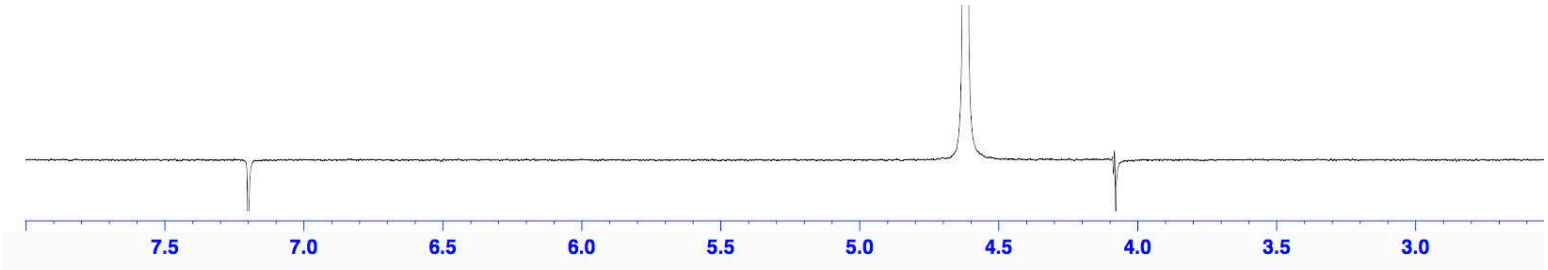
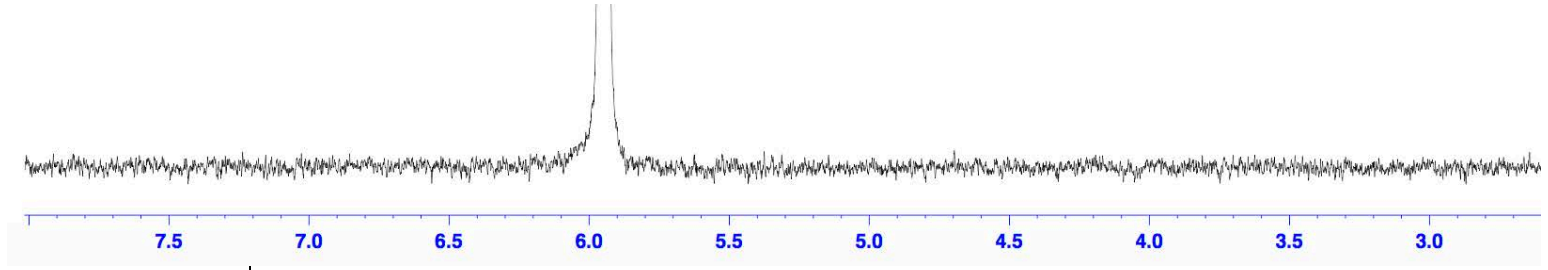
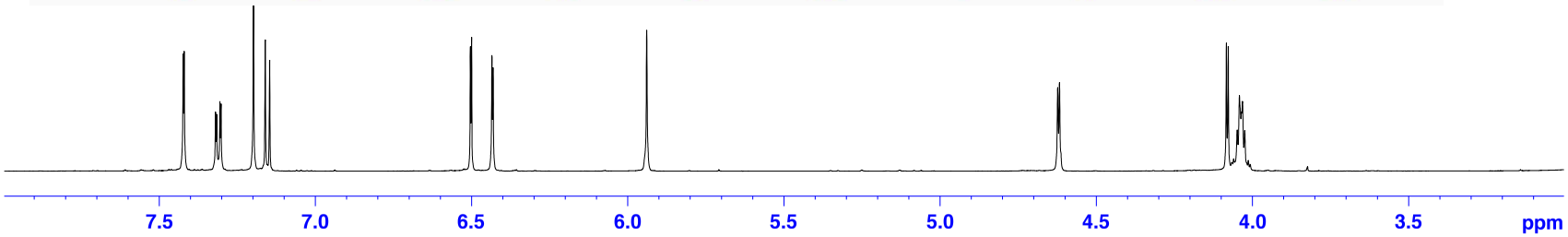






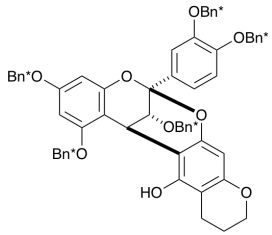



```
Current Data Parameters
NAME                  VB-310-1A
EXPNO                        20
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20190514
Time                      19.53
INSTRUM                   spect
PROBHD    5 mm CPPBBO BB
PULPROG                   zg30
TD                       65536
SOLVENT                Acetone
NS                            16
DS                             2
SWH                 12019.230 Hz
FIDRES                0.183399 Hz
AQ                    2.7262976 sec
RG                        31.94
DW                       41.600 usec
DE                       10.00 usec
TE                       298.1 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1               600.1337060 MHz
NUC1                        1H
P1                       12.00 usec
PLW1               21.00000000 W

F2 - Processing parameters
SI                       65536
SF                 600.1300000 MHz
WDW                         EM
SSB             0
LB                        0.30 Hz
GB              0
PC                        1.00
```



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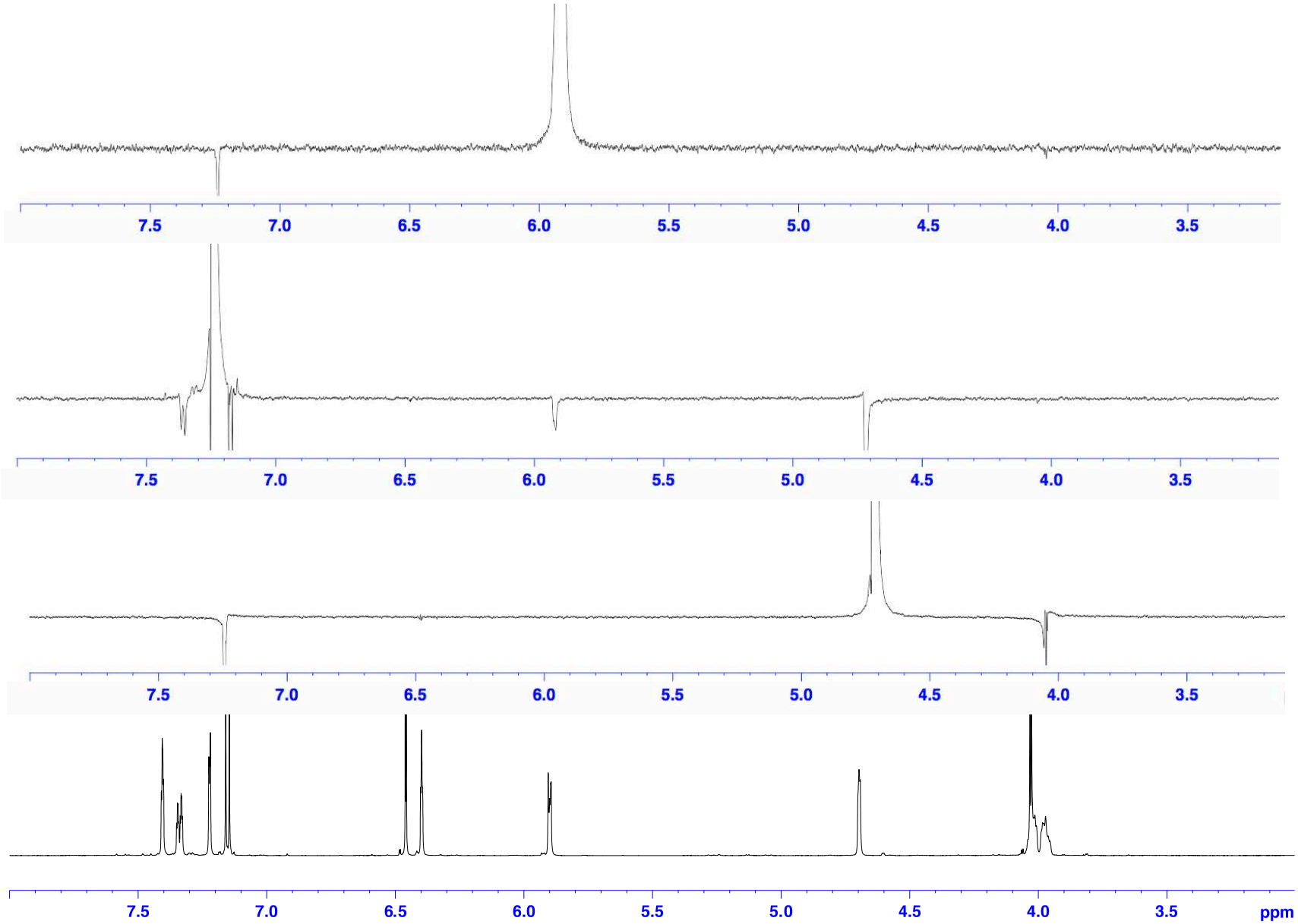


```
Current Data Parameters
NAME            VB-310-1B
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190514
Time                19.57
INSTRUM             spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                    16
DS                     2
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7262976 sec
RG                 31.94
DW                41.600 usec
DE                10.00 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          600.1337060 MHz
NUC1                    1H
P1                  12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                 65536
SF            600.1300109 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```