Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

De novo Synthesis of Dimerization-Ready Flavan Unit via Intramolecular Pummerer/Friedel–Crafts Cascade

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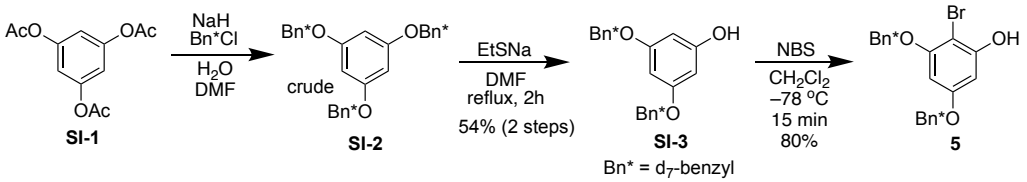
General

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 (tetramethylsilane 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 bromophenol 5

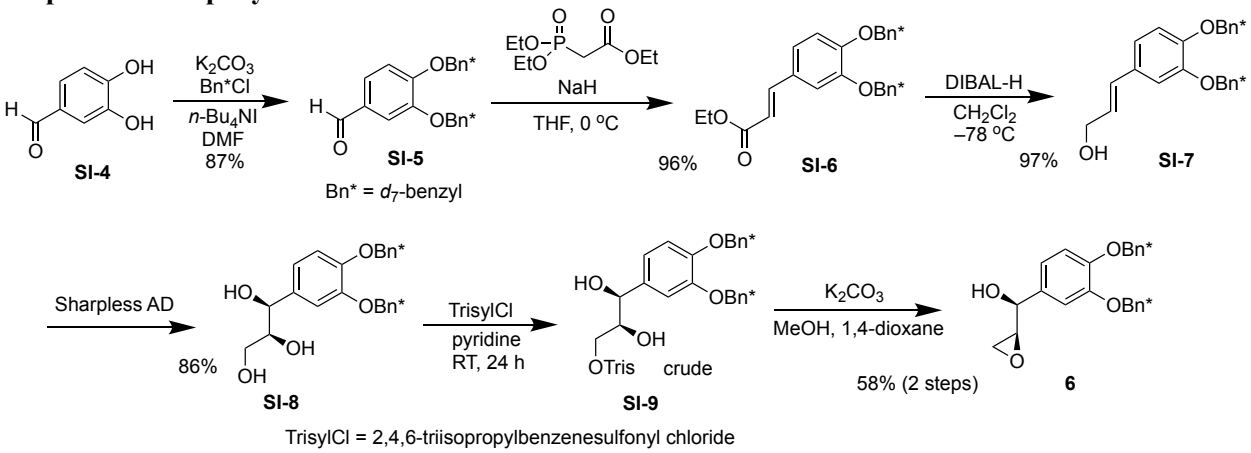


Phenol SI-3[1,2]**:** To a suspension of NaH (1.1g, 63% dispersion in mineral oil, 29 mmol) in DMF (10 mL) at 0 °C was added a solution of 1,3,5-triacetoxy benzene **SI-1** (1.0 g, 4.0 mmol) in DMF (10 mL), tetrabutyl ammonium iodide (TBAI) (0.4 g, 1 mmol) and stirred for 10 min. Bn*Cl (d_7-benzyl chloride, 1.5 mL, 13 mmol) and H_2O (215 μL, 11.9 mmol) was successively added and stirred at 15 °C for 10 h. The reaction was quenched at 0 °C by adding Et_2NH followed by H_2O, and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo to afford crude 1,3,5-tribenzyloxy benzene **SI-2** (1.5 g) which was used for the next reaction without further purification. At 0 °C, ethanethiol (1.1 mL, 15 mmol) in DMF (5 mL) was added to a suspension of NaH (0.25 g, 63 % dispersion in mineral oil, 6.6 mmol) in DMF (10 mL) over a period of 10 min. After 30 min, solution of crude **SI-2** (1.5 g) in DMF (10 mL) was added over a period of 5 min. The reaction mixture was stirred at 150 °C for 2 h. The reaction was quenched at 0 °C by adding H_2O and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/7) to afford phenol **SI-3** (0.68 g, 54%, 2 steps) as a white solid: R_f = 0.55 (EtOAc/hexane = 3/1); mp = 93–94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.80 (s, 1H), 6.10 (d, J = 1.8 Hz, 2H), 6.24 (t, J = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 69.6 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 95.1, 95.5, 127.3 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.7 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.3 (t, $J_{C\text{-}d}$ = 24.0 Hz), 136.6, 157.4, 161.0; IR (neat) 3295, 1608, 1591, 1503, 1360, 1203, 1165, 1148, 1026, 972, 819 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_5D_{14}O_3$ [(M+H)$^+$] *m/z* 321.2208, found *m/z* 321.2211.

Bromophenol 5[3]**:** To a solution of phenol **SI-3** (0.51 g, 1.6 mmol) in CH_2Cl_2 (30 mL) at –78 °C was added *N*-bromosuccinimide (0.30 g, 1.7 mmol) and stirred for 15 min. The reaction was quenched by adding 10% aqueous K_2CO_3 solution and the mixture was extracted with CH_2Cl_2 (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/7) to afford bromophenol **5** (0.51 g, 80%) as a white solid. R_f = 0.65 (EtOAc/Hexane = 2/1); mp = 81–82°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.67 (s), 6.24 (d, J = 3.0 Hz, 1H), 6.35 (d, J = 3.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 69.8 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 70.3 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 92.2, 94.7, 94.9, 126.8 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.3 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.7 (t, $J_{C\text{-}d}$ =

24.0 Hz), 127.8 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.26 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.32 (t, $J_{C\text{-}d}$ = 24.0 Hz), 136.2, 136.3, 154.1, 156.1, 159.9; IR (neat) 3481, 1580, 1493, 1479, 1370, 1200, 1188, 1105, 1009, 975, 800, 654, 632 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_4D_{14}BrO_3$ [$(M+H)^+$] *m/z* 401.1293, found *m/z* 401.1276.

Preparation of epoxy alcohol 6[4]



Aldehyde SI-5: To a solution of aldehyde **SI-4** (5.0 g, 36 mmol) in DMF (50 mL) was added K_2CO_3 (20.0 g, 147 mmol), Bn*Cl (d_7-benzyl chloride, 14.0 mL, 116 mmol), tetrabutylammonium iodide (2.7 g, 7.2 mmol) and stirred at 70 °C for 3 h. It was cooled to room temperature, quenched by adding Et_2NH followed by H_2O and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed successively with aqueous HCl (1 M), H_2O, brine and dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/1) to afford **SI-5** (10.5 g, 87%) as a white solid. R_f = 0.65 (EtOAc/Hexane = 1/1); mp = 92–93 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 70.0–70.1 (m), 112.6, 113.3, 126.8 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.1 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.5 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.3 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.4 (t, $J_{C\text{-}d}$ = 24.0 Hz), 136.1, 136.4, 149.4, 154.5, 191.0; IR (neat) 1677, 1596, 1598, 1350, 1278, 1169, 1182, 1137, 1077, 982, 953, 922, 871, 750, 725, 630 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_5D_{14}O_3$ [$(M+H)^+$] *m/z* 333.2207, found *m/z* 333.2214.

Ester SI-6: To a suspension of NaH (0.29 g, 63% dispersion in mineral oil, 7.6 mmol) in THF (20 mL) at 0 °C was added triethyl phosphonoacetate (1.4 mL, 7.1 mmol) in THF (5 mL) and stirred for 1 h. A solution of **SI-5** (2.0 g, 6.0 mmol) in THF (10 mL) was added dropwise to the mixture, and the reaction mixture was additionally stirred for 1 h. The reaction was quenched by adding H_2O, and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/1) to afford **SI-6** (2.3 g, 96%) as a white solid. R_f = 0.55 (EtOAc/Hexane = 2/1); mp = 80–81 °C; ^{1}H NMR (600

MHz, $CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 1H), 4.24 (q, J = 7.2 Hz, 1H), 6.22 (d, J = 16.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 7.06 (dd, J = 2.4, 8.4 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 7.56 (d, J = 16.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.5, 60.6, 70.0–70.2 (m), 113.9, 114.5, 116.4, 123.0, 126.9 (t, $J_{C\text{-}d}$ = 22.5 Hz), 127.1 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.6 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.2 (t, $J_{C\text{-}d}$ = 24.0 Hz), 136.7, 136.8, 144.5, 149.1, 151.2, 167.4; IR (neat) 2982, 2184, 1697, 1684, 1594, 1427, 1394, 1367, 1049, 1035, 1022, 991, 835, 820, 800, 751, 732, 648 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{10}D_{14}O_4Na$ [$(M+Na)^+$] *m/z* 425.2445, found *m/z* 425.2445.

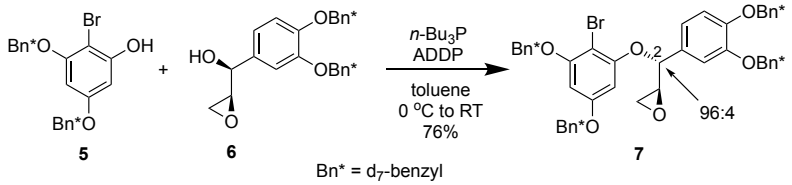
Alcohol SI-7: To a solution of **SI-6** (2.0 g, 5.0 mmol) in THF (25 mL) at –78 ºC was added in DIBAL-H (1.0 M in toluene, 13 mL, 13 mmol) and stirred for 2 h. Reaction was quenched by slowly adding saturated solution of Rochelle salt. It was additionally stirred for 2 h and layers were separated. The aqueous layer was further extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/1) to afford **SI-7** (1.73 g, 97%) as a white solid. R_f = 0.45 (EtOAc/hexane = 1/1); mp = 76–77 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.41 (brm, 1H), 4.28 (d, J = 4.8 Hz, 1H), 6.18 (dt, J = 4.8, 15.6 Hz, 1H), 6.49 (d, J = 15.6 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.89 (dd, J = 1.8, 8.4 Hz, 1H), 7.01 (d, J = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 64.0, 70.1–70.2 (m), 113.1, 115.1, 120.5, 126.9, 127.05 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.11 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.4–127.6 (m), 128.16 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.17 (t, $J_{C\text{-}d}$ = 24.0 Hz), 130.6, 131.2, 137.08, 137.11, 149.0, 149.2; IR (neat) 3357, 2192, 1507, 1461, 1425, 1271, 1238, 1137, 1080, 1053, 1034, 956, 840, 819, 775 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_8D_{14}O_3Na$ [$(M+Na)^+$] *m/z* 383.2340, found *m/z* 383.2332.

Triol SI-8: To a solution of potassium hexacyanoferrate(III) (5.7 g, 17 mmol) in the mixed solvent (140 mL, *t*-BuOH/H_2O = 1/1), was added K_2CO_3 (2.4 g, 17 mmol), methanesulfonamide (0.55 g, 0.58 mmol), $(DHQ)_2PHAL$ (0.23 g, 0.29 mmol), and $K_2OsO_2(OH)_4$ (22 mg, 0.059 mmol) at 0 °C and stirred for 30 min. To this, **SI-7** (2.00 g, 5.55 mmol) was added to rection mixture and stirred for 72 h. The reaction was quenched by adding solid sodium sulfite (5.7 g) and additionally stirred for 24 h at room temperature. It was diluted with H_2O and mixture was extracted with EtOAc (x3). The combined organic extracts were washed with aqueous KOH (2 M), H_2O, brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 4/1) to afford **SI-8** (1.84 g, 86%) as a white solid. R_f = 0.25 (EtOAc/hexane = 4/1); mp = 81–82 °C; $[\alpha]_D^{20}$ = +16 (*c* 0.40, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 2.04 (brs, 1H), 2.75 (brs), 2.90 (brs), 3.39 (dd, J = 5.4, 11.4 Hz, 1H), 3.50 (dd, J = 3.0, 11.4 Hz, 1H), 3.64–3.66 (1H), 4.57 (d, J = 7.2 Hz, 1H), 6.85 (dd, J = 1.8, 8.4 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.95 (d, J =1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 63.4, 70.7 (quint., $J_{C\text{-}d}$ = 21.0 Hz), 74.8, 75.9, 113.8, 115.1, 119.9, 127.1 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.2 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.5 (t, $J_{C\text{-}d}$ = 24.0 Hz), 128.1 (t, $J_{C\text{-}d}$ =

24.0 Hz), 128.2 (t, $J_{C\text{-}d}$ = 24.0 Hz), 133.8, 136.98, 137.02, 149.0, 149.1; IR (neat) 3385, 2882, 1590, 1528, 1490, 1328, 1277, 1165, 1139, 1084, 1051, 1032, 909, 732, 648 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{10}D_{14}O_5Na$ [$(M+Na)^+$] *m/z* 417.2395, found *m/z* 417.2396.

Epoxy alcohol 6: To a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (TrisylCl, 3.7 g, 12 mmol) in pyridine (10 mL) was added triol **SI-8** (1.8 g, 4.6 mmol) at 0 °C. It was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched by adding aqueous HCl (1 M). The mixture was extracted with EtOAc (x3), and the combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was eluted through a silica gel pad and washed with hexane/EtOAc (2/1) to remove unreacted TrisylCl, giving crude **SI-9**. The crude material was dissolved in a mixed solvent (methanol/1,4-dioxane = 2/1, 24 mL), and K_2CO_3 (1.2 g, 8.7 mmol) was added at 0 °C. After stirring for 2 h, the reaction was stopped by adding H_2O, and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/2) to afford epoxy alcohol **6** (1.0 g, 58%, 2 steps) as a colorless viscous oil. R_f = 0.25 (EtOAc/Hexane = 1/1); $[\alpha]_D^{20}$ = +0.34 (*c* 0.87, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.38 (d, *J* = 4.8 Hz, 1H), 2.74 (dd, *J* = 3.0, 4.8 Hz, 1H), 2.79 (t, *J* = 4.8 Hz, 1H), 3.14 (ddd, *J* = 3.0, 4.8, 5.4 Hz, 1H), 4.36 (dd, *J* = 4.8, 5.4 Hz, 1H), 6.91 (dd, *J* = 1.8, 8.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR(150 MHz, $CDCl_3$) δ 45.5, 56.0, 70.7 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 70.8 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 74.3, 113.5, 115.2, 119.6, 127.0 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.2 (t, $J_{C\text{-}d}$ = 24.0 Hz), 127.4–127.6 (m), 128.1 (t, $J_{C\text{-}d}$ = 24.0 Hz), 133.6, 137.0, 137.1, 149.1, 149.2; IR (neat) 3438, 2994, 2205, 1605, 1590, 1509, 1426, 1328, 1271, 1183, 1166, 1031, 993, 919, 852, 819, 801, 748, 542 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_8D_{14}O_4Na$ [$(M+Na)^+$] *m/z* 399.2289, found *m/z* 399.2292.

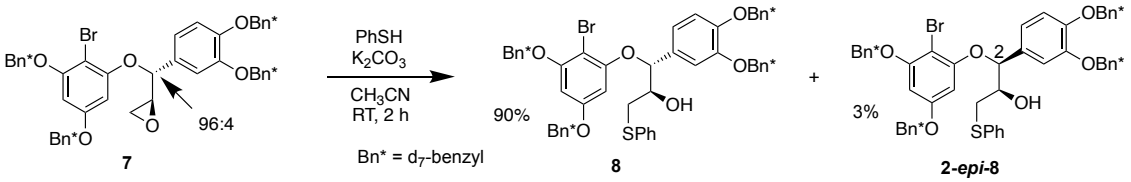
Preparation of epoxy ether 7



To a solution of bromophenol **5** (0.67 g, 1.7 mmol), epoxy-alcohol **6** (0.95 g, 2.5 mmol) and ADDP (1.3 g, 5.2 mmol) in toluene (17 mL) was added *n*-Bu_3P (1.2 mL, 4.8 mmol) at 0 °C. It was warmed to room temperature and stirred for 2 h. The reaction was quenched by adding phosphate buffer (pH = 7) and the mixture extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1/3) to afford **7** as a diastereomeric mixture (0.96 g, 76%, d.r. = 96:4) as an ivory foam.

R_f = 0.75 (EtOAc/hexane = 1/2); $[\alpha]_D^{20}$ = –5.8 (*c* 0.38, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, signals of minor diastereomers are omitted) δ 2.76 (dd, *J* = 3.6, 4.8 Hz, 1H), 2.97 (dd, *J* = 2.4, 4.8 Hz, 1H), 3.23–3.24 (m, 1H), 5.01 (d, *J* = 3.6 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* =1.8, 8.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR(150 MHz, $CDCl_3$, signals of minor diastereomers are omitted) δ 45.1, 54.6, 69.9–70.2 (m), 70.6 (quint, $J_{C\text{-}d}$ = 22.5 Hz), 79.4, 95.0, 95.5, 96.2, 113.4, 114.9, 120.1, 126.6, 126.8–128.5 (m), 136.2, 136.4, 136.9, 137.1, 149.2, 149.3, 155.5, 156.7, 159.2; IR (neat) 2118, 1585, 1491, 1478, 1327, 1272, 1178,1086, 1050, 1032, 988, 730, 610, 574, 542, 513 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{10}D_{28}BrO_6$ $[(M+H)^+]$ *m/z* 757.3604, found *m/z* 757.3609.

Opening of epoxide 7 to give sulfide 8



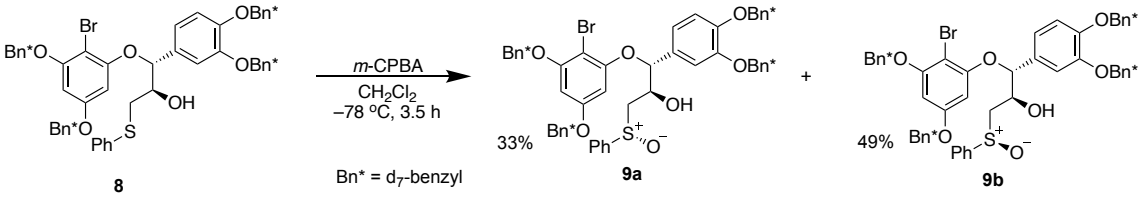
To a solution of epoxide **7** (500 mg, 0.660 mmol) and K_2CO_3 (182 mg, 1.32 mmol) in CH_3CN (6.5 mL) was added PhSH (135 μL, 1.32 mmol) at room temperature. It was stirred for 2 h and diluted with diethyl ether. Reaction mixture was filtered through a Celite® pad and washed with diethyl ether (x3). The combined filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (silica-gel, EtOAc/hexane = 1/5) to afford **8** (514 mg, 90%) as an ivory foam and **2-*epi*-8** (16 mg, 3%) as an colorless oil.

Sulfide 8: R_f = 0.23 (hexane/EtOAc = 7/2); $[\alpha]_D^{20}$ = + 20 (*c* 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.46 (d, *J* = 5.4 Hz, 1H), 3.12 (dd, *J* = 8.4, 13.8 Hz, 1H), 3.27 (dd, *J* = 3.6, 13.8 Hz, 1H), 3.96–4.00 (m, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 5.95 (d, *J* = 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 1.8, 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 1.8 Hz, 1H), 7.11–7.14 (m, 1H), 7.18–7.21 (m, 2H), 7.26–7.27 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.3, 69.4–70.8 (m), 73.4, 82.6, 94.4, 95.3, 95.7, 113.4, 114.8, 120.2, 126.6, 126.6–128.4 (m), 129.1, 129.2, 129.9, 135.6, 136.2, 136.3, 136.7, 137.0, 149.06, 149.12, 155.4, 156.6, 159.2; IR (neat) 3475, 2981, 2119, 1584, 1509, 1327, 1270, 1176, 1085, 1032, 909, 818, 738, 539 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{16}D_{28}O_6BrS$ $[(M+H)^+]$ *m/z* 867.3794, found *m/z* 867.3789.

Sulfide 2-*epi*-8: R_f = 0.25 (hexane/EtOAc = 7/2); $[\alpha]_D^{20}$ = –1.31 (*c* 0.130, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.78 (dd, *J* = 7.2, 13.8 Hz, 1H), 2.96 (d, *J* = 4.2 Hz, 1H), 3.18 (dd, *J* = 4.2, 13.8 Hz, 1H), 4.00–4.03 (m, 1H), 5.09 (d, *J* = 5.4 Hz, 1H), 5.95 (d, *J* = 2.4 Hz, 1H), 6.22 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 1.8,

8.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 1.8 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.24–7.26 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.1, 53.6, 69.4–70.9 (m), 74.0, 82.8, 94.5, 95.4, 95.9, 113.5, 114.9, 120.2, 126.3, 126.6–128.4 (m), 129.1, 129.2, 130.1, 135.9, 136.1, 136.3, 136.7, 137.0, 149.1, 149.3, 155.5, 156.6, 159.2; IR (neat) 3552, 2921, 1584, 1508, 1363, 1271, 1230, 1175, 1085, 1031, 818, 739, 540 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{16}D_{28}O_6BrS$ [(M+H)$^+$] *m/z* 869.3776, found *m/z* 869.3784.

Oxidation of sulfide 8 to hydroxy-sulfoxides 9a and 9b



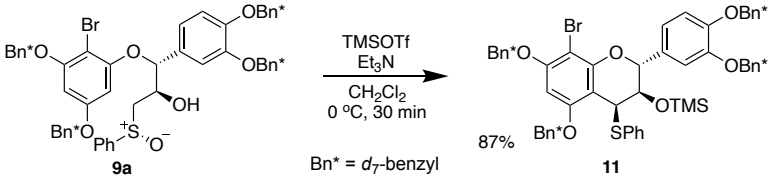
To a solution of sulfide **8** (30.0 mg, 0.0346 mmol) in CH_2Cl_2 (0.7 mL) at –78 °C was added *m*-CPBA (77%, 8.5 mg, 0.038 mmol). After stirring for 3.5 h, the reaction was quenched by adding saturated aqueous Na_2SO_3 solution. The crude products were extracted with EtOAc (x3). Combined organic extracts were washed with water, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica-gel, THF/hexane = 2/7, developed 7 times) to afford less polar hydroxy-sulfoxide **9a** (10.1 mg, 33%) as a viscous oil and more polar hydroxy-sulfoxide **9b** (15.0 mg, 49%) as a viscous oil.

***anti*-isomer 9a**: R_f = 0.30 (EtOAc/hexane = 3/2); $[\alpha]_D^{20}$ = –22 (*c* 0.87, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.91 (dd, J = 1.8, 14.4 Hz, 1H), 3.27 (dd, J = 9.6, 14.4 Hz, 1H), 3.71 (br, 1H), 4.30–4.33 (m, 1H), 5.04 (d, J = 5.4 Hz, 1H), 5.94 (d, J = 2.4 Hz, 1H), 6.21 (d, J = 2.4 Hz, 1H), 6.67 (dd, J = 1.8, 7.8 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 1.8 Hz, 1H), 7.44–7.49 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 56.7, 69.8–70.9 (m), 71.3, 83.2, 94.2, 95.4, 95.6, 113.0, 114.8, 119.9, 124.2, 126.6–129.4 (m), 129.5, 131.1, 136.1, 136.3, 136.8, 137.0, 142.8, 149.0, 149.1, 155.4, 156.6, 159.3; IR (neat) 3322, 1585, 1510, 1427, 1468, 1365, 1271, 1231, 1202, 1176, 1112, 1085, 996, 818, 731, 690 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{15}D_{28}BrO_7SNa$ [(M+Na)$^+$] *m/z* 907.3545, found *m/z* 907.3543.

***syn*-isomer 9b**: R_f = 0.30 (EtOAc/hexane = 3/2); $[\alpha]_D^{20}$ = +31 (*c* 0.67, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.17 (dd, J = 3.0, 13.2 Hz, 1H), 3.20 (dd, J = 8.4, 13.2, 1H), 3.64 (d, J = 3.6 Hz, 1H), 4.37–4.40 (m, 1H), 5.01 (d, J = 5.4 Hz, 1H), 5.95 (d, J = 2.4 Hz, 1H), 6.21 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 1.8, 14.4 Hz, 1H), 6.87 (d, J = 14.4 Hz, 1H), 6.94 (d, J = 1.8 Hz, 1H), 7.50–7.53 (m, 3H), 7.63–7.64 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 53.6, 58.1, 68.9–70.8 (m), 72.6, 83.3, 94.3, 95.4, 95.7, 113.2, 114.9, 120.1, 124.3, 126.6–

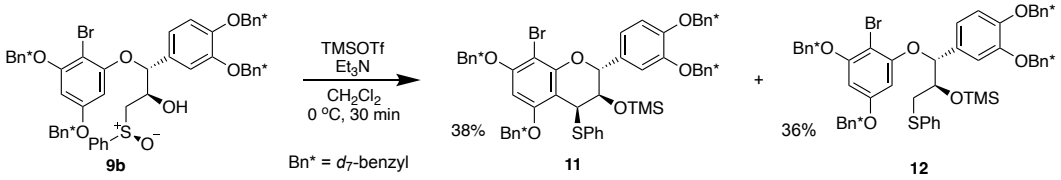
128.4 (m), 129.6, 131.6, 136.1, 136.3, 136.7, 137.0, 143.8, 149.2, 149.3, 155.4, 155.6, 156.6, 159.3; IR (neat) 3330, 1584, 1508, 1427, 1468, 1327, 1271, 1231, 1202, 1176, 1112, 1086, 1032, 818, 747 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{15}D_{28}BrO_7SNa$ [$(M+Na)^+$] *m/z* 905.3563, found *m/z* 905.3561.

Pummerer/Friedel–Crafts cascade of 9a for the preparation of flavan 11



To the solution of **9a** (20.0 mg, 0.0226 mmol) in CH_2Cl_2 (1 mL) at 0 °C, was added Et_3N (26 μL, 0.18 mmol) followed by TMSOTf (30 μL, 0.16 mmol) and stirred for 30 min. The reaction was quenched by adding aqueous saturated $NaHCO_3$ solution and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, EtOAc/hexane = 1/4) to afford flavan **11** (18.3 mg, 87%) as a colorless oil.

Pummerer/Friedel–Crafts cascade of 9b to give flavan 11 and reduced product 12



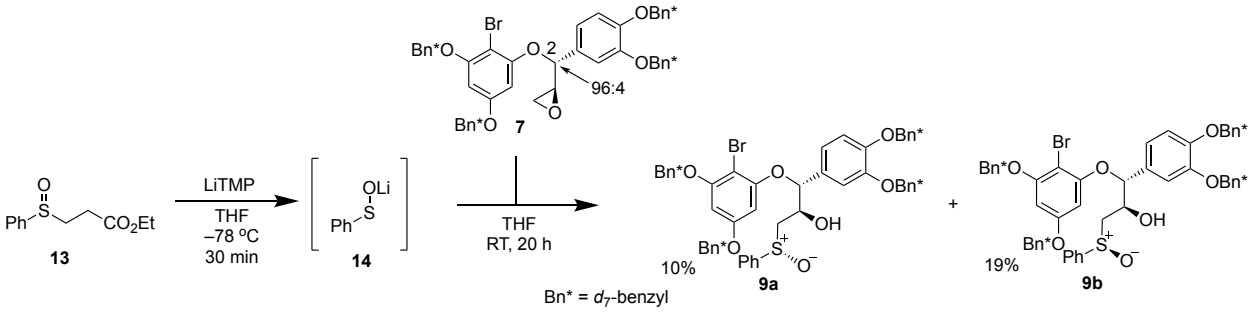
To the solution of **9b** (20.0 mg, 0.0226 mmol) in CH_2Cl_2 (1 mL) at 0 °C, was added Et_3N (26 μL, 0.18 mmol) followed by TMSOTf (30 μL, 0.16 mmol) and stirred for 30 min. The reaction was quenched by adding aqueous saturated $NaHCO_3$ solution and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, EtOAc/hexane = 1/9, developed 4 times) to afford flavan **11** (8.1 mg, 38%) as a colorless oil and sulfide **12** (7.6 mg, 36%) as a colorless oil.

Flavan 11: R_f = 0.70 (EtOAc/hexane = 1/4); $[\alpha]_D^{20}$ = +63 (*c* 0.23, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 0.64 (s, 9H), 3.87 (dd, *J* = 9.0, 4.2 Hz, 1H), 4.53 (d, *J* = 4.2 Hz, 1H), 5.42 (d, *J* = 9.0 Hz, 1H), 6.26 (s, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.02–7.06 (m, 3H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 1H), 7.42–7.44 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 0.1, 50.4, 71.1–72.1 (m), 73.6, 79.0, 93.5, 93.6, 105.9, 115.6,

122.3, 127.6–128.1 (m), 128.2, 128.4–129.4 (m), 129.5, 133.2, 135.2, 137.1, 137.5, 138.2, 138.5, 149.8, 150.0, 152.8, 157.2, 157.4; IR (neat) 2918, 2277,1600, 1511, 1502, 1479, 1414, 1365, 1270, 1184, 1113, 1084, 1051, 1029, 841 cm^{-1}; HRMS (ESI) calcd for $C_{52}H_{22}D_{28}BrO_6SSi$ [$(M+H)^+$] *m/z* 937.4033, found *m/z* 937.4029.

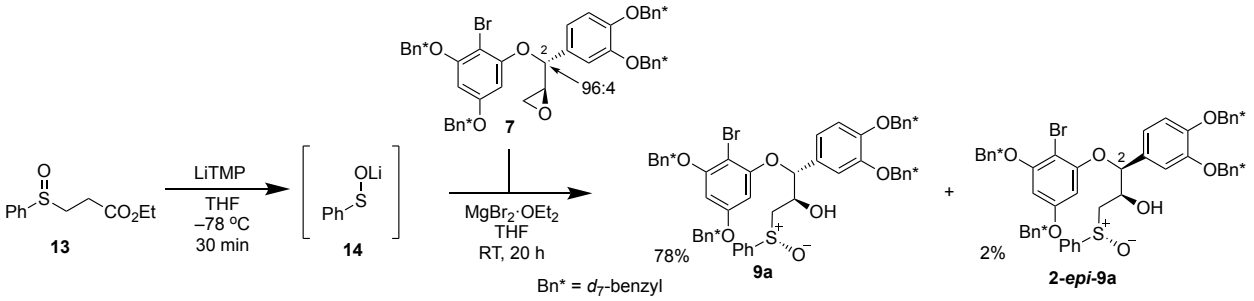
Sulfide 12: R_f = 0.72 (EtOAc/hexane = 1/4); $[\alpha]_D^{20}$ = +11.5 (*c* 1.07, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ –0.18 (s, 9H), 3.20 (dd, *J* = 6.6, 13.8 Hz, 1H), 3.46 (dd, *J* = 3.0, 13.8 Hz, 1H), 4.11 (ddd, *J* = 3.0, 5.4, 6.6 Hz, 1H), 5.01 (d, *J* = 5.4 Hz, 1H), 6.00 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 6.81–6.85 (m, 2H), 7.01 (brs, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, C_6D_6) δ 0.3, 38.8, 69.4–70.7 (m), 75.6, 83.0, 94.8, 95.3, 96.0, 114.5, 115.1, 121.3, 126.9, 127.0–128.5 (m), 129.2, 131.7, 136.8, 137.4, 137.5, 137.7, 149.6, 149.9, 156.2, 157.2, 159.7; IR (neat) 2954, 2119, 1584, 1480, 1469, 1365, 1230, 1177, 1085, 1031, 841, 819, 739, 690, 541 cm^{-1}; HRMS (ESI) calcd for $C_{52}H_{24}D_{28}BrO_6SSi$ [$(M+H)^+$] *m/z* 939.4189, found *m/z* 939.4193.

Ring-opening of epoxide 7 by phenyl sulfinate 14 to provide 9a and 9b (without $MgBr_2 \cdot OEt_2$)



To the solution of 2,2,6,6-tetramethylpipiridine (0.17 mL, 0.99 mmol) in THF (3 mL) at 0 °C, was added *n*-BuLi (0.56 mL, 0.89 mmol) and stirred for 1 h. To this, a solution of sulfoxide **13** (0.18 g, 0.80 mmol) in THF (2 mL) was added at –78 °C. After stirring for 30 min, a solution of **7** (40 mg, 0.053 mmol) in THF (2 mL) was added and stirred for 20 h at room temperature. Reaction was quenched by adding saturated aqueous NH_4Cl solution and the mixture was extracted with EtOAc (x3). Combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, EtOAc/hexane = 1/1) to obtain a mixture of **9a** and **9b** (13.4 mg in total) and starting epoxy-ether **7** (24.5 mg, 61%). **9a** and **9b** was separated by preparative TLC (silica gel, THF/hexane =1/4, developed 6 times) to provide less polar *anti*-isomer **9a** (4.5 mg, 10%) as a viscous oil and more polar *syn*-isomer **9b** (8.8 mg, 19%) as a viscous oil.

Conversion of epoxide 7 to 9a (with $MgBr_2 \cdot OEt_2$)

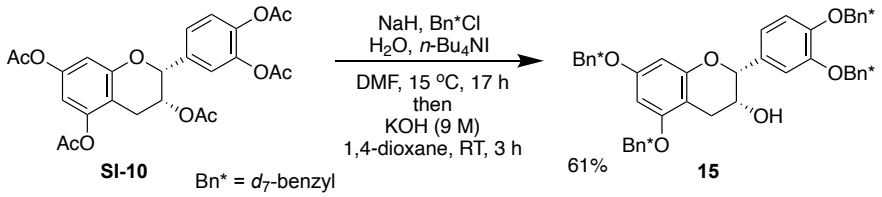


13 14 7 9a 2-*epi*-9a

To a solution of 2,2,6,6-tetramethylpipiridine (0.17 mL, 0.998 mmol) in THF (3 mL) at 0 °C, was added *n*-BuLi (0.56 mL, 0.89 mmol) and stirred for 1 h. To this, a solution of sulfoxide **13** (0.18 g, 0.80 mmol) in THF (2 mL) was added at –78 °C. After stirring for 30 min, $MgBr_2 \cdot OEt_2$ (0.21 g, 0.80 mmol) and a solution of **7** (40 mg, 0.053 mmol) in THF (2 mL) were successively added, and the mixture was stirred for 20 h at room temperature. The reaction was quenched by adding saturated aqueous NH_4Cl solution, and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, EtOAc/hexane = 1/1) to obtain **9a** (36.3 mg, 78%) as an ivory foam and **2-*epi*-9a** (0.8 mg, 2%) as a colorless viscous oil.

2-*epi*-9a: R_f = 0.32 (EtOAc/hexane = 3/2); $[\alpha]_D^{20}$ = –44 (*c* 0.27, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.64 (d, *J* = 12.6 Hz, 1H), 2.86 (dd, *J* = 10.2, 12.6 Hz, 1H), 3.69 (d, *J* = 1.8 Hz, 1H), 4.46–4.48 (m, 1H), 4.87 (d, *J* = 5.4 Hz, 1H), 5.87 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, *J* = 1.8, 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 1.8 Hz, 1H), 7.44–7.51 (m, 3H), 7.57–7.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.9, 57.2, 69,8–71.2 (m), 69.9, 82.9, 94.4, 95.4, 95.6, 113.5, 114.8, 120.4, 124.2, 126.6–128.4 (m), 129.0, 131.1, 136.1, 136.3, 136.8, 137.0, 143.0, 148.9, 149.3, 155.2, 156.6, 159.2; IR (neat) 3329, 1580, 1510, 1425, 1464, 1269, 1230, 1200, 1173, 1109, 1030, 819, 746 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{16}D_{28}BrO_7S$ [$(M+H)^+$] *m/z* 883.3743, found *m/z* 883.3707.

Synthesis of tetra *O*-d_7-benzyl epicatechin 15

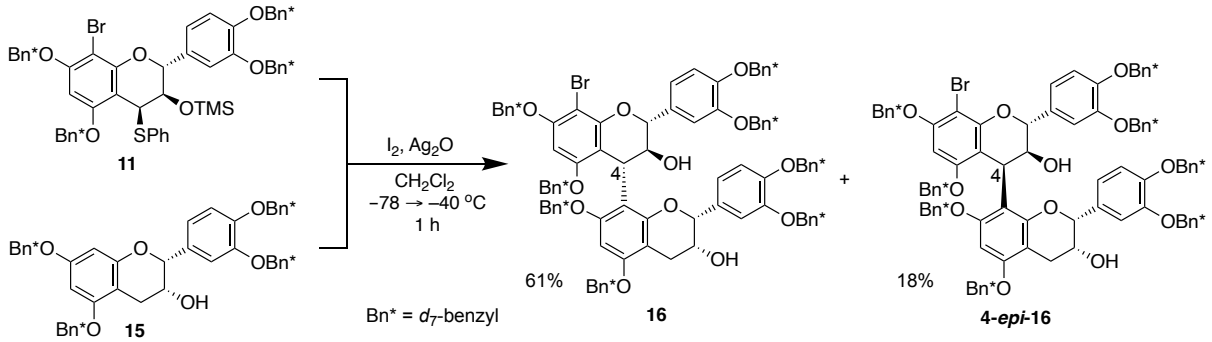


SI-10 15

To a suspension of NaH (0.19 g, 63% dispersion in mineral oil, 5.0 mmol) in DMF (5 mL) at 0 °C was added **SI-10**[5] (0.3 g, 0.6 mmol) in DMF (5 mL) followed by tetrabutylammonium iodide (TBAI) (55 mg,

0.15 mmol). After stirring for 10 min, Bn*Cl (d_7-benzyl chloride, 0.30 mL, 2.5 mmol) and H_2O (43 μL, 2.4 mmol) was successively added and stirred at 15 °C for 17 h. The reaction was quenched by successively adding Et_2NH and H_2O at 0 °C, and the mixture was extracted with EtOAc (x3). The combined organic extracts were washed with water, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was re-dissolved in 1,4-dioxane (12 mL), and aqueous KOH (9 M, 3 mL) was added at 0 °C. After stirring for 3 h, the reaction was quenched by adding H_2O. The mixture was extracted with EtOAc (x3), and the combined organic extracts were successively washed with aqueous 1 M HCl, H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/hexane = 1/4) to afford **15** (0.25 g, 61%) as an ivory foam. R_f = 0.55 (EtOAc/hexane = 1/3); $[\alpha]_D^{20}$ = –13 (*c* 0.91, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.93 (dd, *J* = 4.2, 17.4 Hz, 1H), 2.99 (dd, *J* = 1.8, 17.4 Hz, 1H), 4.22 (s, 1H), 4.92 (s, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.14 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 21.2, 28.4, 60.6, 66.5, 67.8–69.9 (m), 70.1–71.8 (m), 78.6, 94.2, 94.8, 101.1, 113.7, 115.3, 119.6, 126.8–128.4 (m), 131.6, 136.8, 136.9, 137.0, 137.1, 149.0, 149.2, 155.4, 158.5, 159.0, 171.3; IR (neat) 3539, 2269, 1737, 1616, 1593, 1509, 1493, 1327, 1200, 1158, 1141, 1084, 1038, 995, 838, 807, 765, 654 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{11}D_{28}O_6$ [$(M+H)^+$] *m/z* 679.4499, found *m/z* 679.4473.

Attachment of bottom epicatechin unit 15 to sulfide 11 to give 16



To a solution of sulfide **11** (40 mg, 0.043 mmol) and epicatechin derivative **15** (43 mg, 0.063 mmol) in CH_2Cl_2 (3 mL) was added Ag_2O (15 mg, 0.065 mmol) followed by dropwise addition of a solution of I_2 (33 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) at –78 °C. It was stirred for 30 min before warming up to –40 °C over 30 min. The reaction was quenched by adding 10% aqueous $Na_2S_2O_3$ solution and saturated $NaHCO_3$ solution. The mixture was extracted with EtOAc (x3). The combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, $CHCl_3$/EtOAc/CH_2Cl_2 /hexane= 4/1/1/2, developed 2 times) to afford dimer **16** (mixture of rotamers, 37.4 mg, 61%) as an ivory foam and **4-*epi*-16** (mixture of rotamers, 11.0 mg, 18%) as a colorless viscous oil.

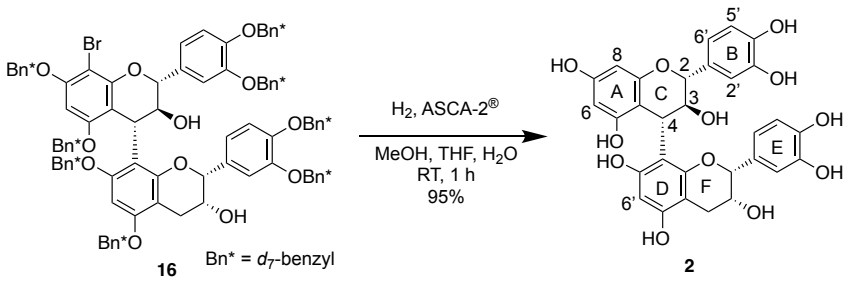
16: R_f = 0.27 ($CHCl_3$/EtOAc/CH_2Cl_2/hexane = 4/1/1/2); $[\alpha]_D^{20}$ = –83 (*c* 0.49, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, rotamer ratio is 1.0:0.55, signals of the minor rotamer are marked with an asterisk) δ *1.52 (br, 0.55H), 1.66 (br, 1H), 2.58 (dd, *J* = 4.2, 16.8 Hz, 1H), *2.87 (dd, *J* = 4.2, 17.4 Hz, 0.55H), 2.88 (d, *J* = 17.4 Hz, 1H), *3.01 (d, *J* = 17.4 Hz, 0.55H), 3.79 (s, 1H), 3.88 (brs, 1H), *4.06 (brm, 0.55H), *4.16 (dt, *J* = 3.6, 9.6 Hz, 0.55H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.58 (d, *J* = 9.6 Hz, 1H), *4.68 (d, *J* = 9.6 Hz, 0.55H), *4.75 (brs, 0.55H), 4.83 (d, *J* = 9.6 Hz, 1H), *4.85 (d, *J* = 9.6 Hz, 0.55H), *5.95 (s, 0.55H), 6.17 (s, 1H), *6.18 (s, 0.55H), *6.21 (dd, *J* = 1.8, 8.4 Hz, 0.55H), 6.22 (s, 1H), *6.68 (d, *J* = 1.8 Hz, 0.55H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 1.8 Hz, 1H), *6.77–6.91 (m, 1.10H), *6.84 (d, *J* = 8.4 Hz, 0.55H), *6.88 (dd, *J* = 1.8, 8.4 Hz, 0.55H), 6.92 (d, *J* = 8.4 Hz, 1H), 7.01–7.02 (m, 2H), 7.14 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$ signals of the minor rotamer are marked with an asterisk) δ 28.3, *29.9, 37.3, *37.6, 66.2, *66.3, *69.0–70.01 (m), 70.03–71.8 (m), *72.5, 73.1, 77.5, *78.3, *82.0, 82.4, 91.3, *92.1, 93.5, *93.8, 93.9, *94.0, 100.9, *102.3, 110.3, *110.9, *111.2, 111.4, *112.7, 113.1, *113.5, 113.8, 114.7, *114.9, *115.1, 115.4, 118.9, *119.7, *120.8, 121.2, [a]126.6–128.4 (m), *130.4, 131.5, *131.5, 132.2, [a]136.2–137.5, 148.5, *148.7, *148.96, *149.00, *149.04, 149.1, 149.15, 149.17, *152.8, *153.4, 153.6, 153.8, 154.3, *154.4, 155.6, *156.3, 156.4, 156.5, *156.9, *157.1; IR (neat) 3441, 2921, 2119, 1598, 1510, 1416, 1357, 1327, 1270, 1201, 1114, 1052, 1030, 909, 819, 731, 544 cm^{-1}; HRMS (ESI) calcd for $C_{86}H_{28}D_{56}BrO_{12}$ [$(M+H)^+$] *m/z* 1433.7873, found *m/z* 1433.7857.

[a] ^{13}C signals of both rotamers are overlapping.

4-*epi*-16: R_f = 0.30 ($CHCl_3$/EtOAc/CH_2Cl_2/hexane = 4/1/1/2); $[\alpha]_D^{20}$ = +26 (c 0.55, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, rotamer ratio = 1.0:0.50, signals of the minor rotamer are marked with an asterisk) δ *2.61 (brd, *J* = 4.2 Hz, 0.5H), 2.86 (br, 1H), 2.92 (dd, *J* = 9.0, 18.0 Hz, 1H), [a]2.96–3.00 (m, 1H), *2.96–3.00 (m, 1H), 3.89 (d, *J* = 3.0 Hz, 0.5H), 4.07 (s, 1H), *4.09–4.11 (m, 0.5H), 4.15–4.19 (m, 1H), *4.15–4.19 (m, 0.5H), *4.88 (s, 0.5H), 5.00 (1H), *5.01 (d, *J* = 6.0 Hz, 0.5H), *5.21 (d, *J* = 7.2 Hz, 0.5H), 5.37 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), *6.16 (s, 0.5H), *6.21 (s, 0.5H), 6.30 (dd, *J* = 1.8, 7.8 Hz, 1H), 6.32 (s, 1H), *6.72 (d, *J* = 7.8 Hz, 0.5H), 6.78–6.87 (m, 3H), *6.78–6.87 (m, 1.5H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), *7.04 (d, *J* = 1.8 Hz, 0.5H), *7.10 (d, *J* = 1.8 Hz, 0.5H), 7.20 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, signals of the minor rotamer are marked with an asterisk) δ 28.86, *28.92, *32.0, 33.4, *66.0, 66.8, *68.0–69.3 (m), 69.7–72.1 (m), *71.0, 71.7, 78.7, *78.8, *79.1, 79.3, 91.8, *92.5, *92.7, 92.9, *93.5, 94.0, *101.6, 103.2, *108.2, 108.5, 108.8, *109.0, 111.5, *113.4, *113.5, 113.6, 114.7, *114.8, *115.0, 115.5, 118.2, *119.5, *119.8, 120.3, [a]126.8–128.3 (m), 130.9, *131.4, *132.1, 132.2, *136.36, *136.40, 136.5, 136.6, *136.8, *136.9, [a]137.0, *137.1, 137.2, *137.3, 137.4, 137.6, 148.5, *148.7, *148.8, *148.9, 149.2, 149.7, 152.1, *152.3, *153.5, 154.7, *155.2, *156.2, 156.6, 156.9, *157.1; IR (neat) 3532, 2922, 1601, 1510, 1583, 1416, 1358, 1272, 1230, 1202, 1189, 1107, 1052, 909, 839, 731 cm^{-1}; HRMS (ESI) calcd for $C_{86}H_{28}D_{56}BrO_{12}$ [$(M+H)^+$] *m/z* 1433.7873, found *m/z* 1433.7877.

[a] ^{13}C signals of both rotamers are overlapping

Synthesis of procyanidin B4 (2)



A solution of tetramer **16** (40.0 mg, 0.0279 mmol) in the presence of ASCA-2® (92.0 mg, 0.0328 mmol) in a mixture of THF, MeOH and H_2O (v/v/v = 2/2/1, 15 mL) was stirred under H_2 atmosphere at room temperature. After stirring for 1 h, it was carefully filtered under argon atmosphere through a glass fiber filter (MeOH) and the filtrate was evaporated to remove organic solvents and lyophilized to give a crude material, which was purified by preparative HPLC [Inertsustain® C18, 20 mm ϕ × 250 mm, MeOH, H_2O (35/65) containing 0.1% TFA, flow rate 8 mL/min, 20 x 250 mm] and lyophilization gave **2**[6] (15.3 mg, 95%) as an ivory amorphous solid. $[\alpha]_D^{25}$ = –198 (*c* 0.560, EtOH); ^{13}C-NMR (150 MHz, CD_3OD, signals of the minor rotamer are marked with an asterisk) δ *30.1, 30.9, *39.6, 39.7, 68.3, *68.6, *74.6, 74.7, *80.7, 80.9, 84.7, *84.9, *97.2–98.0 (m), 98.1–98.9 (m), 100.3, *100.9, 108.1, 108.2, *109.1, *109.6, *115.6, 116.1, 116.7, *116.78, [a]116.82, 116.9, *117.2, 120.0, *121.1, *121.3, 122.1, *132.6, 133.1, *133.3, 133.4, *146.41, *146.44, 146.5, *146.6, 146.8, *146.9, 147.0, 147.3, [a]156.2, *156.6, 156.7, *157.1, 157.2, 158.1, *158.0, *158.2, 158.3, *159.3, 159.5; IR(neat) 3295 (br), 1605, 1519, 1446, 1281, 1260, 1197, 1143, 1062, 800, 609cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{25}O_{12}$ [$(M+H)^+$] *m/z* 577.1351, found *m/z* 577.1338.

[a] ^{13}C signals of both rotamers are overlapping.

Note: Because of deuterium exchange with CD_3OD, the corresponding signals for C4, C8 and C6' are observed as multiplets with decreased intensity levels.

Comparison of ^{1}H NMR data of 2 (600 MHz, CD_3OD, rotamer ratio = 1.0:0.77)

Major rotamer			
Ring	**Carbon number**	**Literature[6]**	**Synthetic**
		^{1}H (400 MHz)	**^{1}H (600MHz)**
Top unit			
C	C-2	4.53 (d, J = 8.0 Hz)[4]	4.67 (d, J = 7.8 Hz)[4]
	C-3	4.48 (dd, J = 8.0, 9.5 Hz)	4.61 (dd, J = 7.8, 10.2 Hz)
	C-4	4.32 (d, J = 9.5 Hz)[4]	4.45 (d, J = 10.2 Hz)[4]
A	C-5	—	—
	C-6	5.74 (d, J = 2.3 Hz)[3]	5.87 (d, J = 1.8 Hz)[3]
	C-7	—	—
	C-8	5.69 (d, J = 2.3 Hz)[3]	5.83 (d, J = 1.8 Hz)[3]
	C-9	—	—
	C-10	—	—
B	C-1’	—	—
	C-2’	6.99 (d, J = 1.9 Hz)[1]	7.12 (d, J = 1.8 Hz)[1]
	C-3’	—	—
	C-4’	—	—
	C-5’	6.69 (d, J = 8.1 Hz)[2]	6.82 (d, J = 8.4 Hz)[2]
	C-6’	6.77 (dd, J = 1.9, 8.1 Hz)[a]	6.89 (dd, J = 1.8, 8.4 Hz)[a]
Bottom Unit			
F	C-2	4.83 (brs)	4.97 (brs)
	C-3	4.16–4.18 (m)	4.26 (brm)
	C-4	2.83 (dd, J = 4.3, 16.8) 2.72 (dd, J = 1.5, 16.8)	2.96 (dd, J = 4.8, 16.8 Hz) 2.87 (dd, J = 1.2, 16.8 Hz)
D	C-5	—	—
	C-6	5.85 (s)	5.99 (s)
	C-7	—	—
	C-8	—	—
	C-9	—	—
	C-10	—	—
E	C-1’	—	—
	C-2’	6.89 (d, J = 1.9 Hz)[1]	7.02 (d, J = 1.8 Hz)[1]
	C-3’	—	—
	C-4’	—	—
	C-5’	6.68 (d, J = 8.1 Hz)[2]	6.80 (d, J = 8.4 Hz)[2]
	C-6’	6.77 (dd, J = 1.9, 8.1 Hz)[a]	6.89 (dd, J = 1.8, 8.4 Hz)[a]

Minor rotamer			
Ring	**Carbon number**	**Literature[6]**	**Synthetic**
		^{1}H (400 MHz)	**^{1}H (600MHz)**
Top unit			
C	C-2	4.22 (d, *J* = 6.1 Hz)	4.34–4.35 (m)[a]
	C-3	4.36 (dd, *J* = 2.2, 6.1 Hz)	4.50 (dd, *J* = 1.2, 6.0 Hz)
	C-4	4.21 (d, *J* = 2.2 Hz)	4.34–4.35 (m)[a]
A	C-5	—	—
	C-6	5.84 (d, *J* = 2.5 Hz)[4]	5.97 (d, *J* = 1.8 Hz)[4]
	C-7	—	—
	C-8	5.79 (d, *J* = 2.5 Hz)[4]	5.93 (d, *J* = 1.8 Hz)[4]
	C-9	—	—
	C-10	—	—
B	C-1’	—	—
	C-2’	6.59 (d, *J* = 1.9 Hz)[2]	6.72 (d, *J* = 1.8 Hz)[2]
	C-3’	—	—
	C-4’	—	—
	C-5’	6.62 (d, *J* = 8.0 Hz)[1]	6.75 (d, *J* = 7.8 Hz)[1]
	C-6’	6.35 (dd, *J* = 1.9, 8.0 Hz)[3]	6.49 (dd, *J* = 1.8, 7.8 Hz)[3]
Bottom Unit			
F	C-2	4.71 (brs)	4.84 (brs)
	C-3	3.95–3.85 (m)	4.09 (brm)
	C-4	2.85–2.70 (m) 2.60 (dd, *J* = 2.2, 17.3)	2.91 (dd, *J* = 5.4, 16.8 Hz) 2.73 (dd, *J* = 2.4, 16.8 Hz)
D	C-5	—	—
	C-6	6.00 (s)	6.13 (s)
	C-7	—	—
	C-8	—	—
	C-9	—	—
	C-10	—	—
E	C-1’	—	—
	C-2’	6.58 (d, *J* = 1.9 Hz)[2]	6.71 (d, *J* = 1.8 Hz)[2]
	C-3’	—	—
	C-4’	—	—
	C-5’	6.51 (d, *J* = 8.0 Hz)[1]	6.64 (d, *J* = 7.8 Hz)[1]
	C-6’	6.31 (dd, *J* = 1.9, 8.0 Hz)[3]	6.45 (dd, *J* = 1.8, 7.8 Hz)[3]

Note: a) Number *1*,*2*,*3* and *4* in each column may be interchanged. b) Symbol *a* in each column represents overlapped signals.

References:

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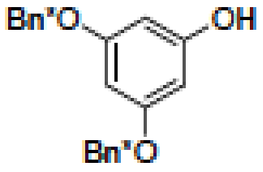
6. A. Saito, N. Nakajima, A. Tanaka and M. Ubukata, *Heterocycles*, 2003, **61**, 287–298.

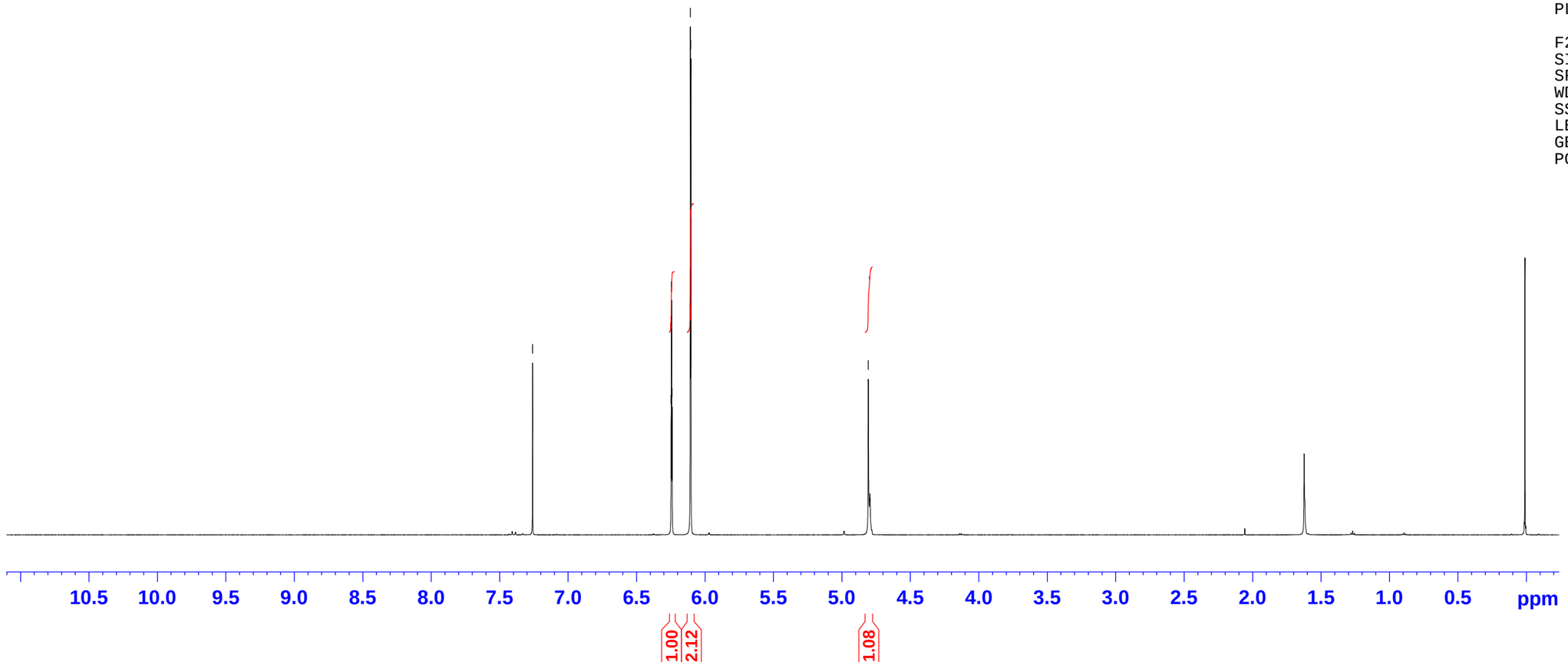
^{1}H NMR of SI-3 (600 MHz $CDCl_3$)



7.260

6.248
6.244
6.241
6.107
6.104

4.808

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Current Data Parameters
NAME                  VB-BnPh
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PROCNO                      1

F2 - Acquisition Parameters
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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              600.1300144 MHz
WDW                           EM
SSB          0
LB                      0.30 Hz
GB           0
PC                         1.00
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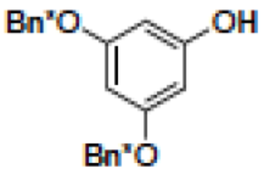
^{13}C NMR of SI-3 (150 MHz, $CDCl_3$)

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Current Data Parameters
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PROCNO                      1

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Date_               20210615
Time                    0.56
INSTRUM                spect
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PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
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                150.9027843 MHz
WDW                         EM
SSB           0
LB                     1.00 Hz
GB            0
PC                     1.40
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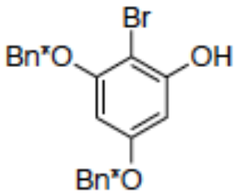
^{1}H NMR of 5 (600 MHz, $CDCl_3$)

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EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_               20210614
Time                   13.16
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              600.1300149 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
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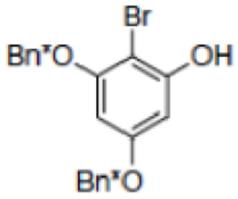
^{13}C NMR of 5 (150 MHz, $CDCl_3$)

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Current Data Parameters
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EXPNO                     41
PROCNO                     1

F2 - Acquisition Parameters
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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                      298.2 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 ========
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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                150.9027825 MHz
WDW                         EM
SSB           0
LB                       1.00 Hz
GB            0
PC                       1.40
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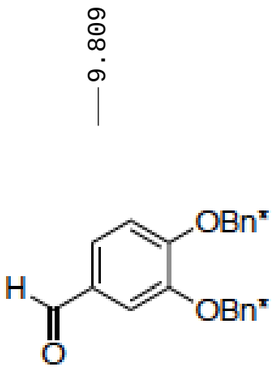
^{1}H NMR of SI-5 (600 MHz, $CDCl_3$)

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Current Data Parameters
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PROCNO                 1

F2 - Acquisition Parameters
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INSTRUM            spect
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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           600.1300144 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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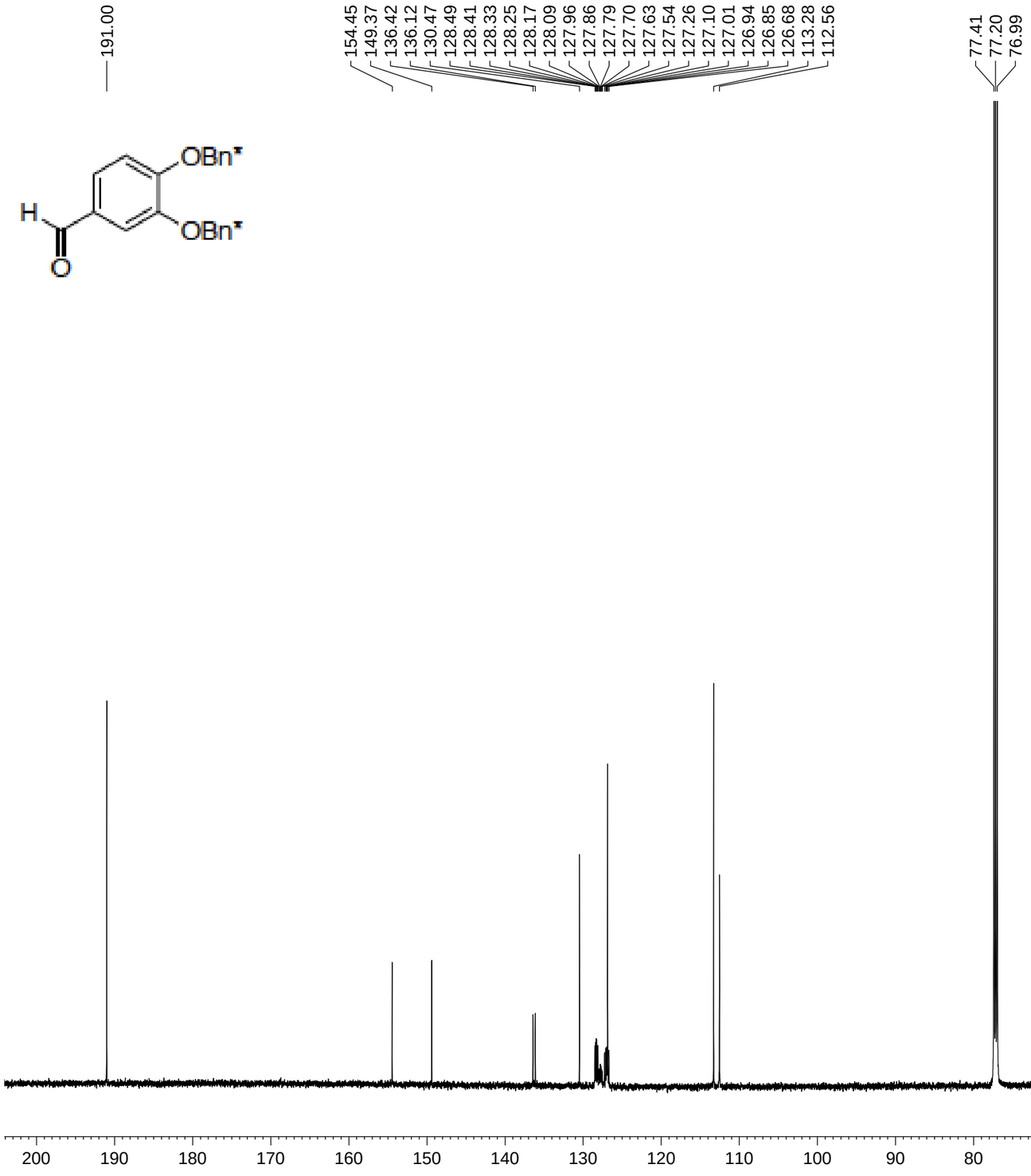
^{13}C NMR of SI-5 (150 MHz, $CDCl_3$)

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Current Data Parameters
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EXPNO                 11
PROCNO                 1

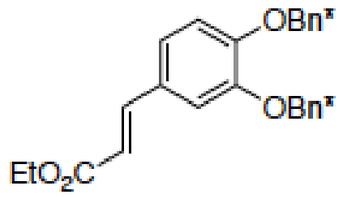
F2 - Acquisition Parameters
Date_           20210603
Time               22.53
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
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          150.9027831 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

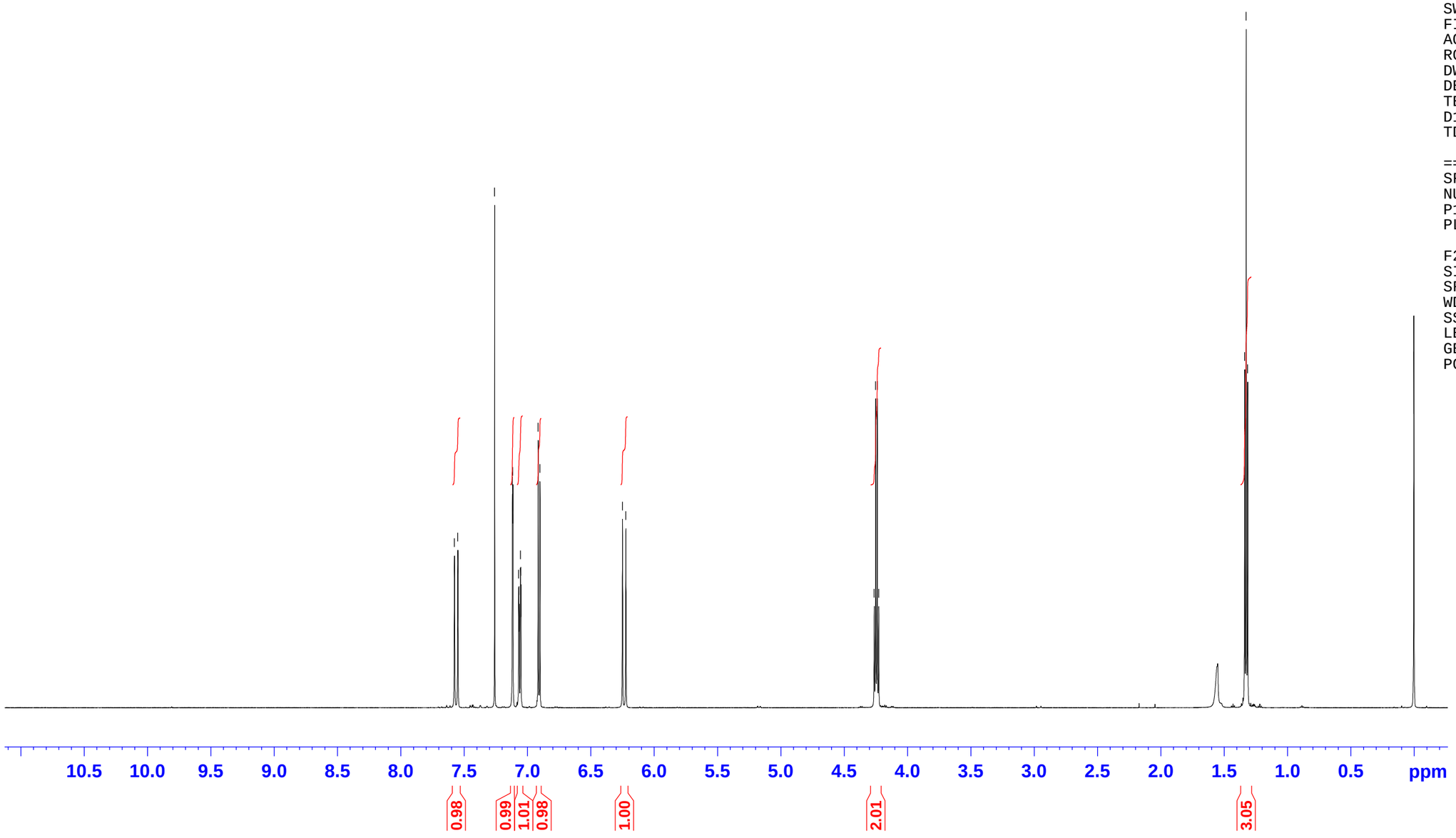
^{1}H NMR of SI-6 (600 MHz, $CDCl_3$)



7.577
7.550
7.260
7.119
7.116
7.070
7.066
7.056
7.053
6.916
6.902
6.250
6.224

4.263
4.251
4.239
4.228

1.339
1.327
1.315



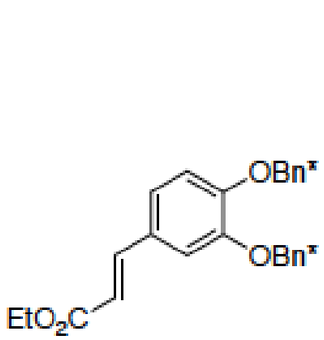

```
Current Data Parameters
NAME                  VB-ester
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20210603
Time                     15.47
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                 600.1300144 MHz
WDW                        EM
SSB             0
LB                       0.30 Hz
GB              0
PC                       1.00
```

^{13}C NMR of SI-6 (150 MHz, $CDCl_3$)




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

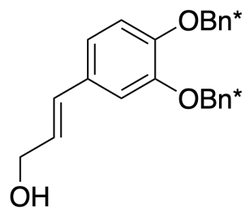
F2 - Acquisition Parameters
Date_           20210604
Time                0.41
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2000
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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          150.9027829 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H NMR of SI-7 (600 MHz, $CDCl_3$)

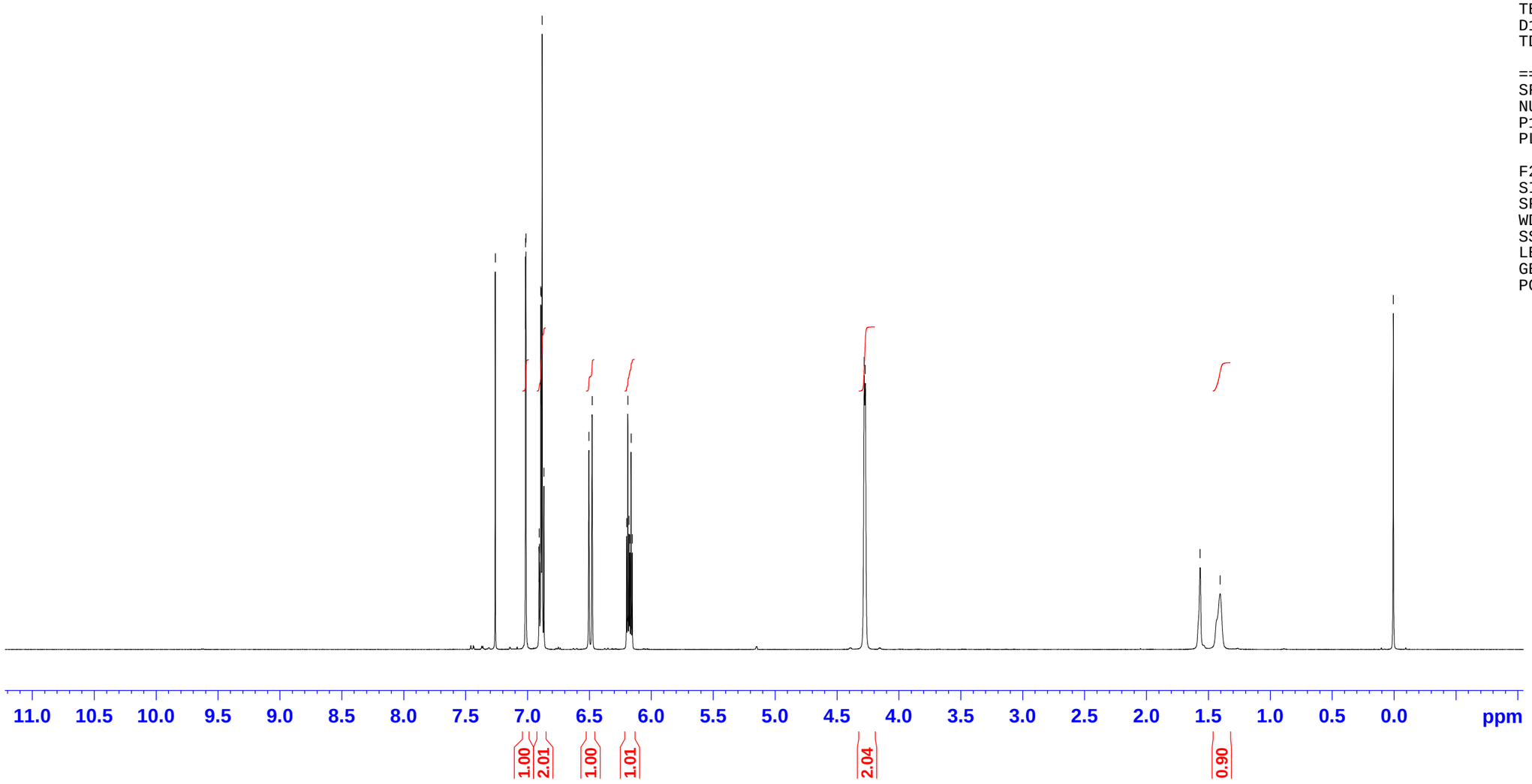


7.260
7.015
7.012
6.906
6.903
6.892
6.889
6.881
6.867
6.504
6.478
6.199
6.189
6.180
6.173
6.163
6.153

4.280
4.272

1.567
1.406

0.006



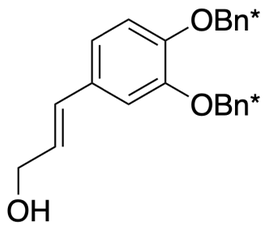

```
Current Data Parameters
NAME                  VB-845
EXPNO                     20
PROCNO                     1

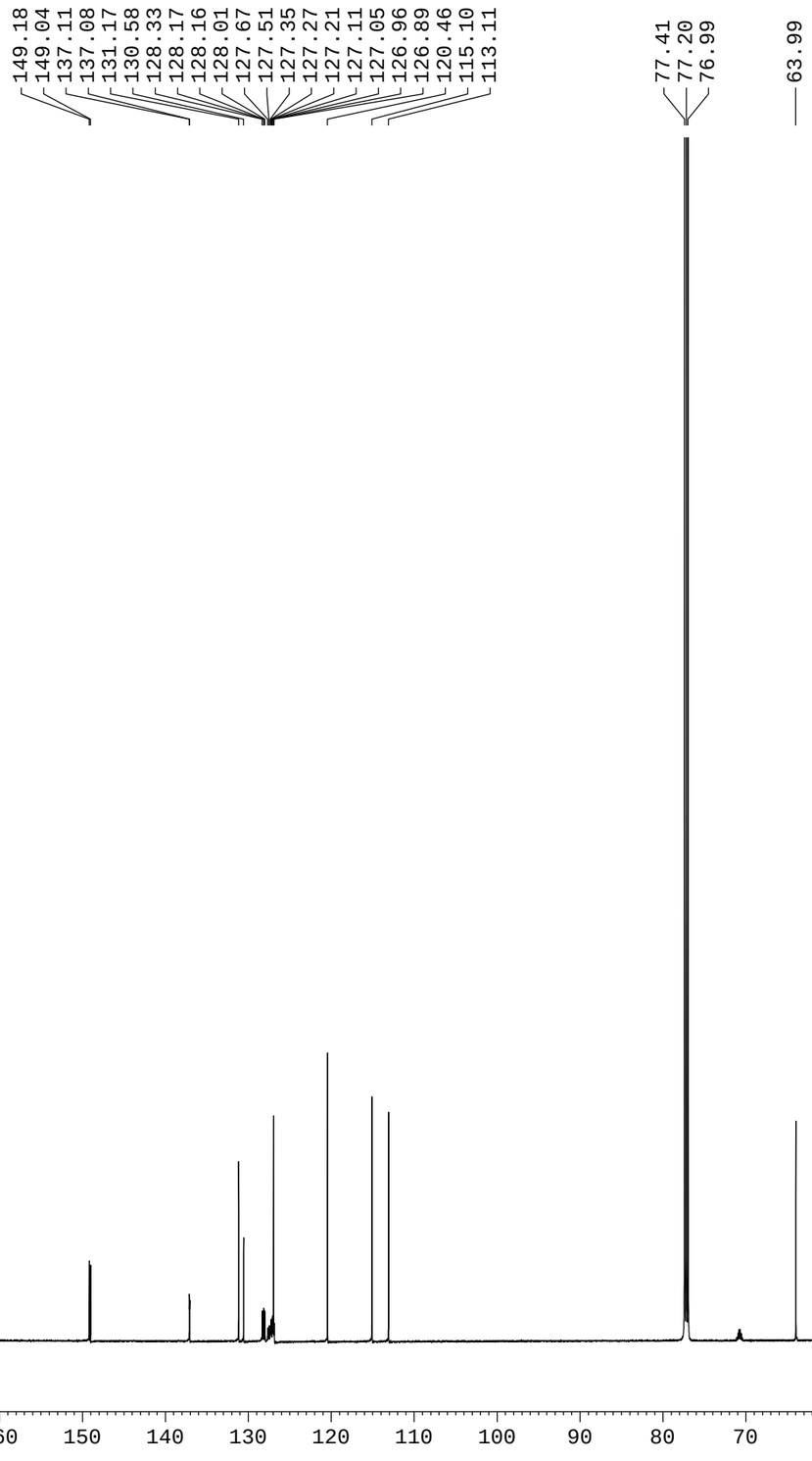
F2 - Acquisition Parameters
Date_               20210906
Time                   17.05
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               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              600.1300144 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

^{13}C NMR of SI-7 (150 MHz, $CDCl_3$)






```
Current Data Parameters
NAME                  VB-845
EXPNO                     21
PROCNO                     1

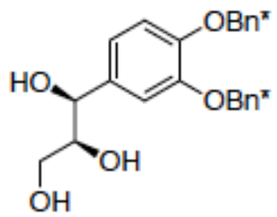
F2 - Acquisition Parameters
Date_               20210907
Time                    1.30
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       4200
DS                          4
SWH                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

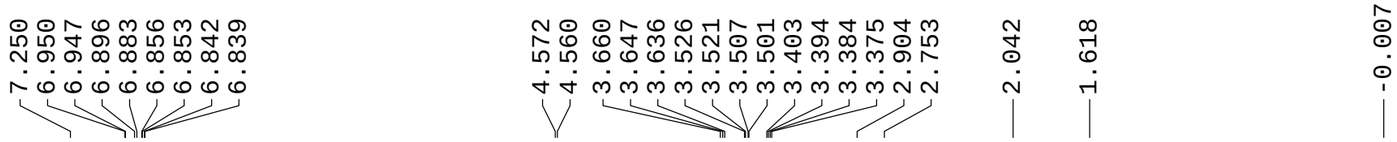
======== CHANNEL f1 ========
SFO1             150.9178981 MHz
NUC1                    13C
P1                      10.00 usec
PLW1              80.00000000 W

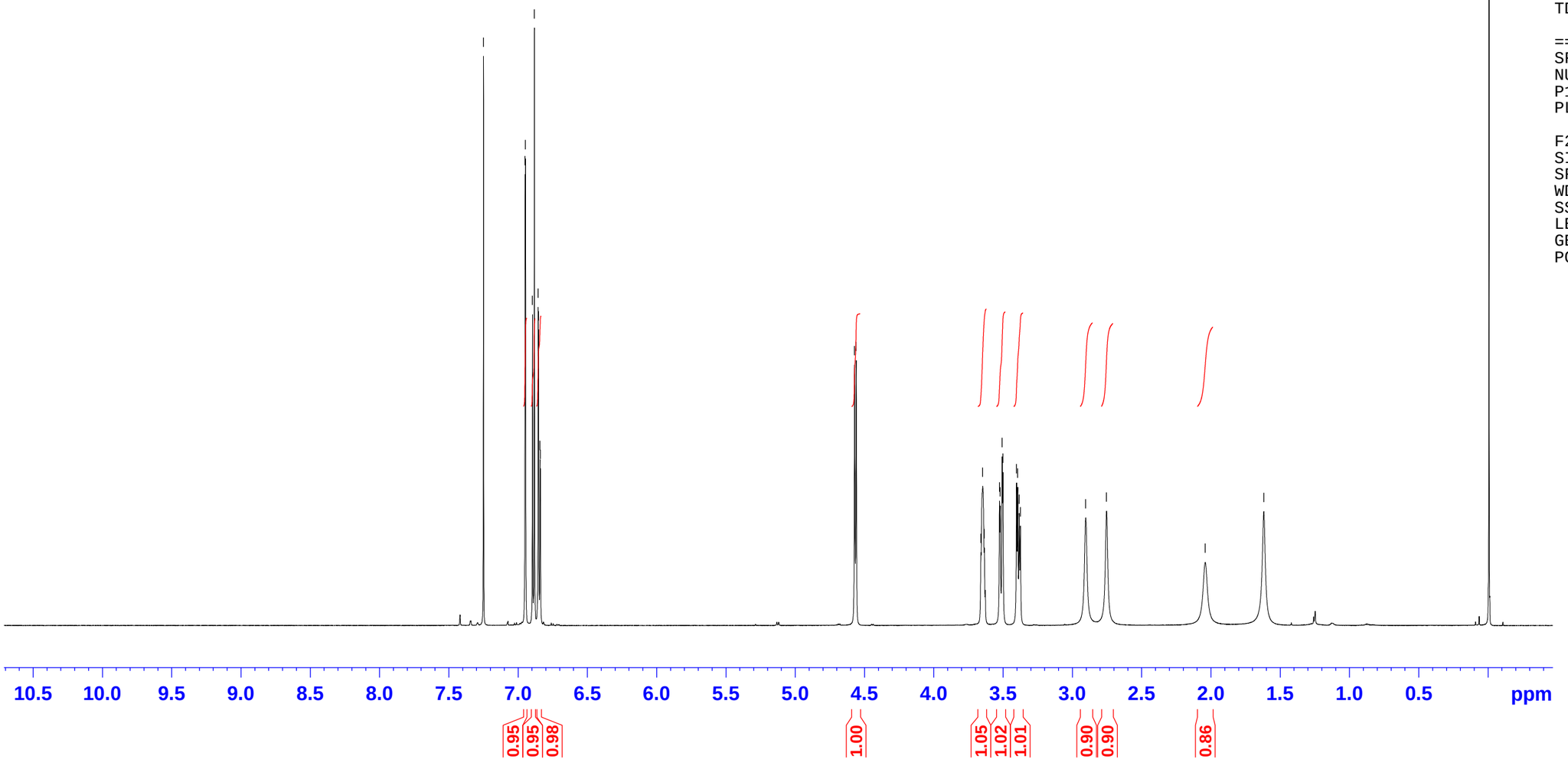
======== CHANNEL f2 ========
SFO2             600.1324005 MHz
NUC2                    1H
CPDPRG[2              waltz16
PCPD2                   70.00 usec
PLW2              13.43999958 W
PLW12              0.61714000 W
PLW13              0.31042001 W

F2 - Processing parameters
SI                      32768
SF               150.9027839 MHz
WDW                        EM
SSB           0
LB                      1.00 Hz
GB            0
PC                      1.40
```

^{1}H NMR of SI-8 (600 MHz, $CDCl_3$)







BRUKER

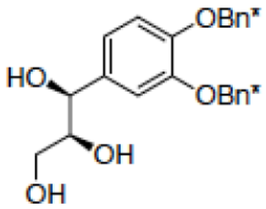
```
Current Data Parameters
NAME                  VB-814
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210527
Time                  19.53
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           600.1300205 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

^{13}C NMR of SI-8 (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME                  VB-814
EXPNO                     21
PROCNO                     1

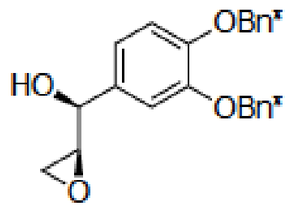
F2 - Acquisition Parameters
Date_               20210527
Time                   23.27
INSTRUM                spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1700
DS                         4
SWH               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

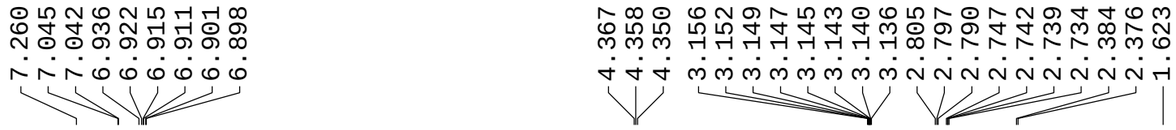
======== CHANNEL f1 ========
SFO1            150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            80.00000000 W

======== 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              150.9027843 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

^{1}H NMR of 6 (600 MHz, $CDCl_3$)





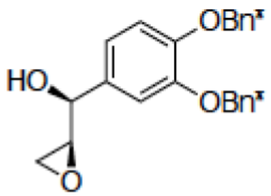

```
Current Data Parameters
NAME                  VB-818
EXPNO                     20
PROCNO                     1

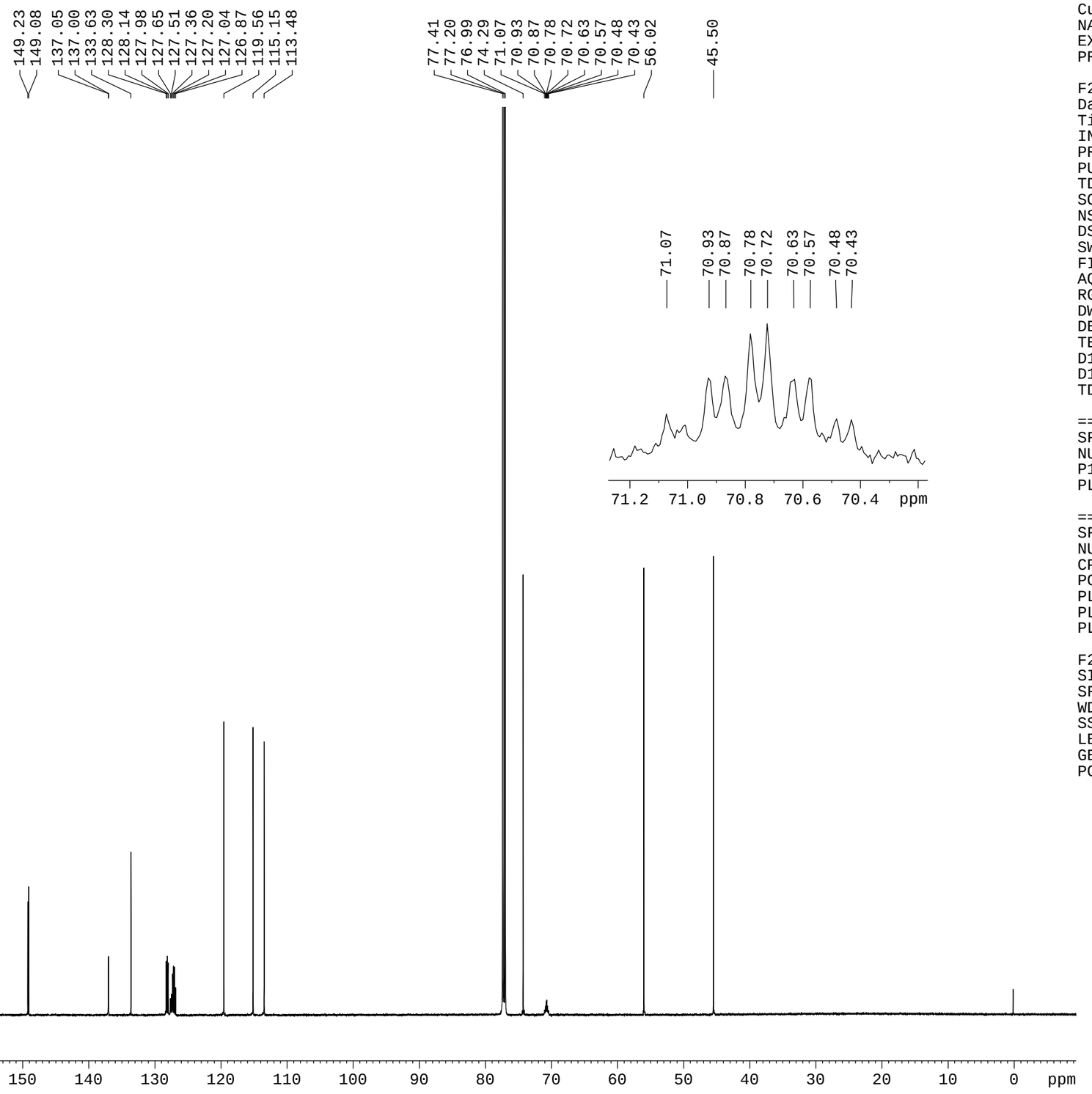
F2 - Acquisition Parameters
Date_               20210531
Time                   16.50
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES              0.183399 Hz
AQ                 2.7262976 sec
RG                      17.5
DW                    41.600 usec
DE                    10.00 usec
TE                    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 6 (150 MHz, $CDCl_3$)






```
Current Data Parameters
NAME                  VB-818
EXPNO                     21
PROCNO                     1

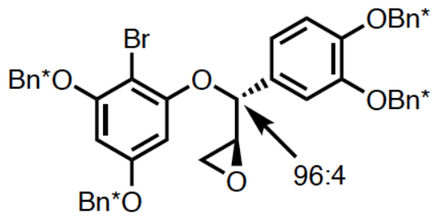
F2 - Acquisition Parameters
Date_              20210531
Time                  22.53
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              36057.691 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

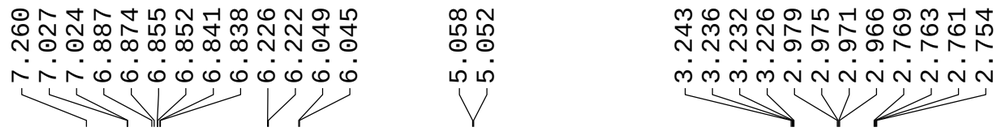
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           80.00000000 W

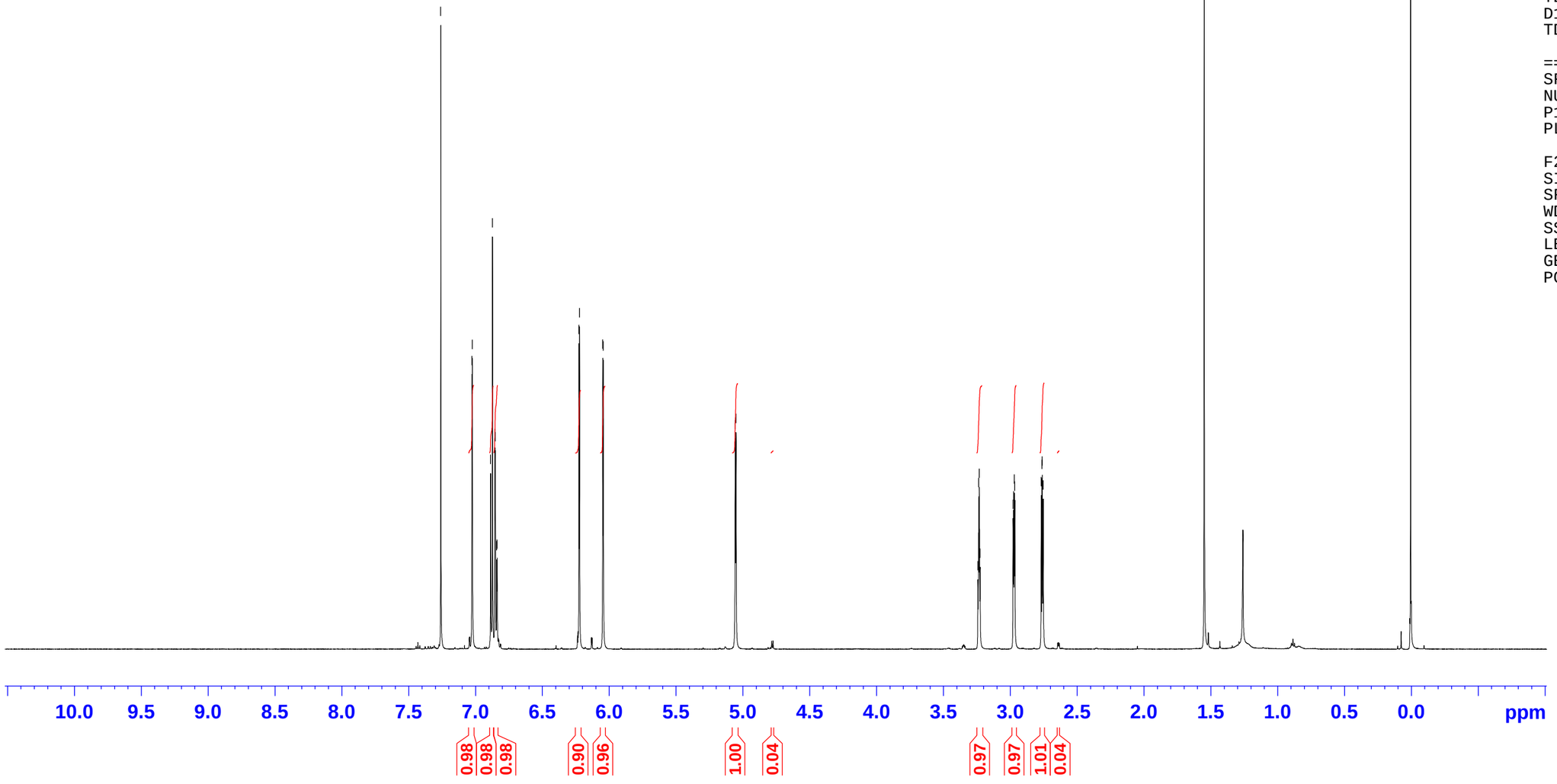
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                    32768
SF             150.9027873 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

^{1}H NMR of 7 (600 MHz, $CDCl_3$)







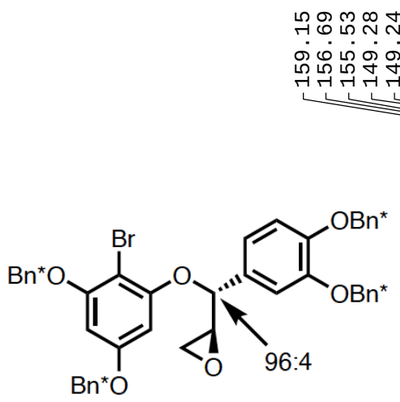

```
Current Data Parameters
NAME                  VB-670
EXPNO                     30
PROCNO                     1

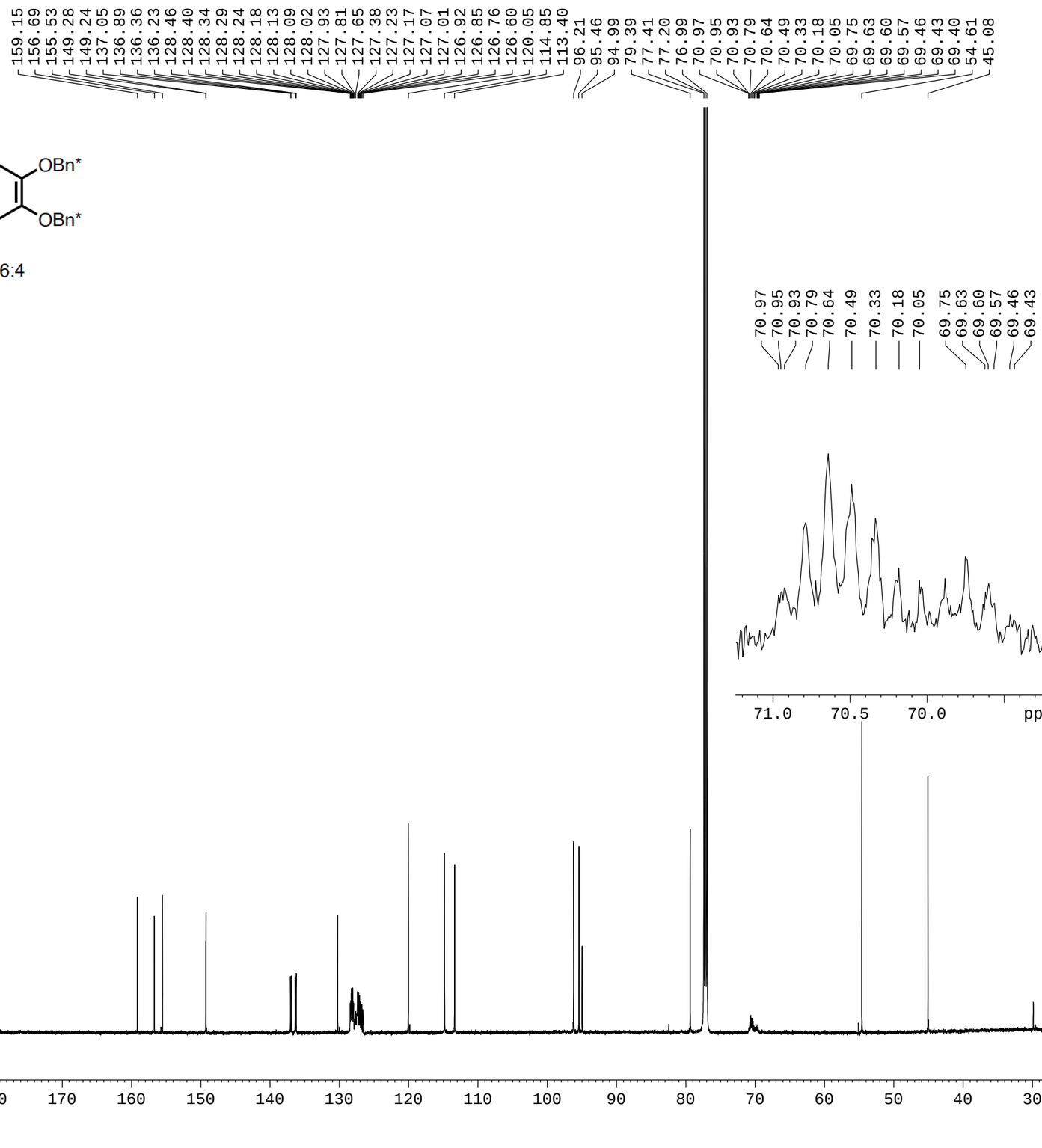
F2 - Acquisition Parameters
Date_               20200929
Time                   18.53
INSTRUM                spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                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              600.1300142 MHz
WDW                           EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

^{13}C NMR of 7 (150 MHz, $CDCl_3$)






```
Current Data Parameters
NAME                  VB-670
EXPNO                     31
PROCNO                     1

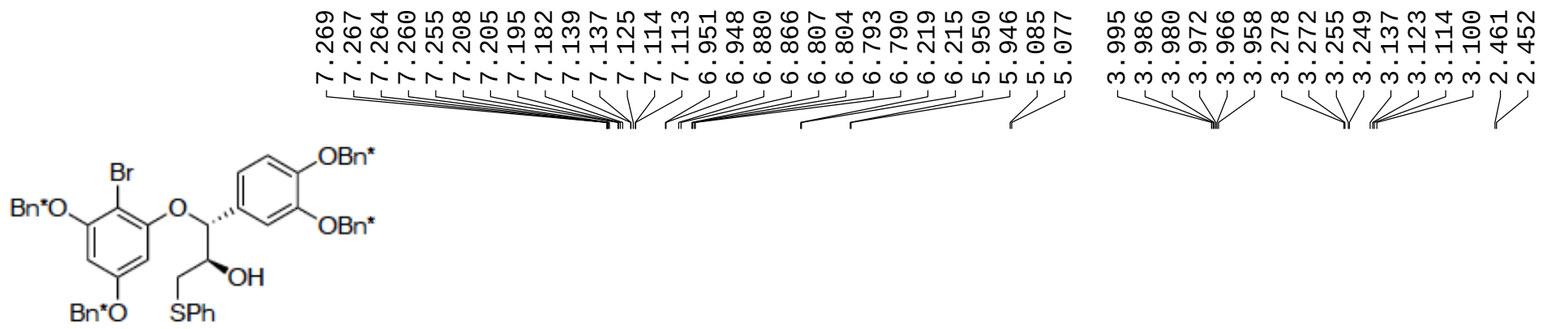
F2 - Acquisition Parameters
Date_              20200930
Time                   9.06
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     4800
DS                        4
SWH              36057.691 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

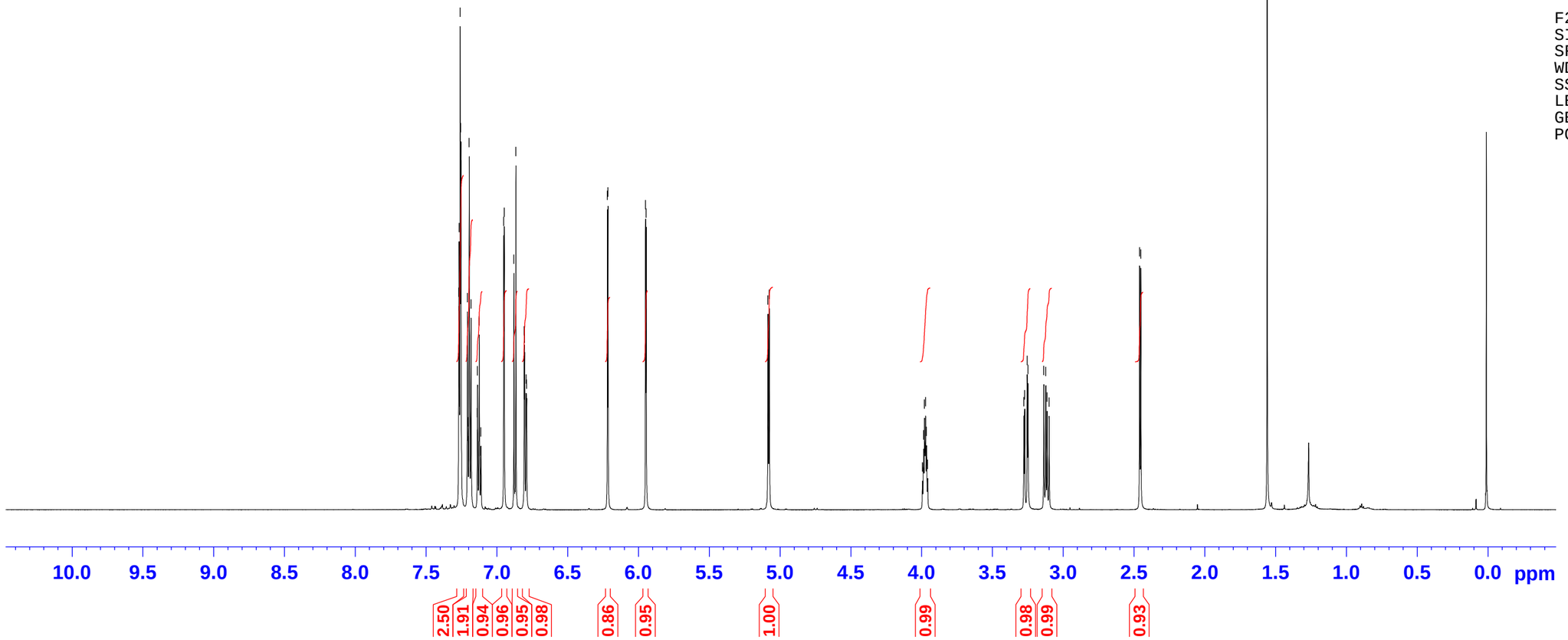
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           80.00000000 W

======== 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               150.9027831 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

^{1}H NMR of 8 (600 MHz, $CDCl_3$)





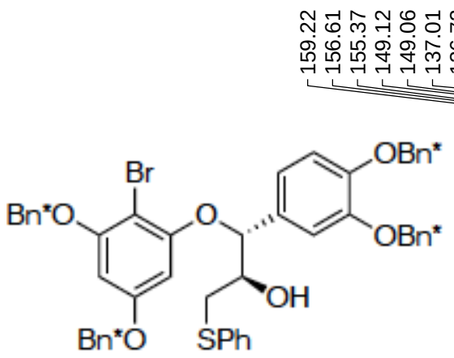

```
Current Data Parameters
NAME                  VB-671-2
EXPNO                       10
PROCNO                       1

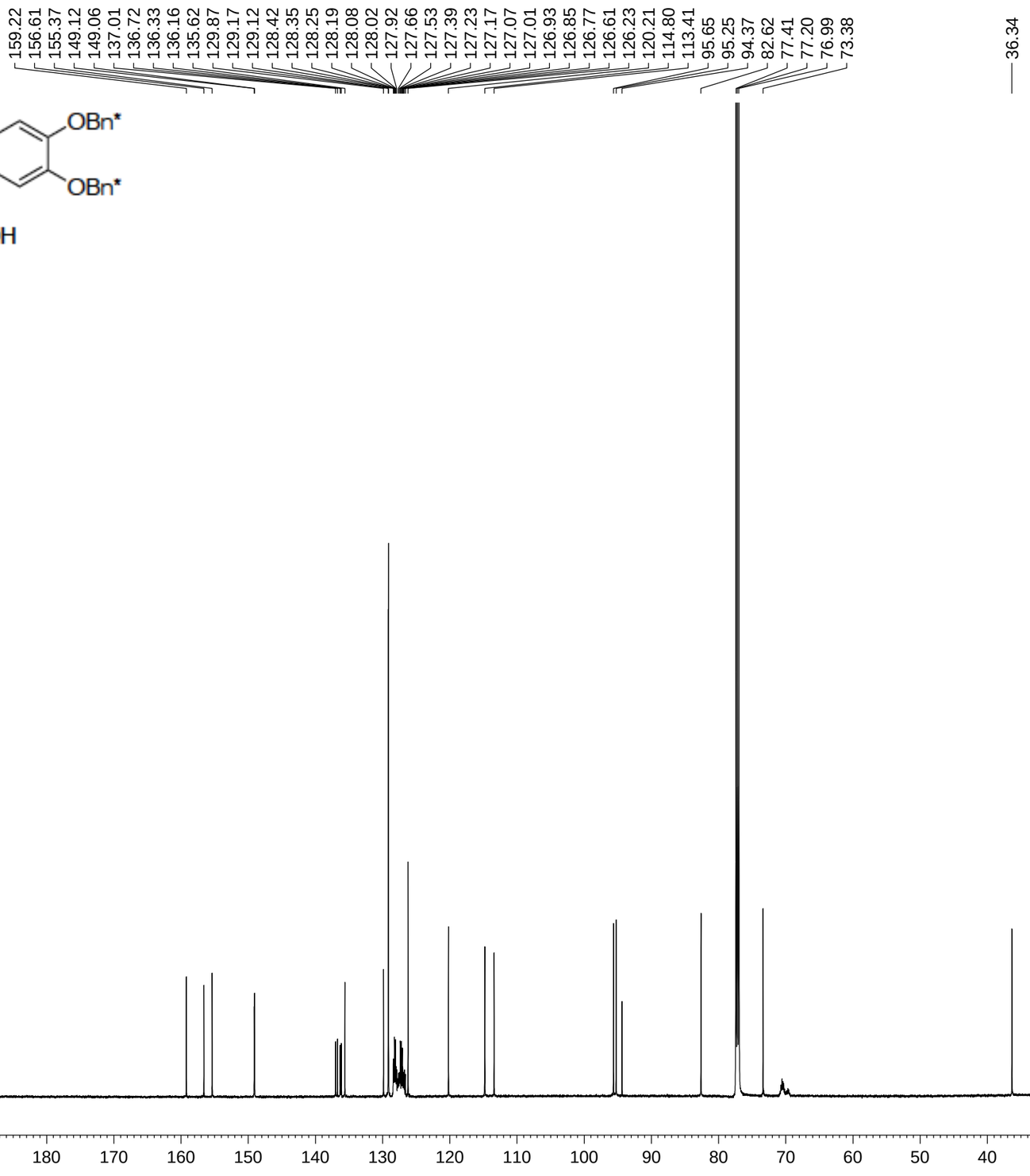
F2 - Acquisition Parameters
Date_                 20201001
Time                     11.04
INSTRUM                  spect
PROBHD   5 mm CPPBBO BB
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 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                  600.1300142 MHz
WDW                            EM
SSB              0
LB                       0.30 Hz
GB               0
PC                       1.00
```

^{13}C NMR of 8 (150 MHz, $CDCl_3$)






```
Current Data Parameters
NAME            VB-671-2
EXPNO                 11
PROCNO                 1

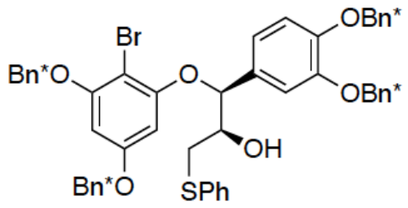
F2 - Acquisition Parameters
Date_           20201002
Time                3.10
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  5000
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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          150.9027854 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H NMR of 2-*epi*-8 (600 MHz, $CDCl_3$)



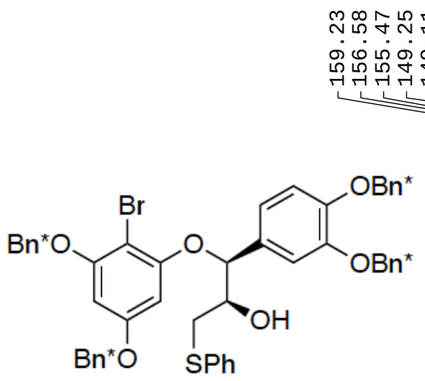

```
Current Data Parameters
NAME                  VB-890
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20211001
Time                  19.13
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                   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            600.1300154 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

^{13}C NMR of 2-*epi*-8 (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME                  VB-890
EXPNO                     31
PROCNO                     1

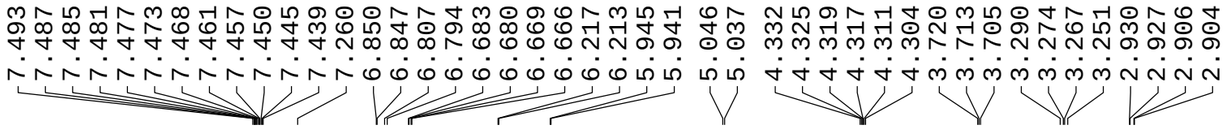
F2 - Acquisition Parameters
Date_              20211002
Time                   3.49
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     7000
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                   175.56
DW                  13.867 usec
DE                   18.00 usec
TE                   298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

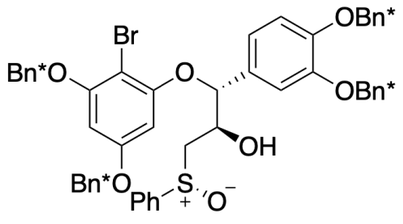
======== CHANNEL f1 ========
SFO1           150.9178981 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           80.00000000 W

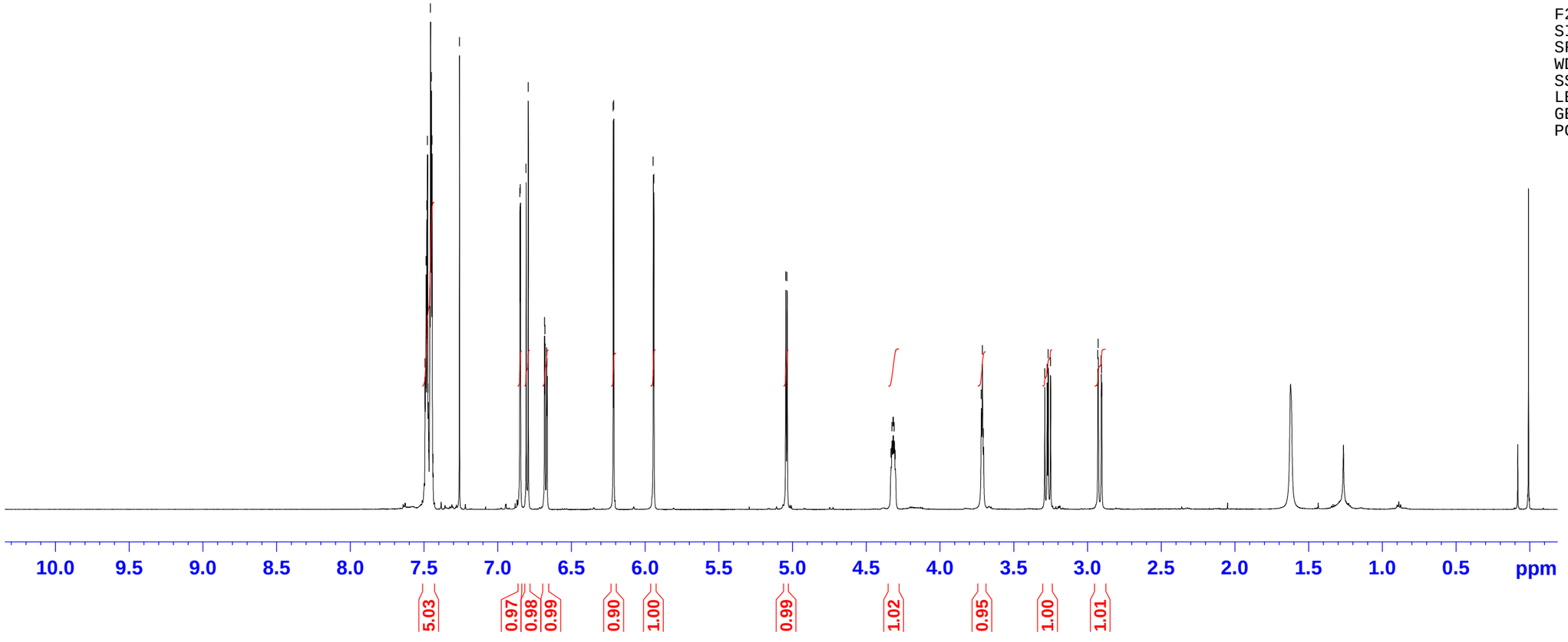
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

F2 - Processing parameters
SI                     32768
SF             150.9027825 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```

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







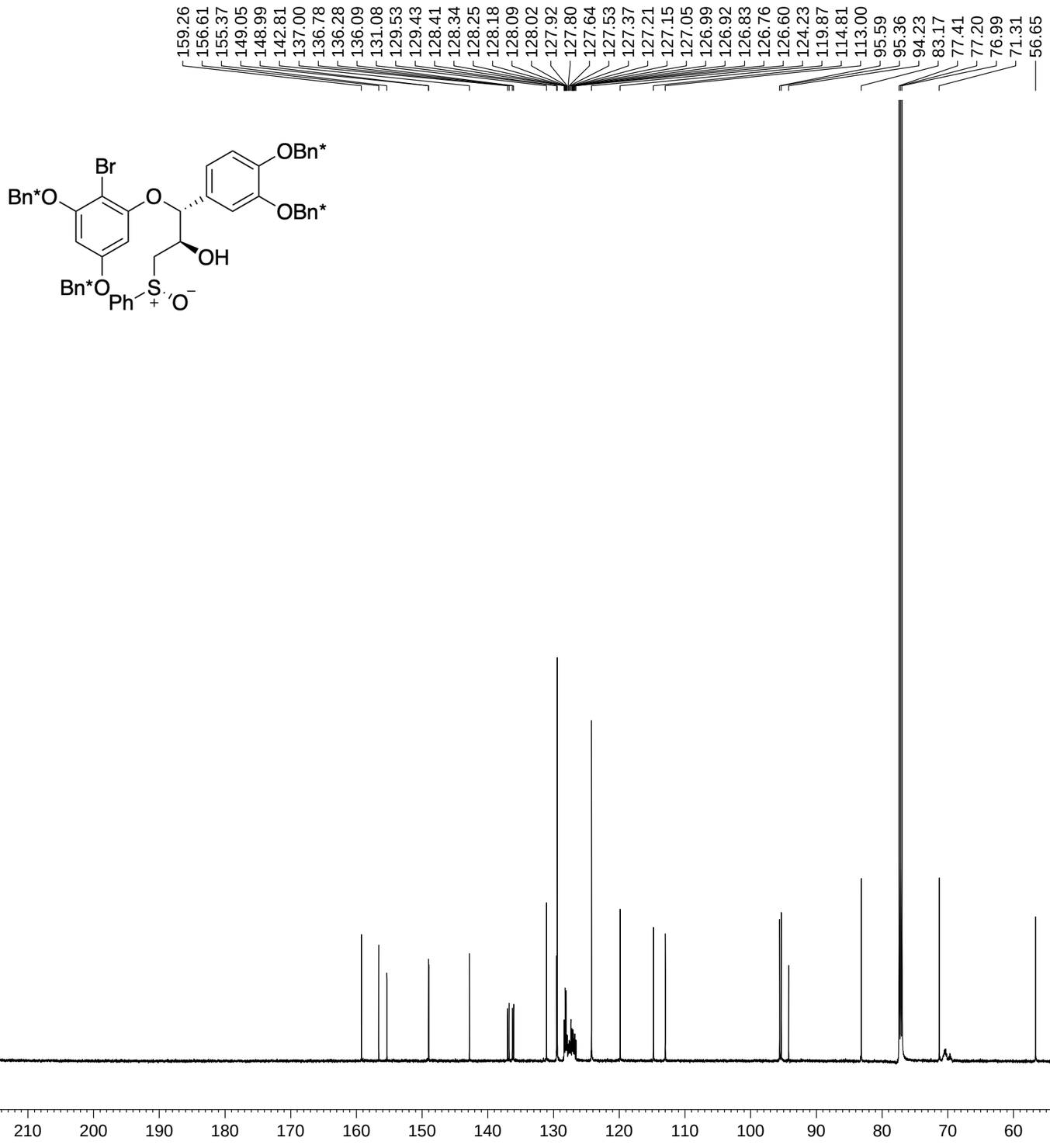

```
Current Data Parameters
NAME                  VB-824
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210610
Time                  16.44
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           600.1300144 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

^{13}C NMR of 9a (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME                  VB-824
EXPNO                     31
PROCNO                     1

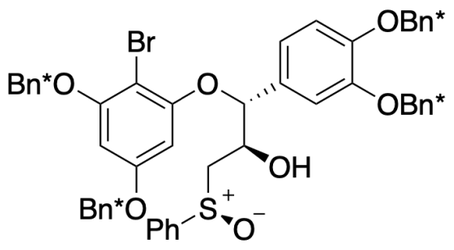
F2 - Acquisition Parameters
Date_              20210610
Time                  23.41
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2000
DS                        4
SWH              36057.691 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             150.9027860 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

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



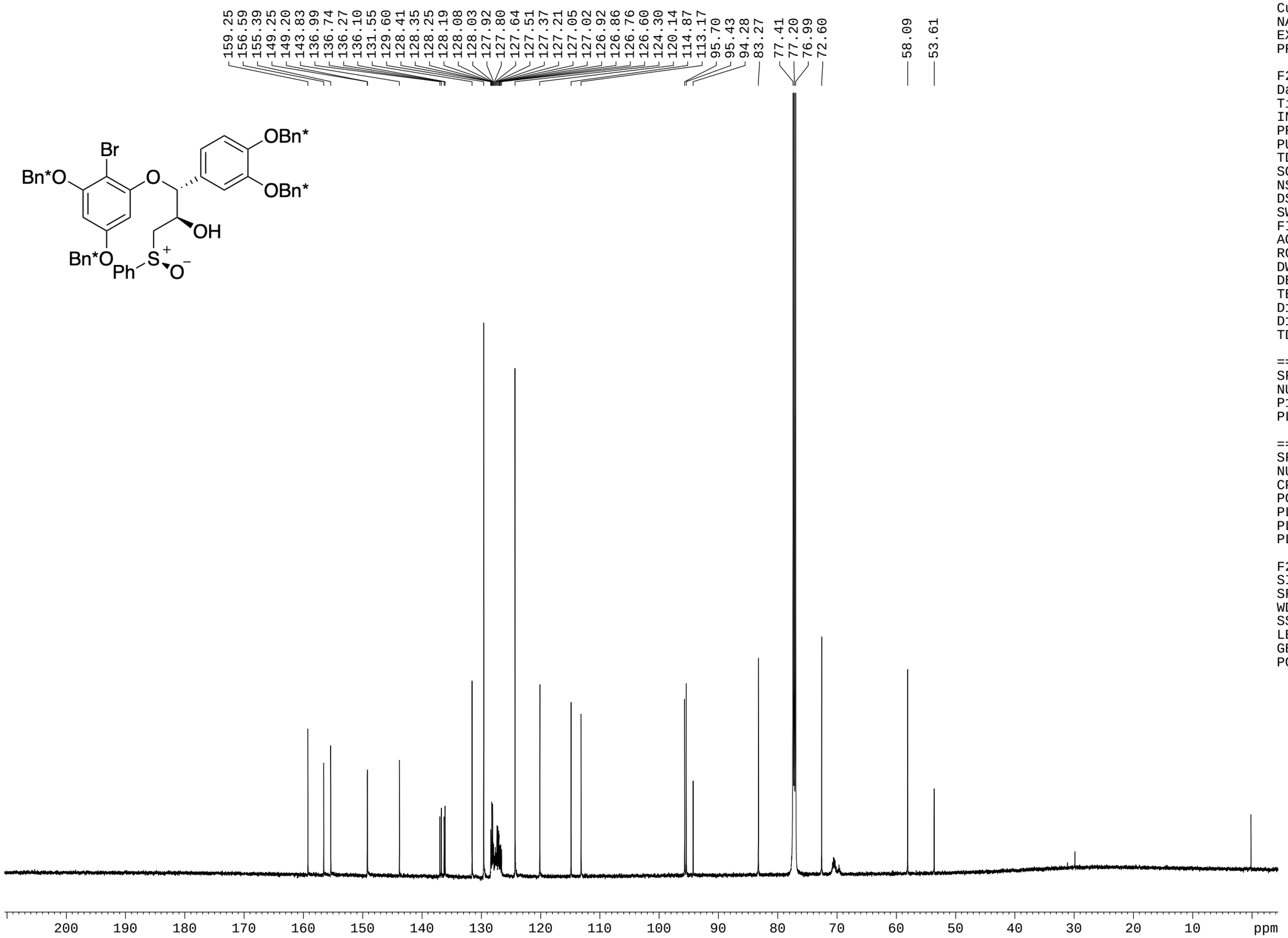

```
Current Data Parameters
NAME            VB-847-2
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210906
Time               19.06
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          600.1300147 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of 9b (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME            VB-847-2
EXPNO                 51
PROCNO                 1

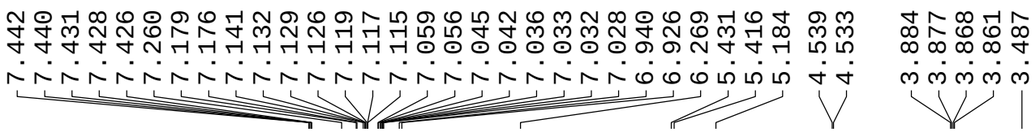
F2 - Acquisition Parameters
Date_           20210907
Time                6.21
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  5000
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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

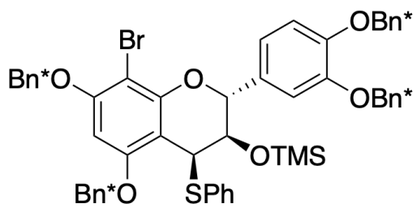
======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1                10.00 usec
PLW1        80.00000000 W

======== 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          150.9027843 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

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





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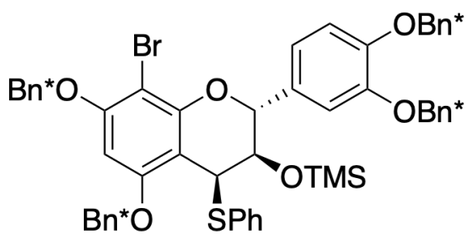
```
Current Data Parameters
NAME          VB-867-2A
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20210903
Time              18.49
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          600.1300144 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

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




```
Current Data Parameters
NAME          VB-867-2A
EXPNO                33
PROCNO                1

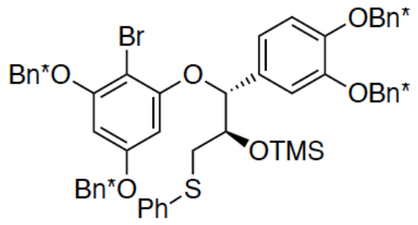
F2 - Acquisition Parameters
Date_          20210904
Time               8.34
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                12240
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            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          150.9026314 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

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



7.366 7.353 7.260 7.228 7.215 7.202 7.120 7.107 7.095 7.014 6.852 6.838 6.825 6.812 6.196 6.192 6.000 5.996 5.016 5.005 4.116 4.111 4.105 4.100 4.095 4.089 3.468 3.463 3.445 3.439 3.211 3.200 3.188 3.177 1.570 -0.176

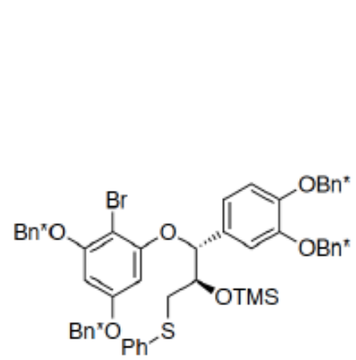

```
Current Data Parameters
NAME            VB-867-1
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210913
Time               21.55
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                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 12 (150 MHz, C_6D_6)




```
Current Data Parameters
NAME            VB-867-1
EXPNO                 71
PROCNO                 1

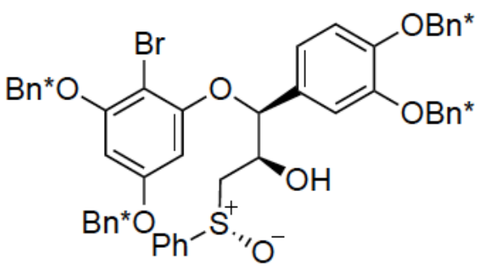
F2 - Acquisition Parameters
Date_           20220716
Time                2.12
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT              C6D6
NS                   5000
DS                      4
SWH           36057.691 Hz
FIDRES         0.550197 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          150.9027533 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

^{1}H NMR of 2-*epi*-9a (600 MHz, $CDCl_3$)



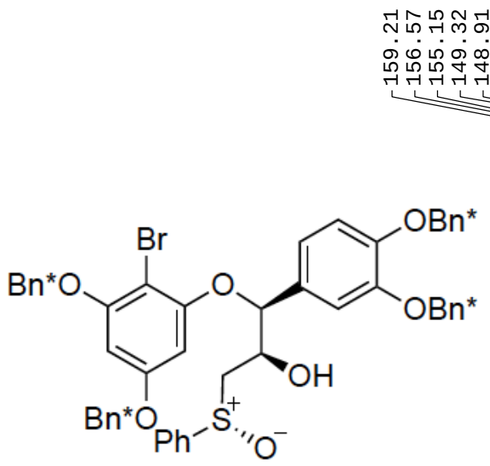

```
Current Data Parameters
NAME          VB-888-1A
EXPNO                10
PROCNO                1

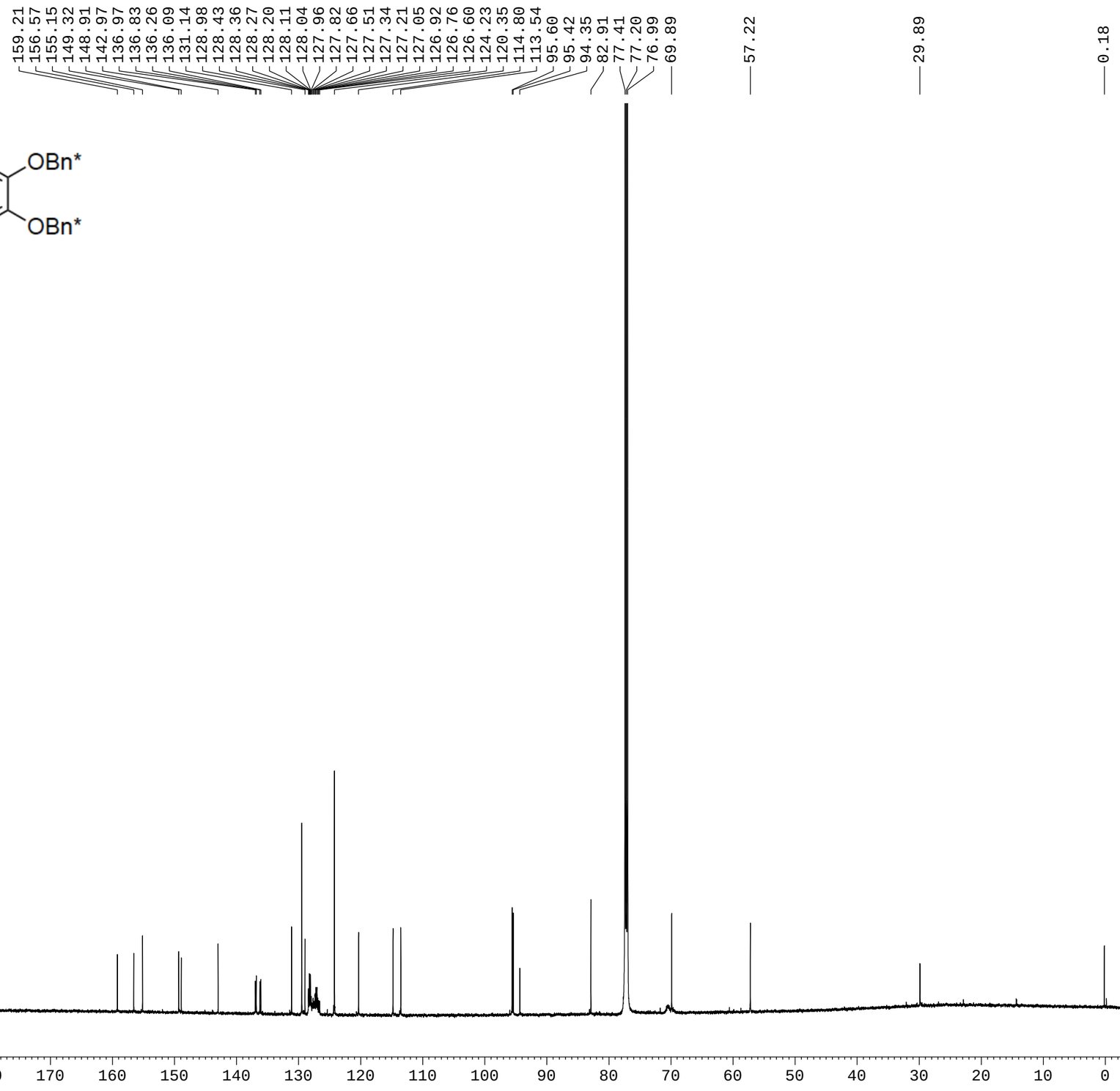
F2 - Acquisition Parameters
Date_          20211006
Time              15.38
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12019.230 Hz
FIDRES         0.183399 Hz
AQ             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          600.1300148 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{13}C NMR of 2-*epi*-9a (150 MHz, $CDCl_3$)






```
Current Data Parameters
NAME           VB-888-1A
EXPNO                 12
PROCNO                 1

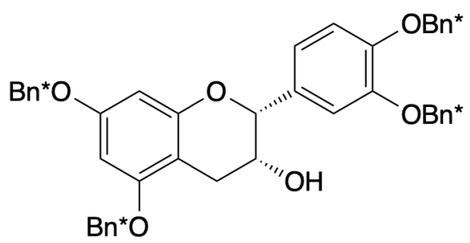
F2 - Acquisition Parameters
Date_           20211007
Time                5.03
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  8500
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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

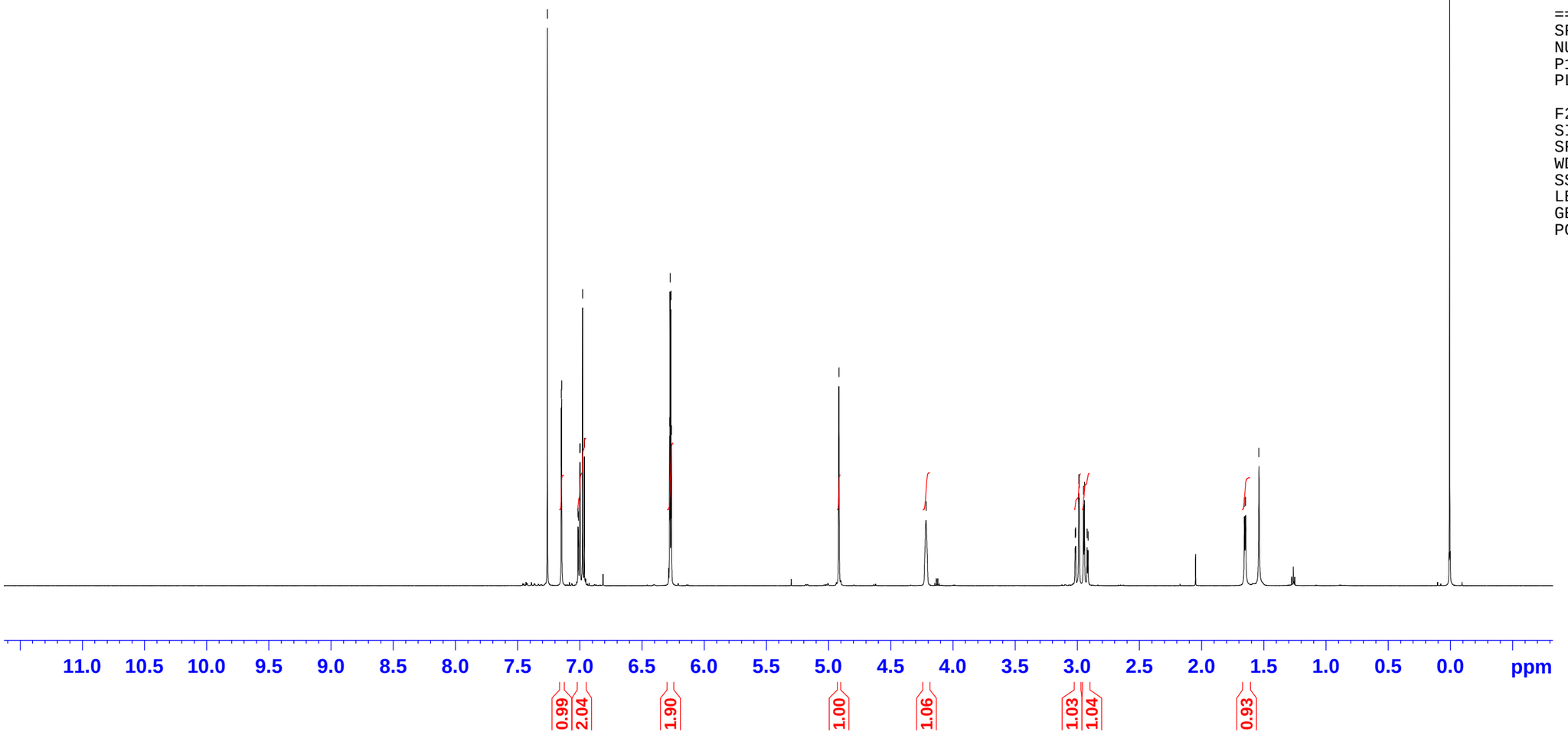
======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        13.43999958 W
PLW12        0.61714000 W
PLW13        0.31042001 W

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

^{1}H NMR of 15 (600 MHz, $CDCl_3$)



7.260 7.148 7.145 7.013 7.010 6.999 6.996 6.977 6.963 6.277 6.273 6.266 6.262 — 4.916 — 4.215 — 3.016 3.013 2.987 2.984 2.949 2.942 2.920 2.913 — 1.656 1.647 1.539



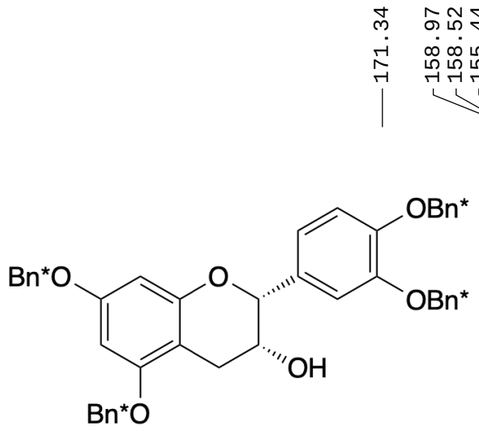

```
Current Data Parameters
NAME            VB-Bn4EC
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211221
Time               18.12
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          600.1300144 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

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




```
Current Data Parameters
NAME                  VB-Bn4EC
EXPNO                       21
PROCNO                       1

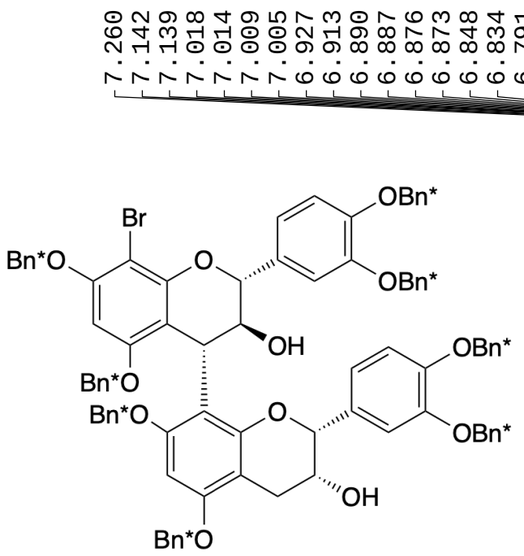
F2 - Acquisition Parameters
Date_                 20211222
Time                     22.54
INSTRUM                  spect
PROBHD   5 mm CPPBBO BB
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                 36057.691 Hz
FIDRES               0.550197 Hz
AQ                   0.9087659 sec
RG                      175.56
DW                      13.867 usec
DE                      18.00 usec
TE                      298.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                      10.00 usec
PLW1               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 16 (600 MHz, $CDCl_3$)



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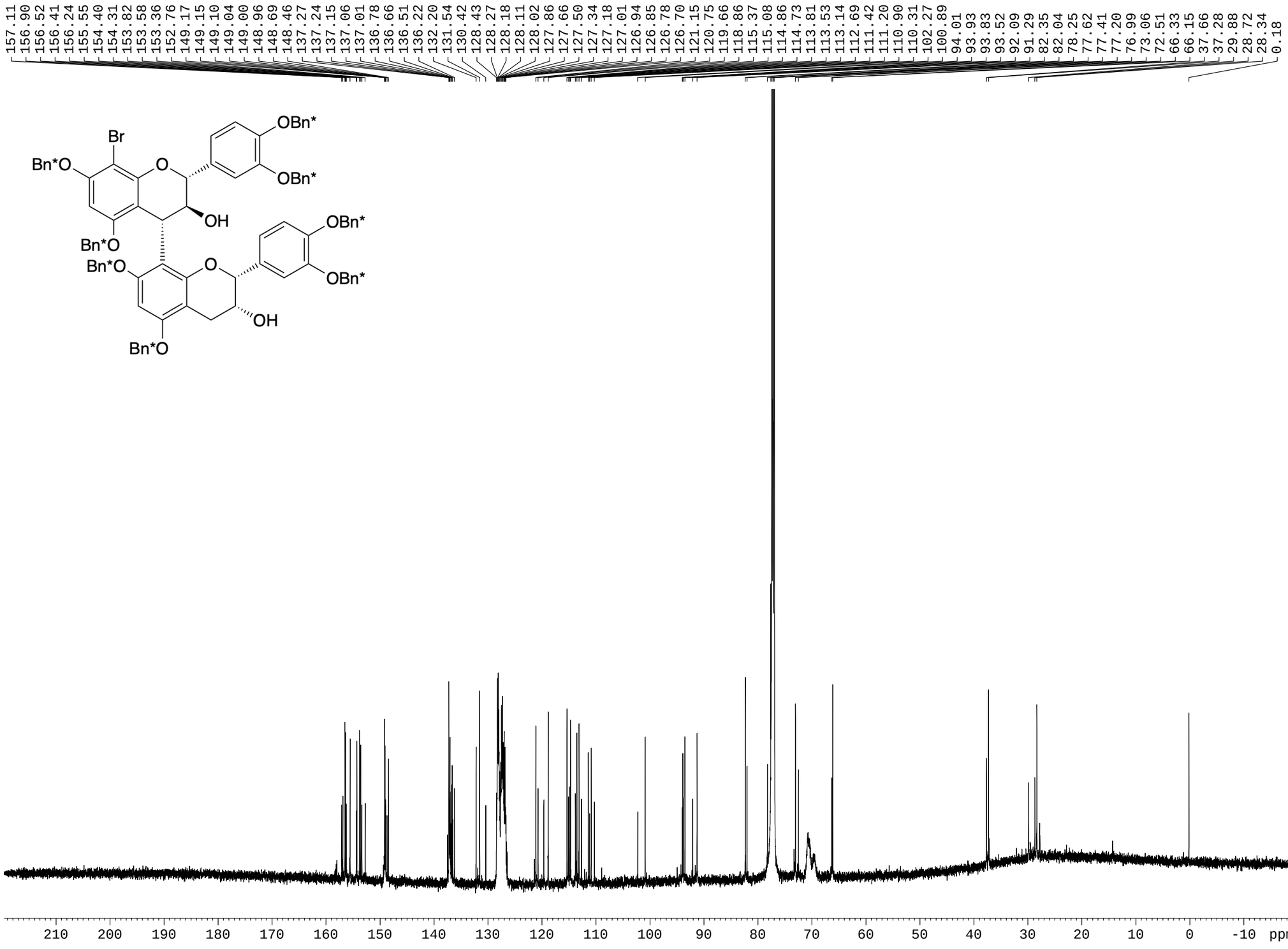
```
Current Data Parameters
NAME          VB-861-2A1
EXPNO                 23
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211221
Time               12.27
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   100
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           600.1300145 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of 16 (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME          VB-CA-EC-2
EXPNO                 21
PROCNO                 1

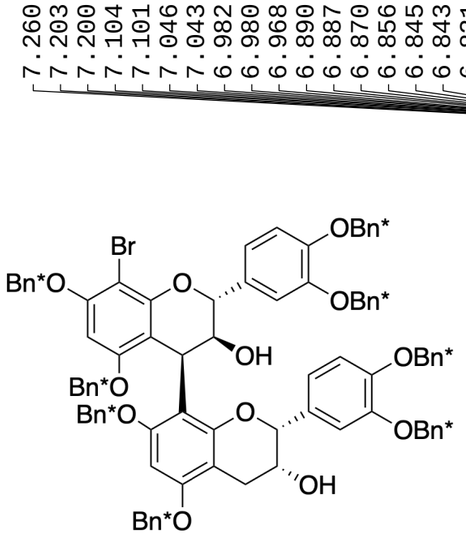
F2 - Acquisition Parameters
Date_           20210908
Time                4.49
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  7000
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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          150.9027847 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{1}H NMR of 4-*epi*-16 (600 MHz, $CDCl_3$)



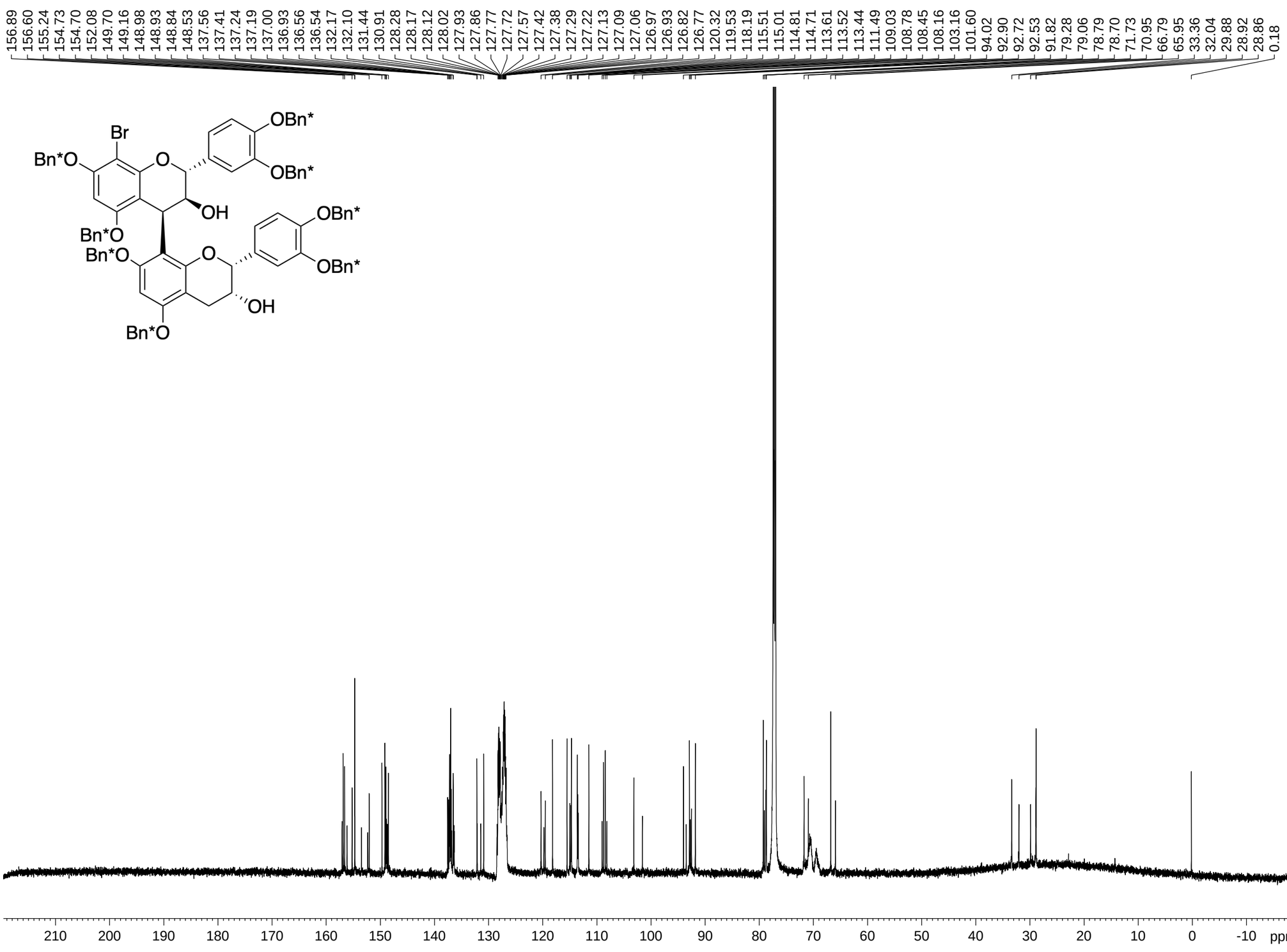

```
Current Data Parameters
NAME            VB-861-1
EXPNO                 22
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210728
Time               15.28
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   100
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          600.1300150 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of 4-*epi*-16 (150 MHz, $CDCl_3$)




```
Current Data Parameters
NAME            VB-861-1
EXPNO                 23
PROCNO                 1

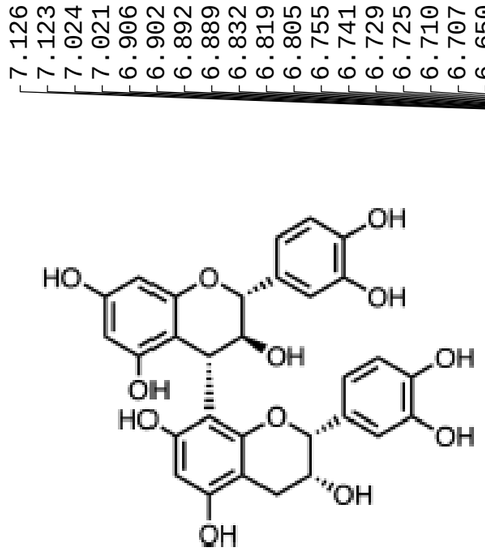
F2 - Acquisition Parameters
Date_           20210729
Time                7.06
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  8500
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 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 2 (600 MHz, $CDCl_3$)



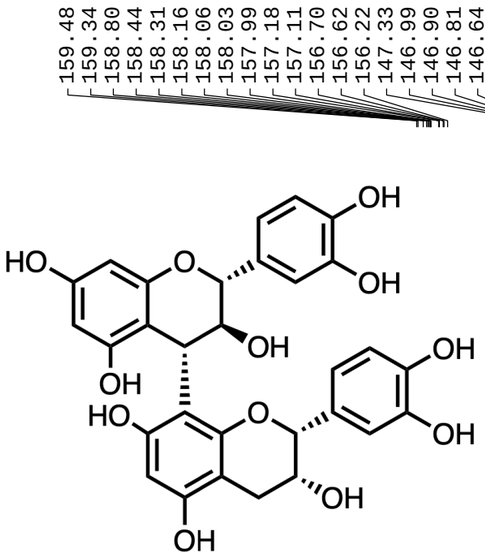

```
Current Data Parameters
NAME                  VB-865
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210803
Time                  11.55
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                      100
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            600.1299933 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

^{13}C NMR of 2 (150 MHz, CD_3OD)




```
Current Data Parameters
NAME                 VB-865
EXPNO                    13
PROCNO                    1

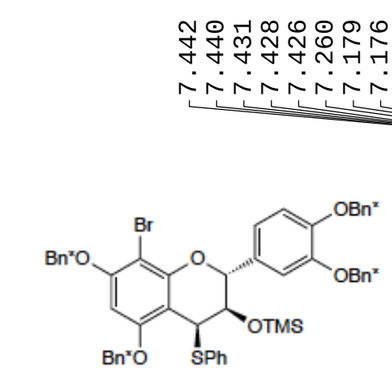
F2 - Acquisition Parameters
Date_              20210804
Time                   4.15
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                     7500
DS                        4
SWH              36057.691 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

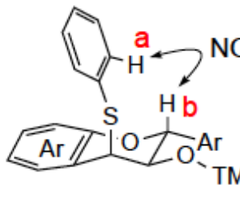
======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                 70.00 usec
PLW2           13.43999958 W
PLW12           0.61714000 W
PLW13           0.31042001 W

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

NOE of 11



Bn* = d_7-benzyl



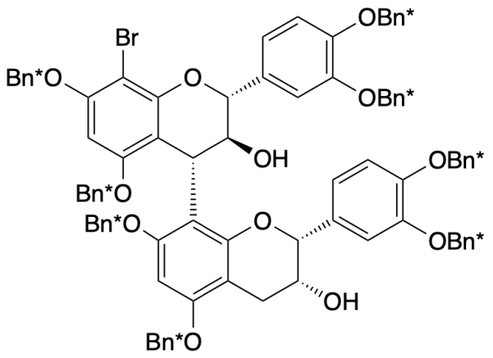

```
Current Data Parameters
NAME          VB-867-2A
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20210903
Time              18.49
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          600.1300144 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

COSY of 16 (600 MHz, $CDCl_3$)




```
Current Data Parameters
NAME          VB-861-2A1
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211221
Time              12.02
INSTRUM           spect
PROBHD   5 mm CPPBBO BB
PULPROG      cosygpppqf
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                    8
SWH            5154.639 Hz
FIDRES         2.516914 Hz
AQ             0.1986560 sec
RG                18.96
DW                97.000 usec
DE                10.00 usec
TE                298.0 K
D0            0.00000300 sec
D1            1.92913902 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00019400 sec

======== CHANNEL f1 ========
SFO1         600.1322140 MHz
NUC1                 1H
P0                12.00 usec
P1                12.00 usec
P17             2500.00 usec
PLW1         21.00000000 W
PLW10         4.83839989 W

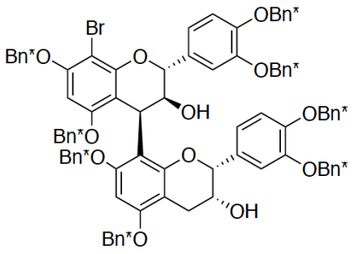
====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            600.1322 MHz
FIDRES         40.270618 Hz
SW                8.589 ppm
FnMODE               QF

F2 - Processing parameters
SI                  1024
SF           600.1300161 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           600.1300161 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
```

COSY of 4-*epi*-16 (600 MHz, $CDCl_3$)



BRUKER

```
Current Data Parameters
NAME                  VB-861-1
EXPNO                       21
PROCNO                       1

F2 - Acquisition Parameters
Date_               20210728
Time                    15.19
INSTRUM                 spect
PROBHD   5 mm CPPBBO BB
PULPROG          cosygpppqf
TD                       2048
SOLVENT                 CDCl3
NS                           1
DS                           8
SWH                 5319.149 Hz
FIDRES               2.597241 Hz
AQ                   0.1925120 sec
RG                      18.96
DW                     94.000 usec
DE                     10.00 usec
TE                     298.1 K
D0                  0.00000300 sec
D1                  1.93528295 sec
D11                 0.03000000 sec
D12                 0.00002000 sec
D13                 0.00000400 sec
D16                 0.00020000 sec
IN0                 0.00018800 sec

======== CHANNEL f1 ========
SFO1               600.1322288 MHz
NUC1                       1H
P0                      12.00 usec
P1                      12.00 usec
P17                   2500.00 usec
PLW1               21.00000000 W
PLW10               4.83839989 W

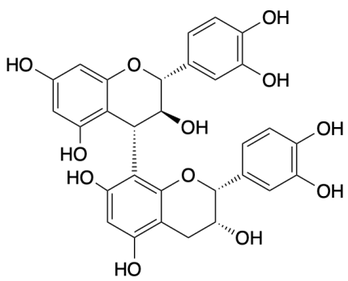
====== GRADIENT CHANNEL =====
GPNAM[1]          SMSQ10.100
GPZ1                    10.00 %
P16                   1000.00 usec

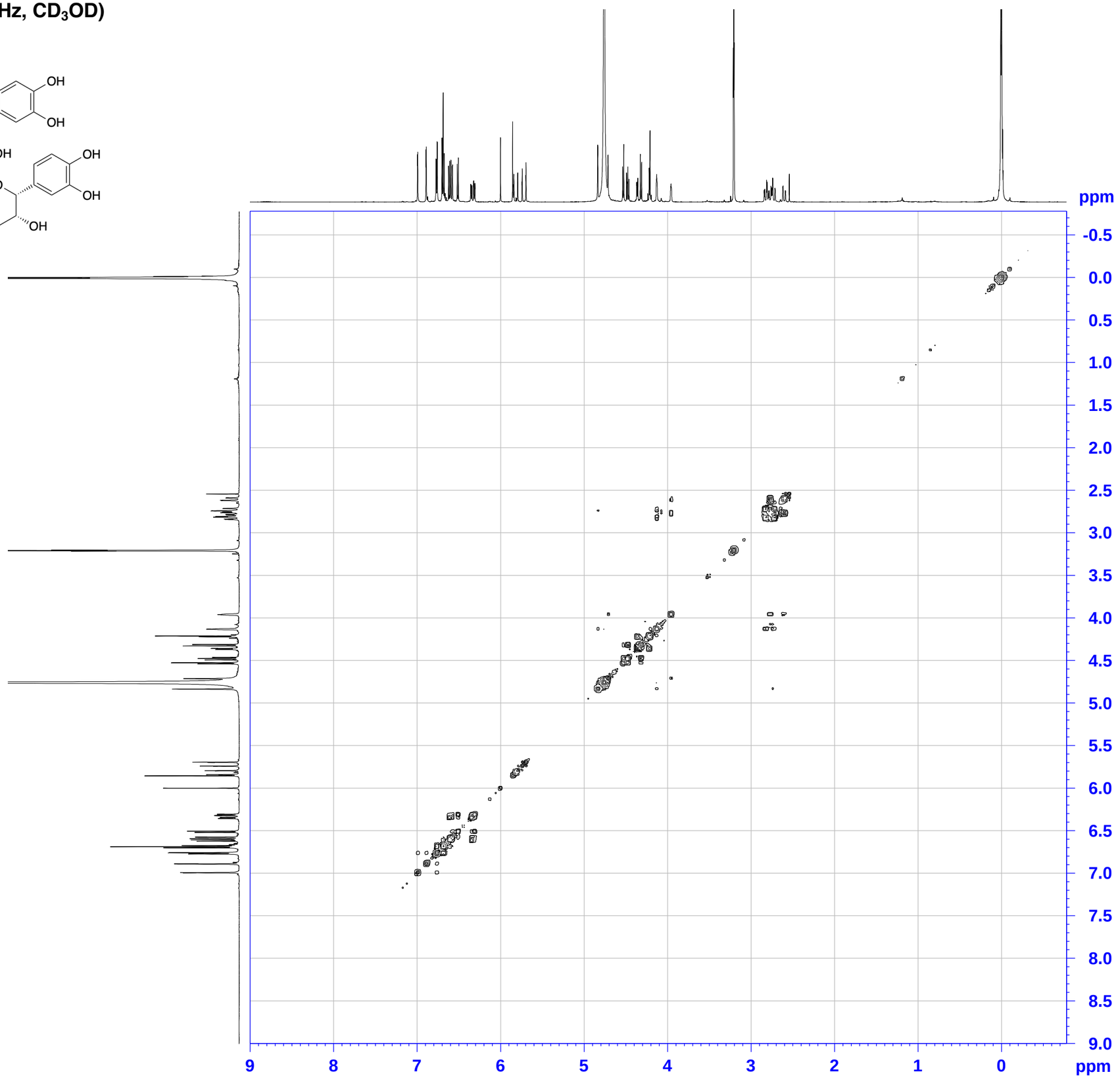
F1 - Acquisition parameters
TD                         128
SFO1                600.1322 MHz
FIDRES             41.555851 Hz
SW                      8.863 ppm
FnMODE                     QF

F2 - Processing parameters
SI                        1024
SF                 600.1300208 MHz
WDW                     QSINE
SSB          0
LB           0 Hz
GB           0
PC                       1.40

F1 - Processing parameters
SI                        1024
MC2                        QF
SF                 600.1300208 MHz
WDW                     QSINE
SSB          0
LB           0 Hz
GB           0
```

COSY of 2 (600 MHz, CD_3OD)





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```
Current Data Parameters
NAME                  VB-865
EXPNO                     12
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210803
Time                  11.56
INSTRUM               spect
PROBHD   5 mm CPPBBO BB
PULPROG        cosygpppqf
TD                     2048
SOLVENT                MeOD
NS                        1
DS                        8
SWH                5000.000 Hz
FIDRES                2.441406 Hz
AQ                 0.2048000 sec
RG                      17.5
DW                  100.000 usec
DE                   10.00 usec
TE                    298.2 K
D0                 0.00000300 sec
D1                 1.92299497 sec
D11                0.03000000 sec
D12                0.00002000 sec
D13                0.00000400 sec
D16                0.00020000 sec
IN0                0.00020000 sec

======== CHANNEL f1 ========
SFO1              600.1321047 MHz
NUC1                      1H
P0                     12.00 usec
P1                     12.00 usec
P17                  2500.00 usec
PLW1              21.00000000 W
PLW10              4.83839989 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       128
SFO1                600.1321 MHz
FIDRES             39.062500 Hz
SW                     8.331 ppm
FnMODE                   QF

F2 - Processing parameters
SI                       1024
SF                600.1300723 MHz
WDW                    QSINE
SSB          0
LB           0 Hz
GB           0
PC                      1.40

F1 - Processing parameters
SI                       1024
MC2                        QF
SF                600.1300723 MHz
WDW                    QSINE
SSB          0
LB           0 Hz
GB           0
```