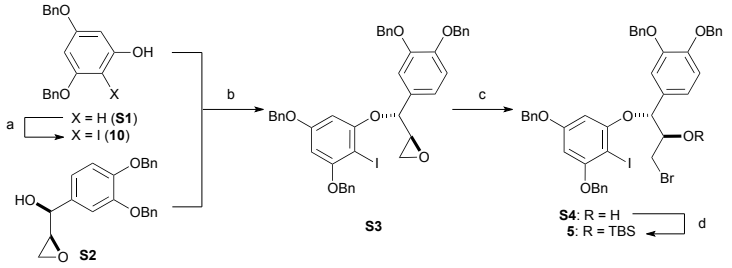
Supporting Information

General Experimental Procedures

All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry argon or nitrogen. Ethereal solvents, toluene and dichloromethane (anhydrous; Kanto Chemical Co., Inc.) were purified under argon using a solvent purification unit (Wako Pure Chemical Industries, Ltd.). *N,N*-Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure and stored over molecular sieves 4A. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, Art 5715, 0.25 mm). Preparative silica gel TLC (PTLC) was performed on 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 Yanaco MP-S3 or MP-500 instrument and are uncorrected. ^{1}H NMR and ^{13}C NMR were measured on a JEOL ECX-500 (500 MHz) or Bruker AV-600 (600MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm), and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Elemental analyses were recorded on an Elementar vario MICRO cube analyzer. Optical rotations ($[\alpha]_D$) were measured on a JASCO P-2300 polarimeter. High-performance liquid chromatography (HPLC) analyses were performed by using a Jasco 880PU instrument with UV detection at 280 nm. Low-resolution mass spectra (LRMS) were obtained on a Shimadzu MALDI–TOF Mass AXIMA® Confidence. High-resolution mass spectra (HRMS) were obtained with micrOTOF-Q II (Bruker Daltonics).

*Synthesis of iodophenol **10***



Scheme S1 (a) I_2, *t*-Bu_2NH, toluene, CH_2Cl_2, –78 ºC, 2 h, 63%; (b) TMAD, *n*-Bu_3P, toluene, 0 ºC, 18 h, 94% (*d.r.* = 97/3); (c) Li_2NiBr_4, THF, 0 °C→r.t. 18 h, 95%; (d) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C, 12 h, 96%.

To a solution of iodine (0.825 g, 3.26 mmol) in toluene (13 mL) was added *t*-$BuNH_2$ (0.690 mL, 6.52 mmol) at room temperature. The reaction mixture was stirred for 1 h at the same temperature. To a solution of di-*O*-benzyl phloroglucinol **S1**[1] (1.00 g, 3.26 mmol) in toluene/CH_2Cl_2 (14/1, 97.5 mL) was added the reaction mixture dropwise over 1 h at –78 ºC. The reaction mixture was stirred for 2 h at the same temperature. The reaction was quenched by adding aqueous 10% $Na_2S_2O_3$. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with saturated aqueous $NaHCO_3$, H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/toluene/EtOAc = 10/10/1 to 5/5/1, gradient elution) to afford iodophenol **10** (0.88 g, 63%) as a light yellow solid.

10: R_f 0.60 (Hexane/toluene/EtOAc = 2/2/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (s, 2H), 5.08 (s, 2H), 5.48 (s, 1H), 6.20 (d, 1H, *J* = 2.6 Hz), 6.38 (d, 1H, *J* = 2.6 Hz), 7.30-7.47 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 68.2, 70.3, 70.9, 94.0, 94.2, 127.0, 127.5, 127.9, 128.2, 128.6, 128.7, 136.3, 136.4, 156.5, 158.1, 161.4; IR (ATR) 3418, 3066, 3022, 2884, 1606, 1577, 1498, 1490, 1455, 1428, 1374, 1355, 1267, 1212, 1164, 1095, 1073, 1030, 1014, 995, 960, 911, 801, 733, 698 cm^{-1}; Anal. Calcd for $C_{20}H_{17}I_1O_3$: C, 55.44; H, 4.26. Found: C, 55.57; H, 3.96.

*Synthesis of epoxy ether **S3***

To a solution of **10** (1.00 g, 2.32 mmol), epoxide **S2**[1] (1.26 g, 3.49 mmol) and TMAD (1.20 g, 6.96 mmol) in toluene (30 mL) was added *n*-Bu_3P (1.41 mL, 6.96 mmol) at 0 ºC. The reaction mixture was stirred for 18 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 6/1 to 4/1, gradient elution) to afford ether **S3** (1.70 g, 94%) as a white amophous.

S3: R_f 0.59 (hexane/EtOAc = 3/1); $[\alpha]_D^{23}$ = +14.1 (*c* 1.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.76 (dd, 1H, *J* = 5.2, 4.1 Hz), 3.07 (dd, 1H, *J* = 5.3, 2.5 Hz), 3.22 (dd, 1H, *J* = 6.3, 3.6 Hz), 4.83 (dd, 2H, *J* = 15.5, 11.9 Hz), 5.07 (s, 2H), 5.10 (d, 1H, *J* = 3.4 Hz), 5.14 (s, 2H), 5.15 (s, 2H), 6.14 (d, 1H, *J* = 2.3 Hz), 6.19 (d, 1H, *J* = 2.3 Hz), 6.84 (dd, 1H, *J* = 8.2, 1.8 Hz), 6.88 (d, 1H, *J* = 8.2 Hz), 7.03 (d,

1H, *J* = 1.8 Hz), 7.25–7.48 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 45.0, 54.5, 69.6, 70.3, 70.9, 71.2, 79.0, 94.6, 95.3, 113.3, 114.7, 119.9, 126.8–128.9 (m), 130.1, 136.4, 136.5, 137.0, 137.2, 149.1 (2C), 157.6, 158.8, 160.7; IR (film) 3462, 3031, 2869, 1980, 1952, 1871, 1812, 1579, 1510, 1498, 1454, 1425, 1380, 1338, 1262, 1218, 1159, 1134, 1103, 1017, 908, 853, 806, 732, 694 cm^{-1}; HRMS (ESI) *m*/*z* 777.1673 ($[M+H]^+$ calcd for $C_{43}H_{37}I_1O_6$: 777.1708); Anal. Calcd for $C_{43}H_{37}I_1O_6$: C, 66.50; H, 4.80. Found: C, 66.40; H, 5.09.

*Synthesis of bromohydrin **S4***

To a solution of **S3** (1.70 g, 2.19 mmol) in THF (40 mL) was added a solution of Li_2NiBr_4 (9.30 mL, ca. 0.4 M THF solution, 3.72 mmol) at 0 ºC. The reaction mixture was stirred for 18 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, toluene/EtOAc = 50/1 to 20/1, gradient elution) to afford ether **S4** (1.78 g, 95%) as a white amorphous solid.

S4: R_f 0.17 (toluene/EtOAc = 20/1); $[\alpha]_D^{23}$ = +49.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (d, 1H, *J* = 5.7 Hz), 3.52 (dd, 1H, *J* = 10.7, 3.7 Hz), 3.72 (dd, 1H, *J* = 10.7, 6.9 Hz), 4.02–4.08 (m 1H), 4.79 (dd, 2H, *J*= 21.2, 11.7 Hz), 5.07 (s, 2H), 5.11 (d, 1H, *J* = 5.5 Hz), 5.12–5.14 (m, 4H), 5.94 (d, 1H, *J* = 2.3 Hz), 6.19 (d, 1H, *J* = 2.3 Hz), 6.83 (dd, 1H, *J* = 8.3, 1.8 Hz), 6.88 (d, 1H, *J* = 8.3 Hz), 6.95 (d, 1H, *J* = 1.8 Hz), 7.22–7.48 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.1, 69.1, 70.3, 70.9, 71.13, 71.14, 74.3, 81.7, 94.6, 94.9, 113.3, 114.7, 120.2, 126.8–128.6 (m), 129.1, 136.2, 136.4, 136.8, 137.1, 149.0, 149.2, 157.1, 158.7, 160.8; IR (film) 3532, 3062, 3031, 2868, 1957, 1872, 1812, 1579, 1511, 1498, 1454, 1424, 1380, 1337, 1260, 1216, 1160, 1135, 1103, 1065, 1016, 907, 845, 808, 732, 694 cm^{-1}; HRMS (ESI) *m*/*z* 857.0934 ($[M+H]^+$ calcd for $C_{43}H_{38}Br_1I_1O_6$: 857.0969); Anal. Calcd for $C_{43}H_{38}Br_1I_1O_6$: C, 60.22; H, 4.47. Found: C, 66.47; H, 4.65.

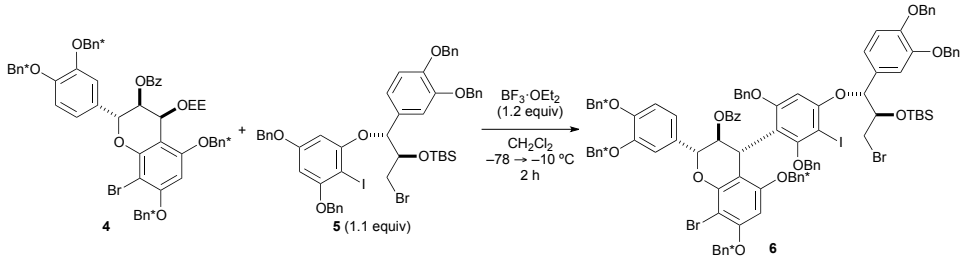
*Synthesis of silyl ether **5***

To a solution of **S4** (1.46 g, 1.70 mmol) in CH_2Cl_2 (30 mL) were added 2,6-lutidine (594 μL, 5.10 mmol) and TBSOTf (704 μL, 3.06 mmol) at 0 ºC. The reaction mixture was stirred for 12 h at the same temperature. The reaction was quenched by adding saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 6/1 to 4/1, gradient elution) to afford ether **5** (1.58 g, 96%) as a white amorphous solid.

5: R_f 0.69 (hexane/EtOAc = 4/1); $[\alpha]_D^{23}$ = +54.9 (*c* 0.950, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ –0.50 (s, 3H), –0.08 (s, 3H), 0.78 (s, 9H), 3.49 (dd, 1H, *J* = 10.7, 3.5 Hz), 3.94–3.97 (m 1H), 4.10 (dd,

1H, *J* = 10.7, 2.9 Hz), 4.76 (d, 1H, *J* = 11.6 Hz), 4.83 (d, 1H, *J* = 11.6 Hz), 5.05–5.16 (m, 7H), 6.02 (d, 1H, *J* = 2.3 Hz), 6.16 (d, 1H, *J* = 2.3 Hz), 6.83 (d, 1H, *J* = 8.2 Hz), 6.85 (dd, 1H, *J* = 8.2, 1.6 Hz), 7.01 (d, 1H, *J* = 1.6 Hz), 7.20–7.49 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ –5.5, –4.9, 17.9, 25.7, 37.3, 69.0, 70.2, 70.9, 71.2, 74.0, 81.1, 94.4, 94.7, 113.7, 114.7, 121.4, 126.8–128.6 (m), 130.9, 136.4, 136.6, 137.1, 137.2, 148.8, 149.0, 157.5, 158.7, 160.8; IR (film) 3063, 3032, 2951, 2928, 2883, 2855, 1949, 1873, 1811, 1579, 1511, 1498, 1454, 1425, 1382, 1328, 1256, 1218, 1161, 1104, 1078, 1017, 956, 903, 835, 827, 808, 778, 732, 694 cm^{-1}; HRMS (ESI) *m/z* 971.1790 ([M+H]$^+$ calcd for $C_{49}H_{52}Br_1I_1O_6Si_1$: 971.1834); Anal. Calcd for $C_{49}H_{52}Br_1I_1O_6Si$: C, 60.56; H, 5.39. Found: C, 60.30; H, 5.66.

Lewis acid catalyzed coupling reaction of **4** with **5**

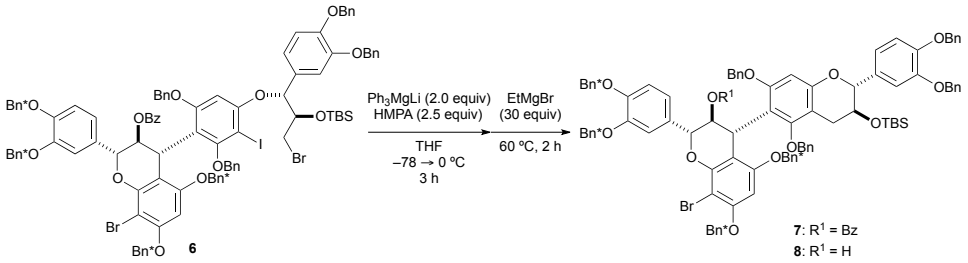


To a solution of bromo-capped benzoate **4**[2] (358 mg, 0.377 mmol) and **5** (403 mg, 0.414 mmol) in CH_2Cl_2 (15 mL) was added a solution of $BF_3{\cdot}OEt_2$ (0.283 M CH_2Cl_2 solution, 1.60 mL, 0.452 mmol) at –78 ºC. The reaction mixture was gradually warmed to –10 ºC over 2 h. The reaction was quenched by adding Et_3N and saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 4/1) to afford 655 mg of **6** (95%) as a white amorphous solid.

6: R_f 0.66 (toluene/EtOAc = 15/1); $[\alpha]_D^{23}$ = –105 (*c* 1.02, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, ratio of rotational isomer = 84:16) δ –0.55 (s, 0.42H), –0.42 (s, 2.58H), –0.11 (s, 0.42H), –0.05 (s, 2.58H), 0.77 (s, 9H), 3.43 (dd, 0.86H, *J* = 10.6, 3.8 Hz), 3.50–3.56 (m, 0.28H), 3.85 (d, 0.14H, *J* = 12.2 Hz), 3.91–3.99 (m, 1.86H), 4.04–4.09 (m, 1H), 4.21 (d, 0.14H, *J* = 10.5 Hz), 4.52–4.58 (m, 1.72H), 4.72 (d, 0.86H, *J* = 11.5 Hz), 4.80–4.89 (m, 1.86H), 4.91–4.96 (m, 0.28H), 5.02–5.13 (m, 5H), 5.68–5.76 (m, 0.86H), 5.77 (s, 0.14H), 5.82–5.88 (m, 0.14H), 6.12 (s, 0.86H), 6.21 (s, 0.14H), 6.28 (s, 0.86H), 6.66–6.98 (m, 6H), 7.09–7.40 (m, 22H), 7.41–7.48 (m, 1.28H), 7.70 (d, 1.72H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, signals for the minor rotational isomer were omitted) δ –5.3, –4.8, 17.9, 25.7, 36.6, 38.0, 70.3, 71.2, 72.5, 74.0, 75.6, 80.0, 82.1, 92.9, 93.6, 96.7, 108.4, 113.8, 114.1, 114.8, 114.9, 117.9, 120.4, 121.2, 126.4–128.5 (m), 129.6, 130.0, 130.2, 131.5, 132.5, 135.3, 136.0, 136.5, 137.0, 137.1, 138.1, 148.7, 148.8, 149.0, 149.3, 153.0, 154.6, 156.2, 156.3, 157.8, 158.0, 164.7; IR (film) 3032, 2928, 2856, 2275, 2198, 1727, 1575, 1510, 1484, 1454, 1428, 1410, 1362, 1328, 1263,

1201, 1179, 1094, 1026, 958, 905, 835, 808, 781, 732, 710, 696 cm^{-1}; HRMS (ESI) *m/z* 1829.5399 ($[M+H]^+$ calcd for $C_{99}H_{63}D_{28}Br_2I_1O_{13}Si_1$: 1829.5471); Anal. Calcd for $C_{99}H_{63}D_{28}Br_2IO_{13}Si$: C, 65.02; H(D), 5.30. Found: C, 64.91; H(D), 5.01.

*Synthesis of **7** and **8***



To a solution of PhMgBr (45 μL, 0.052 mmol, 1.14 mol/L Et_2O solution) and HMPA (11 μL, 0.065 mmol) in THF (0.5 mL) was added PhLi (102 μL, 0.103 mmol, 1.01 M cyclohexane/ether solution) at 0 ºC. The reaction mixture was stirred for 30 min at the same temperature, the reaction mixture was cooled to –78 ºC. To the reaction mixture was added a solution of *seco*-catechin **6** (43.7 mg, 0.0258 mmol) in THF (1 mL) slowly. The reaction was gradually warmed to 0 ºC and stirred for 3 h at the temperature. The reaction was stopped by adding saturated NH_4Cl solution. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (toluene/EtOAc = 15/1) to afford 26.9 mg of **7** (67%) and 8.3 mg of **8** (22%) as a white amorphous solid.

7: R_f 0.57 (toluene/EtOAc = 15/1); $[\alpha]_D^{23}$ = –75.8 (*c* 0.935, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 55:45) δ –0.56 (s, 1.35H), –0.55 (s, 1.65H), –0.38 (s, 1.65H), –0.26 (s, 1.35H), 0.57 (s, 4.95H), 0.66 (s, 4.05H), 2.17 (dd, 0.55H, *J* = 16.0, 9.4 Hz), 2.51 (dd, 0.55H, *J* = 16.3, 5.9 Hz), 2.68 (dd, 0.45H, *J* = 15.4, 9.6 Hz), 3.03 (dd, 0.45H, *J* = 15.4, 5.3 Hz), 3.45 (d, 0.45H, *J* = 11.4 Hz), 3.69 (dd, 0.55H, *J* = 14.7, 8.7 Hz), 3.81 (dd, 0.45H, *J* = 14.4, 8.5 Hz), 3.92 (d, 0.55H, *J* = 12.4 Hz), 4.27–4.39 (m, 1.45H), 4.42 (d, 0.45H, *J* = 11.2 Hz), 4.58 (d, 0.45H, *J* = 8.8 Hz), 4.70 (d, 0.55H, *J* = 12.4 Hz), 4.81–4.98 (m, 2.55H), 5.09–5.22 (m, 4.55H), 5.91-6.07 (m, 1.45), 6.15 (s, 0.55H), 6.17 (s, 0.45H), 6.23 (s, 0.55H), 6.27 (s, 0.45H), 6.34 (s, 0.55H), 6.72–7.47, (m, 29H), 7.65 (d, 1.10H, *J* = 8.4 Hz), 7.74 (d, 0.90H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, signals of two rotational isomers were not distinguished) δ –5.6, –5.5, –5.1, –4.9, 17.7, 17.8, 25.5, 25.6, 29.65, 29.69, 31.0, 32.0, 35.1, 37.0, 69.26, 69.32, 69.6, 70.1, 71.2, 71.3, 71.5, 72.7, 73.3, 75.9, 80.1, 80.4, 81.7, 82.2, 93.8, 94.4 (2C), 95.0, 95.4, 96.2, 97.5, 106.7, 107.0, 107.6, 109.3, 114.1 (2C), 114.2, 114.5, 115.0, 115.1, 115.21, 115.24, 116.5, 117.8, 120.6, 120.9, 121.1, 121.5, 126.7–128.6 (m), 129.4, 129.6, 130.2, 130.4, 130.7, 131.0, 132.4, 132.5, 132.8, 132.9, 136.1, 136.3, 136.5, 136.7, 136.9, 136.98, 137.02, 137.1, 137.28, 137.33, 137.4, 138.2, 138.4, 148.88, 148.92, 149.0, 149.1, 154.1, 156.2, 156.4, 156.7, 156.8, 156.9, 157.9, 158.0, 158.30, 158.32; IR (film) 3062, 3031, 2927,

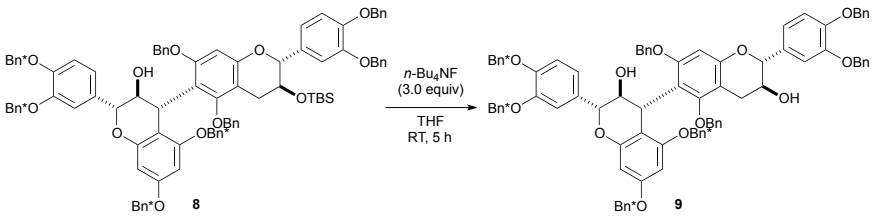
2854, 2346, 2277, 2202, 2118, 1728, 1611, 1588, 1511, 1454, 1429, 1375, 1328, 1314, 1268, 1204, 1178, 1157, 1111, 1027, 910, 836, 819, 734, 711, 697 cm^{-1}; HRMS (ESI) *m*/*z* 1545.8076 ($[M+H]^+$ calcd for $C_{99}H_{64}D_{28}O_{13}Si_1$: 1545.8137).

8: R_f 0.51 (toluene/EtOAc = 15/1); $[\alpha]_D^{23}$ = –59.1 (*c* 0.950, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 60:40) δ –0.56 (s, 1.20 H), –0.48 (s, 1.80H), –0.29 (s, 1.20H), –0.25 (s, 1.80H), 0.66 (s, 5.4H), 0.67 (s, 3.6H), 1.43 (s, 0.40H), 1.77 (s, 0.60H), 2.59 (dd, 0.60H, *J* = 16.1, 9.5 Hz), 2.68–2.79 (m, 1H), 3.01 (dd, 0.40H, *J* = 15.8, 5.6 Hz), 3.43 (d, 0.40H, *J* = 10.9 Hz), 3.74–3.82 (m, 1H), 4.17–4.22 (m, 1.20H), 4.33 (d, 0.40H, *J* = 10.9 Hz), 4.43–4.48 (m, 1H), 4.49–4.61 (m, 2H), 4.65 (d, 0.40H, *J* = 8.9 Hz), 4.69 (d, 0.60H, *J* = 11.7 Hz), 4.73 (d, 0.40H), 4.78–4.84 (m, 1.6H), 5.10–5.23 (m, 4H), 6.10 (s, 0.60H), 6.16 (s, 0.40H), 6.17 (s, 0.40H), 6.20 (s, 0.60H), 6.22 (s, 0.40H), 6.38 (s, 0.60H), 6.88–7.12 (m, 6H), 7.22–7.48 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$, signals of minor rotational isomer are marked with asterisks) δ –5.6*, –5.4, –5.1, –4.9*, 17.8, 25.58, 25.59*, 31.4, 32.1, 37.3*, 38.9, 69.5, 70.0, 70.2*, 71.3*, 71.4, 71.5, 72.4*, 72.6, 73.1*, 73.78*, 73.82, 81.9, 82.0, 82.26*, 82.32, 94.1, 94.7*, 95.0, 95.3*, 97.0*, 97.6, 106.9*, 107.3, 107.9, 109.2*, 113.95, 114.04*, 114.3*, 114.5, 115.0*, 115.1, 115.2*, 115.3, 117.9, 118.8*, 121.0 (2C), 121.1, 121.3*, 126.5–128.5 (m), 131.6*, 131.7, 132.72, 132.74*, 136.2*, 136.4, 136.5*, 136.7*, 136.8, 137.0, 137.26*, 137.30, 137.32, 137.4*, 137.96, 137.99*, 146.9*, 148.86, 148.89*, 149.05, 149.07*, 149.12, 154.0 (2C), 155.8*, 155.9, 156.7* 156.80, 156.84, 157.5*, 157.8, 157.9*, 158.2, 158.3*; IR (film) 3570, 3064, 3032, 2929, 2856, 2275, 2199, 2116, 1980, 1610, 1587, 1508, 1471, 1455, 1429, 1372, 1329, 1269, 1204, 1178, 1157, 1107, 1084, 1028, 907, 871, 836, 816, 778, 733, 696 cm^{-1}; HRMS (ESI) *m*/*z* 1441.7547 ($[M+H]^+$ calcd for $C_{92}H_{60}D_{28}O_{12}Si_1$: 1441.7875); Anal. Calcd for $C_{92}H_{60}D_{28}O_{12}Si$: C, 76.63; H(D), 6.15. Found: C, 76.65; H(D), 6.42.

<u>One-pot synthesis of **8**</u>

To a solution of PhMgBr (112 μL, 0.109 mmol, 0.979 mol/L Et_2O solution) and HMPA (24 μL, 0.14 mmol) was added PhLi (248 μL, 0.218 mmol, 0.881 M cyclohexane/ether solution) at 0 ºC. The reaction mixture was stirred for 30 min at the same temperature, the reaction mixture was cooled to –78 ºC. To the reaction mixture was added a solution of *seco*-catechin **6** (100 mg, 0.0546 mmol) in THF (1.5 mL) slowly. The reaction was gradually warmed to 0 ºC and stirred for 3 h at 0 ºC until the starting material **6** was completely consumed. Then to the reaction mixture was added EtMgBr (1.1 mL, 1.64 mmol, 1.48 M THF solution). The reaction mixture was warmed to 60 ºC and stirred for 2 h. The reaction was quenched by adding saturated NH_4Cl solution. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 4/1) to afford 72.1 mg of **8** (92%) as a white amorphous solid.

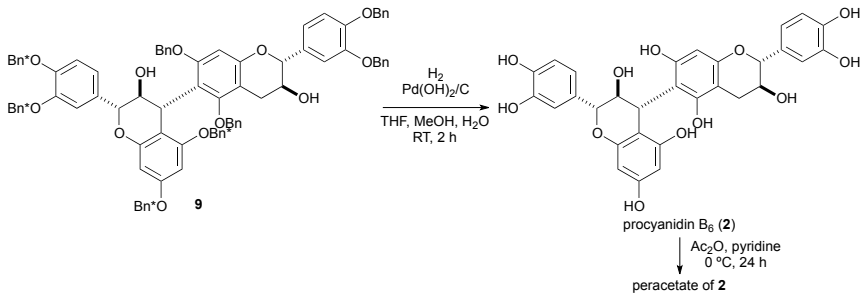
*Synthesis of diol **9***



To a solution of **8** (74.3 mg, 0.0515 mmol) in THF (1.5 mL) was added a solution of *n*-Bu_4NF (155 μL, 0.155 mmol, 1.0 M THF solution) at 0 °C. The reaction mixture was stirred for 5 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 1/1) to afford **9** (65.5 mg, 95%) as white amorphous solid.

9: R_f 0.22 (hexane/EtOAc = 1/1); $[\alpha]_D^{23}$ = –85.0 (*c* 1.35, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 65:35) δ 1.46 (d, 0.35H, *J* = 2.3 Hz, OH), 1.56 (brs, 1H, OH), 1.71 (d, 0.65H, *J* = 2.1 Hz, OH), 2.62 (dd, 0.65H, *J* = 16.0, 9.2 Hz), 2.73 (dd, 0.35H, *J* = 15.4, 10.0 Hz), 2.78 (dd, 0.65H, *J* = 16.0, 5.5 Hz), 3.14 (dd, 0.35H, *J* = 15.4, 5.2 Hz), 3.41 (d, 0.35H, *J* = 11.3 Hz), 3.79–3.87 (m, 1H), 4.24 (ddd, 0.65H, *J* = 9.3, 8.2, 2.1 Hz), 4.45 (d, 0.35H, *J* = 11.1 Hz), 4.49 (d, 0.65H, *J* = 11.4 Hz), 4.50–4.54 (m, 1.35H), 4.55 (d, 0.65H, *J* = 8.5 Hz), 4.58 (d, 0.35H, *J* = 9.2 Hz), 4.59 (d, 0.65H, *J* = 8.7 Hz), 4.64 (d, 0.35H, *J* = 9.1 Hz), 4.68 (d, 0.65H, *J* = 11.7 Hz), 4.76 (d, 0.35H, *J* = 11.9 Hz), 4.78–4.82 (m, 1.30H), 4.84 (d, 0.35H, *J* = 8.5 Hz), 5.15–5.23 (m, 4H), 6.01 (d, 0.35H, *J* = 2.3 Hz), 6.09 (d, 0.65H, *J* = 2.3 Hz), 6.18 (d, 0.65H, *J* = 2.3 Hz), 6.196 (s, 0.35H), 6.201 (d, 0.35H, *J* = 2.3 Hz), 6.37 (s, 0.65H), 6.84–7.12 (m, 6H), 7.22–7.45 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$, signals of minor rotational isomers are marked with asterisks) δ 28.4, 29.4*, 37.3*, 38.7, 68.3, 68.4*, 70.1, 70.2*, 71.2, 71.3*, 71.4, 72.5, 72.6*, 73.5, 74.0*, 81.5, 82.0, 82.3*, 94.2, 94.6*, 94.9, 95.3*, 97.0*, 97.5, 106.7, 106.8*, 108.0, 108.9*, 113.87*, 113.94, 114.05*, 114.11, 115.00*, 115.03*, 115.06, 115.09, 118.2, 119.2*, 120.6, 120.98*, 121.01, 121.04*, 127.0–129.6 (m), 130.7*, 130.8, 131.6, 136.2*, 136.4, 136.5*, 136.7*, 136.77, 136.81*, 136.95*, 137.01, 137.1, 137.4*, 137.9*, 138.0, 149.15, 149.18*, 149.5, 149.6*, 153.5, 153.8*, 155.6*, 156.1, 156.8, 157.6*, 157.8, 158.2, 158.3*; IR (film) 3067, 3063, 3032, 2873, 2276, 2208, 2120, 1608, 1587, 1508, 1454, 1428, 1375, 1328, 1267, 1203, 1175, 1157, 1082, 1028, 909, 839, 816, 734, 696 cm^{-1}; HRMS (ESI) *m*/*z* 1327.6972 ($[M+H]^+$ calcd for $C_{86}H_{46}D_{28}O_{12}$: 1327.7011); Anal. Calcd for $C_{86}H_{46}D_{28}O_{12}$: C, 77.80; H(D), 5.62. Found: C, 77.81; H(D), 5.92.

*Synthesis of procyanidin B_6 (**2**)*



A mixture of **9** (75.0 mg, 0.0565 mmol) and ASCA-2® (138 mg) in MeOH (1.5 mL), THF (1.5 mL), and H_2O (0.75 mL) was hydrogenated under H_2 atmosphere at room temperature for 1.5 h. The mixture was filtered through a glass fiber filter under Ar atmosphere. To the filtrate was added H_2O and evaporated only partially so as to remove most of the organic solvents. The residue was purified by preparative HPLC [Mightysil® RP-18 GP (0.20 cm ϕ x 25 cm), $H_2O/CH_3CN/HCOOH$ = 90/10/0.1, flow rate 5.0 mL/min] to collect a fraction including **2**. The fraction was added H_2O and evaporated only partially so as to remove most of the organic solvents. The solution was lyophilized to afford procyanidin B_6 (**2**) (21.6 mg, 66%) as an off-white powder.

procyanidin B_6 (**2**): $[\alpha]_D^{26}$ = –144 (*c* 0.475, EtOH), {lit[3a]. $[\alpha]_D$ = –130 (*c* 0.50, EtOH), lit[3b]. $[\alpha]_D^{21}$ = –153 (*c* 0.79, EtOH)}; IR (ATR) 3228 (br), 1603, 1519, 1447, 1372, 1282, 1202, 1144, 1112, 1067, 1029, 926, 872, 817, 780 cm^{-1}; HRMS (ESI) *m*/*z* 579.1496 ($[M+H]^+$ calcd for $C_{30}H_{27}O_{12}$: 579.1497).

*Synthesis of per-acetylated procyanidin B_6 (**2-perAc**)*

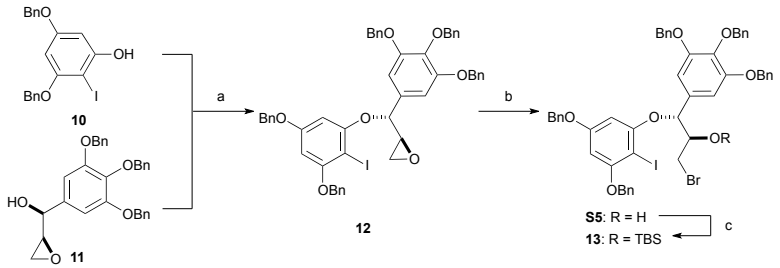
A mixture of **9** (150 mg, 0.113 mmol) and ASCA-2® (276 mg) in MeOH (3 mL), THF (3 mL), and H_2O (1.5 mL) was hydrogenated under H_2 atmosphere at room temperature for 1.5 h. The mixture was filtrated through a glass fiber filter under Ar atmosphere. To the filtrate was added H_2O and evaporated only partially so as to remove most of the organic solvents. The solution was lyophilized to afford procyanidin B_6 (**2**) (71.6 mg, quant.) as an off-white powder.

2 (70.0 mg) was dissolved in pyridine/acetic anhydride (3.0 mL, 1:1 v/v) at 0 ºC. The reaction mixture was stirred for 24 h at 0 ºC. The reaction mixture was diluted CH_2Cl_2, and quenched by adding 10% aqueous $CuSO_4$ solution at 0 ºC. The products were extracted with CH_2Cl_2 (×3). The combined organic extracts were washed successively with 10% aqueous $CuSO_4$ solution, water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash column chromatography (toluene/acetone = 8/1) to afford acetate **2-perAc** (92.6 mg, 2 steps 84%) as a white solid.

2-perAc: R_f 0.50 (toluene/acetone = 4/1); $[\alpha]_D^{26}$ = –31 (*c* 0.46, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 50:50) δ 1.68–2.34 (m, 30H), 2.48 (dd, 0.5H, *J* = 16.1, 9.5 Hz), 2.60 (dd, 0.5H, *J* = 16.7, 8.5 Hz), 2.90 (dd, 0.5H, *J* = 15.8, 4.5 Hz), 2.93–3.01 (m, 0.5H), 4.39 (d, 0.5H, *J* =

9.0 Hz), 4.48 (d, 0.5H, *J* = 8.9 Hz), 4.83 (d, 0.5H, *J* = 11.5 Hz), 4.85 (d, 0.5H, *J* = 10.1 Hz), 4.91 (d, 0.5H, *J* = 8.9 Hz), 5.03 (d, 0.5H, *J* = 8.0 Hz), 5.05–5.10 (m, 0.5H), 5.10–5.17 (m, 0.5H), 5.67–5.74 (m, 0.5H), 5.74–5.81 (m, 0.5H), 6.46 (d, 0.5H, *J* = 2.1 Hz), 6.50 (d, 0.5H, *J* = 2.3 Hz), 6.60 (s, 0.5H), 6.66-6.69 (m, 1.5H), 7.19–7.26 (m, 4H), 7.29–7.32 (m, 1H), 7.35–7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.9–21.1 (m), 29.3, 29.7, 36.6, 37.1, 68.5, 68.6, 71.6, 71.8, 77.7, 78.3, 79.7, 108.5, 108.6, 108.9, 110.4, 110.6, 110.8, 113.3, 113.5, 115.6, 115.7, 117.9, 118.0, 122.4, 122.8, 122.97, 122.99, 123.4, 123.5, 124.9, 125.3, 125.45, 125.50, 134.6, 134.7, 135.6, 135.7, 141.80, 141.83, 141.84, 142.0, 142.2, 142.3, 142.45, 142.48, 147.9, 148.0, 148.1, 148.2, 149.6, 149.9, 150.0, 150.1, 153.0, 153.3, 155.78, 155.79, 166.5, 167.4, 167.5, 167.9, 168.00, 168.03, 168.3, 168.6, 168.85, 168.89, 169.1, 169.4, 170.0; IR (neat) 3026 (br), 3025, 2937, 1772, 1620, 1592, 1507, 1481, 1430, 1371, 1260, 1206, 1185, 1125, 1111, 1050, 1015, 900, 753 cm^{-1}; HRMS (ESI) *m*/*z* 999.2545 ([M+H]$^+$ calcd for $C_{50}H_{47}O_{13}$: 999.2554).

*Synthesis of epoxy ether **12***



Scheme S2 (a) TMAD, *n*-Bu_3P, toluene, RT, 22 h, 93% (*d.r.* = >99/1); (b) Li_2NiBr_4, THF, 0 °C→RT, 13 h, quant.; (d) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C, 5 h, quant.

To a solution of **10** (200 mg, 0.464 mmol), epoxide **11**[1] (325 mg, 0.694 mmol) and TMAD (239 mg, 1.39 mmol) in toluene (6 mL) was added *n*-Bu_3P (347 μL, 1.39 mmol) at 0 ºC. The reaction mixture was stireed for 22 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 6/1 to 4/1, gradient elution) to afford ether **12** (379 mg, 93%, d.r. = >25:1) as a white amorphous solid.

12: R_f 0.67 (toluene/hexane/actetone = 2/2/1); $[\alpha]_D^{23}$ = +35.8 (*c* 1.20, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.75–2.78 (m, 1H), 3.05 (m, 1H), 3.22 (s, 1H), 4.83 (s, 2H), 5.02–5.12 (m, 9H), 6.01 (s, 1H), 6.21 (s, 1H), 6.71 (s, 2H), 7.23–7.48 (m, 25H);^{13}C NMR (150 MHz, $CDCl_3$) δ 45.1, 54.5, 69.6, 70.3, 70.9, 71.2, 75.1, 79.3, 94.6, 95.3, 106.2, 127.0, 127.4–128.6 (m), 132.5, 136.3, 136.4, 136.9, 137.8, 138.4, 153.0, 157.5, 158.8, 160.8; IR (film) 3463, 3029, 2873, 2373, 2343, 1722, 1580, 1498, 1454, 1429, 1373, 1335, 1229, 1212, 1164, 1110, 1017, 908, 841, 809, 735, 696 cm^{-1}; HRMS (ESI) *m*/*z* 883.2080 ([M+H]$^+$ calcd for $C_{50}H_{43}I_1O_7$: 883.2126).

*Synthesis of bromohydrin **S5***

To a solution of **12** (137 mg, 0.155 mmol) in THF (4 mL) was added a solution of Li_2NiBr_4 (0.66 mL, 0.26 mmol, ca. 0.4 M THF solution) at 0 ºC. The reaction mixture was stirred for 19 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (toluene/EtOAc = 15/1) to afford ether **S5** (146 mg, 98%) as a white amorphous solid.

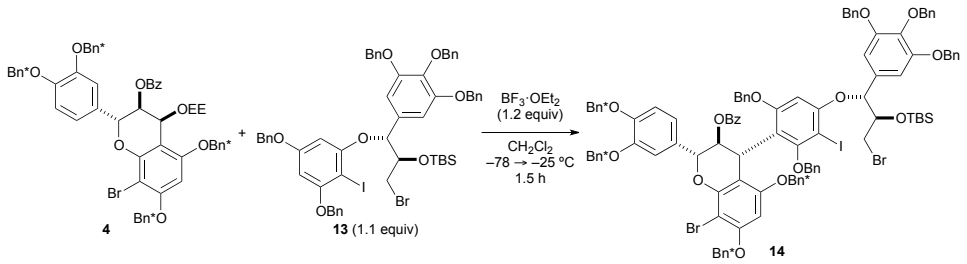
S5: R_f 0.35 (toluene/EtOAc = 15/1); $[\alpha]_D^{21}$ = +66.7 (*c* 1.13, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (d, 1H, *J* = 2.8 Hz, OH), 3.45 (dd, 1H, *J* = 10.7, 3.7 Hz), 3.70 (dd, 1H, *J* = 10.7, 7.0 Hz), 4.03–4.07 (m, 1H), 4.73 (dd, 2H, *J* = 20.6, 11.8 Hz), 5.02–5.10 (m, 8H), 5.11 (d, 1H, *J* = 5.4 Hz), 5.94 (d, 1H, *J* = 2.2 Hz), 6.21 (d, 1H, *J* = 2.2 Hz), 6.63 (s, 2H), 7.23–7.49 (m, 25H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.0, 69.1, 70.3, 70.9, 71.2, 74.3, 75.1, 81.9, 94.6, 94.9, 106.4, 127.0, 127.4–128.6 (m), 131.5, 136.2, 136.4, 136.7, 137.8, 138.5, 153.0, 157.1, 158.8, 160.8; IR (film) 3484, 3088, 3063, 3031, 2932, 2872, 1952, 1876, 1811, 1581, 1498, 1454, 1429, 1373, 1335, 1227, 1163, 1111, 1079, 1028, 1017, 908. 810, 736, 696 cm^{-1}; HRMS (ESI) *m*/*z* 963.1335 ($[M+H]^+$ calcd for $C_{50}H_{44}Br_1I_1O_7$: 963.1388).

*Synthesis of silyl ether **13***

To a solution of **S5** (146 mg, 0.151 mmol) in CH_2Cl_2 (2 mL) were added 2,6-lutidine (53 μL, 0.45 mmol) and TBSOTf (63 μL, 0.27 mmol) at 0 ºC. The reaction mixture was stirred for 6 h at the same temperature. The reaction was quenched by adding saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 3/1) to afford ether **13** (157 mg, 96%) as a white amorphous solid.

13: R_f 0.73 (hexane/EtOAc = 3/1); $[\alpha]_D^{26}$ = +72.4 (*c* 1.04, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ –0.42 (s, 3H), –0.06 (s, 3H), 0.82 (s, 9H), 3.48 (dd, 1H, *J* = 10.7, 3.5 Hz), 3.97 (ddd, 1H, *J* = 7.0, 3.5, 2.9 Hz), 4.09 (dd, 1H, *J* = 10.7, 2.9 Hz), 4.78 (d, 1H, *J* = 11.5 Hz), 4.84 (d, 1H, *J* = 11.5 Hz), 5.01 (s, 2H), 5.04–5.10 (m, 7H), 6.06 (d, 1H, *J* = 2.3 Hz), 6.19 (d, 1H, *J* = 2.3 Hz), 6.72 (s, 2H), 7.22–7.48 (m, 25H); ^{13}C NMR (150 MHz, $CDCl_3$) δ –5.3, –4.9, 17.9, 25.7, 37.3, 69.0, 70.3, 70.9, 71.1, 74.0, 75.1, 81.3, 94.4, 94.8, 107.3, 127.0, 127.4–128.6 (m), 133.3, 136.3, 136.5, 136.9, 137.8, 138.3, 152.8, 157.4, 158.7, 160.8; IR (film) 3063, 3031, 2951, 2928, 2883, 2856, 1950, 1808, 1726, 1582, 1498, 1454, 1430, 1372, 1258, 1227, 1164, 1113, 1078, 1029, 1017, 956, 904. 836, 826, 811, 736, 696 cm^{-1}; HRMS (ESI) *m*/*z* 1077.2184 ($[M+H]^+$ calcd for $C_{56}H_{58}Br_1I_1O_7Si_1$: 1077.2253).

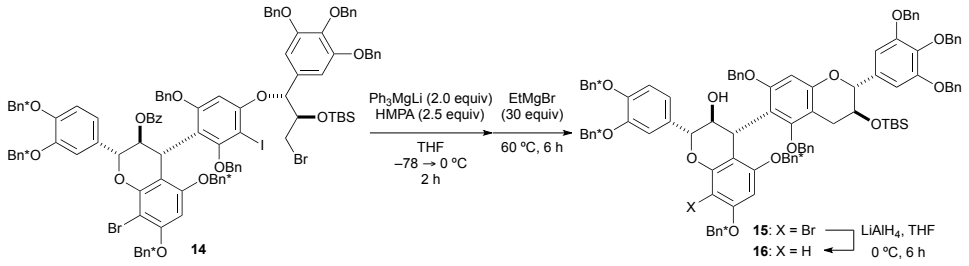
Lewis acid catalyzed coupling reaction between **4** and **13**



To a solution of bromo-capped benzoate **4** (177 mg, 0.186 mmol) and **13** (220 mg, 0.204 mmol) in CH_2Cl_2 (8 mL) was added a solution of $BF_3{\cdot}OEt_2$ (0.310 M CH_2Cl_2 solution, 720 μL, 0.223 mmol) at –78 ºC. The reaction mixture was gradually warmed to –25 ºC over 1.5 h. The reaction was quenched by adding Et_3N and saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3/1) to afford 325 mg of **14** (90%) as a white amorphous solid.

14: R_f 0.66 (toluene/EtOAc = 15/1); $[\alpha]_D^{22}$ = –83.8 (*c* 1.02, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, ratio of rotational isomes = 85:15) δ –0.47 (s, 0.45H), –0.36 (s, 2.55H), –0.07 (s, 0.45H), –0.03 (s, 2.55H), 0.80 (s, 7.65H), 0.81 (s, 1.35), 3.42 (dd, 0.85H, *J* = 10.6, 4.1 Hz), 3.51–3.54 (m, 0.30H), 3.88 (d, 0.15H, *J* = 11.5 Hz), 3.94–3.98 (m, 2H), 4.06–4.09 (m, 1H), 4.21 (d, 0.15H, *J* = 8.6 Hz), 4.55 (d, 1.70H, *J* = 11.8 Hz), 4.74 (d, 0.85H, *J* = 11.5 Hz), 4.82–4.90 (m, 1.85H), 4.91–5.04 (m, 6H), 5.06 (d, 0.85H, *J* = 6.6 Hz), 5.08–5.12 (m, 0.30H), 5.71–5.77 (m, 0.85H), 5.82 (s, 0.15H), 5.84–5.89 (m, 0.15H), 6.12 (s, 0.85H), 6.21 (s, 0.15H), 6.33 (s, 0.85H), 6.60 (s, 0.30H), 6.74 (d, 0.85H, *J* = 8.3 Hz), 6.80–6.84 (m, 1H), 6.85 (s, 1.70H), 6.86–6.89 (m, 0.15H), 6.92 (d, 0.85H, *J* = 1.7 Hz), 6.94 (d, 1.70H, *J* = 7.3 Hz), 6.97–6.99 (m, 0.15H), 7.14–7.41 (m, 26.60H), 7.71 (d, 1.70H, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, signals of the minor rotational isomer are marked with asterisks, and weak signals for the isomer were partially omitted) δ −5.4*, –5.2, –5.0*, –4.8, 18.0, 25.7, 29.4*, 29.7, 36.6, 38.1*, 70.4, 71.1*, 71.2, 72.6, 73.9, 75.07*, 75.14, 75.7, 77.5, 80.0, 80.1, 81.6*, 82.5, 92.8, 93.6, 93.9*, 95.7*, 96.8, 107.3, 109.3, 113.8, 114.8, 118.1, 120.4, 126.6–128.5 (m), 129.2*, 129.7, 130.0*, 130.2*, 132.5, 133.3*, 133.9, 135.3, 135.9, 136.4, 136.5*, 136.8, 136.9*, 137.01*, 137.04, 137.7, 137.9*, 138.0, 138.2*, 138.4, 148.8, 148.8, 152.9*, 153.0, 153.1, 154.56* 154.64, 155.9*, 156.1, 156.4, 157.7*, 157.9, 158.1, 164.7; IR (film) 3089, 3064, 3031, 2952, 2928, 2856, 2353, 2278, 2203, 2118, 1728, 1584, 1507, 1483, 1453, 1436, 1411, 1372, 1327, 1265, 1202, 1181, 1111, 1098, 1052, 1028, 1000, 959, 906, 838, 826, 811, 735, 709, 697 cm^{-1}; HRMS (ESI) *m*/*z* 1935.5862 ($[M+H]^+$ calcd for $C_{106}H_{69}D_{28}Br_2I_1O_{14}Si_1$: 1935.5889).

Synthesis of ***16***

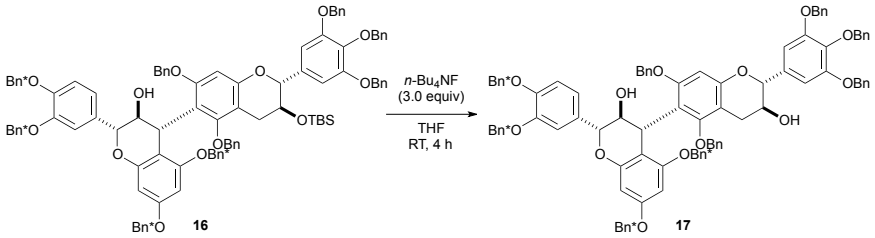


To a solution of PhMgBr (210 μL, 0.103 mmol, 0.979 mol/L Et_2O solution) and HMPA (45 μL, 0.26 mmol) in THF (3 mL) was added PhLi (477 μL, 0.412 mmol, 0.881 M cyclohexane/ether solution) at 0 ºC. The reaction mixture was stirred for 30 min at the same temperature, the reaction mixture was cooled to –78 ºC. To the reaction mixture was added a solution of *seco*-gallocatechin **14** (200 mg, 0.103 mmol) in THF (1.5 mL) slowly. The reaction was gradually warmed to 0 ºC and stirred for 2 h at 0 ºC until the starting material **14** was completely consumed. Then to the reaction mixture was added EtMgBr (2.1 mL, 3.1 mmol, 1.48 M THF solution). The reaction mixture was warmed to 60 ºC and stirred for 6 h. The reaction was stopped by adding saturated NH_4Cl solution. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 3/1) to afford mixture of bromide **15** and debrominated product **16**. To the mixture of **15** and **16** (113 mg) in THF (4 mL) was added $LiAlH_4$ (21.2 mg, 0.560 mmol) at 0 ºC. The reaction mixture was stirred for 6 h at the same temperature. The reaction was quenched by adding saturated potassium sodium tartrate solution and stirred for 1 h. The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 2/1) to afford 92.3 mg of **16** (58%, 2 steps) as a white amorphous solid.

16: R_f 0.39 (hexane/EtOAc = 3/1); $[\alpha]_D^{23}$ = –52.7 (*c* 1.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 60:40) δ –0.50 (s, 1.2H), –0.44 (s, 1.8H), –0.26 (s, 1.2H), –0.24 (s, 1.8H), 0.68 (s, 5.4H), 0.70 (s, 3.6H), 1.43 (s, 0.4H), 1.76 (s, 0.6H), 2.60 (dd, 0.6H, *J* = 16.2, 9.7 Hz), 2.69–2.76 (m, 1H), 3.02 (dd, 0.4H, *J* = 15.5, 5.5 Hz), 3.44 (d, 0.4H, *J* = 11.1 Hz), 3.76–3.82 (m, 1H), 4.20 (dt, 0.6H, *J* = 2.9, 9.2 Hz), 4.24 (d, 0.6H, *J* = 12.0 Hz), 4.32 (d, 0.4H, *J* = 10.9 Hz), 4.44 (d, 0.6H, *J* = 8.9 Hz), 4.48 (d, 0.4H, *J* = 11.9 Hz), 4.52 (dt, 0.4H, *J* = 3.1, 9.1 Hz), 4.56 (d, 0.6H, *J* = 9.6 Hz), 4.59 (d, 0.6H, *J* = 8.8 Hz), 4.60 (d, 0.4H, *J* = 9.7 Hz), 4.64 (d, 0.4H, *J* = 8.9 Hz), 4.71 (d, 0.6H, *J* = 11.8 Hz), 4.74 (d, 0.4H, *J* = 11.9 Hz), 4.80–4.85 (m, 1.6H), 4.99–5.18 (m, 6H), 6.10 (d, 0.6H, *J* = 2.4 Hz), 6.16 (d, 0.4H, *J* = 2.4 Hz), 6.19 (s, 0.4H), 6.21 (d, 0.6H, *J* = 2.4 Hz), 6.23 (d, 0.4H, *J* = 2.4 Hz), 6.40 (s, 0.6H), 6.776 (s, 0.8H), 6.780 (s, 1.2H), 6.88–6.94 (m, 1.6H), 6.99 (s, 0.6H), 7.01 (dd, 0.4H, *J* = 8.3, 1.8 Hz), 7.04–7.09 (m, 1.2H), 7.12 (d, 0.4H, *J* = 1.8 Hz), 7.22–7.44 (m, 23.8H); ^{13}C NMR

(150 MHz, $CDCl_3$, signals of two rotational isomers were not distinguished) δ –5.5, –5.4, –5.0, –4.9, 17.8, 25.59, 25.61, 29.7, 31.5, 32.1, 37.3, 38.8, 69.9, 70.0, 70.2, 71.3, 72.6, 73.8, 73.9, 75.4, 81.9, 82.3, 82.4, 82.6, 84.2, 94.7, 95.0, 95.3, 96.9, 97.6, 106.9, 107.3, 107.58, 107.61, 107.8, 109.2, 114.0, 114.1, 115.0, 115.1, 118.1, 118.9, 121.0, 126.7–128.7(m), 131.56, 131.62, 134.8, 134.9, 136.2, 136.4, 136.5, 136.7, 136.8, 137.0, 137.1, 137.2, 137.4, 137.8, 137.9, 137.8, 137.9, 138.6, 149.07, 149.13, 149.2, 152.8, 153.8, 153.9, 155.8, 155.9, 156.7, 156.8, 156.9, 157.5, 157.8, 157.9, 158.2, 158.3; IR (film) 3063, 3031, 2950, 2927, 2883, 2856, 2277, 2201, 2119, 1610, 1589, 1509, 1489, 1454, 1436, 1371, 1330, 1271, 1203, 1178, 1157, 1111, 1029, 907, 876, 837, 820, 736, 697 cm^{-1}; HRMS (ESI) *m*/*z* 1547.8217 ($[M+H]^+$ calcd for $C_{99}H_{66}D_{28}O_{13}Si_1$: 1547.8294).

*Synthesis of diol **17***

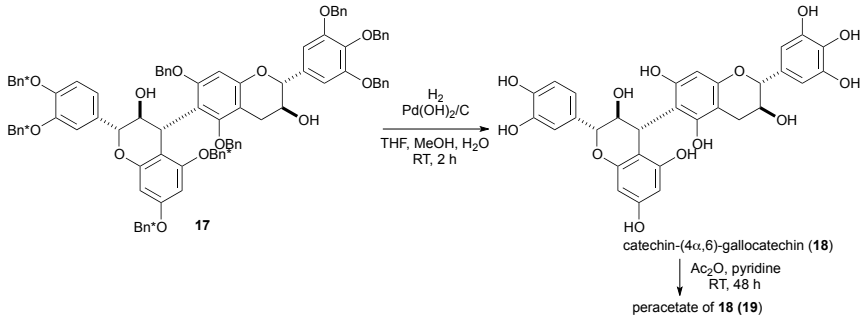


To a solution of **16** (47.3 mg, 0.0306 mmol) in THF (1 mL) was added a solution of *n*-Bu_4NF (92 μL, 0.092 mmol, 1.0 M THF solution) at 0 °C. The reaction mixture was stirred for 4 h at room temperature. The reaction was quenched by adding phosphate buffer (pH = 7). The mixture was extracted with EtOAc (×3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 1/1) to afford **17** (33.9 mg, 78%) as a white amorphous solid.

17: R_f 0.26 (hexane/EtOAc = 1/1); $[\alpha]_D^{25}$ = –82.1 (*c* 0.985, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 67:33) δ 1.45 (s, 0.33H, OH), 1.56 (s, 1H, OH), 1.70 (s, 0.67H, OH), 2.61 (dd, 0.67H, *J* = 16.0, 9.4 Hz), 2.73 (dd, 0.33H, *J* = 15.4, 10.0 Hz), 2.82 (dd, 0.67H, *J* = 16.0, 5.7 Hz), 3.15 (dd, 0.33H, *J* = 15.4, 5.4 Hz), 3.42 (d, 0.33H, *J* = 11.2 Hz), 3.75–3.83 (m, 1H), 4.25 (ddd, 0.67H, *J* = 9.5, 8.9, 2.0 Hz), 4.45 (d, 0.33H, *J* = 11.2 Hz), 4.49–4.55 (m, 2.67H), 4.58 (d, 0.33H, *J* = 9.7 Hz), 4.60 (d, 0.67H, *J* = 8.8 Hz), 4.63 (d, 0.33H, *J* = 8.9 Hz), 4.70 (d, 0.67H, *J* = 11.7 Hz), 4.77 (d, 0.33H, *J* = 11.9 Hz), 4.78–4.82 (m, 1.34H), 4.85 (d, 0.33H, *J* = 8.5 Hz), 5.06–5.18 (m, 6H), 6.02 (d, 0.33H, *J* = 2.4 Hz), 6.10 (d, 0.67H, *J* = 2.4 Hz), 6.18 (d, 0.67H, *J* = 2.4 Hz), 6.21 (d, 0.33H, *J* = 2.4 Hz), 6.22 (s, 0.33H), 6.38 (s, 0.67H), 6.765 (s, 1.34H), 6.768 (s, 0.66), 6.86 (dd, 0.67H, *J* = 8.3, 1.9 Hz), 6.89 (d, 0.67H, *J* = 8.3 Hz), 6.93 (d, 0.33H, *J* = 8.2 Hz), 6.97 (d, 0.67H, *J* = 1.9 Hz), 7.01 (dd, 0.33H, *J* = 8.3, 1.9 Hz), 7.07–7.09 (m, 1.34H), 7.12 (d, 0.33H, *J* = 1.9 Hz), 7.22–7.44 (m, 23.66H); ^{13}C NMR (150 MHz, $CDCl_3$, signals of minor rotational isomers are marked with asterisks) δ 28.5, 29.4*, 37.3*, 38.6, 68.4, 68.5*, 70.1, 70.2*, 71.25*, 71.33, 72.5, 72.7*, 73.5, 74.0*, 75.22*, 75.34, 81.8, 82.0, 82.2*, 82.3*, 94.3, 94.6*, 95.0, 95.2*, 97.0*, 97.5, 106.72*, 106.74, 107.0,

107.1*, 108.0, 108.9*, 113.88*, 113.93, 115.02*, 115.05, 118.4, 119.3*, 120.99, 121.02*, 126.7–128.6 (m), 131.5, 133.07*, 133.13, 136.2*, 136.4, 136.5*, 136.7*, 136.75, 136.79, 136.82, 137.0, 137.3*, 137.71, 137.73*, 137.9*, 138.0, 139.0, 149.2, 139.2, 153.08*, 153.13, 153.4, 153.6*, 155.6*, 156.1, 156.9, 157.6*, 157.8, 158.2, 158.3*; IR (film) 3671, 3573, 3062, 3031, 2921, 2277, 2204, 2119, 1731, 1610, 1589, 1505, 1489, 1453, 1434, 1372, 1329, 1270, 1203, 1176, 1160, 1107, 1028, 910, 839, 820, 737, 697 cm^{-1}; HRMS (ESI) *m/z* 1433.7362 ($[M+H]^+$ calcd for $C_{93}H_{52}D_{28}O_{13}$: 1433.7429).

*Synthesis of catechin-(4α,6)-gallocatechin (**18**)*



A mixture of **17** (33.9 mg, 0.0236 mmol) and ASCA-2® (65 mg) in MeOH (1 mL), THF (1 mL), and H_2O (0.5 mL) was hydrogenated under H_2 atmosphere at room temperature for 2 h. The mixture was filtered through a glass fiber filter under Ar atmosphere. To the filtrate was added H_2O and evaporated only partially so as to remove most of the organic solvents. The residue was purified by preparative HPLC [Mightysil® RP-18 GP (0.20 cm ϕ x 25 cm), $H_2O/CH_3CN/HCOOH$ = 90/10/0.1, flow rate 5.0 mL/min] to collect a fraction including **18**. The fraction was added H_2O and evaporated only partially so as to remove most of the organic solvents. The solution was lyophilized to afford catechin-(4α,6)-gallocatechin (**18**) (2.5 mg, 18%) as off-white powders.

18: $[\alpha]_D^{26}$ = –150 (*c* 0.250, EtOH); IR (ATR) 3215 (br), 1603, 1515, 1448, 1343, 1283, 1203, 1144, 1113, 1066, 1030, 874, 818, 784 cm^{-1}; HRMS (ESI) *m/z* 595.1417 ($[M+H]^+$ calcd for $C_{30}H_{26}O_{13}$: 595.1446), 593.1279 ($[M-H]^-$ calcd for $C_{30}H_{26}O_{13}$: 593.1301).

*Synthesis of peracetate **19***

A mixture of **17** (30 mg, 0.021 mmol) and ASCA-2® (57 mg) in MeOH (1 mL), THF (1 mL), and H_2O (0.5 mL) was hydrogenated under H_2 atmosphere at room temperature for 2 h. The mixture was filtered through a glass fiber filter under Ar atmosphere. To the filtrate was added H_2O and evaporated only partially so as to remove most of the organic solvents. The solution was lyophilized to afford catechin-(4α,6)-gallocatechin (**18**) (19.2 mg) as an off-white powder.

18 (18.0 mg) was dissolved in pyridine/acetic anhydride (1:1 v/v) at 0 ºC. The reaction mixture was stirred for 48 h at room temperature. The reaction mixture was diluted CH_2Cl_2, and quenched by adding 10% $CuSO_4$ solution at 0 ºC. The products were extracted with CH_2Cl_2 (×3). The combined organic extracts were washed successively with 10% aqueous $CuSO_4$ solution, water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by PTLC (toluene/acetone = 5/1) to afford peracetate **19** (8.5 mg, 2 steps 41%) as a white solid.

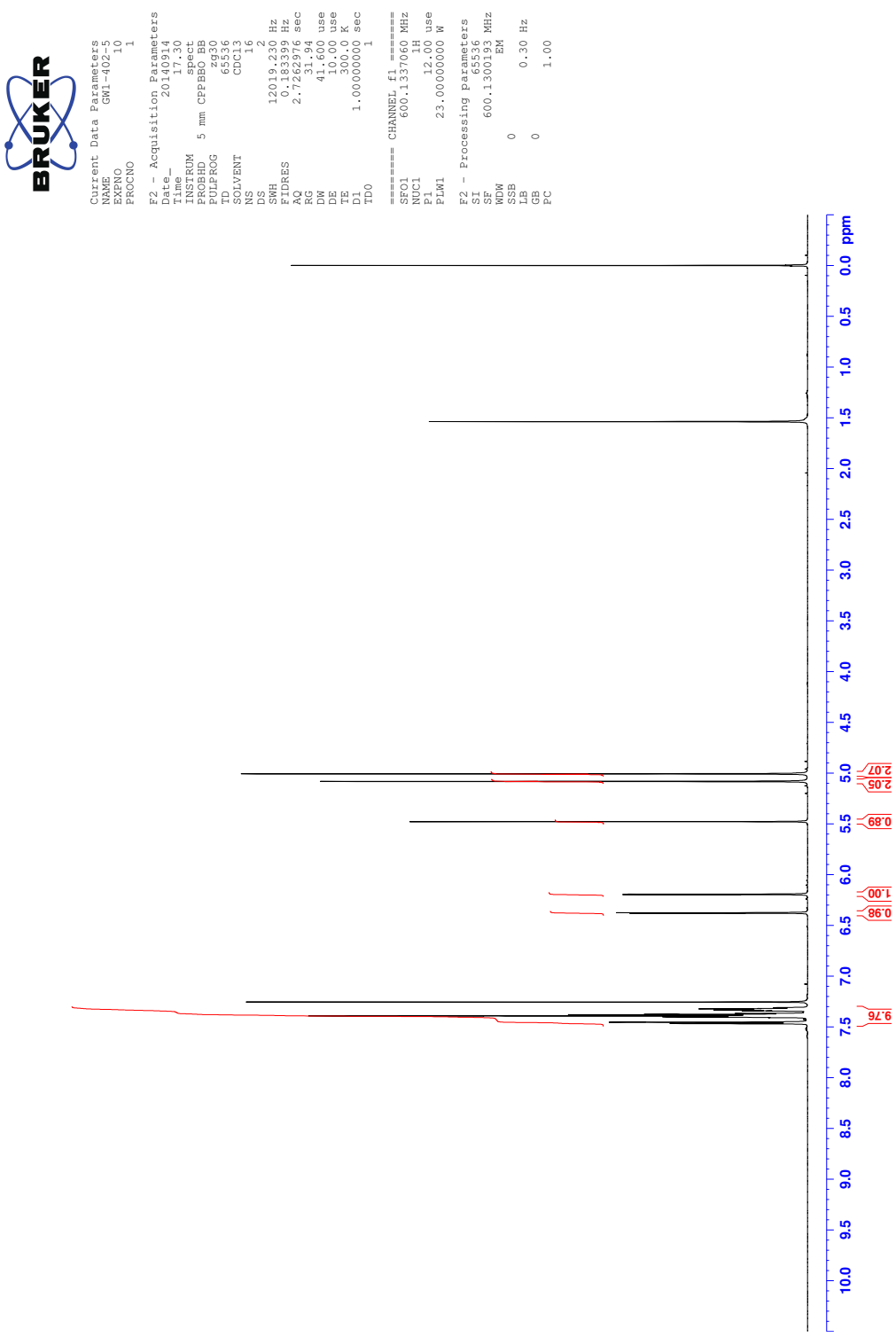
19: R_f 0.25 (toluene/acetone = 4/1); $[\alpha]_D^{24}$ = –27.1 (*c* 0.600, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, ratio of rotational isomers = 50:50) δ 1.94–2.34 (m, 33H), 2.46 (dd, 0.5H, *J* = 16.0, 9.7 Hz), 2.59 (dd, 0.5H, *J* = 16.1, 8.5 Hz), 2.93 (dd, 0.5H, *J* = 16.1, 4.8 Hz), 2.99 (dd, 0.5H, *J* = 15.4, 4.7 Hz), 4.39 (d, 0.5H, *J* = 9.0 Hz), 4.48 (d, 0.5H, *J* = 8.9 Hz), 4.81–4.85 (m, 1.0H), 4.89 (d, 0.5H, *J* = 9.2 Hz), 4.98–5.03 (m, 1.0H), 5.05–5.10 (m, 0.5H), 5.65–5.82 (m, 1.0H), 6.46 (d, 0.5H, *J* = 2.0 Hz), 6.49 (d, 0.5H, *J* = 2.2 Hz), 6.61 (s, 0.5H), 6.66–6.69 (m, 1.5H), 7.16 (s, 1.0H), 7.17 (s, 1.0H), 7.22–7.26 (m, 2H), 7.36–7.39 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.9–21.1 (m), 29.4, 29.7, 36.6, 37.1, 68.5, 68.6, 78.1, 79.7, 108.5, 108.6, 108.9, 110.4, 110.7, 110.8, 113.3, 115.5, 118.1, 119.4, 119.8, 123.0, 123.5, 125.47, 125.52, 134.6, 134.68, 134.70, 141.81, 141.83, 142.46, 142.49, 143.2, 143.3, 147.8, 148.0, 148.1, 148.2, 149.6, 149.9, 150.0, 150.1, 152.9, 153.1, 155.8, 166.8–170.0 (m); IR (film) 3027, 2920, 2851, 1774, 1620, 1593, 1506, 1478, 1431, 1371, 1319, 1186, 1125, 1052, 898, 756 cm^{-1}; HRMS (ESI) *m*/*z* 1079.2423 ($[M+Na]^+$ calcd for $C_{52}H_{48}O_{24}$: 1079.2427).

[1] T. Higuchi, K. Ohmori and K. Suzuki, *Chem. Lett.* 2006, **35**, 1006. See, also reference 7.

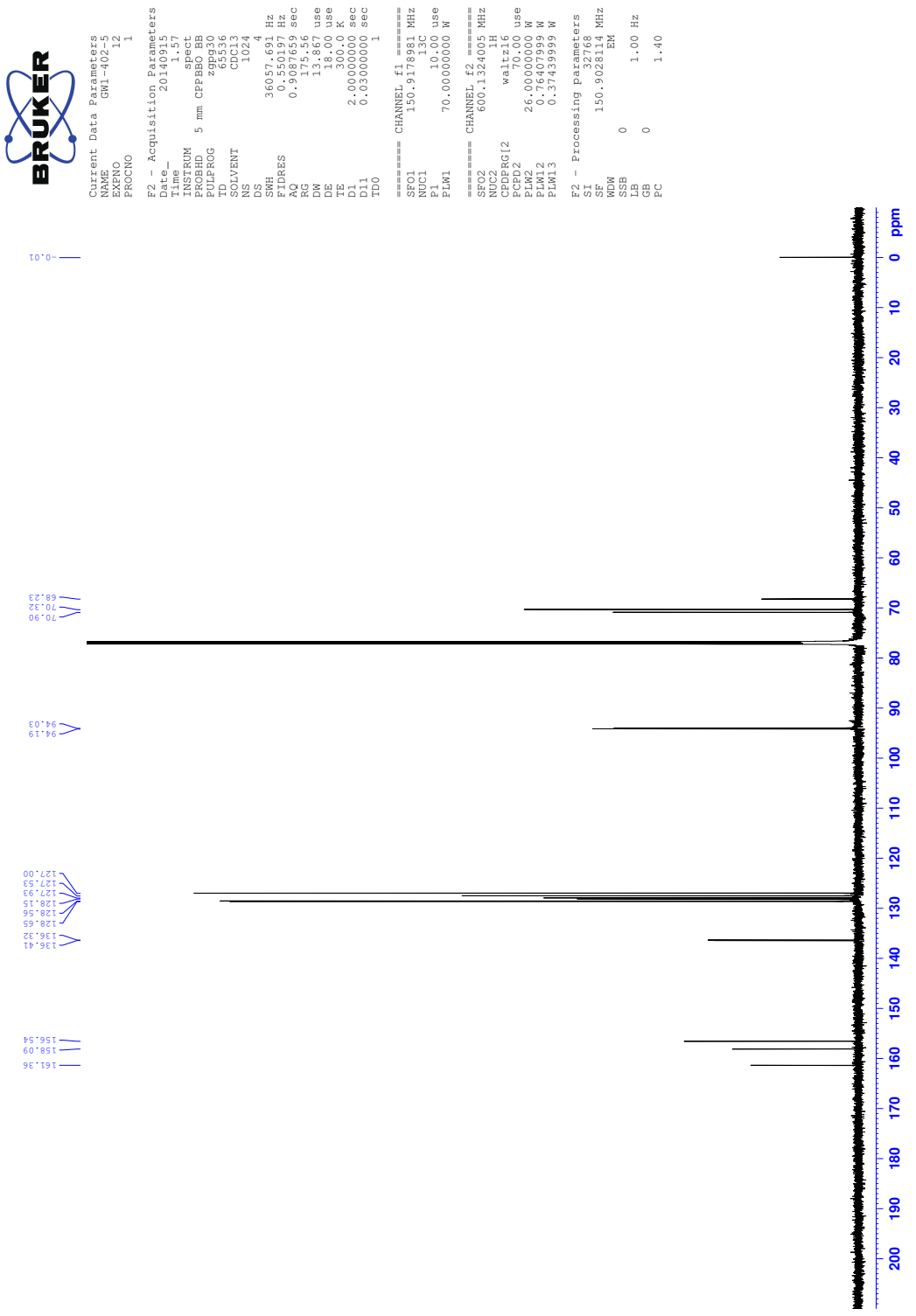
[2] G. Watanabe, K. Ohmori and K. Suzuki, *Chem. Commun.* 2013, **49**, 5210.

[3] (*a*) R. S. Thompson, D. Jacques, E. Haslam and R. J. N. Tanner, *J. Chem. Soc., Perkin Trans. 1* 1972, 1387; (*b*) C. Ma, N. Nakamura, H. Miyashiro, M. Hattori and K. Shimotohno, *Chem. Pharm. Bull.* 1999, **47**, 141.

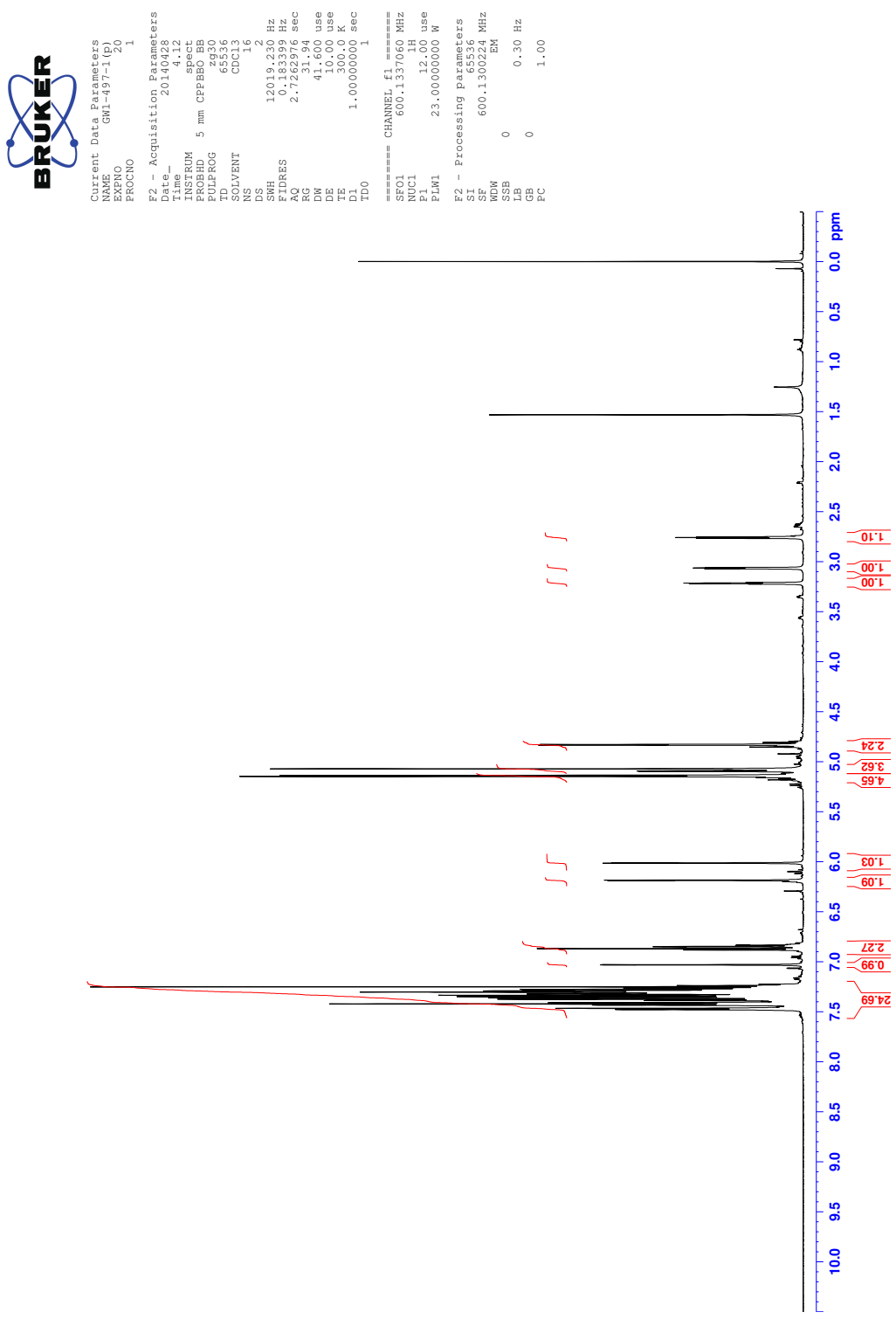
Compound **10** (^{1}H NMR, 600 MHz, $CDCl_3$)



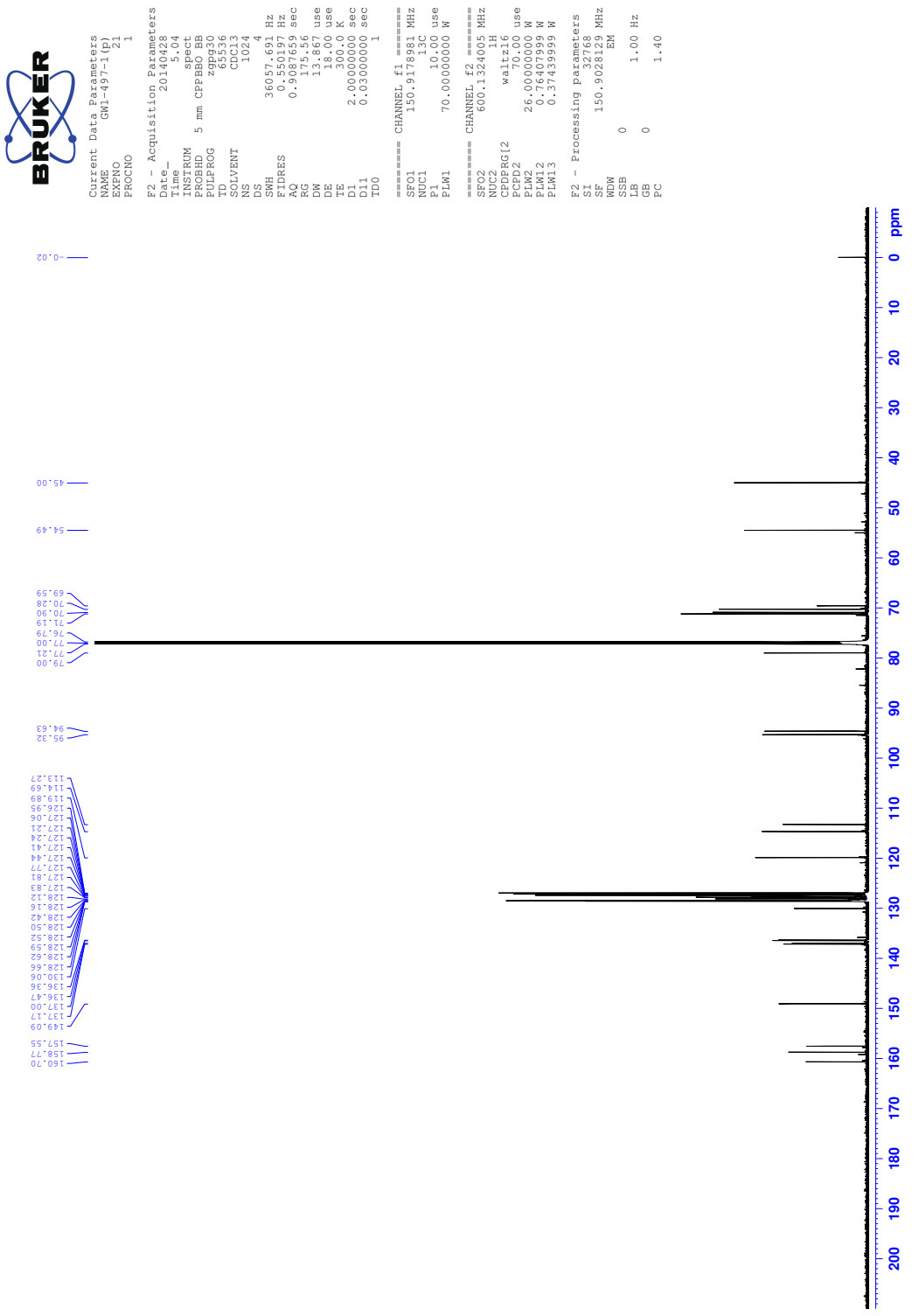
Compound **10** (^{13}C NMR, 150 MHz, $CDCl_3$)



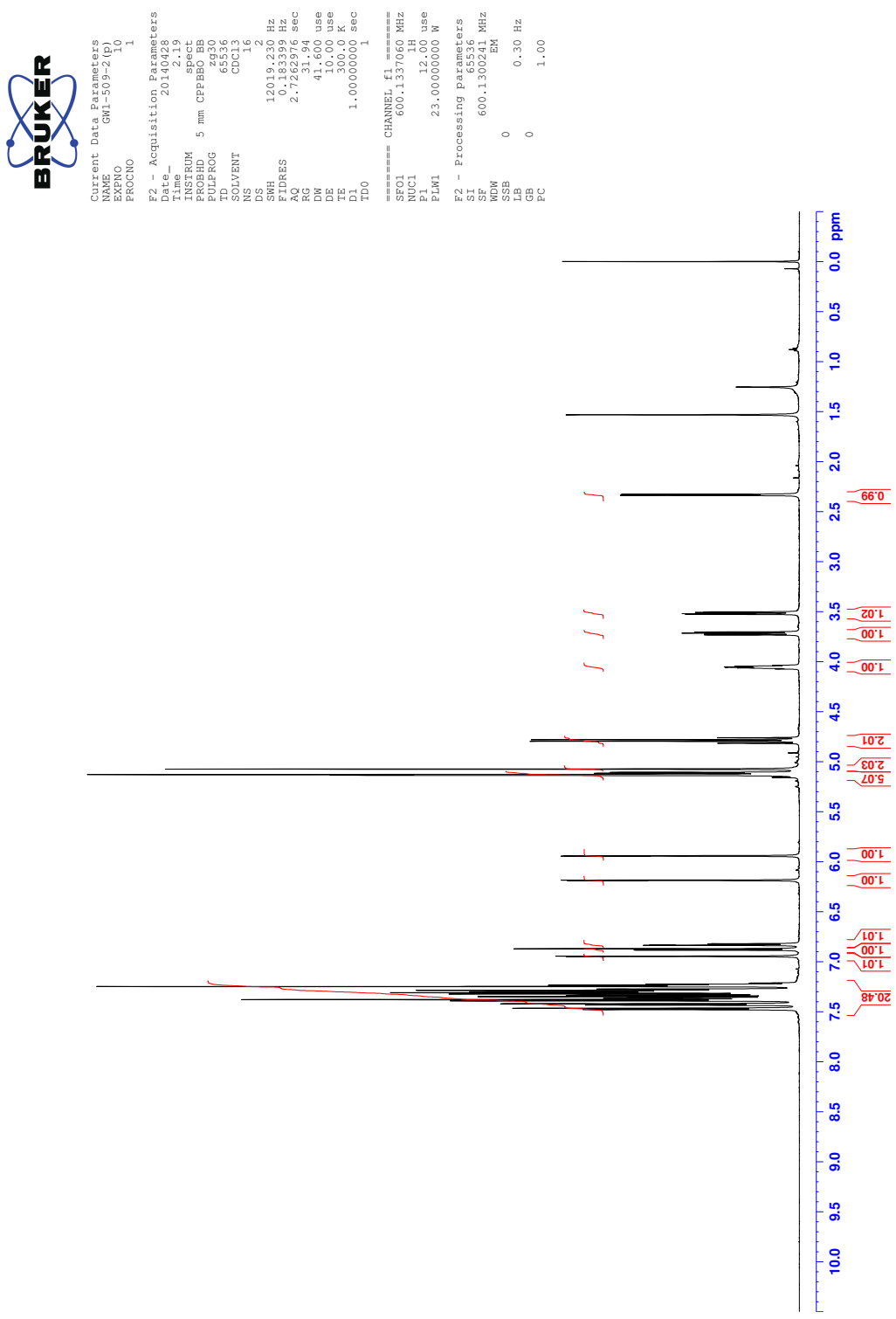
Compound **S3** (^{1}H NMR, 600 MHz, $CDCl_3$)



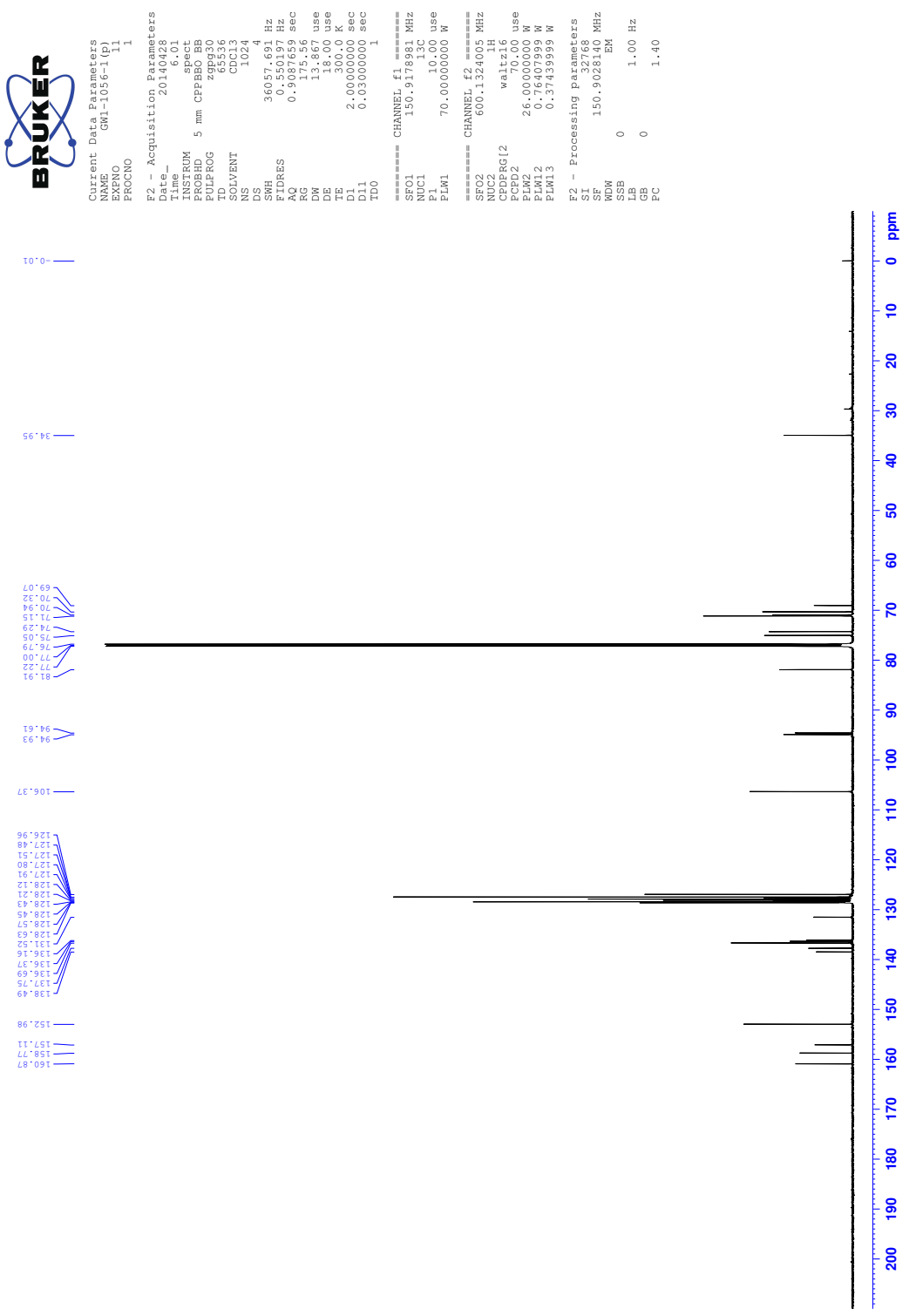
Compound **S3** (^{13}C NMR, 150 MHz, $CDCl_3$)



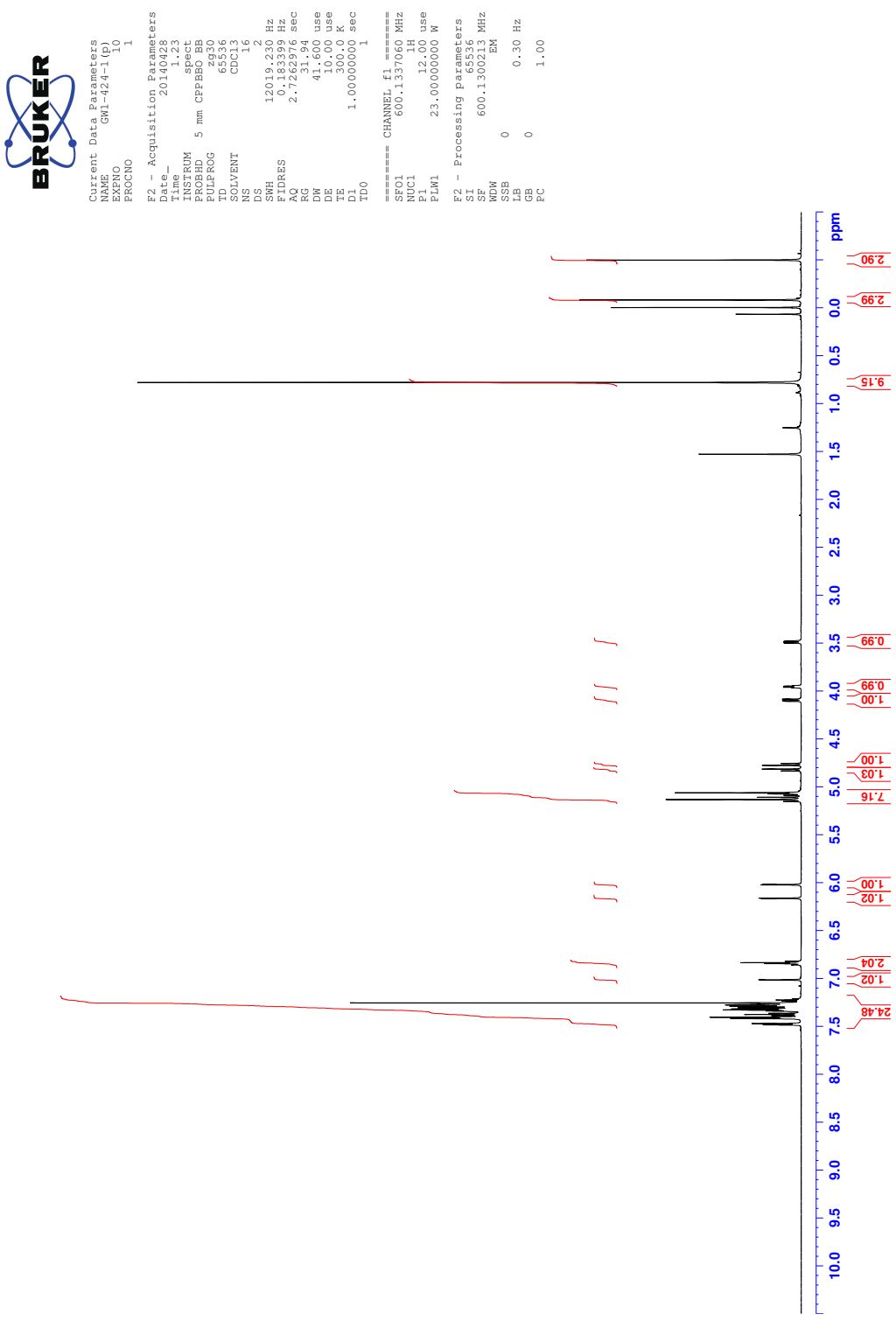
Compound **S4** (^{1}H NMR, 600 MHz, $CDCl_3$)



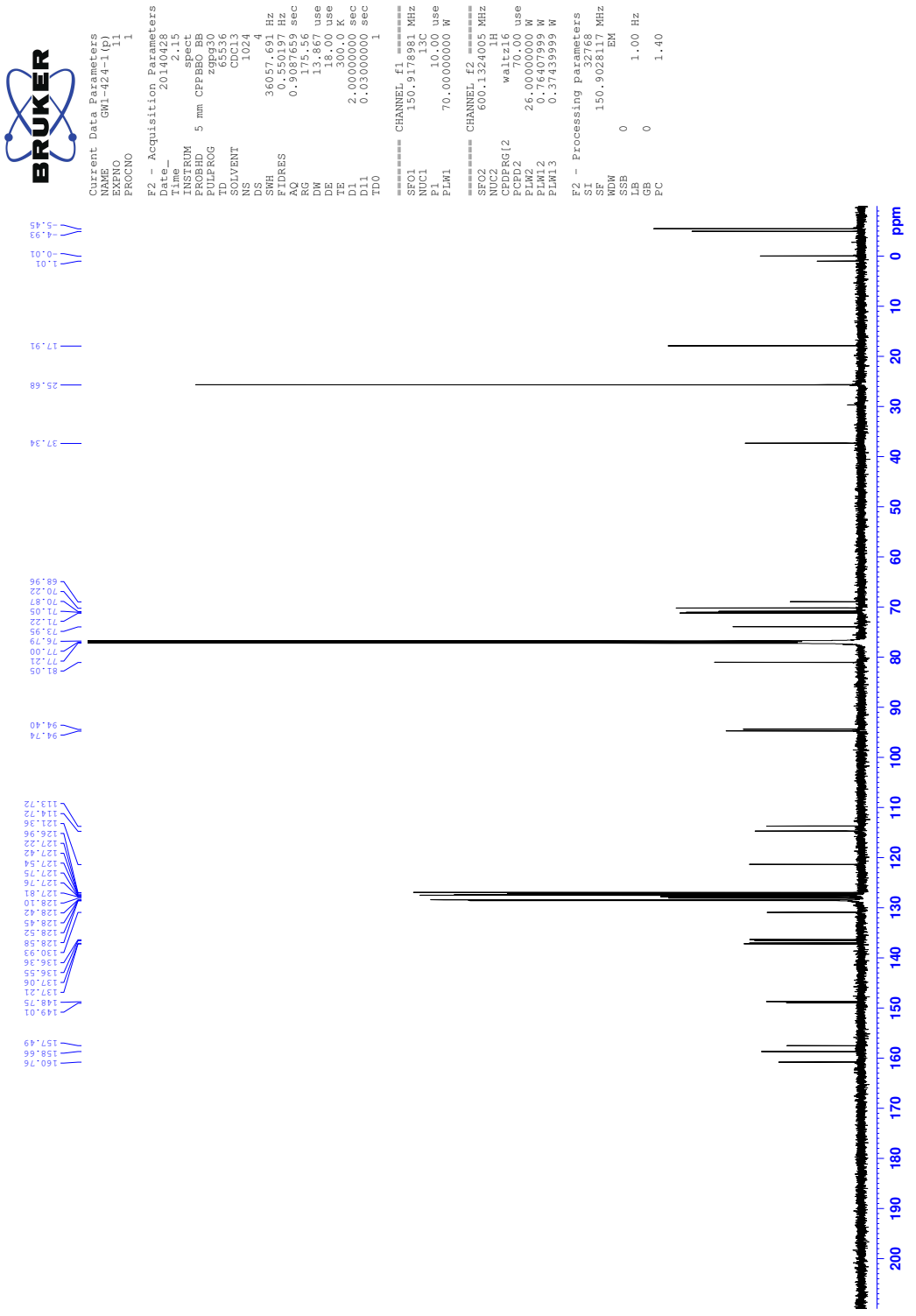
Compound **S4** (^{13}C NMR, 150 MHz, $CDCl_3$)



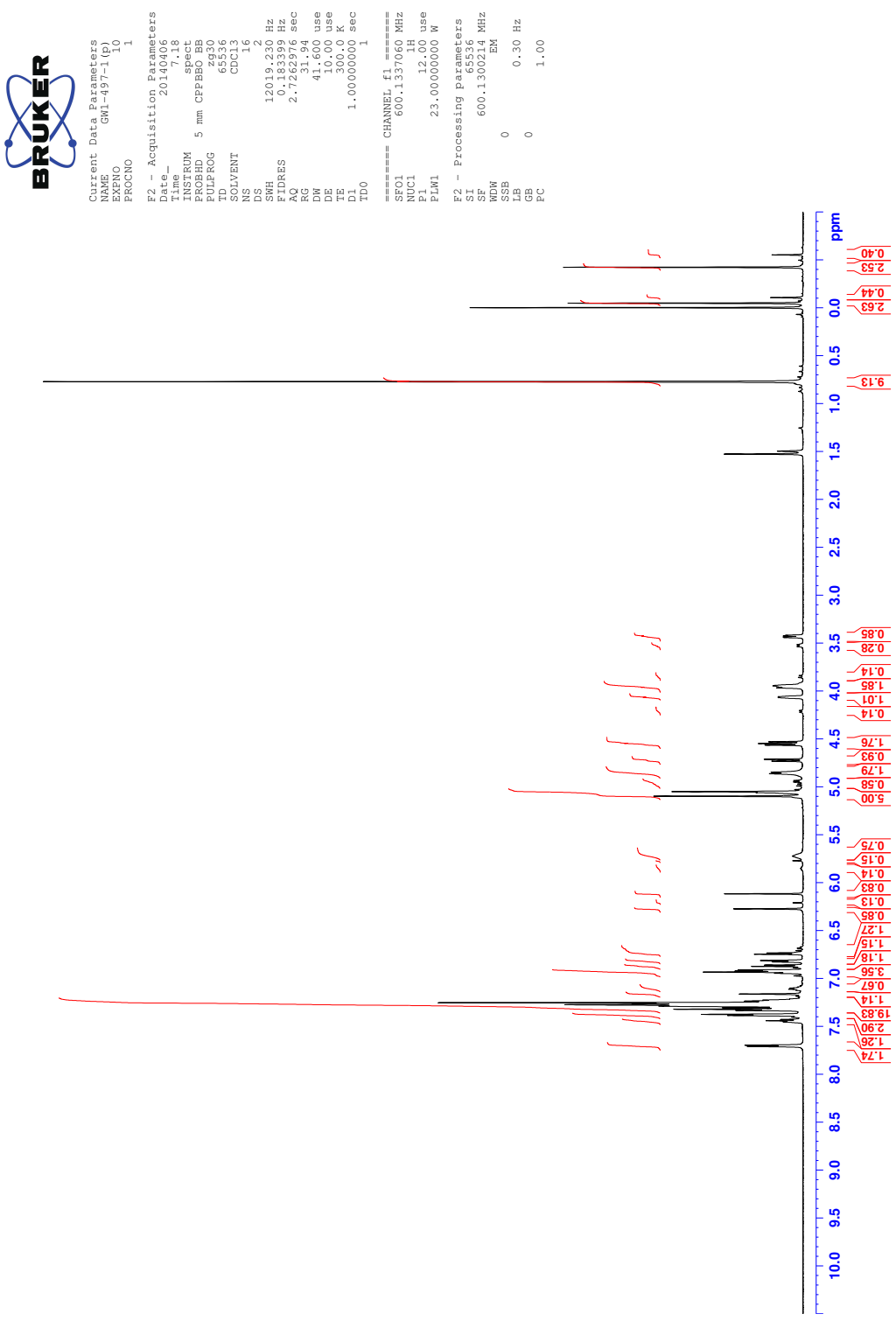
Compound **5** (^{1}H NMR, 600 MHz, $CDCl_3$)



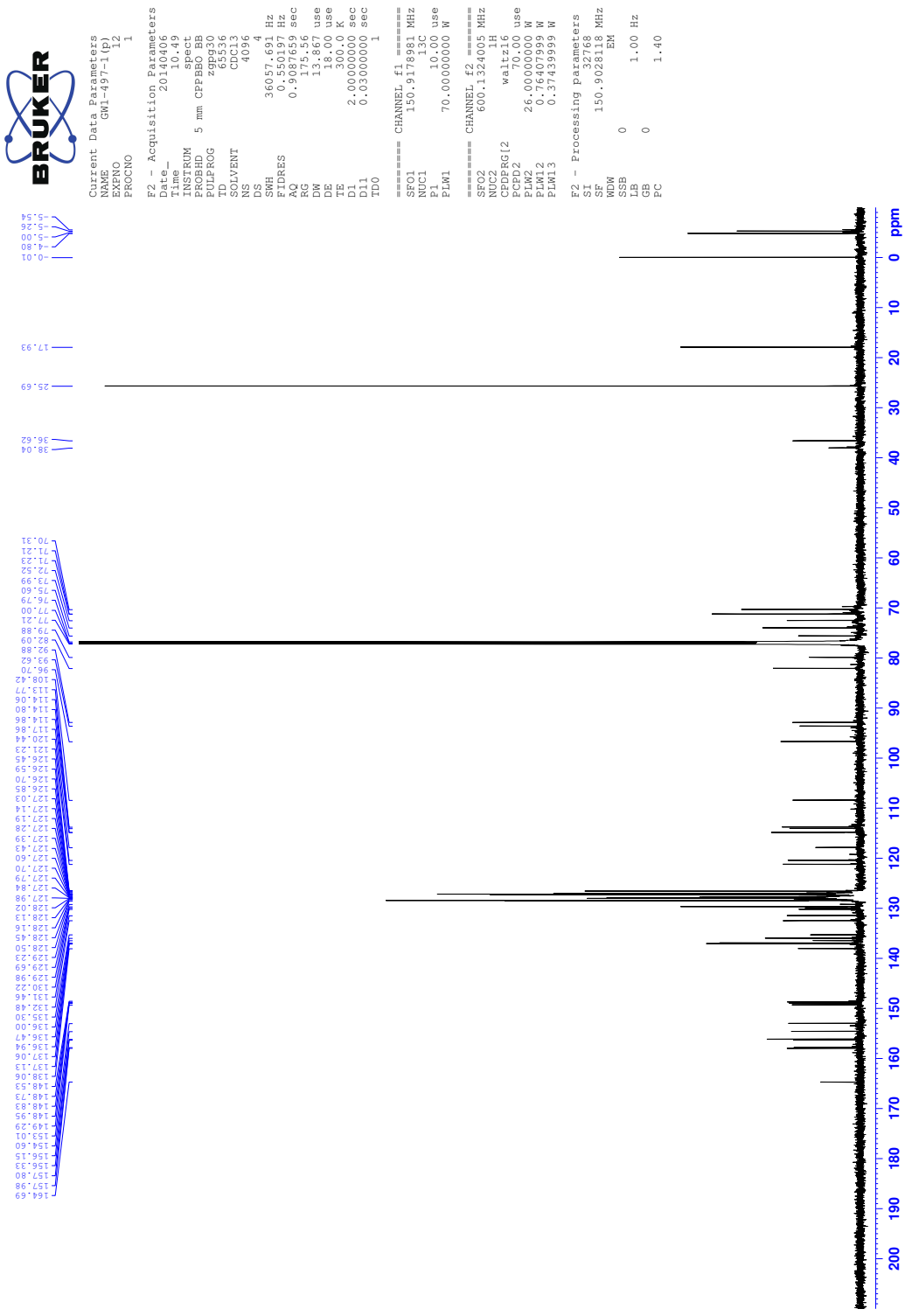
Compound **5** (^{13}C NMR, 150 MHz, $CDCl_3$)



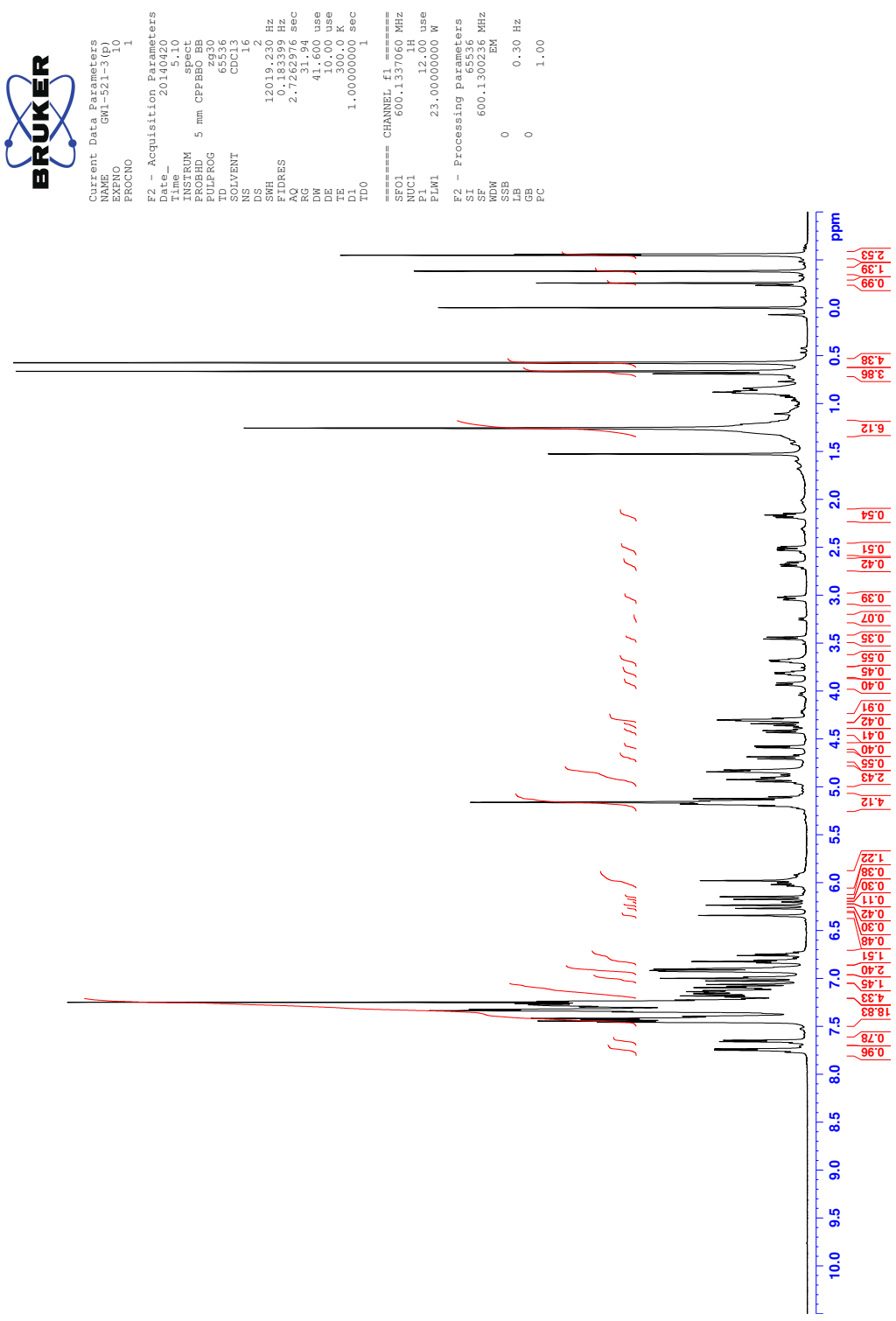
Compound **6** (^{1}H NMR, 600 MHz, $CDCl_3$)



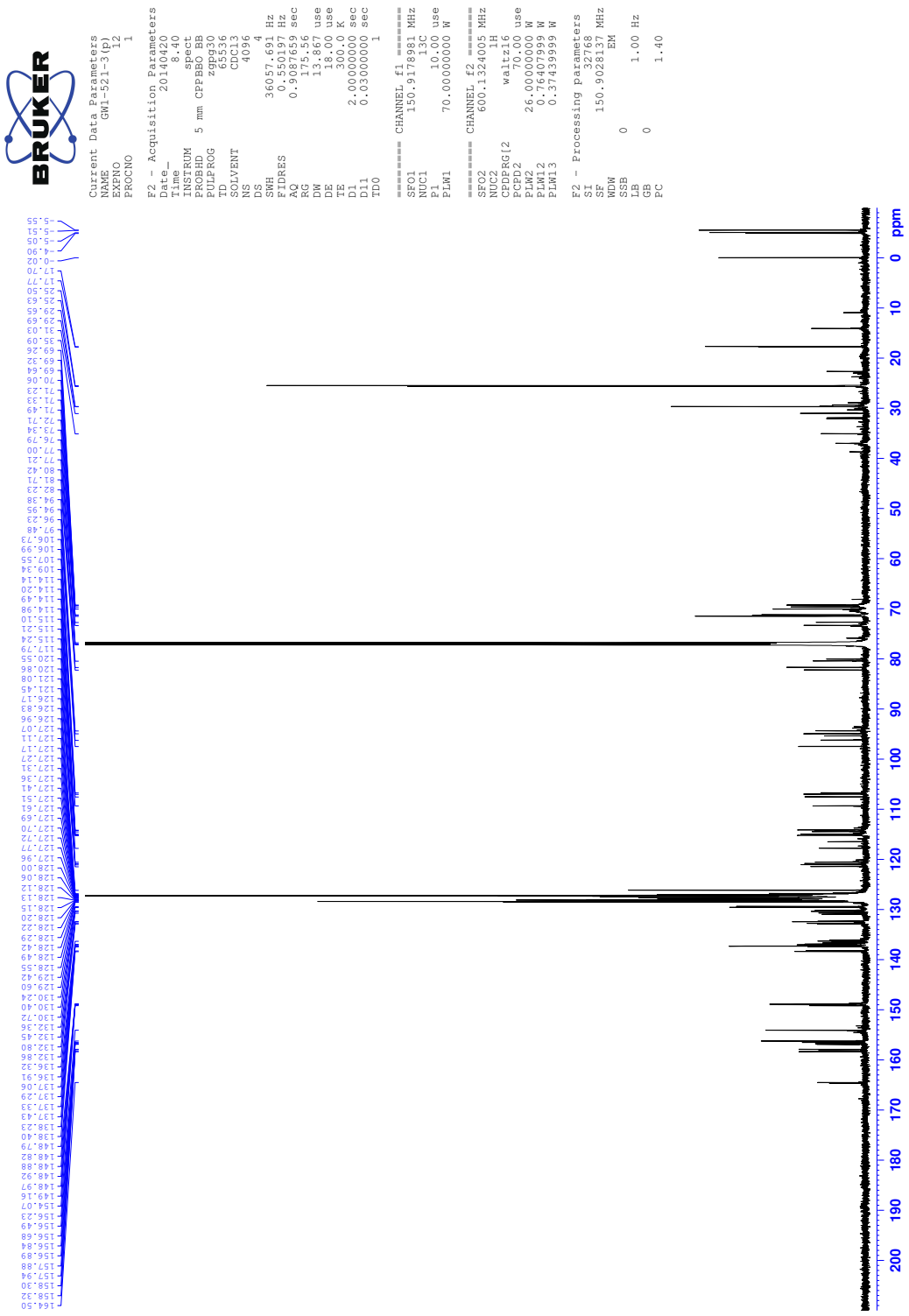
Compound **6** (^{13}C NMR, 150 MHz, $CDCl_3$)



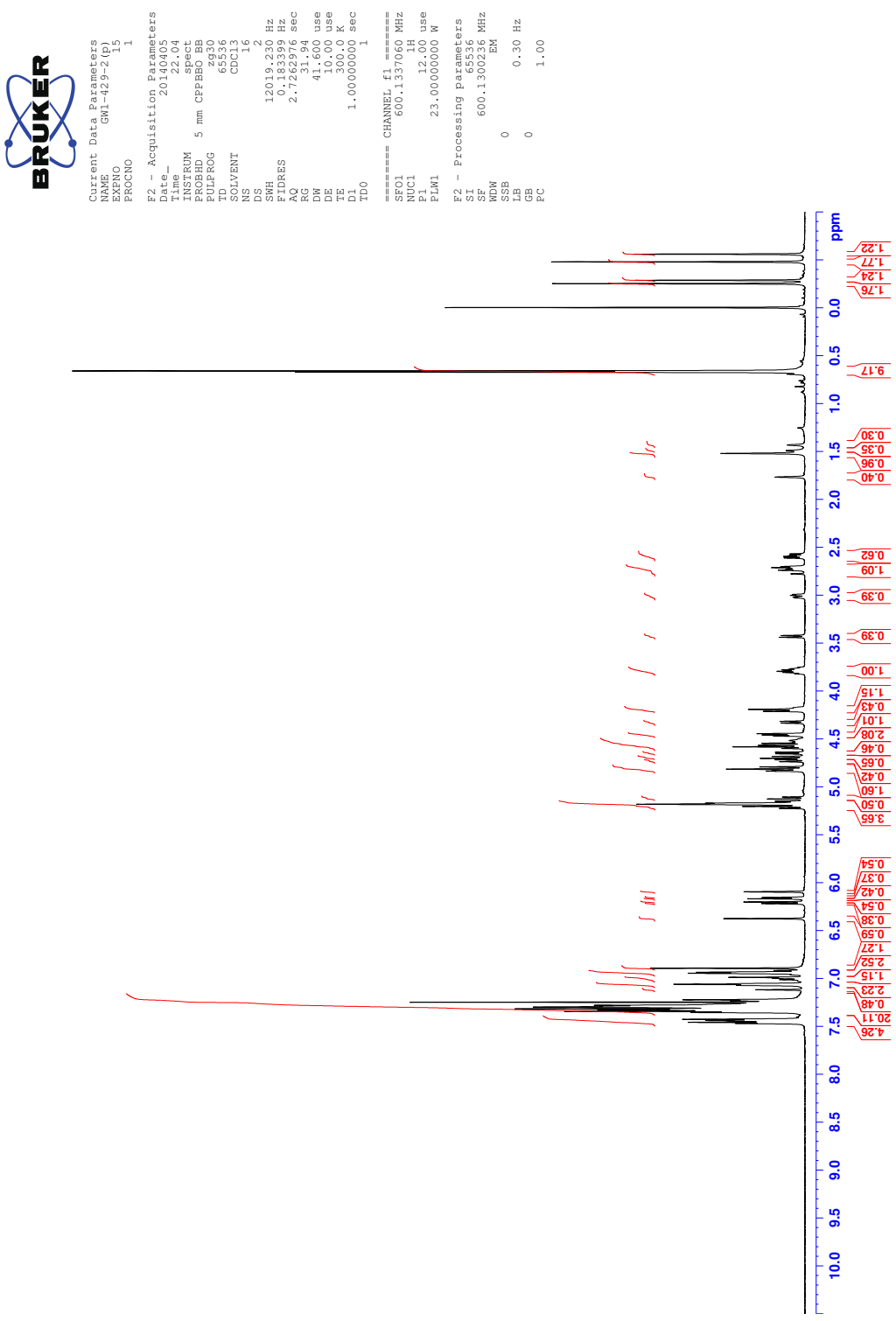
Compound **7** (^{1}H NMR, 600 MHz, $CDCl_3$)



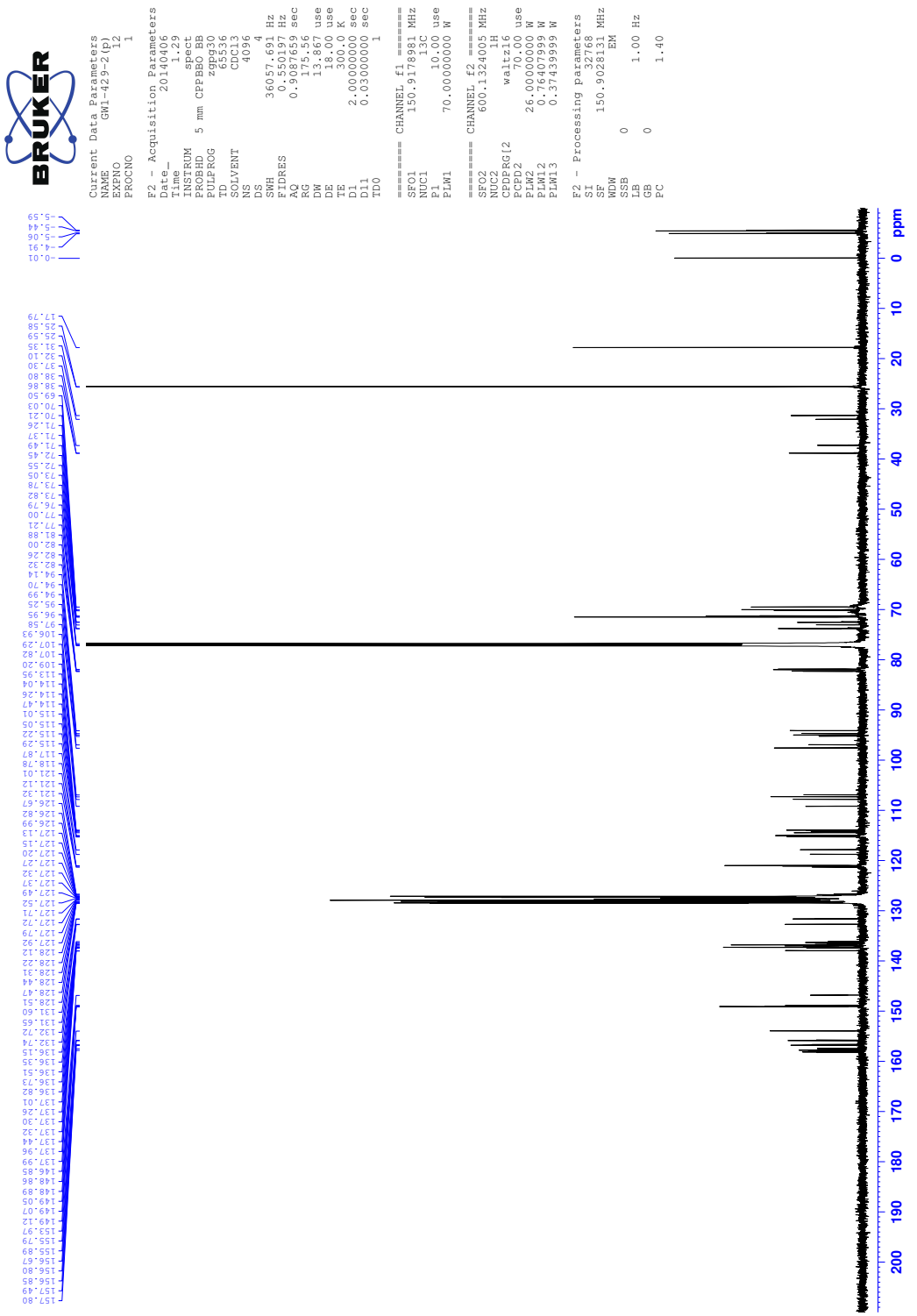
Compound **7** (^{13}C NMR, 150 MHz, $CDCl_3$)



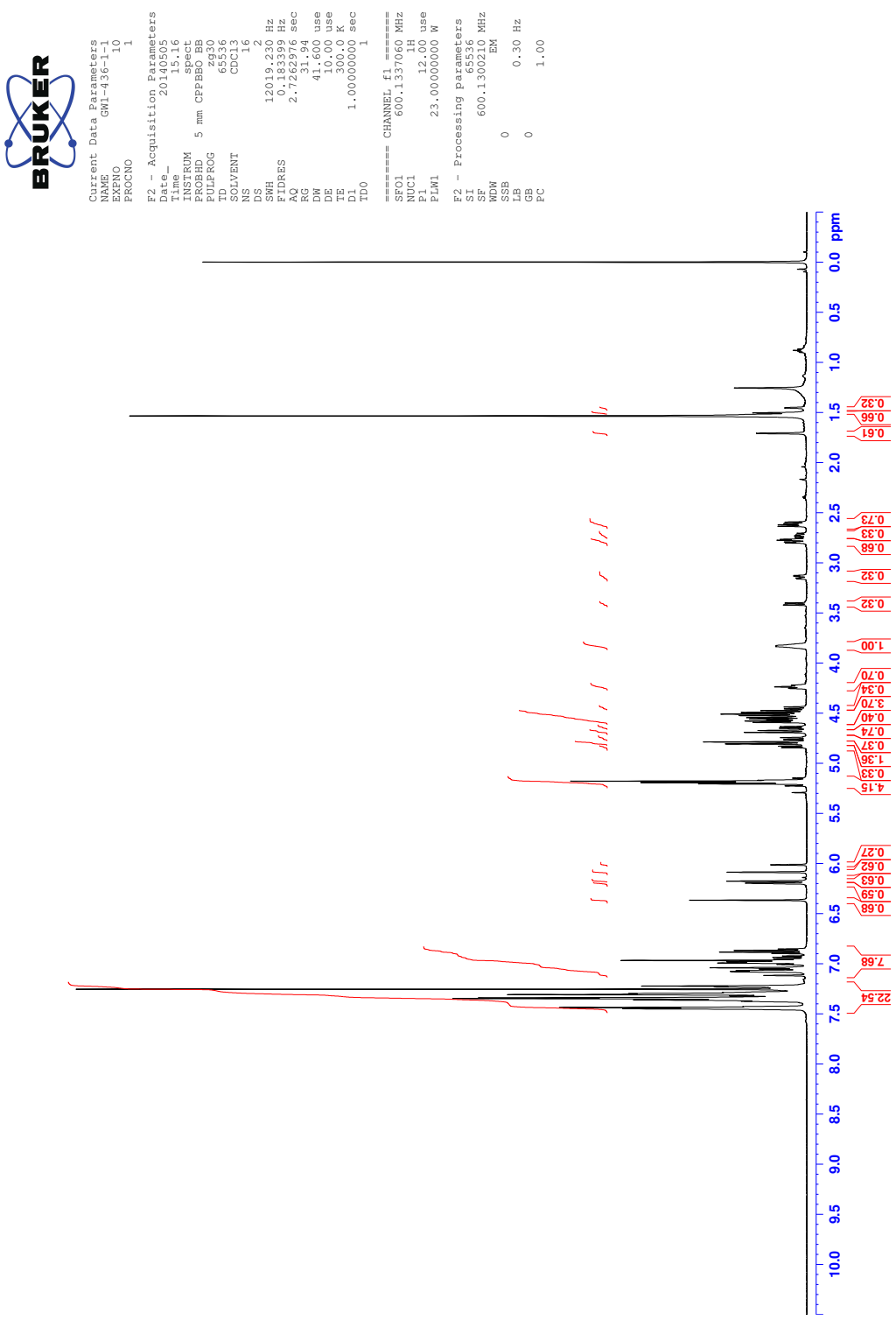
Compound **8** (^{1}H NMR, 600 MHz, $CDCl_3$)



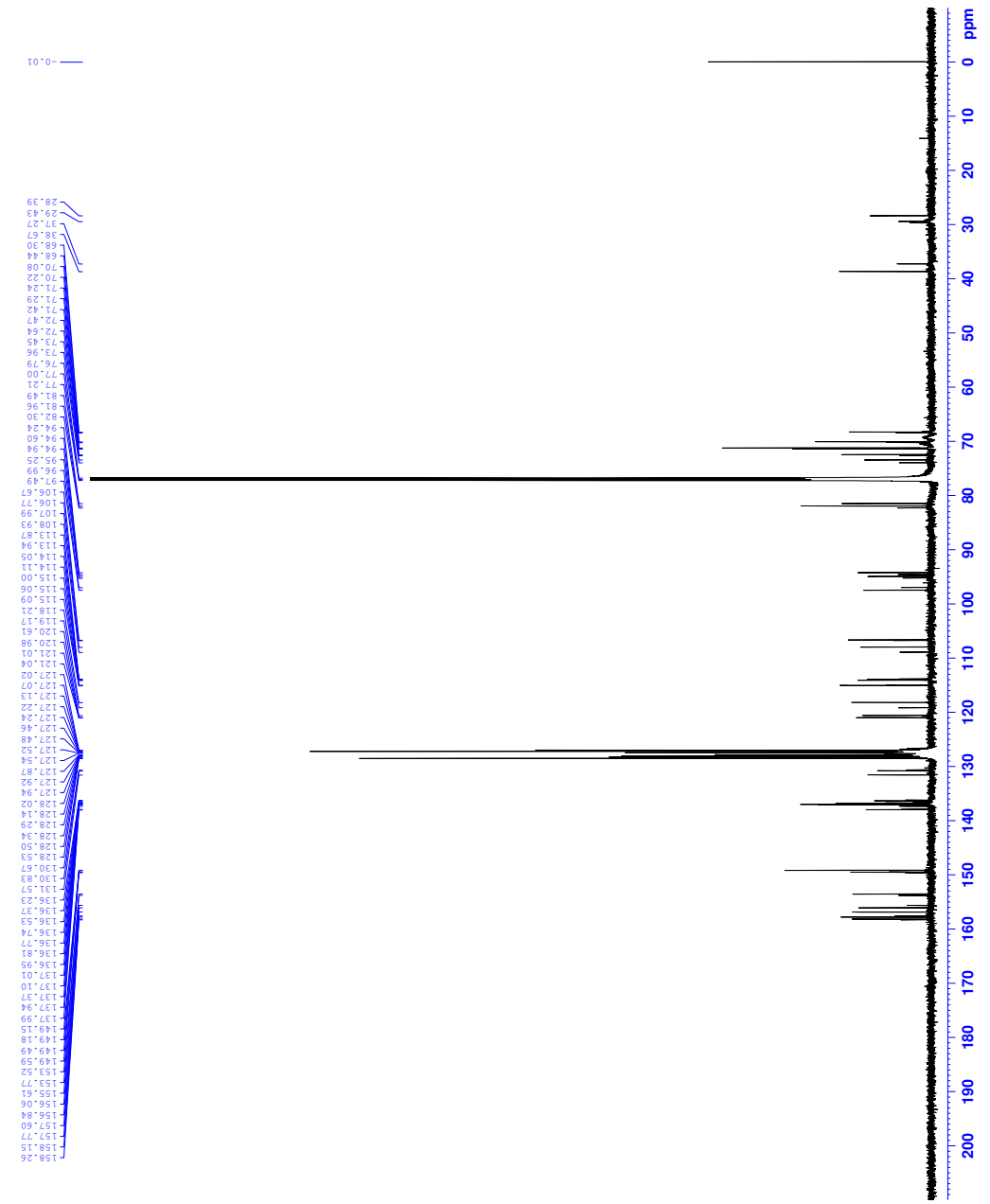
Compound **8** (^{13}C NMR, 150 MHz, $CDCl_3$)



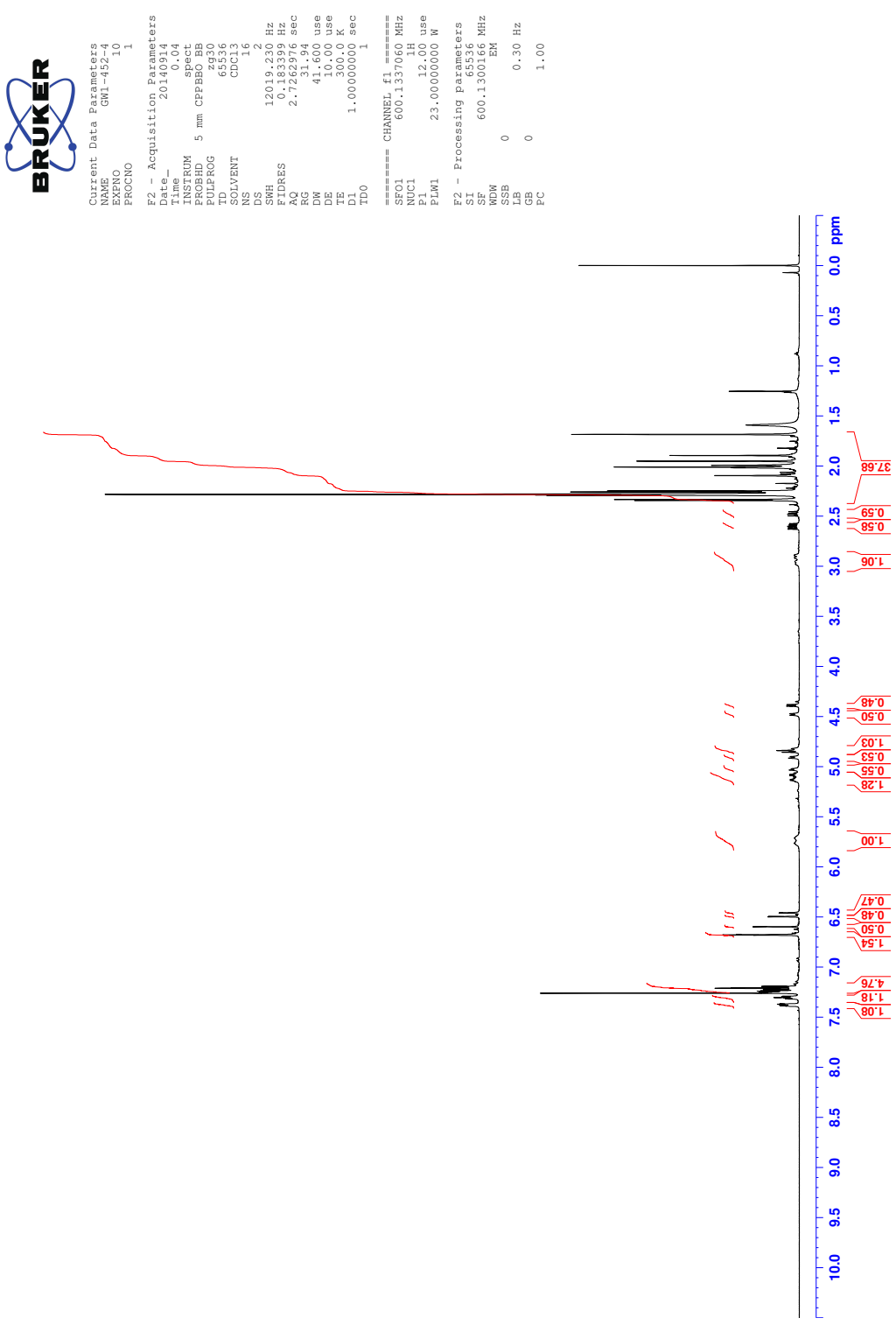
Compound **9** (^{1}H NMR, 600 MHz, $CDCl_3$)



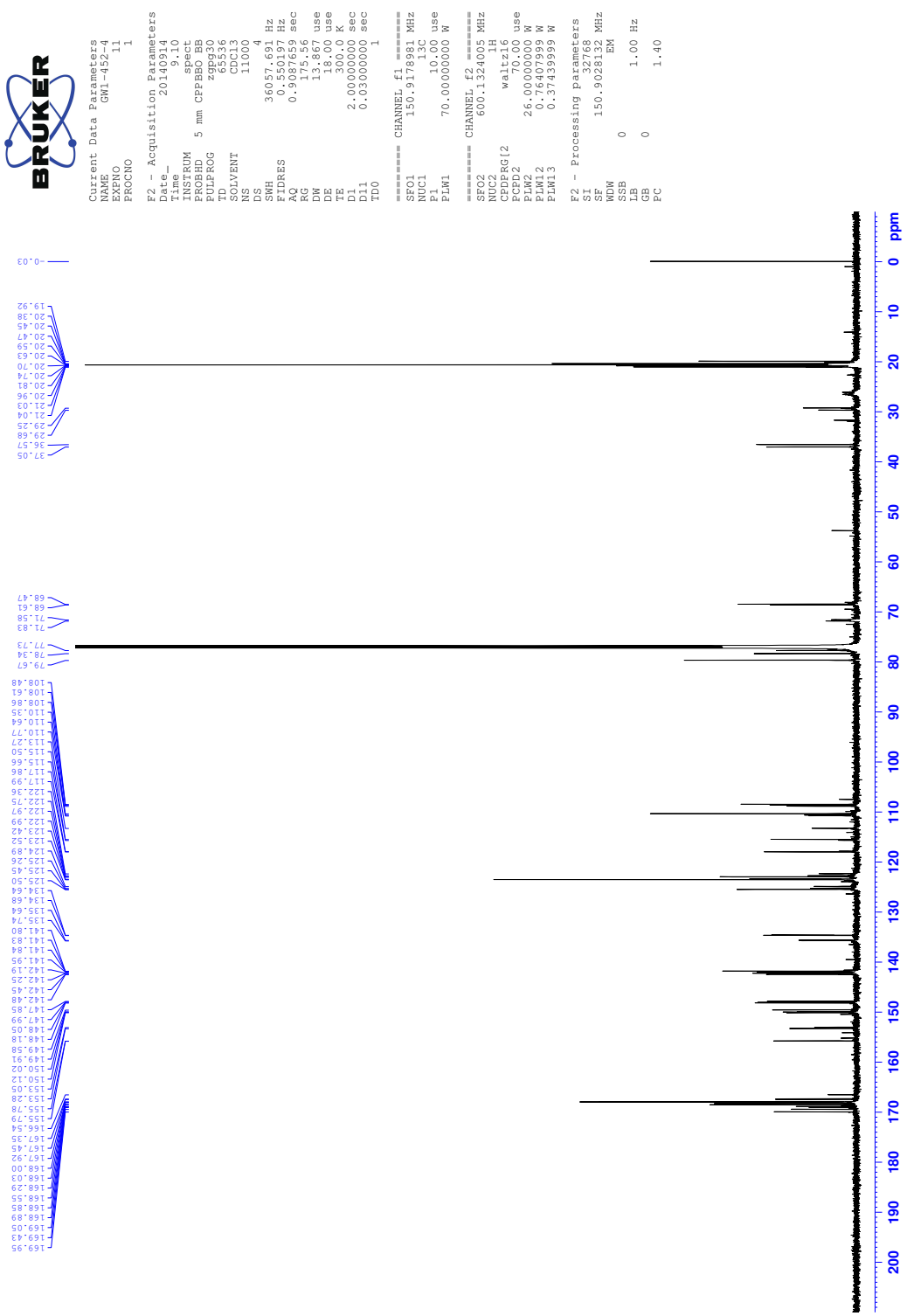
Compound **9** (^{13}C NMR, 150 MHz, $CDCl_3$)



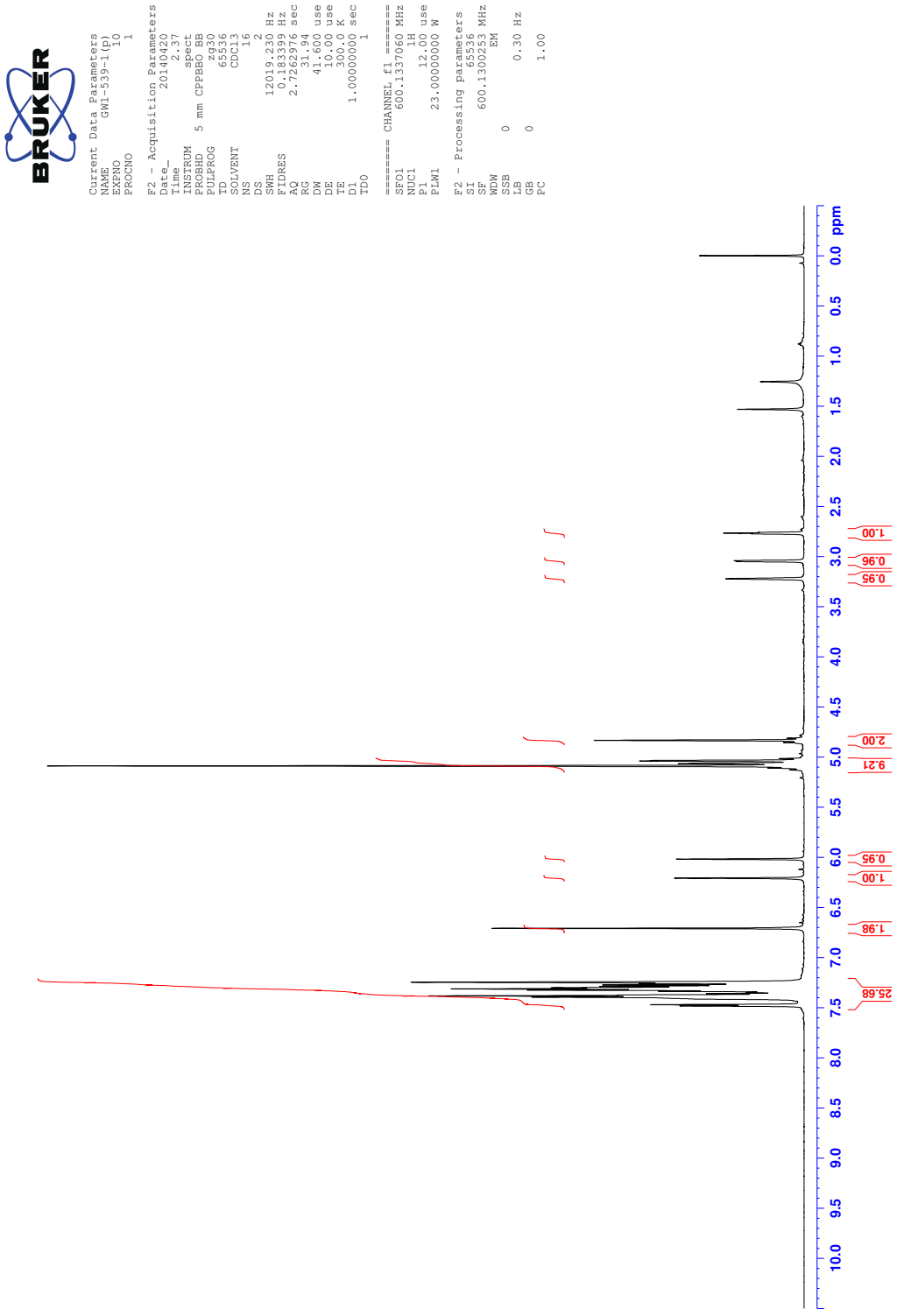
Compound **2-perAc** (^{1}H NMR, 600 MHz, $CDCl_3$)



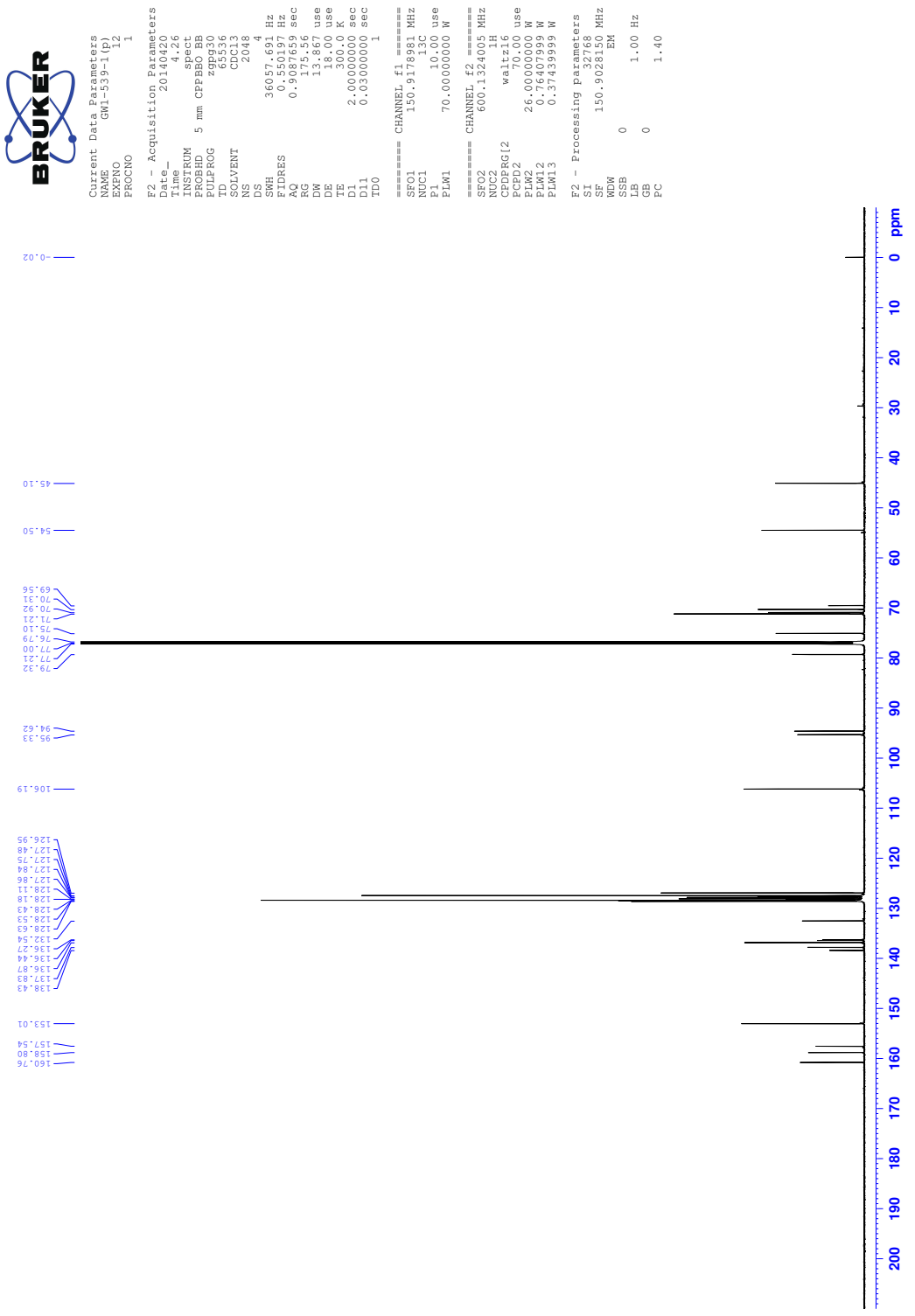
Compound **2-perAc** (^{13}C NMR, 150 MHz, $CDCl_3$)



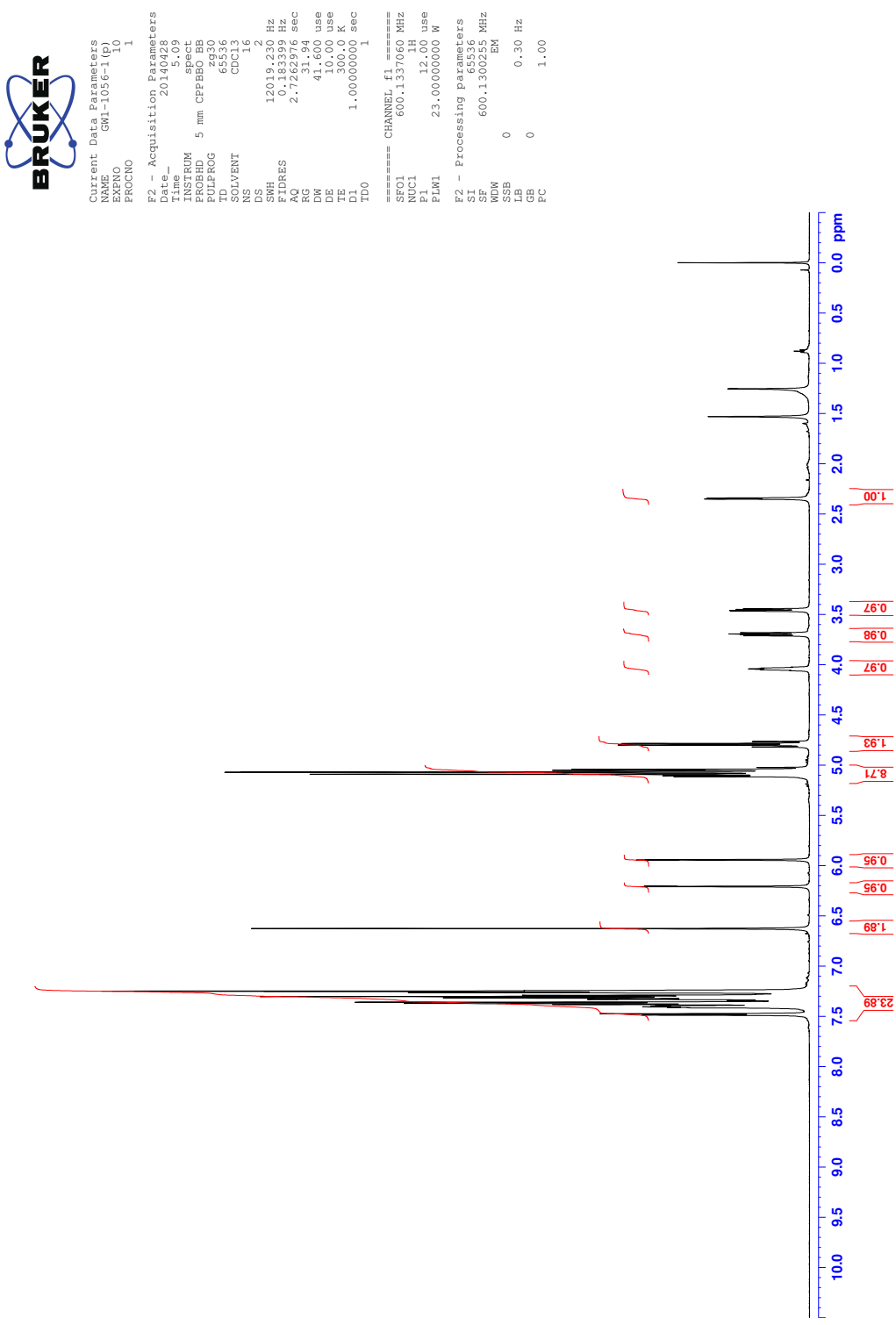
Compound **12** (^{1}H NMR, 600 MHz, $CDCl_3$)



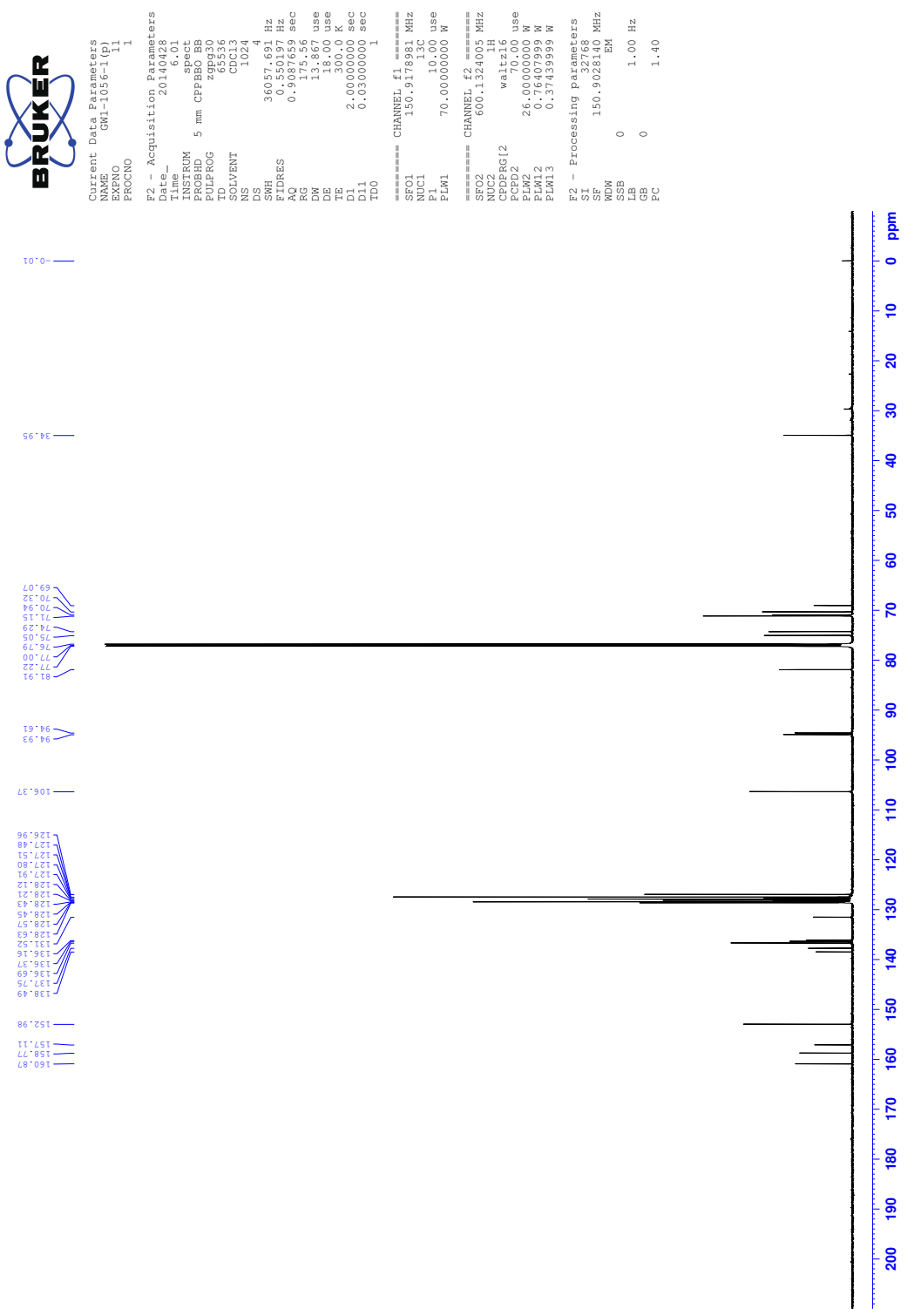
Compound **12** (^{13}C NMR, 150 MHz, $CDCl_3$)



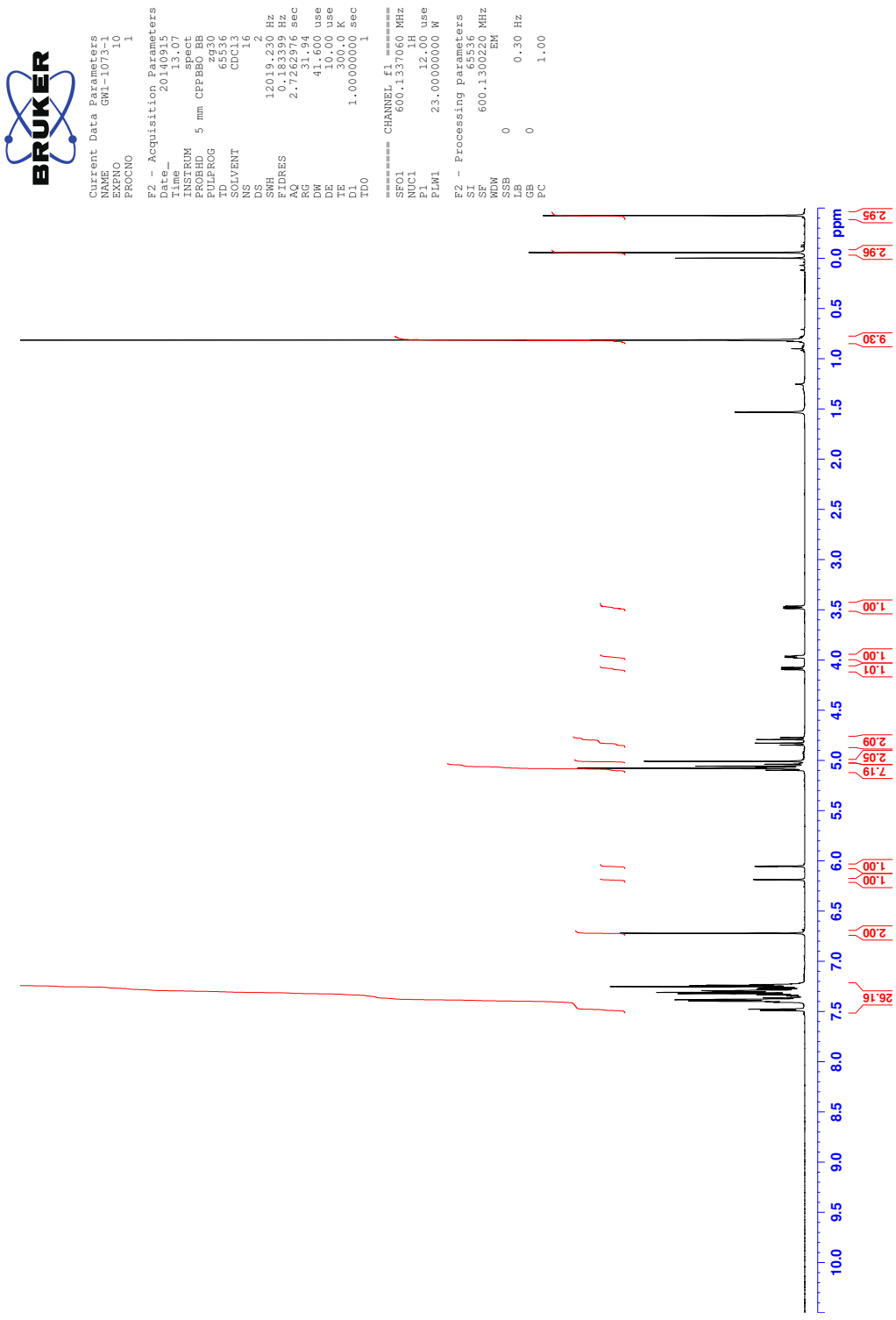
Compound **S5** (^{1}H NMR, 600 MHz, $CDCl_3$)



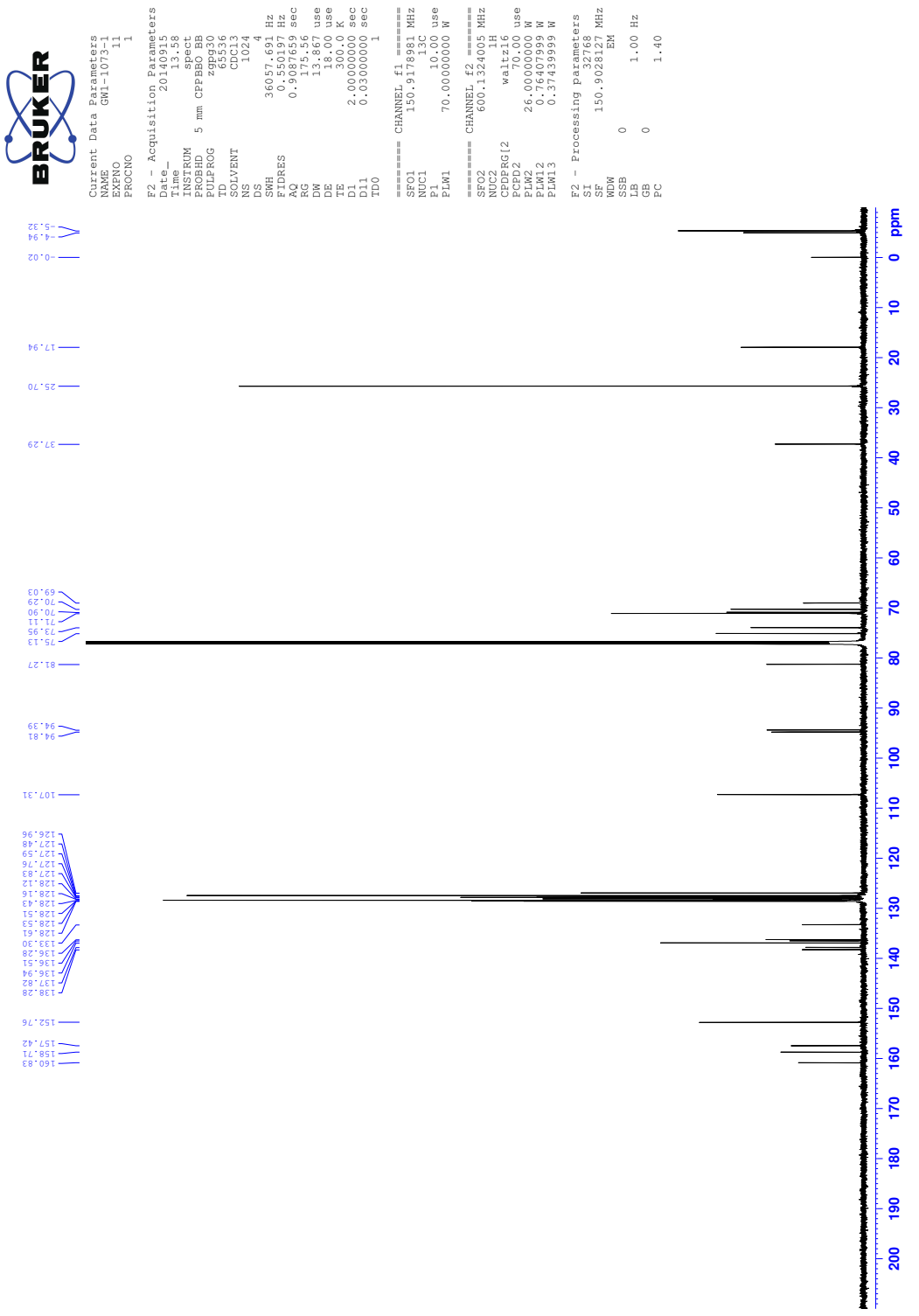
Compound **S5** (^{13}C NMR, 150 MHz, $CDCl_3$)



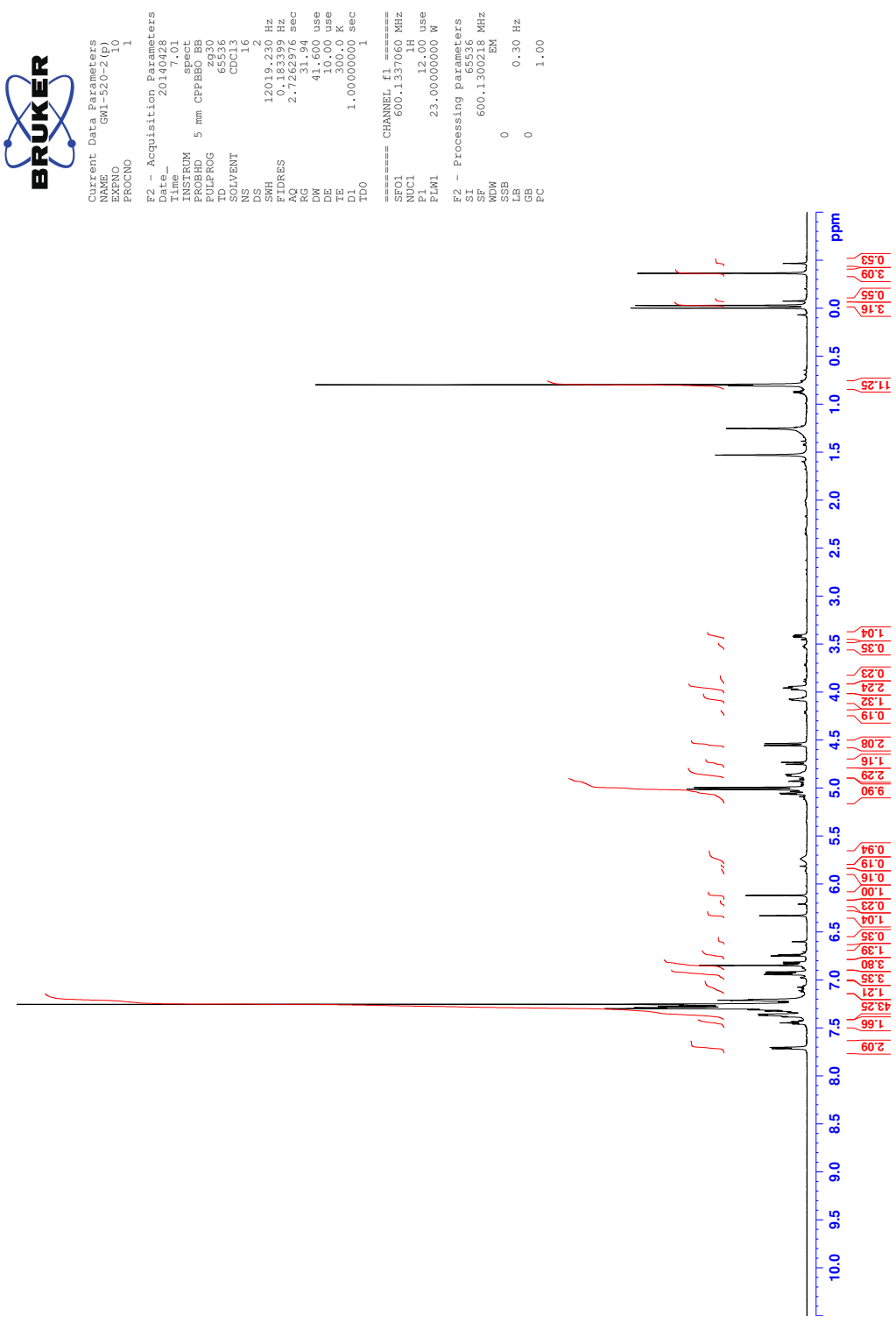
Compound **13** (^{1}H NMR, 600 MHz, $CDCl_3$)



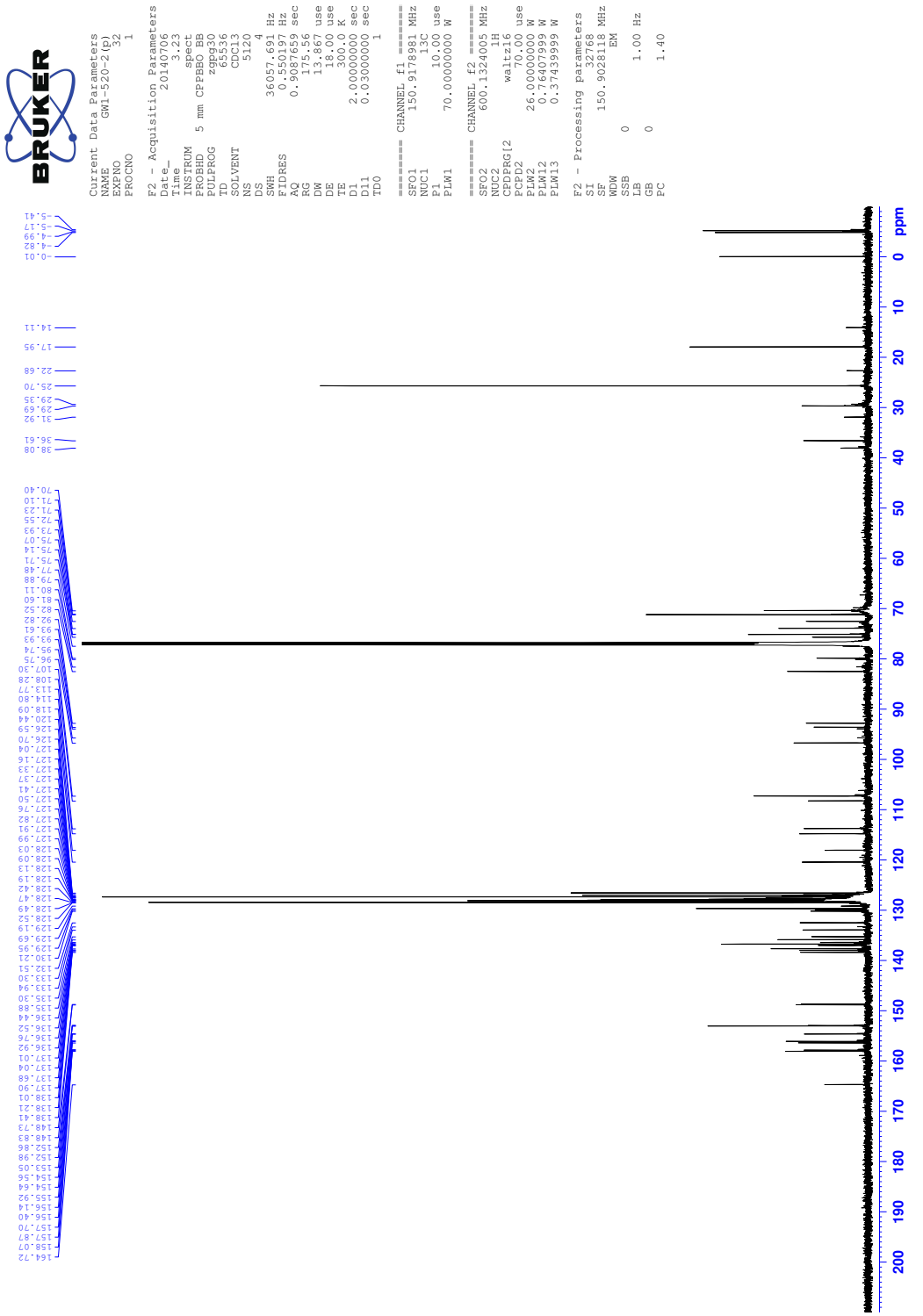
Compound **13** (^{13}C NMR, 150 MHz, $CDCl_3$)



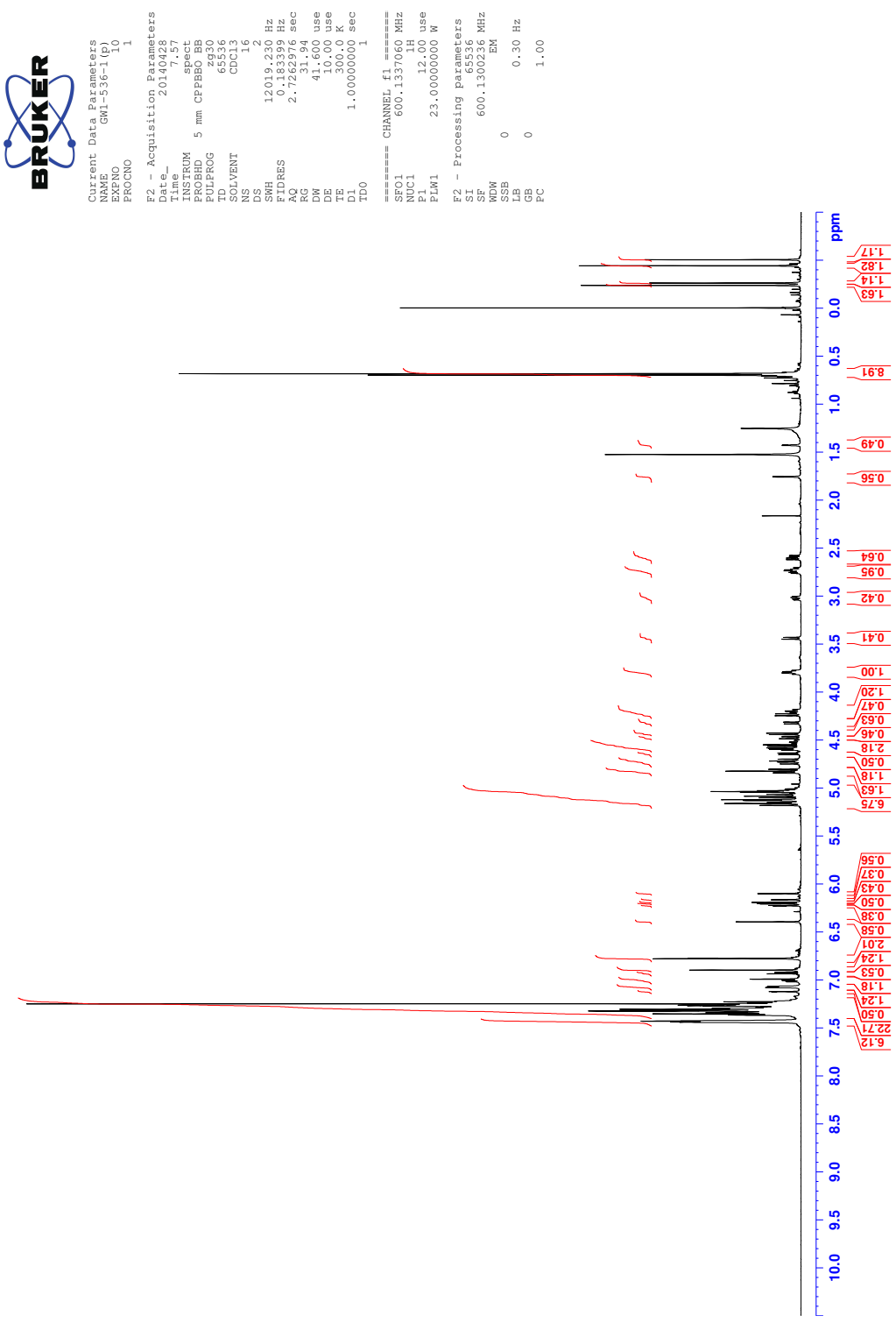
Compound **14** (^{1}H NMR, 600 MHz, $CDCl_3$)



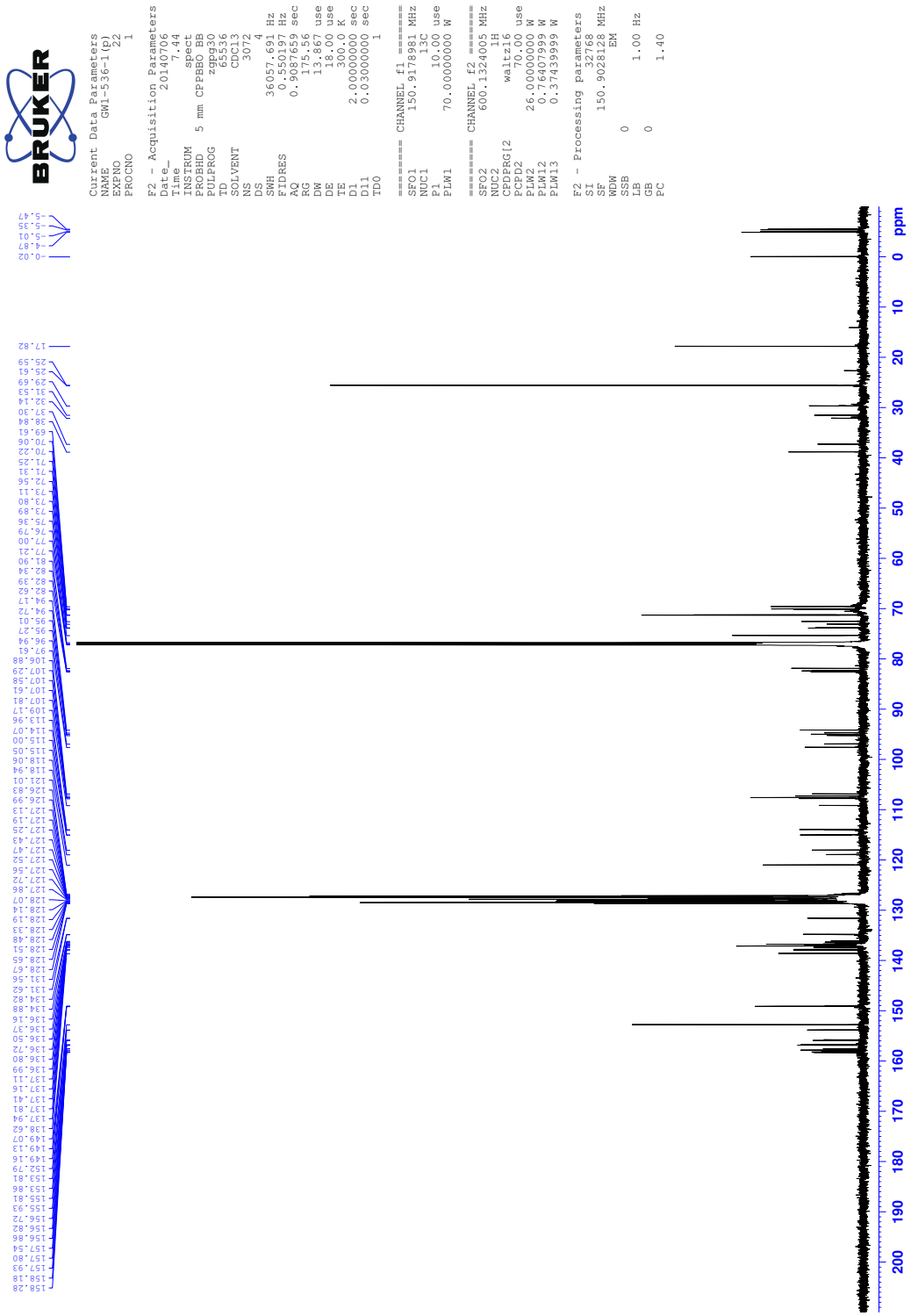
Compound **14** (^{13}C NMR, 150 MHz, $CDCl_3$)



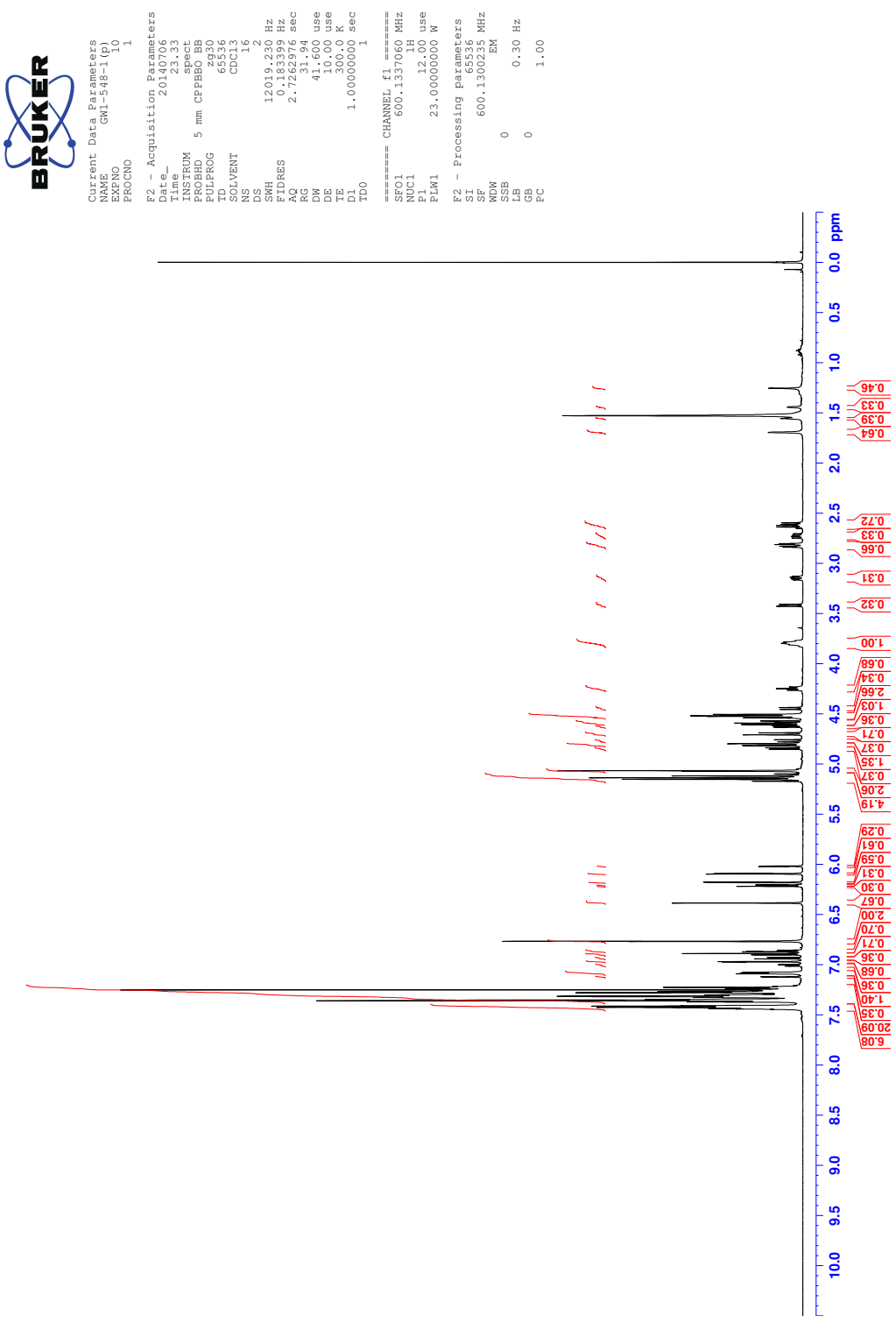
Compound **16** (^{1}H NMR, 600 MHz, $CDCl_3$)



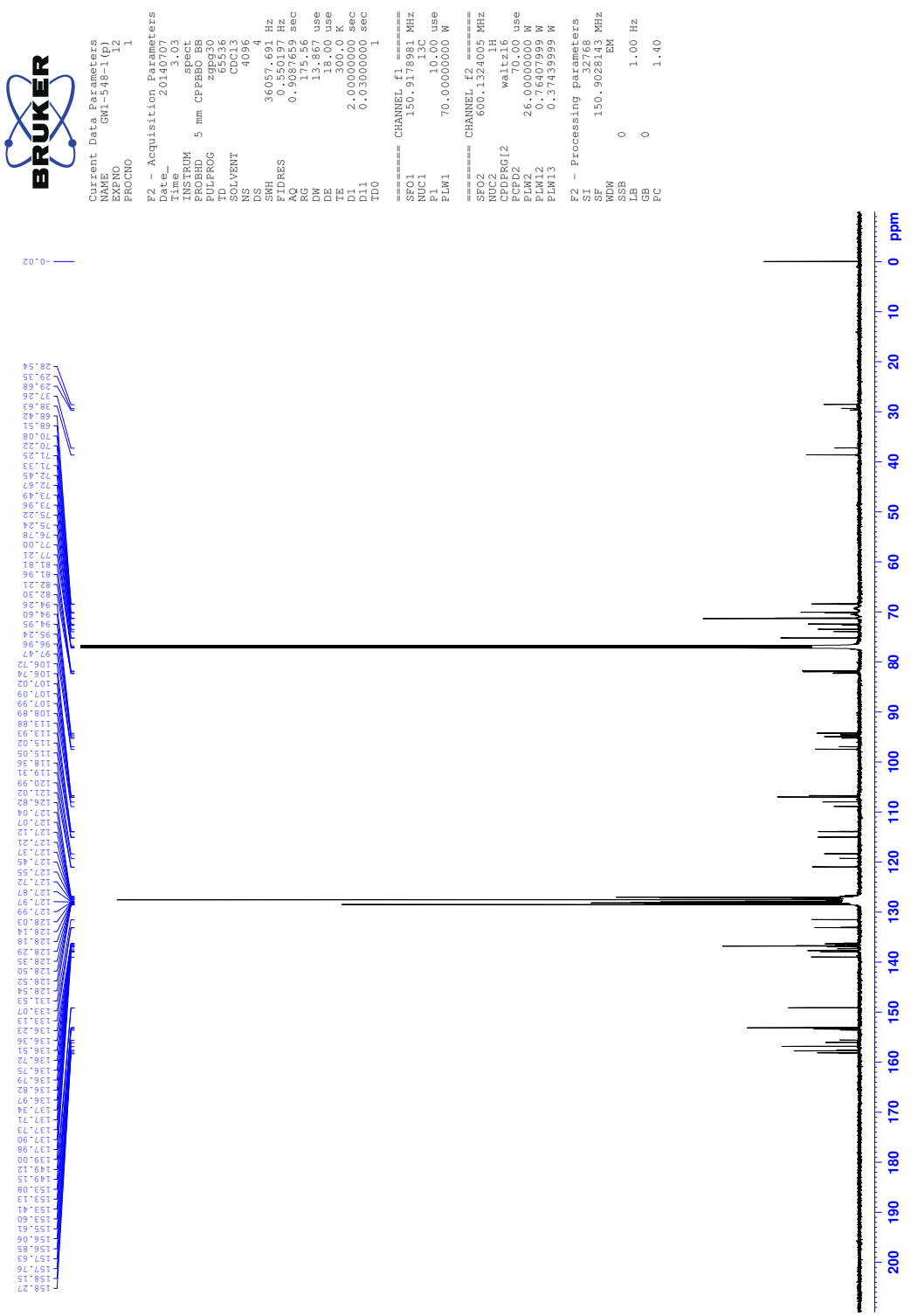
Compound **16** (^{13}C NMR, 150 MHz, $CDCl_3$)



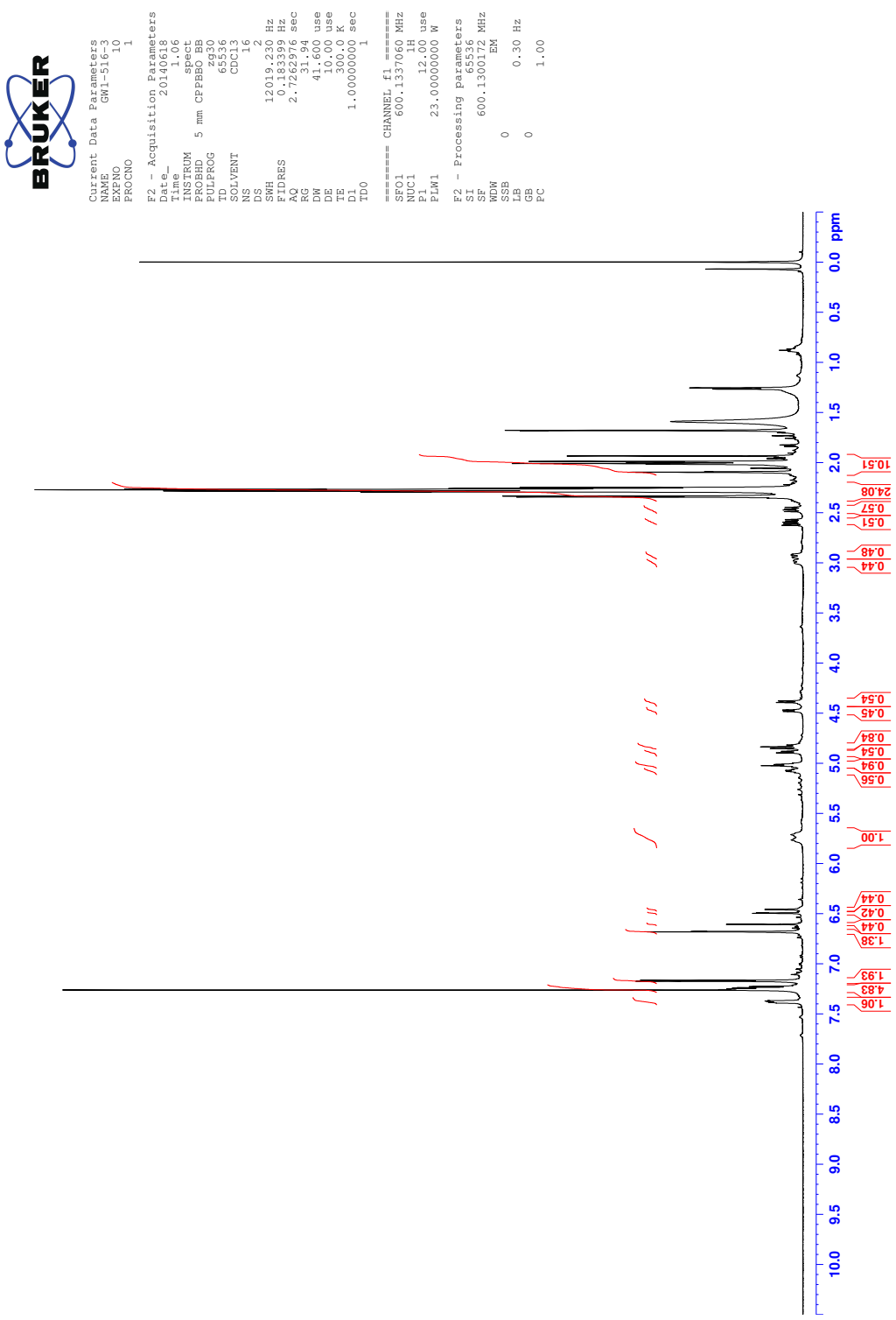
Compound **17** (^{1}H NMR, 600 MHz, $CDCl_3$)



Compound **17** (^{13}C NMR, 150 MHz, $CDCl_3$)



Compound **19** (^{1}H NMR, 600 MHz, $CDCl_3$)



Compound **19** (^{13}C NMR, 150 MHz, $CDCl_3$)