Supplementary Information

Relative stereochemical determination of the C61–C83 fragment of symbiodinolide using a stereodivergent synthetic approach

Hiroyoshi Takamura,* Kosuke Hattori, Takumi Ohashi, Taichi Otsu and Isao Kadota

Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

takamura@cc.okayama-u.ac.jp

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General Methods. Unless otherwise indicated, all reagents were purchased from common commercial suppliers and used as received. All reactions were carried out under an argon atmosphere. Heated reactions were conducted using an oil bath. Reaction solvents were purchased as dehydrated solvents and stored over activated molecular sieves 4Å under argon prior to use. All solvents for the work-up procedures were used as received. Analytical thin layer chromatography (TLC) was performed using aluminum TLC plates (Merck TLC silica gel $60F_{254}$). Column chromatography was performed on Fuji Silysia silica gel BW-300 or Kanto Chemical silica gel 60N. IR spectra were recorded on JASCO FT/IR-460 plus or JASCO FT/IR-FT-001. NMR spectra were recorded on JEOL JNM-AL400, Varian 400-MR, or Varian NMR System PS600. Chemical shifts in the NMR spectra are reported in ppm with reference to the internal residual solvent (for ^{1}H NMR, $CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm, CD_3OD: 3.30 ppm; for ^{13}C NMR, $CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm, CD_3OD: 49.0 ppm). The following abbreviations are used to designate the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (*J*) are given in Hertz. High-resolution mass spectra were recorded on Bruker micrOTOF II (ESI–TOF–MS) or Waters Micromass LCT (ESI–TOF–MS).

Tetraacetate 12. To a solution of acetoxy ether **10** (1.07 g, 3.22 mmol) in MeCN (32 mL) were added 2-[(acetoxymethyl)allyl]trimethylsilane (**11**, 0.83 mL, 3.86 mmol) and TMSOTf (0.24 mL, 1.29 mmol) at –20 ºC. The mixture was warmed up to 0 °C and stirred at the same temperature for 10 min. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 2:1) gave tetraacetate **12** (1.15 g, 93%): colorless oil; R_f = 0.49 (hexane/EtOAc = 1:1); $[\alpha]_D^{24}$ +28.9 (*c* 0.96, $CHCl_3$); IR (neat) 3084, 2956, 2888, 1731, 1653 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (s, 1 H), 5.13–5.10 (m, 1 H), 5.07 (s, 1 H), 4.85 (t, *J* = 7.2 Hz, 1 H), 4.59 (d, *J* = 13.2 Hz, 1 H), 4.53 (d, *J* = 13.2 Hz, 1 H), 4.36 (dd, *J* = 11.9, 6.4 Hz, 1 H), 4.20–4.17 (m, 1 H), 4.07 (dd, *J* = 11.9, 3.4 Hz, 1 H), 3.94–3.90 (m, 1 H), 2.54 (dd, *J* = 14.8, 8.9 Hz, 1 H), 2.28 (dd, *J* = 14.8, 5.5 Hz, 1 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04–1.96 (m, 1 H), 1.90–1.83 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 169.8, 169.6, 140.0, 115.5, 70.9, 68.6, 68.6, 68.5, 66.5, 62.0, 36.3, 32.4, 21.1, 20.9, 20.9, 20.8; HRMS (ESI–TOF) calcd for $C_{18}H_{26}O_9Na$ $[M + Na]^+$ 409.1475, found 409.1476.

Tetrakis-TBS Ether 13. To a solution of tetraacetate **12** (1.10 g, 2.85 mmol) in MeOH (29 mL) was added NaOMe (231 mg, 4.28 mmol) at 0 ºC. The mixture was stirred at room temperature for 1 h. The mixture was neutralized with 1.0 M aqueous HCl at 0 ºC. The mixture was diluted with MeOH and dried over Na_2SO_4. Concentration gave the corresponding tetraol (1.14 g), which was used for the next step without further purification.

To a solution of the tetraol obtained above (1.14 g) in DMF (29 mL) were added DMAP (279 mg, 2.28 mmol), imidazole (3.10 g, 45.6 mmol), and TBSCl (3.44 g, 22.8 mmol) at room temperature. The mixture was stirred at 80 ºC for 2 h. To the mixture were added DMAP (140 mg, 1.14 mmol), imidazole (1.55 g, 22.8 mmol), and TBSCl (1.72 g, 11.4 mmol) at room temperature. The mixture was stirred at 80 ºC for 2 h. The reaction was quenched with saturated aqueous NH_4Cl at 0 ºC. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane, hexane/EtOAc = 50:1) gave tetrakis-TBS ether **13** (1.56 g, 81% in two steps): colorless oil; R_f = 0.41 (hexane/EtOAc = 10:1); $[\alpha]_D^{22}$ +0.6 (*c* 1.09, $CHCl_3$); IR (neat) 2955, 2929, 2886, 2857, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (brs, 1 H), 4.91 (s, 1 H), 4.11–4.04 (m, 2 H), 3.97–3.85 (m, 3 H), 3.80 (d, *J* = 3.2 Hz, 1 H), 3.73 (t, *J* = 6.9 Hz, 1 H), 3.60 (d, *J* = 3.4 Hz, 1 H), 2.30 (dd, *J* = 14.4, 6.6 Hz, 1 H), 2.10 (dd, *J* = 14.4, 6.6 Hz, 1 H), 1.82–1.76 (m, 1 H), 1.39 (d, *J* = 13.9 Hz, 1 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.06 (s, 6 H), 0.06 (s, 6 H), 0.06 (s, 6 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 110.5, 80.1, 69.7, 67.9, 66.0, 64.0, 61.6, 39.4, 33.8, 25.9, 25.9, 25.9, 25.8, 18.4, 18.3, 18.0, 18.0, –4.8, –4.8, –5.0, –5.3, –5.4; HRMS (ESI–TOF) calcd for $C_{34}H_{74}O_5Si_4Na$ $[M + Na]^+$ 697.4511, found 697.4508.

Diol S1. To a solution of tetrakis-TBS ether **13** (415 mg, 0.614 mmol) in CH_2Cl_2 (3.1 mL) and MeOH (3.1 mL) was added CSA (42.7 mg, 0.184 mmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 2:1) gave diol **S1** (246 mg, 90%): colorless oil; R_f = 0.51 (hexane/EtOAc = 1:1); $[\alpha]_D^{23}$ –1.9 (*c* 1.03, $CHCl_3$); IR (neat) 3399, 2953, 2929, 2894, 2858, 1649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1 H), 4.94 (s, 1 H), 4.22–4.16 (m, 1 H), 4.10–4.08 (m, 3 H), 3.85–3.82 (m, 1 H), 3.80 (d, *J* = 3.2 Hz, 1 H), 3.47–3.44 (m, 1 H), 3.37 (d, *J* = 2.8 Hz, 1 H), 2.91 (brs, 1 H), 2.34–2.29 (m, 3 H), 1.98–1.92 (m, 1 H), 1.39 (d, *J* = 13.4 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 113.9, 80.2, 69.4, 69.1, 66.6, 64.9, 60.5, 40.2, 34.0, 25.8, 18.0, –4.6, –4.7, –4.7, –4.8; HRMS (ESI–TOF) calcd for $C_{22}H_{46}O_5Si_2Na$ $[M + Na]^+$ 469.2782, found 469.2782.

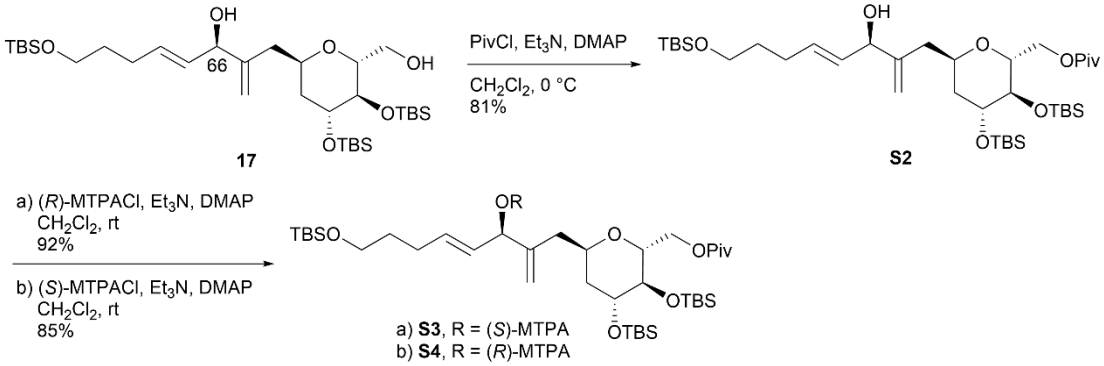
Aldehyde 14. To a solution of diol **S1** (13.3 mg, 29.8 μmol) in CH_2Cl_2 (1.0 mL) was added MnO_2 (13.0 mg, 0.150 mmol) at room temperature. The mixture was stirred at the same temperature for 5 h. To the mixture was added MnO_2 (13.0 mg, 0.150 mmol) at room temperature. The mixture was stirred at the same temperature for 12 h. The mixture was filtered through a Celite pad and washed with EtOAc. Concentration gave aldehyde **14** (13.2 mg, quant): yellow oil; R_f = 0.58 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +0.2 (*c* 1.06, $CHCl_3$); IR (neat) 3436, 2954, 2928, 2892, 2857, 1691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1 H), 6.49 (s, 1 H),

6.11 (s, 1 H), 4.10–4.06 (m, 2 H), 3.79–3.75 (m, 2 H), 3.47 (dd, *J* = 11.5, 3.2 Hz, 1 H), 3.35 (s, 1 H), 2.51 (dd, *J* = 14.4, 7.9 Hz, 1 H), 2.41 (dd, *J* = 14.4, 4.2 Hz, 1 H), 1.92–1.85 (m, 1 H), 1.43 (d, *J* = 13.4 Hz, 1 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.06 (s, 3 H), 0.06 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.6, 136.2, 79.3, 69.6, 69.5, 64.0, 60.9, 34.4, 33.2, 25.9, 18.1, 18.1, –4.4, –4.6, –4.7; HRMS (ESI–TOF) calcd for $C_{22}H_{44}O_5Si_2Na$ $[M + Na]^+$ 467.2625, found 467.2622.

Diols 16 and 17. To a solution of alkenyl iodide **15** (12.0 g, 36.6 mmol) in hexane (76 mL) was added *n*-BuLi (1.56 M in hexane, 23.5 mL, 36.6 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min. To the mixture was added aldehyde **14** (4.07 g, 9.15 mmol) in hexane (5.0 mL + 5.0 mL + 5.0 mL) at 0 ºC. The mixture was stirred at the same temperature for 10 min and stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave diols **16** (3.33 g, 57%) and **17** (1.96 g, 33%). Diol **16**: colorless oil; R_f = 0.43 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ –7.3 (*c* 1.00, $CHCl_3$); IR (neat) 3427, 2954, 2929, 2894, 2858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (dt, *J* = 15.3, 7.2 Hz, 1 H)), 5.51 (dd, *J* = 15.3, 6.6 Hz, 1 H), 5.14 (s, 1 H), 4.96 (s, 1 H), 4.56 (d, *J* = 6.6 Hz, 1 H), 4.19 (dd, *J* = 11.8, 9.7 Hz, 1 H), 4.15–4.11 (m, 1 H), 3.84–3.79 (m, 2 H), 3.61 (t, *J* = 6.5 Hz, 2 H), 3.43 (d, *J* = 11.2 Hz, 1 H), 3.35 (d, *J* = 2.7 Hz, 1 H), 2.98 (brs, 1 H), 2.33 (dd, *J* = 14.5, 4.1 Hz, 1 H), 2.25 (dd, *J* = 14.5, 7.7 Hz, 1 H), 2.11 (q, *J* = 7.2 Hz, 2 H), 1.97–1.90 (m, 1 H), 1.68–1.57 (m, 2 H), 1.39 (d, *J* = 13.7 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.07 (s, 6 H), 0.06 (s, 6 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 131.9, 131.2, 113.8, 80.2, 75.7, 69.4, 69.1, 64.6, 62.6, 60.4, 39.0, 34.0, 32.4, 28.6, 26.0, 25.8, 18.4, 18.1, 18.0, –4.6, –4.7, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{33}H_{68}O_6Si_3Na$ $[M + Na]^+$ 667.4221 found 667.4220. Diol **17**: colorless oil; R_f = 0.51 (hexane/EtOAc = 2:1); $[\alpha]_D^{21}$ +15.3 (*c* 1.07, $CHCl_3$); IR (neat) 3409, 2955, 2929, 2894, 2857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (dt, *J* = 15.4, 6.8 Hz, 1 H), 5.49 (dd, *J* = 15.4, 6.1 Hz, 1 H), 5.14 (s, 1 H), 4.95 (s, 1 H), 4.54 (d, *J* = 6.1 Hz, 1 H), 4.19 (dd, *J* = 11.8, 9.7 Hz, 1 H), 4.02 (t, *J* = 8.3 Hz, 1 H), 3.84 (d, *J* = 9.5 Hz, 1 H), 3.79 (d, *J* = 2.9 Hz, 1 H) 3.61 (t, *J* = 6.4 Hz, 2 H), 3.43–3.34 (m, 3 H), 2.35 (dd, *J* = 14.4, 9.0 Hz, 1 H), 2.22 (brs, 1 H), 2.14–2.08 (m, 3 H), 1.96–1.89 (m, 1 H), 1.64–1.57 (m, 2 H), 1.44 (d, *J* = 13.7 Hz, 1 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.07 (s, 6 H), 0.06 (s, 6 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 131.5, 131.5, 113.6, 80.3, 75.8, 69.5, 69.0, 65.8, 62.6, 60.2, 37.9, 34.5, 32.4, 28.6, 26.0, 25.8, 18.4, 18.1, 18.0, –4.6, –4.7, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{33}H_{68}O_6Si_3Na$ $[M + Na]^+$ 667.4221, found 667.4216.

Stereochemical Determination of 17. The primary hydroxy group of diol **17** was selectively protected with PivCl/Et_3N/DMAP to give pivalate **S2** (Scheme S1). The absolute configuration at the C66 position of **S2** was determined by the modified Mosher method.[1] Thus, treatment of

alcohol **S2** with MTPACl/Et_3N/DMAP provided (*S*)-MTPA ester **S3** and (*R*)-MTPA ester **S4**, respectively. The results for calculating the chemical shift differences ($\Delta\delta_{S-R}$) of **S3** and **S4** are described in Figure S1. The signs at the left side of the C66 position were positive and those at the right side of the C66 position showed negative. Therefore, the absolute stereochemistry at the C66 position of **17** was determined as shown in Scheme S1.



Scheme S1. Transformation of diol **17** for its stereochemical determination. MTPA = α-methoxy-α-(trifluoromethyl)phenylacetyl).

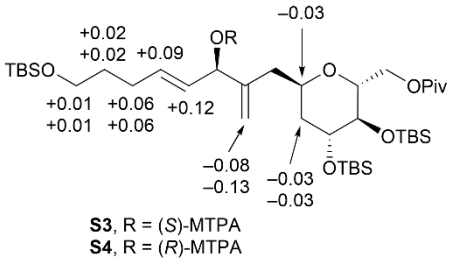


Figure S1. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S3** and **S4**.

Pivalate S2. To a solution of diol **17** (10.0 mg, 15.5 μmol) in CH_2Cl_2 (1.0 mL) were added DMAP (0.2 mg, 1.55 μmol), Et_3N (8.7 μL, 62.0 μmol), and PivCl (2.3 μL, 18.6 μmol) at 0 ºC. The mixture was stirred at the same temperature for 30 min. To the mixture were added Et_3N (17 μL, 0.124 mmol) and PivCl (4.6 μL, 37.2 μmol) at 0 ºC. The mixture was stirred at the same temperature for 30 min. To the mixture were added Et_3N (26 μL, 0.186 mmol) and PivCl (6.9 μL, 55.8 μmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 15:1) gave pivalate **S2** (9.1 mg, 81%): colorless oil; R_f = 0.54 (hexane/EtOAc = 7:1); $[\alpha]_D^{22}$ +20.3 (*c* 0.41, $CHCl_3$); IR (neat) 3442, 2954, 2929, 2892, 2857, 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 15.2, 6.8 Hz, 1 H), 5.47 (dd, *J* = 15.2, 6.2 Hz, 1 H), 5.08 (s, 1 H), 4.93 (s, 1 H), 4.70 (dd, *J* = 11.4, 8.5 Hz, 1 H), 4.52 (d, *J* = 6.2 Hz, 1 H), 4.06–4.02 (m, 2 H), 3.96–3.92 (m, 1 H), 3.81 (brs, 1 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 3.53 (brs, 1 H),

3.46 (d, *J* = 3.0 Hz, 1 H), 2.31 (dd, *J* = 11.4, 8.5 Hz, 1 H), 2.11–2.07 (m, 3 H), 1.91 (t, *J* = 11.4 Hz, 1 H), 1.64–1.57 (m, 2 H), 1.40 (d, *J* = 13.1 Hz, 1 H), 1.21 (s, 9 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.08 (s, 6 H), 0.07 (s, 6 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 148.3, 131.6, 131.2, 113.2, 77.7, 75.4, 69.3, 68.5, 65.4, 62.6, 61.8, 38.8, 38.3, 34.0, 32.4, 28.6, 27.3, 26.0, 25.8, 18.4, 18.1, 18.0, –4.7, –4.7, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{38}H_{76}O_7Si_3Na$ $[M + Na]^+$ 751.4797, found 751.4792.

(*S*)-MTPA Ester S3. To a solution of alcohol **S2** (5.2 mg, 7.13 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (1.7 mg, 14.3 μmol), Et_3N (1.4 μL, 9.98 μmol), and (*R*)-MTPACl (1.6 μL, 8.56 μmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 40:1) gave (*S*)-MTPA ester **S3** (6.2 mg, 92%): yellow oil; R_f = 0.46 (hexane/EtOAc = 10:1); $[\alpha]_D^{22}$ –11.7 (*c* 0.31, $CHCl_3$); IR (neat) 2952, 2928, 2857, 1748, 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2 H), 7.39–7.36 (m, 3 H), 5.91–5.82 (m, 2 H), 5.47 (dd, *J* = 15.1, 7.8 Hz, 1 H), 5.06 (s, 1 H), 5.04 (s, 1 H), 4.52 (dd, *J* = 11.4, 8.1 Hz, 1 H), 4.23 (dd, *J* = 11.4, 5.8 Hz, 1 H), 4.09–4.02 (m, 1 H), 3.91 (t, *J* = 6.7 Hz, 1 H), 3.81 (d, *J* = 2.7 Hz, 1 H), 3.59 (t, *J* = 6.4 Hz, 2 H), 3.56 (s, 3 H), 3.50 (d, *J* = 3.4 Hz, 2 H), 2.20–2.10 (m, 3 H), 1.94 (dd, *J* = 15.5, 5.3 Hz, 1 H), 1.86–1.79 (m, 1 H), 1.62–1.55 (m, 2 H), 1.38 (d, *J* = 13.6 Hz, 1 H), 1.20 (s, 9 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.08 (s, 6 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 165.1, 142.5, 137.0, 132.5, 129.4, 128.2, 127.4, 125.8, 113.4, 79.5, 69.4, 68.5, 63.9, 62.4, 55.5, 38.8, 38.0, 33.7, 32.1, 29.8, 28.6, 27.3, 26.0, 25.9, 25.8, 18.4, 18.1, 18.0, –4.7, –4.7, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{48}H_{83}F_3O_9Si_3Na$ $[M + Na]^+$ 967.5195, found 967.5191.

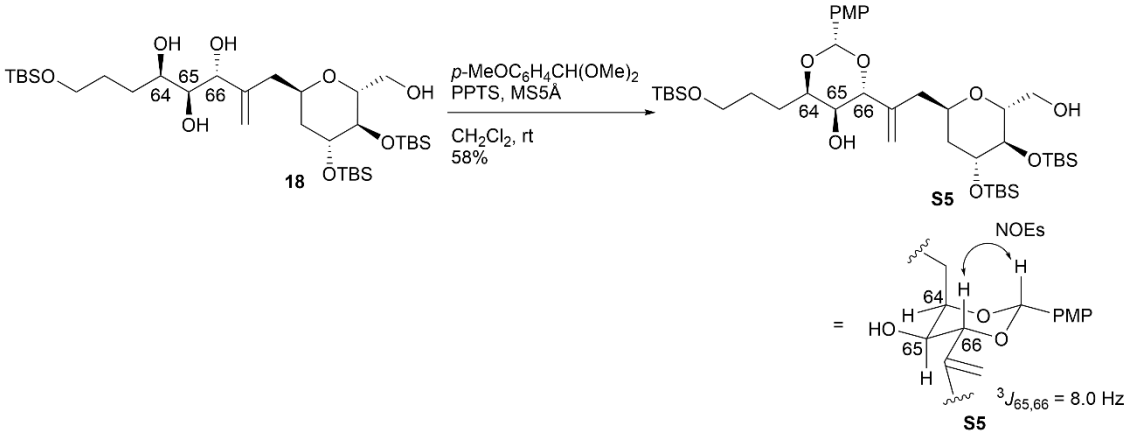
(*R*)-MTPA Ester S4. To a solution of alcohol **S2** (6.0 mg, 8.23 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (2.0 mg, 16.5 μmol), Et_3N (1.6 μL, 11.5 μmol), and (*S*)-MTPACl (1.8 μL, 9.88 μmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture were added Et_3N (1.6 μL, 11.5 μmol) and (*S*)-MTPACl (1.8 μL, 9.88 μmol) at room temperature. The mixture was stirred at the same temperature for 10 min. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 40:1) gave (*R*)-MTPA ester **S4** (6.6 mg, 85%): yellow oil; R_f = 0.45 (hexane/EtOAc = 10:1); $[\alpha]_D^{21}$ +11.7 (*c* 0.33, $CHCl_3$); IR (neat) 2954, 2929, 2857, 1748, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2 H), 7.38–7.37 (m, 3 H), 5.85 (d, *J* = 7.4 Hz, 1 H), 5.78 (dt, *J* = 15.2, 6.6 Hz, 1 H), 5.35 (dd, *J* = 15.2, 7.4 Hz, 1 H), 5.19 (s, 1 H), 5.13 (s, 1 H), 4.54 (dd, *J* = 11.4, 8.2 Hz, 1 H), 4.24 (dd, *J* = 11.4, 5.5 Hz, 1 H), 4.09 (brs, 1 H), 3.92 (t, *J* = 6.9 Hz, 1 H), 3.81 (s, 1 H), 3.58 (t, *J* = 6.1 Hz, 2 H), 3.55 (s, 3 H), 3.50 (s, 2 H), 2.29 (dd,

J = 15.1, 7.3 Hz, 1 H), 2.11–2.02 (m, 3 H), 1.86 (t, J = 12.2 Hz, 1 H), 1.59–1.52 (m, 2 H), 1.39 (d, J = 14.0 Hz, 1 H), 1.21 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.07 (s, 6 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 165.2, 142.5, 136.3, 132.4, 129.4, 128.2, 127.5, 125.6, 114.0, 79.5, 69.4, 68.5, 63.9, 62.4, 55.6, 39.2, 38.8, 38.0, 33.8, 32.1, 28.6, 27.3, 26.0, 25.9, 25.8, 18.4, 18.1, 18.0, –4.7, –4.7, –4.8, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{48}H_{83}F_3O_9Si_3Na$ $[M + Na]^+$ 967.5195, found 967.5192.

Tetrakis-TBS Ether 19. To a solution of allylic alcohol **16** (56.4 mg, 87.4 μmol) in acetone (1.5 mL) and H_2O (0.3 mL) were added NMO (20.5 mg, 0.175 mmol) and OsO_4 (0.05 M in 2-propanol, 87 μL, 4.37 μmol) at 0 ºC. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 6:1, 1:1) gave tetraol **18** (19.8 mg) and allylic alcohol **16** (7.2 mg, 13% recovery). Tetraol **18** was used for the next step without further purification.
To a solution of tetraol **18** obtained above (19.8 mg) in CH_2Cl_2 (1.0 mL) were added imidazole (5.9 mg, 87.3 μmol) and TBSCl (10.5 mg, 69.8 μmol) at 0 ºC. The mixture was stirred at the same temperature for 1 h. To the mixture were added imidazole (5.9 mg, 87.3 μmol) and TBSCl (10.5 mg, 69.8 μmol) at 0 ºC. The mixture was stirred at the same temperature for 1 h., To the mixture were added imidazole (5.9 mg, 87.3 μmol) and TBSCl (10.5 mg, 69.8 μmol) at 0 ºC. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 5:1) gave tetrakis-TBS ether **19** (16.1 mg, 23% in two steps): colorless oil; R_f = 0.49 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +2.3 (c 0.81, $CHCl_3$); IR (neat) 3410, 2956, 2929, 2889, 2858, 1645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1 H), 5.07 (s, 1 H), 4.23 (dd, J = 6.6, 4.2 Hz, 1 H), 4.07–4.01 (m, 1 H), 4.02 (dd, J = 10.1, 7.7 Hz, 1 H), 3.93 (d, J = 4.4 Hz, 1 H), 3.87–3.86 (m, 1 H), 3.80–3.74 (m, 2 H), 3.72–3.63 (m, 3 H), 3.56–3.48 (m, 3 H), 3.01 (d, J = 6.6 Hz, 1 H), 2.37 (dd, J = 14.4, 3.9 Hz, 1 H), 2.22 (dd, J = 14.4, 7.1 Hz, 1 H), 1.98–1.94 (m, 1 H), 1.69–1.64 (m, 4 H), 1.32 (d, J = 13.6 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.07 (s, 6 H), 0.07 (s, 6 H), 0.04 (s, 6 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 116.2, 80.6, 77.2, 72.9, 71.2, 69.4, 67.9, 65.0, 63.6, 61.0, 37.7, 33.5, 30.9, 29.5, 26.0, 25.9, 25.8, 18.4, 18.0, –4.7, –4.8, –4.9, –5.2, –5.3; HRMS (ESI–TOF) calcd for $C_{39}H_{84}O_8Si_4Na$ $[M + Na]^+$ 815.5141, found 815.5140.

Stereochemical Determination of 18. The purified tetraol **18** was treated with *p*-$MeOC_6H_4CH(OMe)_2$/PPTS/MS5Å to give *p*-methoxybenzylidene acetal **S5** in 58% yield (Scheme S2). The observed coupling constant ($^3J_{65,66}$ = 8.0 Hz) in **S5** indicates that H-65 and H-66 possess the axial-axial relationship, and the C65 hydroxy group is arranged in the

equatorial position. The C64 stereochemistry was determined based on the *syn*-addition reaction mechanism of OsO_4-catalyzed dihydroxylation. The stereochemistry at the acetal carbon of **S5** was elucidated by the NOE correlations as shown in arrows.



Scheme S2. Stereochemical determination of tetraol **18**.

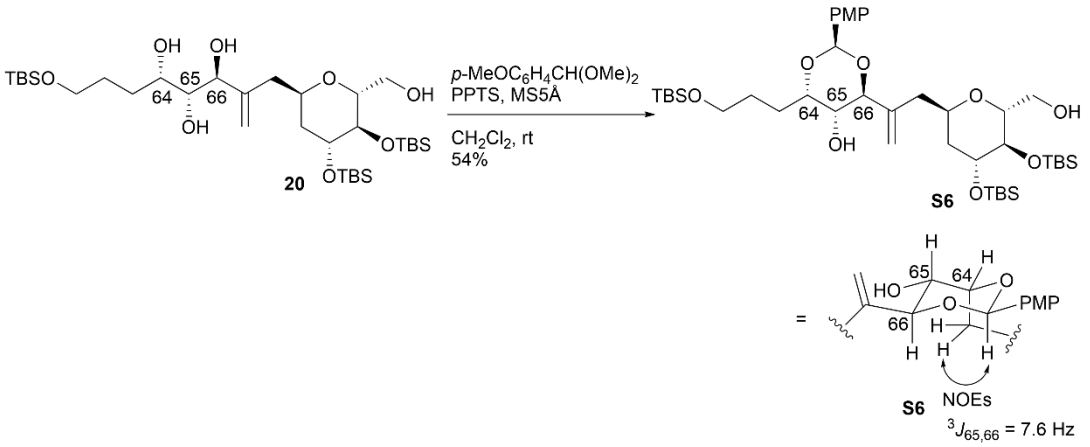
***p*-Methoxybenzylidene Acetal S5.** To a solution of tetraol **18** (14.8 mg, 21.8 μmol) in CH_2Cl_2 (1.0 mL) were added MS5Å (21.8 mg), *p*-$MeOC_6H_4CH(OMe)_2$ (5.6 μL, 32.7 μmol), and PPTS (0.5 mg, 2.18 μmol) at room temperature. The mixture was stirred at the same temperature for 4 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave *p*-methoxybenzylidene acetal **S5** (7.7 mg, 58%): colorless oil; R_f = 0.55 (hexane/EtOAc = 2:1); $[\alpha]_D^{21}$ +3.5 (*c* 0.25, $CHCl_3$); IR (neat) 3436, 2953, 2928, 2896, 2885, 2857, 1616 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 5.84 (s, 1 H), 5.29 (s, 1 H), 5.07 (s, 1 H), 4.30–4.22 (m, 3 H), 4.20–4.12 (m, 3 H), 3.93 (t, *J* = 6.9 Hz, 1 H), 3.80 (s, 3 H), 3.70 (d, *J* = 6.3 Hz, 1 H), 3.65 (t, *J* = 5.9 Hz, 2 H), 3.46 (d, *J* = 12.4 Hz, 1 H), 3.36 (s, 1 H), 2.51 (dd, *J* = 14.4, 4.1 Hz, 1 H), 2.24 (dd, *J* = 14.4, 6.7 Hz, 1 H), 2.02 (t, *J* = 13.4 Hz, 1 H), 1.83–1.76 (m, 2 H), 1.73–1.66 (m, 2 H), 1.35 (d, *J* = 13.1 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H) 0.90 (s, 9 H), 0.07 (s, 6 H), 0.07 (s, 6 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.3, 130.2, 128.1, 116.6, 113.6, 103.2, 81.4, 80.6, 80.1, 75.0, 69.2, 68.9, 64.9, 63.2, 60.4, 55.3, 39.4, 33.5, 30.6, 29.3, 26.1, 25.8, 18.4, 18.1, 18.0, –4.6, –4.8, –4.8, –5.2; HRMS (ESI–TOF) calcd for $C_{41}H_{76}O_9Si_3Na$ $[M + Na]^+$ 819.4695, found 819.4696.

Candidate Compound 3a from 19. To a solution of tetrakis-TBS ether **19** (10.9 mg, 13.7 μmol) in MeOH (1.2 mL) was added 1.0 M aqueous HCl (0.14 mL, 0.140 mmol) at room temperature. The mixture was stirred at the same temperature for 2 h. To the mixture was added 1.0 M aqueous HCl (0.14 mL, 0.140 mmol) at room temperature. The mixture was stirred at the

same temperature for 1 h. To the mixture was added 1.0 M aqueous HCl (0.28 mL, 0.280 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was diluted with MeOH. Concentration and column chromatography (CH_2Cl_2/MeOH = 4:1) gave candidate compound **3a** (4.6 mg, quant): colorless oil; R_f = 0.42 (CH_2Cl_2/MeOH = 2:1); $[\alpha]_D^{21}$ +35.2 (*c* 0.29, CH_3OH); IR (neat) 3405, 2920, 2850 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 5.21 (s, 1 H), 5.11 (s, 1 H), 4.25–4.23 (m, 1 H), 4.20–4.18 (m, 1 H), 3.85 (brs, 1 H), 3.81–3.78 (m, 1 H), 3.76 (dd, *J* = 11.7, 2.7 Hz, 1 H), 3.70 (dd, *J* = 11.7, 6.0 Hz, 1 H), 3.58 (t, *J* = 6.0 Hz, 2 H), 3.53 (ddd, *J* = 8.1, 6.0, 2.7 Hz, 1 H), 3.42–3.40 (m, 1 H), 3.21 (t, *J* = 8.1 Hz, 1 H), 2.55 (dd, *J* = 15.0, 9.0 Hz, 1 H), 2.36 (dd, *J* = 15.0, 6.0 Hz, 1 H), 2.00–1.97 (m, 1 H), 1.74–1.57 (m, 5 H); ^{13}C NMR (150 MHz, CD_3OD) δ 148.6, 115.1, 76.7, 76.0, 74.7, 73.3, 72.5, 71.4, 70.0, 63.1, 63.0, 36.7, 35.1, 31.4, 30.2; HRMS (ESI–TOF) calcd for $C_{15}H_{28}O_8Na$ $[M + Na]^+$ 359.1682, found 359.1678.

Tetraol 20. To a solution of allylic alcohol **17** (75.0 mg, 0.116 mmol) in acetone (1.9 mL) and H_2O (0.4 mL) were added NMO (27.2 mg, 0.232 mmol) and OsO_4 (0.05 M in 2-propanol, 0.12 mL, 5.80 μmol) at 0 ºC. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1, 1:1) gave tetraol **20** (37.9 mg, 24%) and allylic alcohol **17** (24.3 mg, 33% recovery). Tetraol **20**: colorless oil; R_f = 0.50 (hexane/EtOAc = 1:2); $[\alpha]_D^{22}$ +8.8 (*c* 0.39, $CHCl_3$); IR (neat) 3398, 2952, 2928, 2889, 2857, 1644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.22 (s, 1 H), 5.13 (s, 1 H), 4.23–4.16 (m, 2 H), 4.12 (s, 1 H), 4.08–4.01 (m, 1 H), 3.88–3.79 (m, 3 H), 3.72–3.60 (m, 3 H), 3.46–3.41 (m, 2 H), 3.35 (d, *J* = 3.2 Hz, 1 H), 2.59 (d, *J* = 6.8 Hz, 1 H), 2.38 (dd, *J* = 14.4, 9.5 Hz, 1 H), 2.27 (brs, 1 H), 2.22 (dd, *J* = 14.4, 3.1 Hz, 1 H), 1.96–1.90 (m, 1 H), 1.69–1.63 (m, 3 H), 1.46 (d, *J* = 13.1 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.07 (s, 6 H), 0.06 (s, 6 H), 0.06 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 115.6, 80.5, 76.8, 73.9, 70.6, 69.3, 69.0, 66.2, 63.6, 60.3, 38.1, 34.5, 31.3, 29.5, 26.0, 25.8, 25.8, 18.4, 18.1, 18.0, –4.6, –4.7, –4.8, –5.2, –5.3; HRMS (ESI–TOF) calcd for $C_{33}H_{70}O_8Si_3Na$ $[M + Na]^+$ 701.4276, found 701.4273.

Stereochemical Determination of 20. Tetraol **20** was treated with *p*-$MeOC_6H_4CH(OMe)_2$/PPTS/MS5Å to give *p*-methoxybenzylidene acetal **S6** in 54% yield (Scheme S3). The observed coupling constant ($^3J_{65,66}$ = 7.6 Hz) in **S6** indicates that H-65 and H-66 possess the axial-axial relationship, and the C65 hydroxy group is arranged in the equatorial position. The C64 stereochemistry was determined based on the *syn*-addition reaction mechanism of OsO_4-catalyzed dihydroxylation. The stereochemistry at the acetal carbon of **S6** was elucidated by the NOE correlations as shown in arrows.



Scheme S3. Stereochemical determination of tetraol **20**.

***p*-Methoxybenzylidene Acetal S6.** To a solution of tetraol **20** (21.4 mg, 31.5 μmol) in CH_2Cl_2 (1.0 mL) were added MS5Å (35.1 mg), *p*-$MeOC_6H_4CH(OMe)_2$ (8.1 μL, 47.3 μmol), and PPTS (0.8 mg, 3.15 μmol) at room temperature. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave *p*-methoxybenzylidene acetal **S6** (13.6 mg, 54%): colorless oil; R_f = 0.51 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +1.2 (*c* 0.34, $CHCl_3$); IR (neat) 3434, 2952, 2928, 2889, 2857, 1639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 5.85 (s, 1 H), 5.23 (s, 1 H), 5.09 (s, 1 H), 4.30–4.26 (m, 1 H), 4.20 (dd, *J* = 11.8, 9.9 Hz, 1 H), 4.11 (d, *J* = 6.6 Hz, 1 H), 4.02–3.97 (m, 2 H), 3.87–3.82 (m, 3 H), 3.80 (s, 3 H), 3.67 (t, *J* = 5.8 Hz, 2 H), 3.41 (d, *J* = 11.5 Hz, 1 H), 3.35 (d, *J* = 2.9 Hz, 1 H), 2.41 (dd, *J* = 14.1, 9.3 Hz, 1 H), 2.20 (dd, *J* = 14.1, 2.8 Hz, 1 H), 2.11 (brs, 1 H), 1.98–1.91 (m, 1 H), 1.83–1.65 (m, 4 H), 1.44 (d, *J* = 13.9 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H) 0.90 (s, 9 H), 0.07 (s, 6 H), 0.06 (s, 6 H), 0.06 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.8, 130.1, 128.1, 116.7, 113.7, 102.5, 82.6, 80.6, 79.6, 76.0, 69.3, 68.9, 66.3, 63.0, 60.2, 55.3, 38.3, 34.4, 30.2, 29.3, 26.1, 25.8, 25.8, 18.4, 18.1, 18.0, –4.6, –4.7, –4.8, –5.1; HRMS (ESI–TOF) calcd for $C_{41}H_{76}O_9Si_3Na$ $[M + Na]^+$ 819.4695, found 819.4691.

Candidate Compound 3b from 20. To a solution of tris-TBS ether **20** (11.0 mg, 16.2 μmol) in MeOH (1.5 mL) was added 1.0 M aqueous HCl (0.16 mL, 0.160 mmol) at room temperature. The mixture was stirred at the same temperature for 30 min. To the mixture was added 1.0 M aqueous HCl (0.32 mL, 0.320 mmol) at room temperature. The mixture was stirred at the same temperature for 30 min. To the mixture was added 1.0 M aqueous HCl (0.32 mL, 0.320 mmol) at room temperature. The mixture was stirred at the same temperature for 3 h. The mixture was diluted with MeOH. Concentration and column chromatography (CH_2Cl_2/MeOH = 4:1) gave candidate compound **3b** (5.4 mg, 99%): colorless oil; R_f = 0.46 (CH_2Cl_2/MeOH = 2:1); $[\alpha]_D^{23}$

+23.4 (*c* 0.36, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 5.18 (s, 1 H), 5.09 (s, 1 H), 4.29–4.28 (m, 1 H), 4.20 (d, *J* = 7.8 Hz, 1 H), 3.85 (brs, 1 H), 3.81–3.79 (m, 1 H), 3.77 (dd, *J* = 11.7, 2.4 Hz, 1 H), 3.65 (dd, *J* = 11.7, 6.3 Hz, 1 H), 3.58 (t, *J* = 5.7 Hz, 2 H), 3.53 (ddd, *J* = 8.4, 6.3, 2.4 Hz, 1 H), 3.41 (brs, 1 H), 3.12 (t, *J* = 8.4 Hz, 1 H), 2.65 (dd, *J* = 14.4, 9.0 Hz, 1 H), 2.32 (dd, *J* = 14.4, 5.4 Hz, 1 H), 1.97–1.94 (m, 1 H), 1.72–1.57 (m, 5 H); ^{13}C NMR (150 MHz, CD_3OD) δ 148.0, 115.6, 76.5, 75.6, 75.0, 73.5, 71.8, 71.4, 70.1, 63.2, 63.1, 36.8, 35.7, 31.4, 30.3; HRMS (ESI–TOF) calcd for $C_{15}H_{28}O_8Na$ $[M + Na]^+$ 359.1682, found 359.1678.

Alcohol 21. To a solution of diol **16** (85.6 mg, 0.133 mmol) in CH_2Cl_2 (1.3 mL) were added DMAP (3.2 mg, 26.6 μmol), imidazole (27.2 mg, 0.399 mmol), and TBSCl (48.1 mg, 0.319 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture were added imidazole (27.2 mg, 0.399 mmol) and TBSCl (48.1 mg, 0.319 mmol) at room temperature. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane, hexane/EtOAc = 70:1) gave the corresponding pentakis-TBS ether (110 mg), which was used for the next step without further purification.
A mixture of the alkene obtained above (110 mg) and 9-BBN (88.6 mg, 0.726 mmol) in THF (1.2 mL) was stirred at 50 ºC for 1 h. To the mixture were added 3.0 M aqueous NaOH (1.0 mL, 3.00 mmol) and 30% aqueous H_2O_2 (1.0 mL, 9.75 mmol) at 0 ºC. The mixture was stirred at room temperature for 1 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 20:1) gave alcohol **21** (90.4 mg, 76% in two steps): colorless oil; R_f = 0.49 (hexane/EtOAc = 10:1); $[\alpha]_D^{28}$ +2.2 (*c* 0.82, $CHCl_3$); IR (neat) 3435, 2954, 2929, 2886, 2857, 1642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (dt, *J* = 15.3, 7.2 Hz, 1 H), 5.42 (dd, *J* = 15.3, 7.1 Hz, 1 H), 4.15 (dd, *J* = 7.1, 4.6 Hz, 1 H), 3.91–3.85 (m, 3 H), 3.80 (d, *J* = 3.2 Hz, 1 H), 3.75–3.68 (m, 2 H), 3.61 (t, *J* = 6.5 Hz, 2 H), 3.61–3.58 (m, 2 H), 2.07 (q, *J* = 7.2 Hz, 2 H), 1.89–1.83 (m, 1 H), 1.69 (brs, 1 H), 1.67–1.65 (m, 1 H), 1.61–1.55 (m, 3 H), 1.50–1.47 (m, 1 H), 1.37 (d, *J* = 13.4 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.07 (s, 6 H), 0.06 (s, 6 H), 0.05 (s, 6 H), 0.05 (s, 6 H), 0.02 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 131.3, 80.0, 75.9, 69.8, 68.2, 65.1, 64.2, 62.6, 61.6, 45.2, 35.2, 34.9, 32.5, 28.5, 26.0, 25.9, 18.4, 18.4, 18.1, 18.1, –3.9, –4.6, –4.8, –4.8, –5.2, –5.2; HRMS (ESI–TOF) calcd for $C_{45}H_{98}O_7Si_5Na$ $[M + Na]^+$ 913.6057, found 913.6061.

Sulfide 22. To a solution of alcohol **21** (83.1 mg, 93.0 μmol) in CH_2Cl_2 (0.9 mL) were added Et_3N (26 μL, 0.186 mmol), DMAP (2.3 mg, 18.8 μmol), and TsCl (21.4 mg, 0.112 mmol) at 0 ºC. The mixture was stirred at room temperature for 4 h. To the mixture were added Et_3N (26 μL, 0.186 mmol) and TsCl (21.4 mg, 0.112 mmol) at 0 ºC. The mixture was stirred at room

temperature for 4 h. To the mixture were added Et_3N (26 μL, 0.186 mmol) and TsCl (21.4 mg, 0.112 mmol) at 0 ºC. The mixture was stirred at room temperature for 14 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 70:1) gave the corresponding tosylate (87.3 mg), which was used for the next step without further purification.

To a solution of the tosylate obtained above (87.3 mg) in DMF (0.8 mL) was added NaI (249 mg, 1.66 mmol) at room temperature. The mixture was stirred at 100 ºC for 7 h. To the mixture was added NaI (124 mg, 0.830 mmol) at room temperature. The mixture was stirred at 100 ºC for 3 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 80:1) gave the corresponding alkyl iodide (67.0 mg), which was used for the next step without further purification.

To a solution of the alkyl iodide obtained above (67.0 mg) in benzene (0.7 mL) were added PhSH (27 μL, 0.264 mmol) and DBU (47 μL, 0.317 mmol) at 4 ºC. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 70:1) gave sulfide **22** (61.4 mg, 68% in three steps): yellow oil; R_f = 0.49 (hexane/EtOAc = 40:1); $[\alpha]_D^{28}$ –7.6 (*c* 1.32, $CHCl_3$); IR (neat) 2954, 2929, 2886, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2 H), 7.23 (t, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 5.57 (dt, *J* = 15.5, 7.2 Hz, 1 H), 5.40 (dd, *J* = 15.5, 7.0 Hz, 1 H), 4.36 (dd, *J* = 7.0, 4.5 Hz, 1 H), 3.92 (dd, *J* = 9.9, 7.5 Hz, 1 H), 3.87–3.85 (m, 1 H), 3.80–3.76 (m, 2 H), 3.66 (t, *J* = 7.1 Hz, 1 H), 3.62–3.59 (m, 1 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 3.10 (dd, *J* = 12.8, 6.2 Hz, 1 H), 2.90 (dd, *J* = 12.8, 7.2 Hz, 1 H), 2.06 (q, *J* = 7.2 Hz, 2 H), 1.92–1.87 (m, 1 H), 1.81–1.74 (m, 1 H), 1.68–1.50 (m, 4 H), 1.34 (d, *J* = 3.2 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.86 (s, 9 H), 0.08–0.01 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 131.7, 130.7, 128.7, 128.6, 125.3, 79.5, 73.8, 70.0, 68.3, 64.7, 62.7, 61.9, 42.0, 34.9, 34.8, 34.8, 32.5, 28.6, 26.1, 26.0, 18.4, 18.3, 18.2, 18.1, –3.9, –4.5, –4.7, –4.8, –5.1; HRMS (ESI–TOF) calcd for $C_{51}H_{102}O_6SSi_5Na$ $[M + Na]^+$ 1005.6141, found 1005.6141.

Alkene 24. To a solution of alkene **22** (33.7 mg, 34.3 μmol) in pyridine (0.3 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 0.8 mL, 40.0 μmol) at room temperature. The mixture was stirred at the same temperature for 2 h. To the mixture were added $NaHSO_3$ (272 mg), H_2O (1.2 mL), and pyridine (1.1 mL) at room temperature. The mixture was stirred at the same temperature for 12 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration gave diol **23** (34.5 mg), which was used for the next step without further purification.

To a solution of sulfide **23** obtained above (34.5 mg) in CH_2Cl_2 (0.5 mL) was added *m*CPBA

(69–75%, 11.0 mg, 44.0–47.8 μmol) at –78 ºC. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with 2-methyl-2-butene. The mixture was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. Concentration gave the corresponding sulfoxide (36.2 mg), which was used for the next step without further purification.

To a solution of the sulfoxide obtained above (36.2 mg) in xylene (0.4 mL) was added $NaHCO_3$ (11.8 mg, 0.140 mmol) at room temperature. The mixture was stirred at reflux for 15 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 15:1) gave alkene **24** (17.2 mg, 56% in three steps): colorless oil; R_f = 0.41 (hexane/EtOAc = 10:1); $[\alpha]_D^{28}$ +3.2 (*c* 0.86, $CHCl_3$); IR (neat) 3435, 2954, 2929, 2891, 2857, 1645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 1 H), 5.12 (s, 1 H), 4.19 (d, *J* = 6.8 Hz, 1 H), 4.03–3.95 (m, 2 H), 3.80–3.68 (m, 3 H), 3.63 (t, *J* = 5.9 Hz, 2 H), 3.51 (d, *J* = 3.2 Hz, 1 H), 3.40–3.38 (m, 2 H), 2.55 (brs, 1 H), 2.21 (dd, *J* = 15.2, 9.4 Hz, 1 H), 2.02 (dd, *J* = 15.2, 3.2 Hz, 1 H), 1.91–1.84 (m, 1 H), 1.66–1.53 (m, 5 H), 1.41 (d, *J* = 13.2 Hz, 1 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.10–0.02 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 115.5, 80.3, 78.6, 71.6, 69.6, 69.5, 68.0, 65.9, 63.3, 61.0, 35.8, 34.7, 31.3, 29.5, 26.1, 26.1, 25.9, 25.9, 25.9, 18.5, 18.4, 18.2, 18.1, 18.0, –4.5, –4.6, –4.8, –4.9, –5.0, –5.1, –5.2, –5.3; HRMS (ESI–TOF) calcd for $C_{45}H_{98}O_8Si_5Na$ $[M + Na]^+$ 929.6006, found 929.6005.

Candidate Compound 3a from 24. To a solution of pentakis-TBS ether **24** (4.1 mg, 4.52 μmol) in MeOH (0.5 mL) was added 1.0 M aqueous HCl (0.20 mL, 0.200 mmol) at room temperature. The mixture was stirred at the same temperature for 2 h. To the mixture was added 1.0 M aqueous HCl (0.20 mL, 0.200 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture was added 1.0 M aqueous HCl (0.20 mL, 0.200 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was diluted with MeOH. Concentration and column chromatography (CH_2Cl_2/MeOH = 4:1) gave candidate compound **3a** (1.5 mg, 99%).

Alcohol 25. To a solution of diol **17** (71.8 mg, 0.111 mmol) in CH_2Cl_2 (1.1 mL) were added DMAP (2.7 mg, 22.4 μmol), imidazole (22.7 mg, 0.333 mmol), and TBSCl (40.1 mg, 0.266 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture were added imidazole (22.7 mg, 0.333 mmol) and TBSCl (40.1 mg, 0.266 mmol) at room temperature. The mixture was stirred at the same temperature for 12 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane, hexane/EtOAc = 70:1) gave the corresponding pentakis-TBS ether (85.0 mg), which was used for the next step without further purification.

A mixture of the alkene obtained above (85.0 mg) and 9-BBN (71.0 mg, 0.582 mmol) in THF (1.0 mL) was stirred at 50 ºC for 1 h. To the mixture were added 3.0 M aqueous NaOH (0.8 mL, 2.40 mmol) and 30% aqueous H_2O_2 (0.8 mL, 7.80 mmol) at 0 ºC. The mixture was stirred at room temperature for 30 min. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 20:1) gave alcohol **25** (73.6 mg, 75% in two steps): colorless oil; R_f = 0.46 (hexane/EtOAc = 10:1); $[\alpha]_D^{28}$ +4.5 (*c* 1.33, $CHCl_3$); IR (neat) 3436, 2954, 2929, 2890, 2857, 1638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.57 (dt, *J* = 15.4, 7.0 Hz, 1 H), 5.47 (dd, *J* = 15.4, 6.6 Hz, 1 H), 4.18 (dd, *J* = 6.4, 4.8 Hz, 1 H), 4.01–3.96 (m, 1 H), 3.92–3.78 (m, 4 H), 3.68 (t, *J* = 6.7 Hz, 1 H), 3.62–3.59 (m, 1 H), 3.61 (t, *J* = 6.4 Hz, 2 H), 3.56–3.54 (m, 1 H), 2.08 (q, *J* = 7.0 Hz, 2 H), 1.95–1.89 (m, 1 H), 1.80–1.76 (m, 1 H), 1.64–1.57 (m, 5 H), 1.32 (d, *J* = 13.9 Hz, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.07–0.02 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 131.1, 79.8, 77.7, 70.0, 68.5, 63.5, 62.7, 62.6, 61.6, 42.3, 34.6, 34.5, 32.5, 28.6, 26.0, 26.0, 25.9, 18.4, 18.3, 18.1, –3.9, –4.5, –4.6, –4.8, –5.2, –5.2; HRMS (ESI–TOF) calcd for $C_{45}H_{98}O_7Si_5Na$ $[M + Na]^+$ 913.6057, found 913.6056.

Sulfide 26. To a solution of alcohol **25** (73.6 mg, 82.6 μmol) in CH_2Cl_2 (0.8 mL) were added Et_3N (23 μL, 0.166 mmol), DMAP (2.3 mg, 17.2 μmol), and TsCl (19.1 mg, 0.100 mmol) at 0 ºC. The mixture was stirred at room temperature for 3 h. To the mixture were added Et_3N (23 μL, 0.166 mmol) and TsCl (19.1 mg, 0.100 mmol) at 0 ºC. The mixture was stirred at room temperature for 3 h. To the mixture were added Et_3N (46 μL, 0.332 mmol) and TsCl (38.2 mg, 0.200 mmol) at 0 ºC. The mixture was stirred at room temperature for 11 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 70:1) gave the corresponding tosylate (70.1 mg), which was used for the next step without further purification.

To a solution of the tosylate obtained above (70.1 mg) in DMF (0.7 mL) was added NaI (30.1 mg, 0.201 mmol) at room temperature. The mixture was stirred at 100 ºC for 2 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 80:1) gave the corresponding alkyl iodide (54.0 mg), which was used for the next step without further purification.

To a solution of the alkyl iodide obtained above (54.0 mg) in benzene (0.5 mL) were added PhSH (22 μL, 0.212 mmol) and DBU (38 μL, 0.254 mmol) at 4 ºC. The mixture was stirred at room temperature for 3 h. To the mixture were added PhSH (22 μL, 0.212 mmol) and DBU (38 μL, 0.254 mmol) at 4 ºC. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography

(hexane/EtOAc = 70:1) gave sulfide **26** (59.1 mg, 72% in three steps): colorless oil; R_f = 0.40 (hexane/EtOAc = 40:1); $[\alpha]_D^{28}$ +3.1 (*c* 1.46, $CHCl_3$); IR (neat) 2954, 2929, 2886, 2857, 1644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2 H), 7.25–7.19 (m, 2 H), 7.11 (t, *J* = 7.2 Hz, 1 H), 5.56 (dt, *J* = 15.3, 7.1 Hz, 1 H), 5.40 (dd, *J* = 15.3, 7.0 Hz, 1 H), 4.26–4.23 (m, 1 H), 3.99–3.93 (m, 1 H), 3.91–3.87 (m, 1 H), 3.79 (brs, 1 H), 3.73 (dd, *J* = 9.8, 6.1 Hz, 1 H), 3.63–3.58 (m, 2 H), 3.61 (t, *J* = 6.7 Hz, 2 H), 3.08 (dd, *J* = 12.7, 5.4 Hz, 1 H), 2.98 (dd, *J* = 12.7, 6.4 Hz, 1 H), 2.07 (q, *J* = 7.1 Hz, 2 H), 1.92–1.88 (m, 1 H), 1.78–1.71 (m, 2 H), 1.61–1.56 (m, 3 H), 1.39–1.33 (m, 1 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.08–0.00 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 131.7, 131.4, 128.6, 128.5, 125.2, 79.4, 74.8, 70.1, 68.3, 64.2, 62.7, 62.0, 40.8, 35.3, 34.9, 34.1, 32.6, 28.6, 26.0, 26.0, 18.4, 18.3, 18.2, 18.1, 18.1, –3.8, –4.5, –4.6, –4.7, –4.8, –5.1; HRMS (ESI–TOF) calcd for $C_{51}H_{102}O_6SSi_5Na$ $[M + Na]^+$ 1005.6141, found 1005.6137.

Alkene 28. To a solution of alkene **26** (51.6 mg, 52.4 μmol) in pyridine (0.5 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 1.2 mL, 60.0 μmol) at room temperature. The mixture was stirred at the same temperature for 2 h. To the mixture was added OsO_4 (0.05 M in CH_2Cl_2, 1.2 mL, 60.0 μmol) at room temperature. To the mixture were added $NaHSO_3$ (472 mg), H_2O (1.2 mL), and pyridine (0.9 mL) at room temperature. The mixture was stirred at the same temperature for 9 h. The mixture was diluted with EtOAc, washed with saturated aqueous $CuSO_4$, H_2O, and brine, and then dried over Na_2SO_4. Concentration gave diol **27** (52.8 mg), which was used for the next step without further purification.

To a solution of sulfide **27** obtained above (52.8 mg) in CH_2Cl_2 (0.5 mL) was added *m*CPBA (69–75%, 17.0 mg, 68.0–73.9 μmol) at –78 ºC. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with 2-methyl-2-butene. The mixture was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. Concentration gave the corresponding sulfoxide (54.6 mg), which was used for the next step without further purification.

To a solution of the sulfoxide obtained above (54.6 mg) in xylene (0.5 mL) was added $NaHCO_3$ (17.5 mg, 0.208 mmol) at room temperature. The mixture was stirred at reflux for 17 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 16:1) gave alkene **28** (26.0 mg, 56% in three steps): colorless oil; R_f = 0.38 (hexane/EtOAc = 10:1); $[\alpha]_D^{28}$ +0.1 (*c* 1.30, $CHCl_3$); IR (neat) 3500, 2955, 2929, 2888, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1 H), 5.13 (s, 1 H), 4.26 (d, *J* = 5.4 Hz, 1 H), 4.09–4.03 (m, 1 H), 3.95–3.86 (m, 2 H), 3.84–3.81 (m, 2 H), 3.70 (t, *J* = 6.7 Hz, 1 H), 3.64–3.60 (m, 1 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 3.38 (brs, 1 H), 2.85 (brs, 1 H), 2.23 (dd, *J* = 15.0, 6.7 Hz, 1 H), 2.14 (dd, *J* = 15.0, 5.5 Hz, 1 H), 1.91–1.84 (m, 1 H), 1.65–1.48 (m, 5 H), 1.39 (d, *J* = 12.9 Hz, 1 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.11–0.04 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 115.1, 80.0,

79.3, 72.6, 69.8, 69.5, 68.1, 64.5, 63.2, 61.5, 37.7, 34.2, 30.9, 29.4, 26.1, 26.0, 26.0, 25.9, 25.9, 18.4, 18.3, 18.2, 18.1, 18.1, –4.6, –4.9, –5.0, –5.2; HRMS (ESI–TOF) calcd for $C_{45}H_{98}O_8Si_5Na$ $[M + Na]^+$ 929.6006, found 929.6002.

Candidate Compound 3b from 28. To a solution of pentakis-TBS ether **28** (5.6 mg, 6.17 μmol) in MeOH (0.5 mL) was added 1.0 M aqueous HCl (60 μL, 60.0 μmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture was added 1.0 M aqueous HCl (0.30 mL, 0.300 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was diluted with MeOH. Concentration and column chromatography (CH_2Cl_2/MeOH = 4:1) gave candidate compound **3b** (2.0 mg, 96%).

Table S1. ^{1}H NMR chemical shifts and their deviations of natural symbiodinolide (**1**) and the synthetic products **3a** and **3b**.[a]

Position	**1**[b]	**3a**[c]	**3b**[c]	$\Delta\delta = \delta_{\mathbf{1}} - \delta_{\mathbf{3a}}$	$\Delta\delta = \delta_{\mathbf{1}} - \delta_{\mathbf{3b}}$
66	4.09	4.19	4.20	–0.10	–0.11
68a	2.33	2.36	2.32	–0.03	+0.01
68b	2.63	2.55	2.65	+0.08	–0.02
69	4.27	4.25	4.28	+0.02	–0.01

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 3.30 ppm). [b] Data reported in reference 2. Recorded at 800 MHz. [c] Recorded at 600 MHz.

Table S2. ^{1}H NMR chemical shifts and their deviations of natural symbiodinolide (**1**) and the synthetic products **3a** and **3b**.[a]

Position	**1**[b]	**3a**[c]	**3b**[c]	$\Delta\delta = \delta_{\mathbf{1}} - \delta_{\mathbf{3a}}$	$\Delta\delta = \delta_{\mathbf{1}} - \delta_{\mathbf{3b}}$
70a	1.64	1.69	1.70	–0.05	–0.06
70b	1.72	1.98	1.96	–0.26	–0.24
71	3.80	3.79	3.80	+0.01	0
72	3.04	3.21	3.18	–0.17	–0.14
73	3.69	3.53	3.53	+0.16	+0.16

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 3.30 ppm). [b] Data reported in reference 2. Recorded at 800 MHz. [c] Recorded at 600 MHz.

Alkyne 41. To a solution of diol **37** (3.71 g, 22.0 mmol) in CH_2Cl_2 (73 mL) was added K_2CO_3 (5.47 g, 39.6 mmol) at room temperature. The mixture was stirred at the same temperature for 4 days. The mixture was filtered and washed with CH_2Cl_2 (80 mL). To the mixture were added $PhI(OAc)_2$ (8.50 g, 26.4 mmol) and TEMPO (516 mg, 3.30 mmol) at room temperature. The mixture was stirred at the same temperature for 20 min. To the mixture was added $Ph_3P{=}CHCO_2Me$ (11.4 g, 33.0 mmol) at 0 ºC. The mixture was stirred at room temperature for

1 h. The mixture was filtered through short column chromatography (hexane/EtOAc = 4:1). The mixture was concentrated, washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 5:1) gave α,β-unsaturated ester **38** (1.95 g), which was used for the next step without further purification.

A mixture of alkene **38** obtained above (1.95 g) and 5% Pd/C (en) (190 mg) in THF (45 mL) was stirred at room temperature for 1 h under H_2 atmosphere. To the mixture was added 5% Pd/C (en) (190 mg) at room temperature. The mixture was stirred at room temperature for 12 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with Et_2O. Concentration gave the corresponding alkane (1.38 g), which was used for the next step without further purification.

To a solution of trimethylsilylacetylene (2.0 mL, 14.4 mmol) in THF (48 mL) was added *n*-BuLi (2.60 M in hexane, 5.5 mL, 14.4 mmol) at –78 ºC. The mixture was stirred at the same temperature for 30 min. To the mixture was added $BF_3{\cdot}OEt_2$ (1.7 mL, 14.4 mmol) at –78 ºC. The mixture was stirred at the same temperature for 1 h. To the mixture was added the epoxide obtained above (1.38 g) in THF (6.0 mL + 5.0mL + 5.0 mL) at –78 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with MeOH and saturated aqueous NH_4Cl. The mixture was diluted with EtOAc and washed with H_2O and brine. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 4:1) gave alcohol **39** (2.09 g), which was used for the next step without further purification.

To a solution of alcohol **39** obtained above (2.09 g) in CH_2Cl_2 (21 mL) were added *i*-Pr_2NEt (5.9 mL, 34.0 mmol), TBAI (628 mg, 1.70 mmol), and BOMCl (3.5 mL, 25.5 mmol) at room temperature. The mixture was stirred at reflux for 11 h. To the mixture were added *i*-Pr_2NEt (5.9 mL, 34.0 mmol) and BOMCl (3.5 mL, 25.5 mmol) at room temperature. The mixture was stirred at reflux for 3 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 10:1) gave the corresponding BOM ether (4.43 g), which was used for the next step without further purification.

To a suspension of $LiAlH_4$ (387 mg, 10.2 mmol) in THF (30 mL) was added the ester obtained above (4.43 g) in THF (3.0 mL + 5.0 mL + 5.0 mL) at 0 ºC. The mixture was stirred at the same temperature for 20 min. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was stirred at room temperature for 1 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 8:1, 3:1) gave alcohol **40** (2.32 g), which was used for the next step without further purification.

To a solution of alcohol **40** obtained above (2.32 g) in CH_2Cl_2 (23 mL) were added *i*-Pr_2NEt (2.4 mL, 13.9 mmol), TBAI (256 mg, 0.694 mmol), and MOMCl (0.79 mL, 10.4 mmol) at room

temperature. The mixture was stirred at the same temperature for 2 h. To the mixture were added *i*-Pr_2NEt (1.2 mL, 6.95 mmol) and MOMCl (0.40 mL, 5.20 mmol) at room temperature. The mixture was stirred at the same temperature for 3 h. To the mixture were added *i*-Pr_2NEt (1.2 mL, 6.95 mmol) and MOMCl (0.40 mL, 5.20 mmol) at room temperature. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, H_2O, and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 1:1) gave the corresponding MOM ether (2.47 g), which was used for the next step without further purification.

To a solution of the alkyne obtained above (2.47 g) in MeOH (33 mL) was added K_2CO_3 (1.80 g, 13.0 mmol) at room temperature. The mixture was stirred at the same temperature for 14 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 8:1) gave alkyne **41** (1.91 g, 28% in seven steps): colorless oil; R_f = 0.42 (hexane/EtOAc = 3:1); $[\alpha]_D^{25}$ +21.4 (*c* 0.99, $CHCl_3$); IR (neat) 3292, 2928, 2880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5 H), 4.88 (d, *J* = 7.2 Hz, 1 H), 4.81 (d, *J* = 7.2 Hz, 1 H), 4.69 (d, *J* = 11.6 Hz, 1 H), 4.63 (d, *J* = 11.6 Hz, 1 H), 4.61 (s, 2 H), 3.81–3.75 (m, 1 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 3.35 (s, 3 H), 2.54–2.42 (m, 2 H), 2.01 (t, *J* = 2.7 Hz, 1 H), 1.73–1.68 (m, 2 H), 1.66–1.60 (m, 2 H), 1.60–1.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 128.3, 127.8, 127.6, 96.4, 93.7, 81.0, 75.6, 70.1, 69.7, 67.6, 55.1, 33.8, 29.7, 24.5, 22.1; HRMS (ESI–TOF) calcd for $C_{18}H_{26}O_4Na$ $[M + Na]^+$ 329.1729, found 329.1726.

Alcohol 43. To a solution of triacetate **42** (1.17 g, 3.84 mmol) in MeOH (13 mL) was added NaOMe (304 mg, 5.63 mmol) at 0 ºC. The mixture was stirred at room temperature for 20 min. The reaction was quenched with 3.0 M aqueous HCl at 0 ºC. The mixture was diluted MeOH and dried over Na_2SO_4. Concentration gave the corresponding triol (975 mg), which was used for the next step without further purification.

To a solution of the triol obtained above (975 mg) in DMF (11 mL) were added imidazole (2.69 g, 39.5 mmol), DMAP (205 mg, 1.68 mmol), and TBSCl (3.04 g, 20.2 mmol) at room temperature. The mixture was stirred at 80 ºC for 13 h. To the mixture were added imidazole (1.84 g, 27.0 mmol) and TBSCl (1.98 g, 13.1 mmol) at room temperature. The mixture was stirred at 80 ºC for 4 h. To the mixture were added imidazole (935 mg, 13.7 mmol) and TBSCl (1.06 g, 7.03 mmol) at room temperature. The mixture was stirred at 80 ºC for 3 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane, hexane/EtOAc = 40:1) gave the corresponding tris-TBS ether (2.70 g), which was used for the next step without further purification.

To a solution of the tris-TBS ether obtained above (2.70 g) in CH_2Cl_2 (19 mL) and MeOH (19

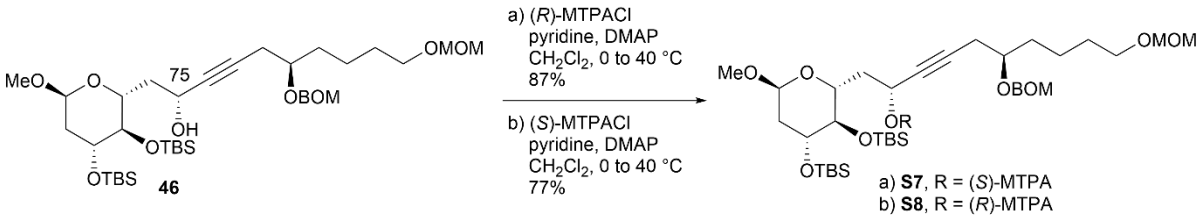
mL) was added CSA (267 mg, 1.15 mmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 6:1) gave alcohol **43** (1.19 g, 76% in three steps): colorless oil; R_f = 0.34 (hexane/EtOAc = 4:1); $[\alpha]_D^{23}$ +63.6 (*c* 1.00, $CHCl_3$); IR (neat) 3501, 2955, 2930, 2896, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73–4.72 (m, 1 H), 4.00–3.94 (m, 1 H), 3.82–3.77 (m, 1 H), 3.72–3.66 (m, 1 H), 3.57–3.52 (m, 1 H), 3.41 (d, *J* = 8.8 Hz, 1 H), 3.31 (s, 3 H), 2.07 (dd, *J* = 13.3, 4.8 Hz, 1 H), 1.93 (t, *J* = 6.4 Hz, 1 H), 1.64 (dd, *J* = 13.3, 3.6 Hz, 1 H), 0.91 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.3, 73.0, 72.8, 70.8, 62.3, 54.7, 39.0, 26.3, 26.1, 18.4, 18.1, –2.8, –3.0, –4.1, –4.6; HRMS (ESI–TOF) calcd for $C_{19}H_{42}O_5Si_2Na$ $[M + Na]^+$ 429.2469, found 429.2467.

Aldehyde 44. To a solution of alcohol **43** (256 mg, 0.629 mmol) in CH_2Cl_2 (6.3 mL) were added Et_3N (0.17 mL, 1.26 mmol), DMAP (14.6 mg, 0.126 mmol), and TsCl (144 mg, 0.755 mmol) at 0 ºC. The mixture was stirred at room temperature for 2 h. To the mixture were added Et_3N (0.51 mL, 3.78 mmol) and TsCl (432 mg, 2.27 mmol) at 0 ºC. The mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 40:1, 10:1) gave the corresponding tosylate (325 mg), which was used for the next step without further purification.
To a solution of the tosylate obtained above (325 mg) in DMSO (5.8 mL) was added NaCN (63.4 mg, 1.33 mmol) at room temperature. The mixture was stirred at 70 ºC for 3 h. To the mixture was added NaCN (35.4 mg, 0.722 mmol) at room temperature. The mixture was stirred at 70 ºC for 1 h. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 20:1) gave the corresponding nitrile (193 mg), which was used for the next step without further purification.
To a solution of the nitrile obtained above (193 mg) in CH_2Cl_2 (4.6 mL) was added DIBAL-H (1.02 M in hexane, 1.0 mL, 1.02 mmol) at –78 ºC. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with MeOH. The mixture was filtered through a Celite pad and washed with EtOAc. Concentration and column chromatography (hexane/EtOAc = 15:1, 10:1) gave aldehyde **44** (146 mg, 55% in three steps): colorless oil; R_f = 0.50 (hexane/EtOAc = 7:1); $[\alpha]_D^{23}$ +59.0 (*c* 0.67, $CHCl_3$); IR (neat) 2952, 2930, 2896, 2857, 1733 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.77 (dd, *J* = 3.4, 0.6 Hz, 1 H), 4.65 (dd, *J* = 3.6, 2.0 Hz, 1 H), 4.09 (ddd, *J* = 10.4, 8.4, 2.4 Hz, 1 H), 3.98 (ddd, *J* = 10.4, 8.4, 4.8 Hz, 1 H), 3.30 (s, 3 H), 3.26 (t, *J* = 8.4 Hz, 1 H), 2.82 (ddd, *J* = 15.5, 2.4, 0.6 Hz, 1 H), 2.49 (ddd, *J* = 15.5, 10.4, 3.4 Hz, 1 H), 2.09 (ddd, *J* = 13.2, 4.8, 2.0 Hz, 1 H), 1.65 (ddd, *J* = 13.2, 10.4, 3.6 Hz, 1 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 200.9, 98.2, 76.2, 70.6, 68.3, 54.9, 46.3, 39.1, 26.3, 26.1, 18.4, 18.1, –2.8, –3.0, –3.9, –4.1; HRMS (ESI–TOF) calcd for $C_{20}H_{42}O_5Si_2Na$ $[M + MeOH + Na]^+$ 473.2731, found 473.2718.

Propargylic Alcohols 45 and 46. To a solution of alkyne **41** (901 mg, 2.94 mmol) in THF (10 mL) was added *n*-BuLi (2.60 M in hexane, 0.93 mL, 2.42 mmol) at –78 ºC. The mixture was stirred at the same temperature for 1 h. To the mixture was added aldehyde **44** (674 mg, 1.61 mmol) in THF (2.0 mL + 2.0 mL + 2.0 mL) at –78 ºC. The mixture was warmed up to room temperature and stirred at the same temperature for 2 h. The reaction was quenched with MeOH and saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 8:1, 5:1, 3:1) gave propargylic alcohols **45** (323 mg, 28%) and **46** (668 mg, 57%). Propargylic alcohol **45**: colorless oil; R_f = 0.32 (hexane/EtOAc = 2:1); $[\alpha]_D^{23}$ +52.8 (*c* 0.83, $CHCl_3$); IR (neat) 3435, 2948, 2930, 2894, 2855 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5 H), 4.86 (d, *J* = 7.0 Hz, 1 H), 4.78 (d, *J* = 7.0 Hz, 1 H), 4.67–4.66 (m, 1 H), 4.64 (s, 2 H), 4.60 (s, 2 H), 4.58–4.56 (m, 1 H), 3.92 (ddd, *J* = 10.8, 8.0, 4.8 Hz, 1 H), 3.76–3.68 (m, 2 H), 3.52 (t, *J* = 6.4 Hz, 2 H), 3.35 (s, 3 H), 3.31 (s, 3 H), 3.21 (t, *J* = 8.3 Hz, 1 H), 2.91 (d, *J* = 3.2 Hz, 1 H), 2.52–2.48 (m, 2 H), 2.23 (ddd, *J* = 13.6, 6.4, 2.0 Hz, 1 H), 2.06 (ddd, *J* = 13.2, 4.8, 1.6 Hz, 1 H), 1.84–1.76 (m, 1 H), 1.72–1.58 (m, 5 H), 1.57–1.50 (m, 1 H), 1.49–1.39 (m, 1 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 127.7, 127.6, 98.2, 96.3, 93.8, 82.4, 81.7, 75.9, 72.0, 70.5, 69.7, 67.6, 62.0, 55.1, 54.9, 40.7, 38.9, 34.0, 29.7, 26.3, 26.2, 24.8, 22.1, 18.3, 18.1, –2.7, –3.0, –3.8, –4.2; HRMS (ESI–TOF) calcd for $C_{38}H_{68}O_9Si_2Na$ $[M + Na]^+$ 747.4300, found 747.4303. Propargylic alcohol **46**: colorless oil; R_f = 0.45 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +52.3 (*c* 0.95, $CHCl_3$); IR (neat) 3465, 2952, 2930, 2892, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5 H), 4.86 (d, *J* = 7.1 Hz, 1 H), 4.78 (d, *J* = 7.1 Hz, 1 H), 4.69–4.68 (m, 1 H), 4.64 (s, 2 H), 4.64–4.60 (m, 1 H), 4.60 (s, 2 H), 4.07 (td, *J* = 10.4, 2.0 Hz, 1 H), 3.98–3.92 (m, 1 H), 3.78–3.73 (m, 1 H), 3.52 (t, *J* = 6.4 Hz, 2 H), 3.38 (s, 3 H), 3.35 (s, 3 H), 3.24 (t, *J* = 8.6 Hz, 1 H), 2.55–2.44 (m, 2 H), 2.15 (ddd, *J* = 14.4, 6.4, 2.0 Hz, 1 H), 2.07 (dd, *J* = 12.8, 4.0 Hz, 1 H), 1.81 (ddd, *J* = 14.4, 10.8, 2.8 Hz, 1 H), 1.72–1.59 (m, 5 H), 1.56–1.51 (m, 1 H), 1.50–1.41 (m, 1 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 127.7, 127.6, 98.3, 96.3, 93.8, 82.5, 81.8, 76.5, 75.9, 70.8, 70.4, 69.7, 67.6, 61.0, 55.2, 55.1, 39.0, 38.9, 34.0, 29.8, 26.3, 26.2, 24.8, 22.2, 18.4, 18.1, –2.6, –3.0, –3.9, –4.1; HRMS (ESI–TOF) calcd for $C_{38}H_{68}O_9Si_2Na$ $[M + Na]^+$ 747.4300, found 747.4298.

Stereochemical Determination of 46. The absolute configuration at the C75 position of **46** was determined by the modified Mosher method[1] as shown in Scheme S4 and Figure S2.



Scheme S4. Transformation of propargylic alcohol **46** for its stereochemical determination.

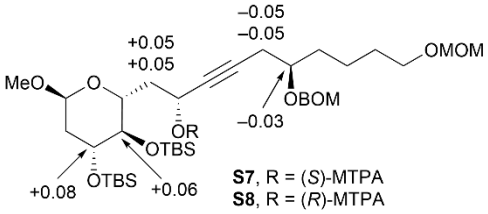


Figure S2. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S7** and **S8**.

(*S*)-MTPA Ester S7. To a solution of alcohol **46** (1.6 mg, 2.21 μmol) in CH_2Cl_2 (0.2 mL) were added pyridine (0.5 μL, 6.63 μmol), DMAP (0.8 mg, 6.55 μmol), and (*R*)-MTPACl (0.8 μL, 4.42 μmol) at 0 ºC. The mixture was stirred at room temperature for 20 min. To the mixture were added pyridine (1.0 μL, 13.3 μmol) and (*R*)-MTPACl (1.6 μL, 8.84 μmol) at room temperature. The mixture was stirred at 40 ºC for 20 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 6:1) gave (*S*)-MTPA ester **S7** (1.8 mg, 87%): colorless oil; R_f = 0.61 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +34.3 (*c* 0.14, $CHCl_3$); IR (neat) 2950, 2928, 2856, 1752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2 H), 7.38–7.26 (m, 8 H), 5.72–5.69 (m, 1 H), 4.84 (d, *J* = 7.1 Hz, 1 H), 4.75 (d, *J* = 7.1 Hz, 1 H), 4.63–4.61 (m, 1 H), 4.62 (s, 2 H), 4.60 (s, 2 H), 3.88–3.82 (m, 1 H), 3.73–3.68 (m, 1 H), 3.54 (s, 3 H), 3.52–3.46 (m, 1 H), 3.50 (t, *J* = 6.4 Hz, 2 H), 3.34 (s, 3 H), 3.17 (s, 3 H), 3.17–3.14 (m, 1 H), 2.47–2.46 (m, 3 H), 2.02 (ddd, *J* = 13.6, 4.8, 2.4 Hz, 1 H), 1.81 (t, *J* = 12.7 Hz, 1 H), 1.65–1.55 (m, 6 H), 1.49–1.40 (m, 1 H), 0.91 (s, 9 H), 0.85 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 137.7, 131.8, 129.4, 128.4, 128.2, 127.8, 127.6, 97.9, 96.4, 93.9, 83.4, 78.4, 76.2, 75.9, 70.8, 69.7, 68.6, 67.6, 63.6, 55.5, 55.1, 55.0, 38.6, 38.1, 34.0, 29.8, 26.3, 26.0, 24.8, 22.1, 18.4, 18.0, –2.8, –3.1, –4.0, –4.2; HRMS (ESI–TOF) calcd for $C_{48}H_{75}F_3O_{11}Si_2Na$ $[M + Na]^+$ 963.4698, found 963.4695.

(*R*)-MTPA Ester S8. To a solution of alcohol **46** (2.8 mg, 3.86 μmol) in CH_2Cl_2 (0.2 mL) were added pyridine (0.9 μL, 11.6 μmol), DMAP (1.4 mg, 11.6 μmol), and (*S*)-MTPACl (1.4 μL, 7.72 μmol) at 0 ºC. The mixture was stirred at room temperature for 1 h. To the mixture were added pyridine (0.9 μL, 11.6 μmol) and (*S*)-MTPACl (1.4 μL, 7.72 μmol) at room temperature.

The mixture was stirred at 40 ºC for 14 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 6:1) gave (*R*)-MTPA ester **S8** (2.8 mg, 77%): colorless oil; R_f = 0.42 (hexane/EtOAc = 3:1); $[\alpha]_D^{22}$ +68.0 (*c* 0.14, $CHCl_3$); IR (neat) 2953, 2928, 2853, 1753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 2 H), 7.38–7.28 (m, 8 H), 5.70–5.67 (m, 1 H), 4.84 (d, *J* = 7.1 Hz, 1 H), 4.76 (d, *J* = 7.1 Hz, 1 H), 4.62 (s, 2 H), 4.60–4.59 (m, 1 H), 4.59 (s, 2 H), 3.80–3.70 (m, 2 H), 3.57 (s, 3 H), 3.50 (t, *J* = 6.4 Hz, 2 H), 3.34 (s, 3 H), 3.28 (t, *J* = 9.8 Hz, 1 H), 3.21 (s, 3 H), 3.09 (t, *J* = 8.1 Hz, 1 H), 2.50 (dd, *J* = 5.8, 1.6 Hz, 2 H), 2.44–2.37 (m, 1 H), 2.01–1.97 (m, 1 H), 1.80–1.73 (m, 1 H), 1.65–1.40 (m, 7 H), 0.90 (s, 9 H), 0.80 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.05 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 137.7, 132.3, 129.4, 128.4, 128.2, 127.8, 127.7, 127.3, 98.0, 96.4, 93.9, 83.6, 78.6, 76.1, 75.8, 70.6, 69.7, 68.5, 67.6, 63.3, 55.4, 55.1, 38.7, 38.4, 34.1, 29.8, 26.3, 26.0, 24.8, 22.1, 18.3, 18.0, –2.7, –3.2, –4.1, –4.2; HRMS (ESI–TOF) calcd for $C_{48}H_{75}F_3O_{11}Si_2Na$ $[M + Na]^+$ 963.4698, found 963.4701.

Allylic Alcohol 47. To a solution of propargylic alcohol **45** (294 mg, 0.406 mmol) in Et_2O (4.1 mL) was added Red-Al (65% in toluene, 1.2 mL, 4.01 mmol) at 0 ºC. The mixture was stirred at reflux for 4 h. The reaction was quenched with saturated aqueous sodium potassium tartrate at 0 ºC. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave allylic alcohol **47** (220 mg, 75%): colorless oil; R_f = 0.49 (hexane/EtOAc = 2:1); $[\alpha]_D^{26}$ +48.9 (*c* 1.78, $CHCl_3$); IR (neat) 3465, 3032, 2952, 2930, 2896, 2857 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5 H), 5.68 (ddd, *J* = 15.6, 7.8, 7.2 Hz, 1 H), 5.54 (dd, *J* = 15.6, 6.6 Hz, 1 H), 4.81 (d, *J* = 7.2 Hz, 1 H), 4.76 (d, *J* = 7.2 Hz, 1 H), 4.70 (d, *J* = 2.4 Hz, 1 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 12.0 Hz, 1 H), 4.60 (s, 2 H), 4.27–4.24 (m, 1 H), 3.91 (ddd, *J* = 10.8, 7.8, 4.8 Hz, 1 H), 3.71–3.65 (m, 2 H), 3.51–3.49 (m, 3 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.19 (t, *J* = 9.0 Hz, 1 H), 2.35–2.25 (m, 2 H), 2.10–2.04 (m, 2 H), 1.66–1.48 (m, 7 H), 1.42–1.36 (m, 1 H), 0.90 (s, 9 H), 0.87 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 135.1, 128.4, 127.8, 127.6, 126.7, 98.4, 96.3, 93.4, 76.9, 76.7, 73.7, 72.7, 70.3, 69.5, 67.7, 55.1, 55.0, 39.3, 38.8, 37.2, 33.9, 29.8, 26.3, 26.1, 22.1, 18.3, 18.0, –2.7, –3.1, –3.9, –4.3; HRMS (ESI–TOF) calcd for $C_{38}H_{70}O_9Si_2Na$ $[M + Na]^+$ 749.4456, found 749.4457.

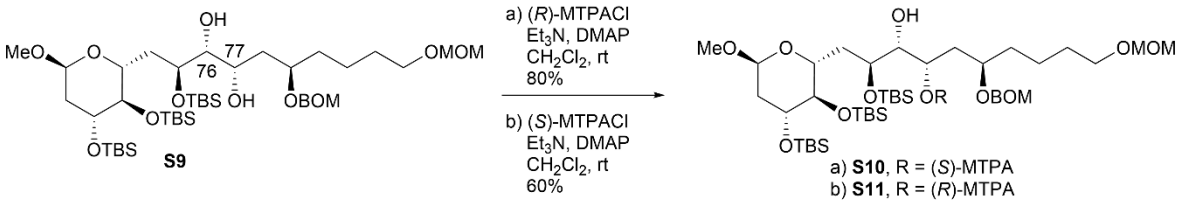
Tris-TBS Ether 48. To a solution of allylic alcohol **47** (113 mg, 0.155 mmol) in CH_2Cl_2 (3.1 mL) were added 2,6-lutidine (54 μL, 0.465 mmol) and TBSOTf (85 μL, 0.372 mmol) at 0 ºC. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 10:1) gave tris-TBS ether **48** (129 mg, 99%): pale yellow oil; R_f = 0.57 (hexane/EtOAc = 4:1);

$[\alpha]_D^{22}$ +52.1 (*c* 1.45, $CHCl_3$); IR (neat) 2955, 2929, 2896, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5 H), 5.60–5.45 (m, 2 H), 4.82 (d, *J* = 7.2 Hz, 1 H), 4.76 (d, *J* = 7.2 Hz, 1 H), 4.66 (d, *J* = 11.6 Hz, 1 H), 4.63 (s, 1 H), 4.60 (s, 2 H), 4.58 (d, *J* = 11.6 Hz, 1 H), 4.27 (ddd, *J* = 10.0, 6.4, 3.6 Hz, 1 H), 3.85 (ddd, *J* = 10.4, 7.6, 4.5 Hz, 1 H), 3.69–3.64 (m, 1 H), 3.50 (t, *J* = 6.2 Hz, 2 H), 3.48–3.43 (m, 1 H), 3.34 (s, 3 H), 3.29 (s, 3 H), 3.16 (t, *J* = 8.0 Hz, 1 H), 2.32–2.25 (m, 2 H), 2.03–1.91 (m, 2 H), 1.69–1.40 (m, 8 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.08 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 135.8, 128.4, 127.8, 127.6, 126.8, 97.8, 96.4, 93.5, 77.1, 76.5, 71.0, 70.7, 70.1, 69.5, 67.7, 55.1, 55.0, 41.2, 38.6, 37.1, 34.0, 29.8, 26.2, 26.1, 25.9, 22.2, 18.2, 18.2, 18.1, –2.9, –3.3, –4.0, –4.3, –4.3, –4.7; HRMS (ESI–TOF) calcd for $C_{44}H_{84}O_9Si_3Na$ $[M + Na]^+$ 863.5321, found 863.5323.

Diol 49. To a solution of alkene **48** (64.0 mg, 76.1 μmol) in pyridine (2.5 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 2.0 mL, 0.100 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. To the mixture were added $NaHSO_3$ (560 mg), H_2O (10.0 mL), and pyridine (9.5 mL) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was diluted with EtOAc and washed with H_2O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave diols **49** (18.2 mg, 28%) and **S9** (37.1 mg, 55%). Diol **49**: colorless oil; R_f = 0.47 (hexane/EtOAc = 3:1); $[\alpha]_D^{22}$ +39.1 (*c* 0.69, $CHCl_3$); IR (neat) 3501, 2954, 2929, 2899, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5 H), 4.78 (d, *J* = 6.8 Hz, 1 H), 4.76 (d, *J* = 6.8 Hz, 1 H), 4.63 (s, 3 H), 4.61 (s, 1 H), 4.59 (s, 2 H), 4.05 (dt, *J* = 10.1, 2.6 Hz, 1 H), 3.95–3.85 (m, 2 H), 3.78–3.76 (m, 1 H), 3.58 (t, *J* = 9.3 Hz, 1 H), 3.50 (t, *J* = 6.5 Hz, 2 H), 3.42–3.38 (m, 1 H), 3.34 (s, 3 H), 3.27 (s, 3 H), 3.17 (s, 1 H), 3.14 (t, *J* = 8.3 Hz, 1 H), 2.55 (d, *J* = 8.4 Hz, 1 H), 2.38–2.32 (m, 1 H), 2.02 (ddd, *J* = 13.3, 4.6, 2.0 Hz, 1 H), 1.85 (ddd, *J* = 14.2, 9.8, 6.5 Hz, 1 H), 1.65–1.43 (m, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.13 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.4, 127.8, 127.6, 98.2, 96.3, 92.9, 77.2, 75.7, 74.4, 70.7, 70.5, 70.2, 69.5, 67.6, 55.2, 55.1, 39.0, 38.2, 36.8, 34.0, 29.9, 26.3, 26.1, 25.8, 21.9, 18.3, 18.0, 18.0, –2.8, –3.1, –3.9, –4.3, –4.8; HRMS (ESI–TOF) calcd for $C_{44}H_{86}O_{11}Si_3Na$ $[M + Na]^+$ 897.5376, found 897.5381. Diol **S9**: colorless oil; R_f = 0.38 (hexane/EtOAc = 3:1); $[\alpha]_D^{14}$ +40.3 (*c* 0.77, $CHCl_3$); IR (neat) 3489, 2952, 2930, 2896, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5 H), 4.83 (s, 2 H), 4.65 (s, 2 H), 4.62 (s, 1 H), 4.59 (s, 2 H), 4.22 (dt, *J* = 9.6, 3.6 Hz, 1 H), 4.17 (dt, *J* = 10.4, 2.4 Hz, 1 H), 3.92–3.86 (m, 2 H), 3.57 (ddd, *J* = 11.2, 8.8, 2.0 Hz, 1 H), 3.49 (t, *J* = 6.8 Hz, 2 H), 3.39 (dd, *J* = 8.9, 4.0 Hz, 1 H), 3.34 (s, 3 H), 3.31 (s, 3 H), 3.23 (d, *J* = 2.5 Hz, 1 H), 3.15 (t, *J* = 8.3 Hz, 1 H), 2.83 (d, *J* = 9.0 Hz, 1 H), 2.14 (ddd, *J* = 14.0, 9.6, 2.0 Hz, 1 H), 2.04 (ddd, *J* = 12.8, 4.4, 2.0 Hz, 1 H), 1.93 (ddd, *J* = 14.0, 10.0, 3.2 Hz, 1 H), 1.70–1.43 (m, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.88

(s, 9 H), 0.12 (s, 3 H), 0.12 (s, 3 H), 0.94 (s, 3 H), 0.94 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 128.4, 127.8, 127.6, 98.3, 96.4, 94.3, 77.5, 75.1, 73.6, 73.5, 70.6, 69.5, 68.9, 67.7, 66.6, 55.4, 55.1, 39.1, 39.0, 36.4, 34.9, 29.9, 26.3, 26.2, 25.8, 21.9, 18.3, 18.0, 17.9, –3.0, –3.0, –3.7, –4.3, –4.6, –4.9; HRMS (ESI–TOF) calcd for $C_{44}H_{86}O_{11}Si_3Na$ [M + Na]$^+$ 897.5376, found 897.5333.

Stereochemical Determination of S9. Treatment of diol **S9** with MTPACl/Et_3N/DMAP provided mono-(*S*)-MTPA ester **S10** and mono-(*R*)-MTPA ester **S11** at the C77 positions, respectively (Scheme S5). The C77 absolute stereochemistry of **S9** was determined by applying the modified Mosher method[1] (Figure S3). The C76 absolute configuration of **S9** was elucidated based on the *syn*-addition reaction mechanism of OsO_4-catalyzed dihydroxylation.



Scheme S5. Transformation of diol **S9** for its stereochemical determination.

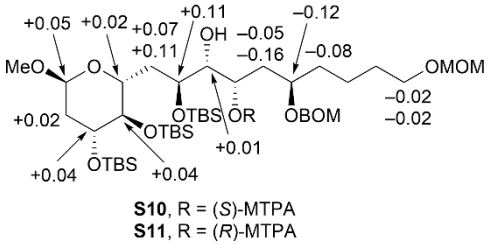


Figure S3. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S10** and **S11**.

(*S*)-MTPA Ester S10. To a solution of diol **S9** (6.1 mg, 6.97 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (1.7 mg, 13.9 μmol), Et_3N (39 μL, 0.279 mmol), and (*R*)-MTPACl (30 μL, 0.209 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 7:1) gave (*S*)-MTPA ester **S10** (6.1 mg, 80%): colorless oil; R_f = 0.43 (hexane/EtOAc = 4:1); $[\alpha]_D^{22}$ +26.0 (*c* 0.065, $CHCl_3$); IR (neat) 3501, 2956, 2928, 2856, 1746 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.63 (m, 2 H), 7.38–7.27 (m, 8 H), 5.49–5.47 (m, 1 H), 4.77 (d, *J* = 7.2 Hz, 1 H), 4.76 (d, *J* = 7.2 Hz, 1 H), 4.67 (d, *J* = 11.8 Hz, 1 H), 4.64 (dd, *J* = 3.6, 1.2 Hz, 1 H), 4.58 (s, 2 H), 4.56 (d, *J* = 11.8 Hz, 1 H), 3.93–3.89 (m, 2 H), 3.81 (t, *J* = 6.5 Hz, 1 H), 3.65–3.63 (m, 1 H), 3.57 (s, 3 H), 3.48–3.41 (m, 3 H), 3.35–3.34 (m,

1 H), 3.33 (s, 3 H), 3.30 (s, 3 H), 3.18 (t, *J* = 8.2 Hz, 1 H), 2.10 (ddd, *J* = 14.4, 6.0, 1.8 Hz, 1 H), 2.06 (ddd, *J* = 13.2, 4.8, 1.8 Hz, 1 H), 1.96 (ddd, *J* = 14.4, 8.5, 3.7 Hz, 1 H), 1.83 (ddd, *J* = 14.4, 8.5, 4.2 Hz, 1 H), 1.72–1.49 (m, 8 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 138.0, 132.0, 129.5, 128.4, 128.3, 127.8, 127.6, 127.6, 98.3, 96.3, 94.5, 77.5, 76.6, 75.1, 74.1, 70.6, 69.9, 69.7, 67.6, 67.5, 55.5, 55.1, 39.3, 37.1, 34.9, 34.0, 29.7, 26.3, 26.3, 25.9, 21.6, 18.3, 18.0, 18.0, –2.9, –3.0, –3.5, –4.1, –4.2, –5.2; HRMS (ESI–TOF) calcd for $C_{54}H_{93}F_3O_{13}Si_3Na$ $[M + Na]^+$ 1113.5774, found 1113.5769.

(*R*)-MTPA Ester S11. To a solution of diol **S9** (3.6 mg, 4.11 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (1.0 mg, 8.19 μmol), Et_3N (21 μL, 0.148 mmol), and (*S*)-MTPACl (19 μL, 98.6 μmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 7:1) gave (*R*)-MTPA ester **S11** (2.7 mg, 60%): colorless oil; R_f = 0.43 (hexane/EtOAc = 4:1); $[\alpha]_D^{21}$ +54.3 (*c* 0.095, $CHCl_3$); IR (neat) 3490, 2956, 2928, 2856, 1744 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62–7.61 (m, 2 H), 7.38–7.28 (m, 8 H), 5.37 (t, *J* = 5.7 Hz, 1 H), 4.78 (d, *J* = 7.2 Hz, 1 H), 4.77 (d, *J* = 7.2 Hz, 1 H), 4.66 (d, *J* = 11.8 Hz, 1 H), 4.59 (s, 2 H), 4.58 (s, 1 H), 4.54 (d, *J* = 11.8 Hz, 1 H), 3.91–3.85 (m, 2 H), 3.70 (t, *J* = 6.5 Hz, 1 H), 3.66–3.63 (m, 1 H), 3.55 (s, 3 H), 3.49–3.46 (m, 1 H), 3.48 (t, *J* = 6.6 Hz, 1 H), 3.33 (s, 3 H), 3.27 (s, 3 H), 3.14 (t, *J* = 8.5 Hz, 1 H), 2.07–2.00 (m, 4 H), 1.66–1.39 (m, 8 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 137.9, 132.0, 129.6, 128.4, 128.4, 127.8, 127.6, 127.5, 98.2, 96.3, 94.5, 77.4, 76.1, 75.3, 74.4, 70.6, 69.8, 69.7, 67.7, 67.6, 55.4, 55.1, 39.2, 36.7, 34.9, 30.3, 29.7, 26.3, 26.3, 25.9, 21.7, 18.0, 18.0, 18.0, –2.9, –3.0, –3.5, –4.0, –4.2, –5.0; HRMS (ESI–TOF) calcd for $C_{54}H_{93}F_3O_{13}Si_3Na$ $[M + Na]^+$ 1113.5774, found 1113.5775.

Triol 50. A mixture of BOM ether **49** (12.4 mg, 14.2 μmol) and 20% $Pd(OH)_2$/C (2.0 mg) in MeOH (0.5 mL) was stirred at room temperature for 2 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (hexane/EtOAc = 3:1) gave triol **50** (11.1 mg, quant): colorless oil; R_f = 0.22 (hexane/EtOAc = 3:1); $[\alpha]_D^{22}$ +32.0 (*c* 0.62, $CHCl_3$); IR (neat) 3436, 2951, 2929, 2894, 2857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65–4.64 (m, 1 H), 4.61 (s, 2 H), 4.02 (dt, *J* = 10.1, 2.6 Hz, 1 H), 3.92–3.82 (m, 3 H), 3.54–3.53 (m, 1 H), 3.52 (t, *J* = 6.4 Hz, 2 H), 3.38–3.33 (m, 1 H), 3.35 (s, 3 H), 3.29 (s, 3 H), 3.15 (t, *J* = 8.2 Hz, 1 H), 2.38–2.31 (m, 1 H), 2.03 (ddd, *J* = 13.0, 4.6, 1.9 Hz, 1 H), 1.66–1.40 (m, 10 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 98.3, 96.4, 77.1, 74.1, 73.6, 71.3, 70.4, 70.1, 69.5, 67.7, 55.2, 55.1, 39.5, 38.9, 37.5, 36.7, 29.7, 26.3, 26.1, 25.8, 22.1, 18.3, 18.0, 17.9, –2.8, –3.1, –3.9, –3.9, –4.3, –4.8; HRMS (ESI–TOF) calcd for $C_{36}H_{78}O_{10}Si_3Na$ $[M + Na]^+$ 777.4800, found 777.4804.

Candidate Compound 4a. To a solution of tris-TBS ether **50** (11.3 mg, 15.0 μmol) in THF (0.3 mL) was added TBAF (1.0 M in THF, 90 μL, 90.0 μmol) at room temperature. The mixture was stirred at the same temperature for 5 h. To the mixture was added TBAF (1.0 M in THF, 90 μL, 90.0 μmol) at room temperature. The mixture was stirred at 40 °C for 3 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4a** (3.8 mg, 61%): colorless oil; R_f = 0.33 (CH_2Cl_2/MeOH = 5:1); $[\alpha]_D^{22}$ +57.3 (*c* 0.19, CH_3OH); IR (neat) 3409, 2960, 2925, 2854 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.73 (d, *J* = 3.0 Hz, 1 H), 4.58 (s, 2 H), 4.00–3.97 (m, 1 H), 3.94–3.91 (m, 1 H), 3.82–3.78 (m, 1 H), 3.74 (ddd, *J* = 11.4, 9.1, 5.0 Hz, 1 H), 3.62 (td, *J* = 9.1, 3.0 Hz, 1 H), 3.52 (t, *J* = 6.5 Hz, 2 H), 3.37–3.36 (m, 1 H), 3.33 (s, 3 H), 3.32 (s, 3 H), 3.06 (t, *J* = 9.1 Hz, 1 H), 2.23 (ddd, *J* = 14.4, 6.0, 3.0 Hz, 1 H), 2.03 (ddd, *J* = 13.3, 5.0, 1.2 Hz, 1 H), 1.74–1.43 (m, 10 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.9, 97.4, 77.5, 75.9, 72.9, 71.9, 71.1, 71.0, 69.6, 68.8, 55.4, 55.4, 41.3, 38.9, 38.2, 36.9, 30.8, 23.2; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2203.

Candidate Compound 4b. To a solution of diol **49** (6.2 mg, 7.08 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (1.0 mg, 8.19 μmol), pyridine (25 μL, 0.315 mmol), and Ac_2O (22 μL, 0.236 mmol) at room temperature. The mixture was stirred at the same temperature for 16 h. To the mixture were added DMAP (1.0 mg, 8.19 μmol), pyridine (25 μL, 0.315 mmol), and Ac_2O (22 μL, 0.236 mmol) at room temperature. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 4:1) gave the corresponding diacetate (6.5 mg), which was used for the next step without further purification.

A mixture of the BOM ether obtained above (6.5 mg) and 20% $Pd(OH)_2$/C (1.3 mg) in MeOH (0.2 mL) was stirred at room temperature for 40 min under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration gave the corresponding alcohol (4.5 mg), which was used for the next step without further purification.

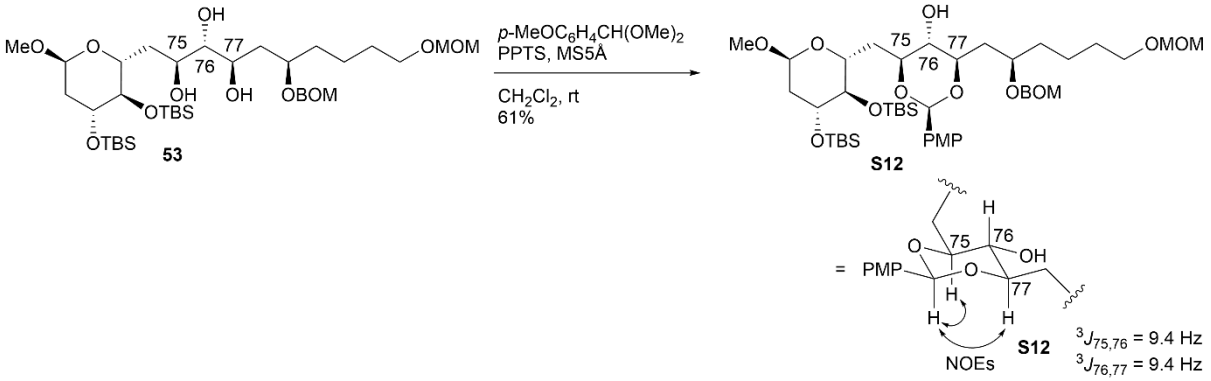
To a mixture of the alcohol obtained above (4.5 mg), Ph_3P (5.6 mg, 21.4 μmol), and *p*-NO_2PhCO_2H (3.6 mg, 21.4 μmol) in THF (0.2 mL) was added DEAD (2.2 M in toluene, 9.7 μL, 21.4 μmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 7:1, 4:1) gave *p*-nitrobenzoate **51** (3.8 mg), which was used

for the next step without further purification.
To a solution of triester **51** obtained above (3.8 mg) in MeOH (0.2 mL) was added NaOMe (1.0 mg, 18.5 μmol) at 0 ºC. The mixture was stirred at room temperature for 14 h. The reaction was quenched with DOWEX 50WX4. The mixture was filtered and washed with EtOAc. Concentration and short column chromatography (hexane/EtOAc = 4:1, 1:1) gave the corresponding triol (2.8 mg), which was used for the next step without further purification.
To a solution of the tris-TBS ether obtained above (2.8 mg) in THF (0.2 mL) was added TBAF (1.0 M in THF, 21 μL, 21.0 μmol) at room temperature. The mixture was stirred at the same temperature for 14 h and at 40 ºC for 8 h. The mixture was filtered through short column chromatography (EtOAc/MeOH = 5:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4b** (1.5 mg, 51% in five steps): colorless oil; R_f = 0.30 (CH_2Cl_2/MeOH = 5:1); $[\alpha]_D^{22}$ +67.3 (*c* 0.070, CH_3OH); IR (neat) 3398, 2959, 2925, 2851 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.73 (d, *J* = 3.5 Hz, 1 H), 4.59 (s, 2 H), 3.99–3.97 (m, 2 H), 3.84–3.80 (m, 1 H), 3.74 (ddd, *J* = 11.4, 9.2, 5.0 Hz, 1 H), 3.61 (td, *J* = 9.2, 2.8 Hz, 1 H), 3.52 (t, *J* = 6.5 Hz, 2 H), 3.33 (s, 3 H), 3.32 (s, 3 H), 3.31–3.30 (m, 1 H), 3.06 (t, *J* = 9.2 Hz, 1 H), 2.23 (ddd, *J* = 14.4, 6.0, 2.8 Hz, 1 H), 2.04 (ddd, *J* = 13.1, 5.0, 0.6 Hz, 1 H), 1.69–1.46 (m, 10 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.9, 97.4, 77.5, 76.8, 71.7, 71.1, 70.8, 69.6, 69.0, 68.8, 55.4, 55.4, 42.2, 39.0, 38.9, 36.9, 30.8, 23.5; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2207.

Triol 53. A mixture of alkyne **45** (9.2 mg, 12.7 μmol) and Lindlar cat (palladium 5% on calcium carbonate poisoned with lead, 3.4 mg) in MeOH (3.0 mL) was stirred at room temperature for 3 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration gave allylic alcohol **52** (10.4 mg), which was used for the next step without further purification.
To a solution of allylic alcohol **52** obtained above (10.4 mg) in pyridine (0.2 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 0.4 mL, 20.0 μmol) at room temperature. The mixture was stirred at the same temperature for 2 h. To the mixture were added $NaHSO_3$ (136 mg), H_2O (0.6 mL), and pyridine (0.6 mL) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was diluted with EtOAc and washed with H_2O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 2:1) gave triol **53** (5.1 mg, 53% in two steps) and its C76,C77-epimer (4.3 mg, 44% in two steps). Triol **53**: colorless oil; R_f = 0.37 (CH_2Cl_2/MeOH = 20:1); $[\alpha]_D^{22}$ +20.8 (*c* 2.01, $CHCl_3$); IR (neat) 3486, 2952, 2928, 2900, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5 H), 4.84 (d, *J* = 6.8 Hz, 1 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.71 (d, *J* = 1.9 Hz, 1 H), 4.64 (s, 2 H), 4.60 (s, 2 H), 4.06 (brs, 1 H), 4.01–3.78 (m, 6 H), 3.50 (t, *J* = 6.5 Hz, 2 H), 3.42 (t, *J* = 6.7 Hz, 1 H), 3.35 (s, 3 H), 3.35 (s, 3 H), 3.21 (t, *J* = 8.4 Hz, 1 H), 2.89 (brs, 1 H), 2.47 (d, *J* = 14.6 Hz, 1 H), 2.08 (ddd, *J* = 13.6, 4.8,

1.6 Hz, 1 H), 1.97 (dt, *J* = 14.8, 2.8 Hz, 1 H), 1.79 (dt, *J* = 14.8, 8.8 Hz, 1 H), 1.69–1.43 (m, 9 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.10 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.4, 127.8, 98.5, 96.4, 93.4, 77.9, 75.7, 74.4, 74.1, 72.6, 70.3, 70.1, 67.6, 55.1, 55.1, 38.9, 37.1, 34.4, 30.0, 26.3, 26.2, 21.4, 18.4, 18.1, –2.7, –3.0, –3.8, –4.2; HRMS (ESI–TOF) calcd for $C_{38}H_{72}O_{11}Si_2Na$ $[M + Na]^+$ 783.4511, found 783.4507.

Stereochemical Determination of 53. Triol **53** was treated with *p*-$MeOC_6H_4CH(OMe)_2$/PPTS/MS5Å to give *p*-methoxybenzylidene acetal **S12** in 61% yield (Scheme S6). The observed coupling constants ($^3J_{75,76}$ and $^3J_{76,77}$ = 9.4 Hz) in **S12** indicate that H-75, H-76, and H-77 possess the axial orientations. The stereochemistry at the acetal carbon of **S12** was elucidated by the NOE correlations as shown in arrows.



Scheme S6. Stereochemical determination of triol **53**.

***p*-Methoxybenzylidene Acetal S12.** To a solution of triol **53** (14.8 mg, 19.4 μmol) in CH_2Cl_2 (0.3 mL) were added MS5Å (24.0 mg), *p*-$MeOC_6H_4CH(OMe)_2$ (5.0 μL, 29.1 μmol), and PPTS (0.5 mg, 1.94 μmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 8:1, 4:1) gave *p*-methoxybenzylidene acetal **S12** (10.5 mg, 61%): colorless oil; R_f = 0.23 (hexane/EtOAc = 3:1); $[\alpha]_D^{22}$ +50.8 (*c* 0.021, $CHCl_3$); IR (neat) 3429, 2956, 2926, 2855 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 7.62 (d, *J* = 8.6 Hz, 2 H), 7.34–7.03 (m, 5 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 5.57 (s, 1 H), 4.78 (d, *J* = 7.2 Hz, 1 H), 4.68 (d, *J* = 7.2 Hz, 1 H), 4.59 (s, 2 H), 4.49 (s, 2 H), 4.49 (s, 1 H), 4.20–4.17 (m, 2 H), 4.09–4.05 (m, 1 H), 3.94–3.86 (m, 2 H), 3.64 (td, *J* = 9.1, 3.2 Hz, 1 H), 3.49–3.48 (m, 1 H), 3.43 (t, *J* = 6.0 Hz, 2 H), 3.25 (s, 3 H), 3.18 (s, 3 H), 3.18 (s, 3 H), 2.57 (ddd, *J* = 14.6, 5.7, 2.3 Hz, 1 H), 2.32 (ddd, *J* = 14.6, 5.7, 4.9 Hz, 1 H), 2.26–2.21 (m, 1 H), 2.15–2.07 (m, 2 H), 1.75–1.51 (m, 8 H), 1.06 (s, 9 H), 0.99 (s, 9 H), 0.25 (s, 3 H), 0.21 (s, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (150 MHz, C_6D_6) δ 128.6, 128.3, 128.1, 128.0, 127.9, 113.7, 101.1, 98.6, 96.6, 93.8, 79.4, 78.7, 77.0, 75.5, 71.6, 71.5, 70.8, 69.8, 67.8, 55.2, 54.9, 54.7, 39.6, 37.9, 35.5, 34.7, 30.3, 26.6, 26.5, 22.6, 18.6, 18.5, –2.3,

–2.7, –3.7, –3.9; HRMS (ESI–TOF) calcd for $C_{46}H_{78}O_{12}Si_2Na$ $[M + Na]^+$ 901.4930, found 901.4932.

Tetraol 54. A mixture of BOM ether **53** (21.7 mg, 28.5 μmol) and 20% $Pd(OH)_2/C$ (4.2 mg) in MeOH (1.0 mL) was stirred at room temperature for 1 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **54** (14.0 mg, 76%): colorless oil; R_f = 0.58 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{24}$ +31.8 (*c* 0.70, $CHCl_3$); IR (neat) 3435, 2952, 2929, 2899, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, *J* = 2.2 Hz, 1 H), 4.61 (s, 2 H), 4.11 (s, 1 H), 3.98–3.85 (m, 4 H), 3.79 (t, *J* = 9.2 Hz, 1 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 3.41 (t, *J* = 6.8 Hz, 1 H), 3.36 (s, 3 H), 3.34 (s, 3 H), 3.22 (t, *J* = 8.5 Hz, 1 H), 2.84 (brs, 1 H), 2.48 (d, *J* = 14.4 Hz, 1 H), 2.08 (ddd, *J* = 13.2, 5.9, 1.3 Hz, 1 H), 1.89 (d, *J* = 14.4 Hz, 1 H), 1.68–1.43 (m, 10 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.5, 96.4, 76.9, 75.7, 74.9, 74.3, 73.9, 71.8, 70.2, 67.7, 55.2, 55.1, 38.8, 38.7, 38.1, 34.6, 29.6, 26.3, 26.1, 22.1, 18.4, 18.1, –2.6, –3.0, –3.8, –4.2; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3932.

Candidate Compound 4c. To a solution of bis-TBS ether **54** (14.0 mg, 21.8 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 65 μL, 65.0 μmol) at room temperature. The mixture was stirred at the same temperature for 19 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (CH_2Cl_2/MeOH = 7:1) gave candidate compound **4c** (7.0 mg, 78%): colorless oil; R_f = 0.57 (CH_2Cl_2/MeOH = 4:1); $[\alpha]_D^{21}$ +52.3 (*c* 0.36, CH_3OH); IR (neat) 3304, 2931, 2895, 2871, 2834 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.76 (d, *J* = 2.4 Hz, 1 H), 4.59 (s, 2 H), 3.87–3.85 (m, 3 H), 3.77–3.70 (m, 2 H), 3.52 (t, *J* = 6.6 Hz, 2 H), 3.40 (t, *J* = 6.3 Hz, 1 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.07 (t, *J* = 9.3 Hz, 1 H), 2.34 (dt, *J* = 14.4, 2.7 Hz, 1 H), 2.04 (ddd, *J* = 13.2, 5.4, 0.6 Hz, 1 H), 1.84 (ddd, *J* = 14.4, 4.5, 2.7 Hz, 1 H), 1.64–1.52 (m, 7 H), 1.48–1.41 (m, 2 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.9, 97.4, 78.2, 77.5, 73.1, 73.0, 72.4, 71.5, 69.5, 68.8, 55.4, 55.3, 39.8, 38.8, 38.2, 36.2, 30.9, 23.2; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2203.

Tetraol 56. To a solution of triol **53** (33.5 mg, 44.0 μmol) in CH_2Cl_2 (0.5 mL) were added pyridine (21 μL, 0.264 mmol), Ac_2O (19 μL, 0.198 mmol), and DMAP (1.0 mg, 8.19 μmol) at 0 °C. The mixture was stirred at room temperature for 2 h. To the mixture were added pyridine (10 μL, 0.126 mmol) and Ac_2O (9.0 μL, 93.8 μmol) at room temperature. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 4:1) gave the

corresponding triacetate (36.0 mg), which was used for the next step without further purification.
A mixture of the BOM ether obtained above (36.0 mg) and 20% $Pd(OH)_2/C$ (10.3 mg) in EtOH (2.0 mL) was stirred at room temperature for 2 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration gave the corresponding alcohol (31.7 mg), which was used for the next step without further purification.
To a mixture of the alcohol obtained above (31.7 mg), Ph_3P (43.3 mg, 0.165 mmol), and *p*-NO_2PhCO_2H (27.6 mg, 0.165 mmol) in THF (0.5 mL) was added DEAD (2.2 M in toluene, 75 μL, 0.165 mmol) at 0 ºC. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 3:1) gave *p*-nitrobenzoate **55** (27.5 mg), which was used for the next step without further purification.
To a solution of tetraester **55** obtained above (27.5 mg) in MeOH (1.0 mL) was added NaOMe (13.8 mg, 0.255 mmol) at 0 ºC. The mixture was stirred at room temperature for 2 h. The reaction was quenched with DOWEX 50WX4. The mixture was filtered and washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **56** (16.7 mg, 59% in four steps): colorless oil; R_f = 0.55 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{23}$ +37.7 (*c* 0.44, $CHCl_3$); IR (neat) 3435, 2952, 2930, 2897, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 1 H), 4.62 (s, 2 H), 4.03–3.88 (m, 4 H), 3.79 (t, *J* = 9.9 Hz, 1 H), 3.54 (t, *J* = 6.3 Hz, 2 H), 3.48 (t, *J* = 6.5 Hz, 1 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.22 (t, *J* = 8.4 Hz, 1 H), 2.46 (d, *J* = 14.2 Hz, 1 H), 2.08 (dd, *J* = 13.2, 4.2 Hz, 1 H), 1.82 (t, *J* = 5.4 Hz, 2 H), 1.67–1.44 (m, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.11 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.5, 96.4, 76.9, 75.5, 75.2, 74.3, 71.5, 70.2, 69.7, 67.7, 55.2, 55.1, 38.8, 37.2, 34.4, 29.6, 26.3, 26.2, 22.5, 18.4, 18.1, –2.7, –3.0, –3.8, –4.2; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3937.

Candidate Compound 4d. To a solution of bis-TBS ether **56** (14.4 mg, 22.5 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 68 μL, 68.0 μmol) at room temperature. The mixture was stirred at the same temperature for 8 h. To the mixture was added TBAF (1.0 M in THF, 68 μL, 68.0 μmol) at room temperature. The mixture was stirred at the same temperature for 15 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (CH_2Cl_2/MeOH = 7:1) gave candidate compound **4d** (7.5 mg, 81%): colorless oil; R_f = 0.59 (CH_2Cl_2/MeOH = 4:1); $[\alpha]_D^{23}$ +67.9 (*c* 0.38, CH_3OH); IR (neat) 3398, 2928, 2849 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.76 (d, *J* = 3.0 Hz, 1 H), 4.59 (s, 2 H), 3.93 (ddd, *J* = 9.6, 6.3, 2.4 Hz, 1 H), 3.89 (ddd, *J* = 7.8, 6.3, 3.0 Hz, 1 H), 3.86–3.82 (m, 1 H), 3.78–3.71 (m, 2 H), 3.52 (t, *J* = 6.6 Hz, 2 H), 3.41 (t, *J* = 6.3 Hz, 1 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.08 (t, *J* = 9.3 Hz, 1 H), 2.33 (dt, *J* = 14.7, 3.0 Hz, 1 H), 2.05 (ddd, *J* = 13.2, 5.4, 1.2 Hz, 1 H), 1.72 (ddd, *J* = 14.4, 10.2, 2.4 Hz, 1 H), 1.66–1.48 (m, 9 H); ^{13}C NMR (150

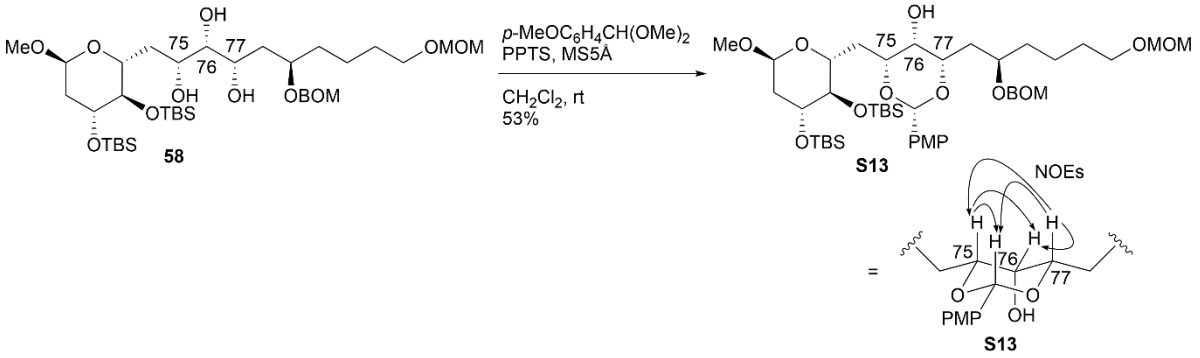
MHz, CD_3OD) δ 99.9, 97.4, 78.5, 77.5, 73.2, 72.4, 70.6, 69.6, 69.1, 68.8, 55.4, 55.3, 40.5, 39.1, 38.8, 36.0, 30.8, 23.5; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2211.

Allylic Alcohol 57. To a solution of propargylic alcohol **46** (45.0 mg, 62.1 μmol) in Et_2O (1.0 mL) was added Red-Al (65% in toluene, 0.19 mL, 0.621 mmol) at 0 ºC. The mixture was stirred at reflux for 3 h. The reaction was quenched with saturated aqueous sodium potassium tartrate at 0 ºC. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave allylic alcohol **57** (33.9 mg, 75%): colorless oil; R_f = 0.60 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +48.7 (*c* 1.13, $CHCl_3$); IR (neat) 3478, 2977, 2952, 2931, 2884, 2859 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5 H), 5.75–5.68 (m, 1 H), 5.58 (dd, *J* = 15.6, 5.6 Hz, 1 H), 4.81 (d, *J* = 7.1 Hz, 1 H), 4.77 (d, *J* = 7.1 Hz, 1 H), 4.68 (brs, 1 H), 4.62 (s, 2 H), 4.60 (s, 2 H), 4.37 (brs, 1 H), 3.93 (ddd, *J* = 10.8, 7.6, 4.4 Hz, 1 H), 3.83 (td, *J* = 10.0, 2.0 Hz, 1 H), 3.71–3.65 (m, 1 H), 3.51 (t, *J* = 6.4 Hz, 2 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.23 (t, *J* = 8.4 Hz, 1 H), 2.52 (d, *J* = 5.4 Hz, 1 H), 2.31 (t, *J* = 6.4 Hz, 2 H), 2.06 (ddd, *J* = 13.1, 4.8, 2.0 Hz, 1 H), 1.99 (ddd, *J* = 14.0, 8.0, 2.0 Hz, 1 H), 1.71–1.38 (m, 7 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.4, 128.3, 127.7, 127.6, 126.6, 98.2, 96.3, 93.4, 76.5, 70.7, 70.0, 69.5, 69.4, 67.7, 55.1, 55.0, 38.9, 38.5, 37.3, 34.0, 29.9, 26.3, 26.2, 22.2, 18.4, 18.2, –2.6, –3.0, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{38}H_{70}O_9Si_2Na$ $[M + Na]^+$ 749.4456, found 749.4460.

Triol 58. To a mixture of allylic alcohol **57** (64.4 mg, 88.6 μmol) and TMEDA (13 μL, 0.107 mmol) in CH_2Cl_2 (6.8 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 2.1 mL, 0.105 mmol) at –78 ºC. The mixture was stirred at the same temperature for 2 h. To the mixture were added TMEDA (13 μL, 0.107 mmol) and OsO_4 (0.05 M in CH_2Cl_2, 2.1 mL, 0.105 mmol) at –78 ºC. The mixture was stirred at the same temperature for 1 h. The mixture was warmed up to room temperature. To the mixture was added ethylenediamine (30 μL, 0.445 mmol) at room temperature. The mixture was stirred at the same temperature for 48 h. The mixture was diluted with EtOAc and washed with brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 2:1) gave triol **58** (32.3 mg, 47%) and its C76,C77-epimer (26.3 mg, 39%). Triol **58**: colorless oil; R_f = 0.37 (hexane/EtOAc = 1:2); $[\alpha]_D^{22}$ +30.4 (*c* 0.98, $CHCl_3$); IR (neat) 3436, 2953, 2930, 2890, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5 H), 4.83 (d, *J* = 7.1 Hz, 1 H), 4.79 (d, *J* = 7.1 Hz, 1 H), 4.68–4.67 (m, 1 H), 4.63 (s, 2 H), 4.60 (s, 2 H), 4.12 (d, *J* = 7.8 Hz, 1 H), 3.99–3.90 (m, 3 H), 3.85 (t, *J* = 8.8 Hz, 1 H), 3.62 (s, 1 H), 3.50 (t, *J* = 6.5 Hz, 2 H), 3.34 (s, 3 H), 3.32 (s, 3 H), 3.23 (t, *J* = 8.3 Hz, 1 H), 2.97 (d, *J* = 7.8 Hz, 1 H), 2.86 (d, *J* = 8.8 Hz, 1 H), 2.13–2.04 (m, 2 H), 2.00 (dt, *J* = 14.4, 8.8 Hz, 1 H), 1.73–1.55 (m, 8

H), 1.47–1.39 (m, 2 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.4, 127.8, 98.1, 96.4, 93.2, 78.0, 75.4, 70.9, 70.8, 70.0, 69.6, 67.5, 55.1, 54.9, 39.0, 37.9, 35.6, 34.2, 29.9, 26.3, 26.2, 21.6, 18.4, 18.1, –2.7, –3.0, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{38}H_{72}O_{11}Si_2Na$ $[M + Na]^+$ 783.4511, found 783.4514.

Stereochemical Determination of 58. Triol **58** was treated with *p*-$MeOC_6H_4CH(OMe)_2$/PPTS/MS5Å to give *p*-methoxybenzylidene acetal **S13** in 53% yield (Scheme S7). The stereochemistries at the C76 and C77 positions were determined by the observed NOEs of H-75/H-76, H75/H-77, and H-76/H-77. The stereochemistry at the acetal carbon of **S13** was elucidated by the NOE correlations as shown in arrows.



Scheme S7. Stereochemical determination of triol **58**.

***p*-Methoxybenzylidene Acetal S13.** To a solution of triol **58** (4.4 mg, 5.78 μmol) in CH_2Cl_2 (0.2 mL) were added MS5Å (6.6 mg), *p*-$MeOC_6H_4CH(OMe)_2$ (3.0 μL, 17.5 μmol), and PPTS (0.5 mg, 1.94 μmol) at room temperature. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with Et_3N. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 8:1, 4:1) gave *p*-methoxybenzylidene acetal **S13** (2.7 mg, 53%): colorless oil; R_f = 0.38 (hexane/EtOAc = 2:1); IR (neat) 3436, 2976, 2928, 2898, 2858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 7 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.84 (s, 1 H), 4.84 (d, J = 6.8 Hz, 1 H), 4.78 (d, J = 6.8 Hz, 1 H), 4.67–4.65 (m, 1 H), 4.64 (s, 2 H), 4.59 (s, 2 H), 4.35–4.30 (m, 1 H), 3.98–3.87 (m, 3 H), 3.81 (s, 3 H), 3.78–3.75 (m, 2 H), 3.51 (t, J = 6.4 Hz, 2 H), 3.34 (s, 3 H), 3.30 (s, 3 H), 3.22 (t, J = 8.4 Hz, 1 H), 2.90 (d, J = 4.8 Hz, 1 H), 2.15–2.01 (m, 3 H), 1.82–1.47 (m, 9 H), 0.90 (s, 9 H), 0.83 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.9, 129.7, 128.4, 128.0, 127.8, 127.6, 113.6, 102.4, 98.2, 96.4, 93.8, 77.1, 76.9, 76.5, 76.0, 75.6, 70.6, 69.9, 69.8, 69.6, 67.6, 55.3, 55.0, 38.9, 34.5, 34.2, 30.3, 29.7, 26.3, 26.1, 22.1, 18.3, 18.0, –2.8, –3.1, –3.9, –4.3; HRMS (ESI–TOF) calcd for $C_{46}H_{78}O_{12}Si_2Na$ $[M + Na]^+$ 901.4930, found 901.4927.

Tetraol 59. A mixture of BOM ether **58** (2.7 mg, 3.55 μmol) and 20% $Pd(OH)_2/C$ (1.0 mg) in MeOH (0.5 mL) was stirred at room temperature for 30 min under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **59** (2.2 mg, 97%): colorless oil; R_f = 0.57 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{23}$ +47.9 (*c* 0.48, $CHCl_3$); IR (neat) 3418, 2952, 2930, 2897, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.69–4.68 (m, 1 H), 4.62 (s, 2 H), 4.17 (d, *J* = 9.5 Hz, 1 H), 3.99–3.93 (m, 4 H), 3.85 (td, *J* = 10.0, 2.0 Hz, 1 H), 3.54 (t, *J* = 6.4 Hz, 2 H), 3.36 (s, 3 H), 3.32 (s, 3 H), 3.25 (t, *J* = 8.2 Hz, 1 H), 3.10 (d, *J* = 5.6 Hz, 1 H), 2.97 (brs, 1 H), 2.13–2.04 (m, 3 H), 1.84 (dt, *J* = 14.4, 10.0 Hz, 1 H), 1.68–1.44 (m, 9 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.12 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.1, 96.4, 76.5, 75.3, 72.3, 72.1, 71.1, 70.8, 69.8, 67.7, 55.2, 54.9, 39.7, 38.8, 38.0, 35.2, 29.6, 26.3, 26.2, 22.1, 18.4, 18.2, –2.7, –3.0, –3.9, –4.1; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3934.

Candidate Compound 4e. To a solution of bis-TBS ether **59** (17.4 mg, 27.1 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 81 μL, 81.0 μmol) at room temperature. The mixture was stirred at the same temperature for 6 h. To the mixture was added TBAF (1.0 M in THF, 81 μL, 81.0 μmol) at room temperature. The mixture was stirred at the same temperature for 14 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4e** (6.4 mg, 57%): colorless oil; R_f = 0.52 (CH_2Cl_2/MeOH = 3:1); $[\alpha]_D^{22}$ +65.4 (*c* 0.32, CH_3OH); IR (neat) 3338, 2934 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.72 (d, *J* = 3.0 Hz, 1 H), 4.59 (s, 2 H), 4.07–4.05 (m, 1 H), 3.91–3.88 (m, 1 H), 3.80–3.73 (m, 3 H), 3.52 (t, *J* = 6.3 Hz, 2 H), 3.33 (s, 3 H), 3.33 (s, 3 H), 3.22–3.21 (m, 1 H), 3.02 (t, *J* = 9.3 Hz, 1 H), 2.05 (ddd, *J* = 12.9, 5.4, 0.9 Hz, 1 H), 1.94 (ddd, *J* = 14.3, 10.2, 2.4 Hz, 1 H), 1.81 (ddd, *J* = 14.3, 9.8, 2.0 Hz, 1 H), 1.75–1.40 (m, 9 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.6, 97.4, 77.5, 77.5, 71.0, 70.4, 69.9, 69.5, 69.3, 68.8, 55.4, 55.1, 41.5, 39.0, 38.4, 37.0, 30.8, 23.2; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2203.

Tetraol 61. To a solution of triol **58** (37.5 mg, 49.3 μmol) in CH_2Cl_2 (0.5 mL) were added pyridine (24 μL, 0.296 mmol), Ac_2O (21 μL, 0.222 mmol), and DMAP (1.0 mg, 8.19 μmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 4:1) gave the corresponding triacetate (42.7 mg), which was used for the next step without further purification.

A mixture of the BOM ether obtained above (42.7 mg) and 20% $Pd(OH)_2/C$ (4.3 mg) in EtOH

(1.0 mL) was stirred at room temperature for 30 min under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration gave the corresponding alcohol (30.3 mg), which was used for the next step without further purification.

To a mixture of the alcohol obtained above (30.3 mg), Ph_3P (41.4 mg, 0.158 mmol), and *p*-NO_2PhCO_2H (26.4 mg, 0.158 mmol) in THF (0.5 mL) was added DEAD (2.2 M in toluene, 72 μL, 0.158 mmol) at 0 ºC. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 3:1) gave *p*-nitrobenzoate **60** (31.1 mg), which was used for the next step without further purification.

To a solution of tetraester **60** obtained above (31.1 mg) in MeOH (1.0 mL) was added NaOMe (2.7 mg, 50.9 μmol) at 0 ºC. The mixture was stirred at room temperature for 2 h. The reaction was quenched with DOWEX 50WX4. The mixture was filtered and washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **61** (18.7 mg, 59% in four steps): colorless oil; R_f = 0.51 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{22}$ +41.1 (*c* 0.94, $CHCl_3$); IR (neat) 3434, 2978, 2952, 2930, 2897, 2883, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.68 (s, 1 H), 4.61 (s, 2 H), 4.23 (d, *J* = 9.3 Hz, 1 H), 4.02–3.92 (m, 4 H), 3.84 (t, *J* = 9.2 Hz, 1 H), 3.53 (t, *J* = 6.4 Hz, 2 H), 3.35 (s, 3 H), 3.31 (s, 3 H), 3.25 (t, *J* = 8.3 Hz, 1 H), 2.13–2.04 (m, 2 H), 2.00–1.93 (m, 1 H), 1.67–1.40 (m, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.2, 96.4, 76.5, 75.4, 71.1, 70.7, 69.8, 69.4, 68.7, 67.7, 55.2, 54.9, 39.5, 38.8, 37.1, 35.0, 29.7, 26.3, 26.2, 22.6, 18.4, 18.2, –2.7, –3.0, –3.9, –4.1; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3938.

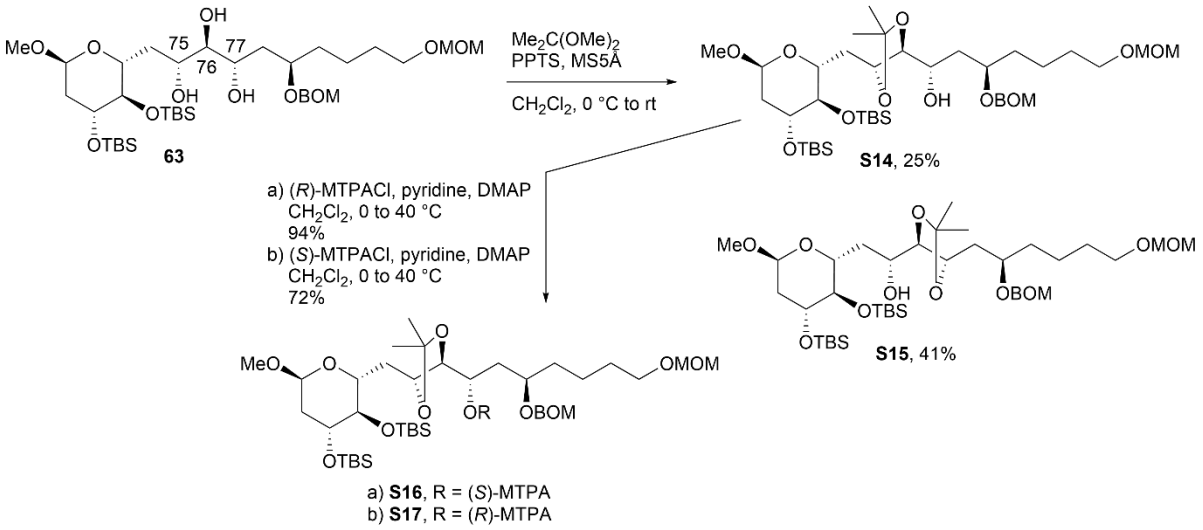
Candidate Compound 4f. To a solution of bis-TBS ether **61** (10.4 mg, 16.2 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 49 μL, 49.0 μmol) at room temperature. The mixture was stirred at the same temperature for 15 h. To the mixture was added TBAF (1.0 M in THF, 60 μL, 60.0 μmol) at room temperature. The mixture was stirred at the same temperature for 8 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4f** (4.4 mg, 66%): white solid; R_f = 0.29 (CH_2Cl_2/MeOH = 5:1); $[\alpha]_D^{18}$ +63.7 (*c* 0.22, CH_3OH); IR (neat) 3366, 2963, 2925, 2854 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.72 (d, *J* = 3.2 Hz, 1 H), 4.59 (s, 2 H), 4.11 (dt, *J* = 10.1, 2.8 Hz, 1 H), 3.90 (ddd, *J* = 10.1, 7.1, 2.2 Hz, 1 H), 3.84–3.73 (m, 3 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 3.33 (s, 3 H), 3.33 (s, 3 H), 3.20–3.18 (m, 1 H), 3.02 (t, *J* = 9.2 Hz, 1 H), 2.05 (ddd, *J* = 13.1, 5.3, 1.2 Hz, 1 H), 1.96 (ddd, *J* = 13.7, 10.1, 2.2 Hz, 1 H), 1.81 (ddd, *J* = 13.7, 10.1, 2.2 Hz, 1 H), 1.75 (ddd, *J* = 14.2, 10.1, 2.8 Hz, 1 H), 1.63–1.41 (m, 8 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.6, 97.4, 78.6, 77.5, 69.9, 69.6, 69.5, 69.2, 68.8, 68.6, 55.4, 55.1, 42.3, 39.0, 39.0, 36.8, 30.8, 23.5; HRMS (ESI–TOF) calcd for

$C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2204.

Triol 63. A mixture of alkyne **46** (102 mg, 0.141 mmol) and Lindlar cat (palladium 5% on calcium carbonate poisoned with lead, 102 mg) in EtOAc (1.4 mL) was stirred at room temperature for 2 h under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration gave allylic alcohol **62** (75.0 mg), which was used for the next step without further purification.

To a solution of allylic alcohol **62** obtained above (75.0 mg) in pyridine (1.0 mL) was added OsO_4 (0.05 M in CH_2Cl_2, 2.7 mL, 0.135 mmol) at room temperature. The mixture was stirred at the same temperature for 20 min. To the mixture were added $NaHSO_3$ (666 mg), H_2O (3.6 mL), and pyridine (3.2 mL) at room temperature. The mixture was stirred at the same temperature for 4 h. The mixture was diluted with EtOAc and washed with H_2O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 1:1) gave triol **63** (36.5 mg, 34% in two steps) and its C76,C77-epimer (27.5 mg, 26% in two steps). Triol **63**: colorless oil; R_f = 0.44 (hexane/EtOAc = 1:2); $[\alpha]_D^{21}$ +22.7 (*c* 1.83, $CHCl_3$); IR (neat) 3456, 2972, 2955, 2930, 2899, 2884, 2860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5 H), 4.85 (d, *J* = 6.8 Hz, 1 H), 4.79 (d, *J* = 6.8 Hz, 1 H), 4.69–4.68 (m, 1 H), 4.64 (s, 1 H), 4.62 (s, 1 H), 4.60 (s, 2 H), 4.17 (d, *J* = 9.0 Hz, 1 H), 3.99–3.91 (m, 3 H), 3.80 (td, *J* = 9.6, 2.0 Hz, 1 H), 3.69 (s, 1 H), 3.50 (t, *J* = 6.4 Hz, 2 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.25 (t, *J* = 9.2 Hz, 1 H), 2.98 (d, *J* = 2.9 Hz, 1 H), 2.74 (d, *J* = 8.0 Hz, 1 H), 2.24 (ddd, *J* = 14.0, 10.0, 2.0 Hz, 1 H), 2.07 (ddd, *J* = 13.2, 4.8, 2.0 Hz, 1 H), 1.89 (ddd, *J* = 14.8, 3.6, 2.0 Hz, 1 H), 1.74 (dt, *J* = 14.8, 9.2 Hz, 1 H), 1.69–1.55 (m, 6 H), 1.53–1.38 (m, 3 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.4, 127.8, 127.7, 98.0, 96.4, 93.1, 78.2, 76.5, 75.9, 73.8, 70.8, 70.1, 69.7, 67.5, 55.1, 54.8, 39.0, 37.8, 35.7, 34.2, 29.9, 26.3, 26.2, 21.6, 18.4, 18.2, –2.7, –3.0, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{38}H_{72}O_{11}Si_2Na$ $[M + Na]^+$ 783.4511, found 783.4510.

Stereochemical Determination of 63. Triol **63** was treated with $Me_2C(OMe)_2$/PPTS/MS5Å to give acetonide **S14** in 25% yield along with acetonide **S15** in 41% yield. (Scheme S8). The obtained alcohol **S14** was transformed to (*S*)-MTPA ester **S16** and (*R*)-MTPA ester **S17**, and the stereochemistry at the C77 position of **S14** was determined the modified Mosher method[1] (Figure S4). The absolute configuration at the C76 position of **63** was elucidated based on the *syn*-addition reaction mechanism of OsO_4-catalyzed dihydroxylation.



Scheme S8. Transformation of triol **63** for its stereochemical determination.

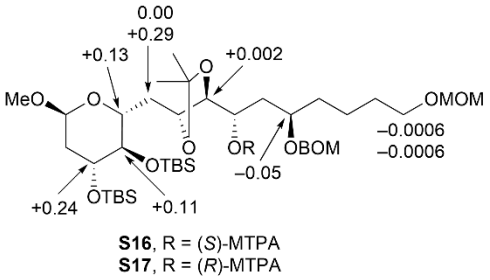


Figure S4. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S16** and **S17**.

Acetonide S14. To a solution of triol **63** (8.5 mg, 11.2 μmol) in CH_2Cl_2 (0.2 mL) were added MS5Å (19.2 mg), $Me_2C(OMe)_2$ (14 μL, 0.112 mmol), and PPTS (1.1 mg, 4.48 μmol) at 0 °C. The mixture was stirred at room temperature for 11 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 4:1) gave acetonide **S14** (2.2 mg, 25%) and acetonide **S15** (3.7 mg, 41%). Acetonide **S14**: colorless oil; R_f = 0.51 (hexane/EtOAc = 2:1); $[\alpha]_D^{22}$ +54.0 (*c* 0.11, $CHCl_3$); IR (neat) 3478, 2952, 2928, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 5 H), 4.79 (d, *J* = 7.1 Hz, 1 H), 4.76 (d, *J* = 7.1 Hz, 1 H), 4.65–4.64 (m, 1 H), 4.63 (s, 1 H), 4.62 (s, 1 H), 4.60 (s, 2 H), 4.28–4.24 (m, 1 H), 3.98–3.92 (m, 1 H), 3.90–3.77 (m, 4 H), 3.51 (t, *J* = 6.5 Hz, 2 H), 3.34 (s, 3 H), 3.30 (s, 3 H), 3.17 (t, *J* = 8.6 Hz, 1 H), 2.12–2.04 (m, 3 H), 1.93 (d, *J* = 6.6 Hz, 1 H), 1.85–1.79 (m, 1 H), 1.65–1.49 (m, 8 H), 1.45 (s, 3 H), 1.34 (s, 3 H), 0.91 (s, 9 H), 0.91 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.3, 127.7, 127.6, 107.8, 97.9, 96.4, 93.4, 80.7, 75.3, 74.1, 70.9, 69.6, 68.5, 67.7, 66.1, 55.1, 54.5, 39.2, 37.4, 34.2, 33.9, 29.9, 27.5, 26.4, 26.2, 25.2, 22.0, 18.4, 18.2, –2.6, –3.0, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{41}H_{76}O_{11}Si_2Na$ $[M + Na]^+$ 823.4824, found 823.4824.

(*S*)-MTPA Ester S16. To a solution of alcohol **S14** (2.1 mg, 2.62 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (2.0 mg, 16.4 μmol), pyridine (1.4 μL, 17.3 μmol), and (*R*)-MTPACl (2.0 μL, 10.7 μmol) at 0 °C. The mixture was stirred at 40 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 7:1) gave (*S*)-MTPA ester **S16** (2.5 mg, 94%): colorless oil; R_f = 0.60 (hexane/EtOAc = 2:1); $[\alpha]_D^{24}$ +38.1 (*c* 0.13, $CHCl_3$); IR (neat) 2953, 2927, 2858, 1753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2 H), 7.38–7.28 (m, 8 H), 5.55 (t, *J* = 8.8 Hz, 1 H), 4.78 (d, *J* = 6.8 Hz, 1 H), 4.74 (d, *J* = 6.8 Hz, 1 H), 4.62 (s, 2 H), 4.62–4.60 (m, 1 H), 4.60 (s, 2 H), 4.14–4.09 (m, 1 H), 4.06 (dd, *J* = 8.3, 5.6 Hz, 1 H), 3.90–3.84 (m, 2 H), 3.58 (s, 3 H), 3.52 (t, *J* = 6.4 Hz, 2 H), 3.50–3.46 (m, 1 H), 3.35 (s, 3 H), 3.19 (s, 3 H), 3.11 (t, *J* = 8.3 Hz, 1 H), 2.28–2.22 (m, 1 H), 2.04–2.00 (m, 1 H), 1.99–1.90 (m, 1 H), 1.61–1.38 (m, 9 H), 1.42 (s, 3 H), 1.22 (s, 3 H), 0.91 (s, 9 H), 0.87 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 137.7, 132.2, 129.3, 128.4, 128.0, 127.8, 127.7, 127.6, 108.7, 98.2, 96.4, 93.4, 79.0, 74.9, 73.9, 71.4, 70.6, 69.6, 68.5, 67.7, 55.5, 55.2, 55.1, 39.2, 34.3, 34.0, 33.6, 30.0, 29.8, 28.0, 26.4, 26.1, 25.9, 22.1, 18.4, 18.0, –2.7, –2.9, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{51}H_{83}F_3O_{13}Si_2Na$ $[M + Na]^+$ 1039.5222, found 1039.5219.

(*R*)-MTPA Ester S17. To a solution of alcohol **S14** (2.2 mg, 2.75 μmol) in CH_2Cl_2 (0.2 mL) were added DMAP (2.0 mg, 16.4 μmol), pyridine (1.4 μL, 17.3 μmol), and (*S*)-MTPACl (2.0 μL, 10.7 μmol) at 0 °C. The mixture was stirred at 40 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and column chromatography (hexane/EtOAc = 7:1) gave (*R*)-MTPA ester **S17** (2.0 mg, 72%): colorless oil; R_f = 0.46 (hexane/EtOAc = 3:1); $[\alpha]_D^{21}$ +65.0 (*c* 0.10, $CHCl_3$); IR (neat) 2953, 2927, 2854, 1754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.63 (m, 2 H), 7.37–7.27 (m, 8 H), 5.58 (t, *J* = 9.4 Hz, 1 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.75 (d, *J* = 6.8 Hz, 1 H), 4.63 (s, 2 H), 4.61–4.60 (m, 1 H), 4.60 (s, 2 H), 4.19–4.14 (m, 1 H), 4.06 (dd, *J* = 8.8, 5.6 Hz, 1 H), 3.91–3.85 (m, 1 H), 3.78–3.72 (m, 1 H), 3.62 (s, 3 H), 3.52 (t, *J* = 6.5 Hz, 2 H), 3.36 (s, 3 H), 3.35 (s, 3 H), 3.24 (t, *J* = 9.6 Hz, 1 H), 3.00 (t, *J* = 8.4 Hz, 1 H), 2.12–1.98 (m, 3 H), 1.74–1.52 (m, 9 H), 1.43 (s, 3 H), 1.31 (s, 3 H), 0.91 (s, 9 H), 0.76 (s, 9 H), 0.10 (s, 3 H), 0.07 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 137.7, 132.7, 129.3, 128.4, 128.1, 127.9, 127.6, 127.4, 108.8, 98.4, 96.4, 93.4, 79.1, 74.9, 74.1, 70.7, 70.5, 69.6, 68.5, 67.7, 55.7, 55.1, 39.2, 34.6, 34.0, 33.6, 29.9, 29.8, 28.1, 26.4, 26.0, 22.0, 18.4, 18.0, 14.2, –2.7, –3.0, –3.9, –4.2; HRMS (ESI–TOF) calcd for $C_{51}H_{83}F_3O_{13}Si_2Na$ $[M + Na]^+$ 1039.5222, found 1039.5217.

Tetraol 64. A mixture of BOM ether **63** (7.1 mg, 9.33 μmol) and 20% $Pd(OH)_2/C$ (1.0 mg) in

MeOH (1.0 mL) was stirred at room temperature for 40 min under H_2 atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **64** (5.7 mg, 95%): colorless oil; R_f = 0.54 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{22}$ +36.5 (*c* 0.29, $CHCl_3$); IR (neat) 3417, 2952, 2929, 2897, 2857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 1 H), 4.62 (s, 2 H), 4.16 (d, *J* = 9.0 Hz, 1 H), 4.00–3.90 (m, 4 H), 3.80 (td, *J* = 9.6, 2.0 Hz, 1 H), 3.54 (t, *J* = 6.4 Hz, 2 H), 3.36 (s, 3 H), 3.33 (s, 3 H), 3.27 (t, *J* = 8.4 Hz, 1 H), 3.08 (brs, 1 H), 2.26–2.20 (m, 1 H), 2.08 (dd, *J* = 13.0, 4.5 Hz, 1 H), 1.77 (d, *J* = 14.6 Hz, 1 H), 1.68–1.43 (m, 10 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.1, 96.4, 76.3, 75.7, 75.3, 72.9, 70.8, 69.9, 67.9, 67.7, 55.2, 54.9, 39.3, 38.9, 38.0, 35.3, 29.6, 26.4, 26.2, 22.1, 18.4, 18.2, –2.6, –3.0, –3.8, –4.1; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3939.

Candidate Compound 4g. To a solution of bis-TBS ether **64** (18.1 mg, 28.2 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 0.14 mL, 0.140 mmol) at room temperature. The mixture was stirred at the same temperature for 7 h. To the mixture was added TBAF (1.0 M in THF, 0.14 mL, 0.140 mmol) at room temperature. The mixture was stirred at the same temperature for 17 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4g** (8.1 mg, 70%): colorless oil; R_f = 0.50 (CH_2Cl_2/MeOH = 3:1); $[\alpha]_D^{22}$ +75.5 (*c* 0.41, CH_3OH); IR (neat) 3366, 2934 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.72 (d, *J* = 3.0 Hz, 1 H), 4.59 (s, 2 H), 4.10 (dt, *J* = 10.2, 2.4 Hz, 1 H), 3.86–3.83 (m, 1 H), 3.82–3.78 (m, 1 H), 3.78–3.75 (m, 1 H), 3.73 (td, *J* = 9.3, 2.4 Hz, 1 H), 3.53 (t, *J* = 6.6 Hz, 2 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.18 (dd, *J* = 7.8, 2.4 Hz, 1 H), 3.00 (t, *J* = 9.3 Hz, 1 H), 2.22 (ddd, *J* = 14.4, 10.2, 2.4 Hz, 1 H), 2.06–2.03 (m, 1 H), 1.92 (ddd, *J* = 13.8, 4.2, 2.4 Hz, 1 H), 1.65–1.41 (m, 9 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.6, 97.4, 78.4, 77.5, 72.3, 71.8, 69.9, 69.6, 68.8, 67.8, 55.4, 55.1, 41.3, 39.0, 38.2, 37.5, 30.9, 23.2; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$ 435.2206, found 435.2206.

Tetraol 66. To a solution of triol **63** (12.5 mg, 16.4 μmol) in CH_2Cl_2 (0.2 mL) were added pyridine (7.9 μL, 98.4 μmol), Ac_2O (7.0 μL, 73.8 μmol), and DMAP (1.0 mg, 8.19 μmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 4:1) gave the corresponding triacetate (13.6 mg), which was used for the next step without further purification.

A mixture of the BOM ether obtained above (13.6 mg) and 20% $Pd(OH)_2$/C (1.4 mg) in EtOH (1.0 mL) was stirred at room temperature for 30 min under H_2 atmosphere. The catalyst was

filtered off and the mixture was washed with EtOAc. Concentration gave the corresponding alcohol (12.6 mg), which was used for the next step without further purification.
To a mixture of the alcohol obtained above (12.6 mg), Ph_3P (17.2 mg, 65.6 μmol), and *p*-NO_2PhCO_2H (11.0 mg, 65.6 μmol) in THF (0.2 mL) was added DEAD (2.2 M in toluene, 30 μL, 66.0 μmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with EtOAc, washed with H_2O and brine, and then dried over Na_2SO_4. Concentration and short column chromatography (hexane/EtOAc = 3:1) gave *p*-nitrobenzoate **65** (12.4 mg), which was used for the next step without further purification.
To a solution of tetraester **65** obtained above (12.4 mg) in MeOH (1.0 mL) was added NaOMe (1.1 mg, 20.4 μmol) at 0 ºC. The mixture was stirred at room temperature for 2 h. The reaction was quenched with DOWEX 50WX4. The mixture was filtered and washed with EtOAc. Concentration and column chromatography (CH_2Cl_2/MeOH = 30:1) gave tetraol **68** (6.7 mg, 64% in four steps): colorless oil; R_f = 0.46 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{23}$ +42.8 (*c* 0.34, $CHCl_3$); IR (neat) 3412, 2952, 2930, 2896, 2860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.70–4.69 (m, 1 H), 4.62 (s, 2 H), 4.18 (d, *J* = 9.8 Hz, 1 H), 4.03–3.94 (m, 3 H), 3.80 (td, *J* = 9.2, 2.8 Hz, 1 H), 3.54 (t, *J* = 6.3 Hz, 2 H), 3.36 (s, 3 H), 3.36–3.33 (m, 1 H), 3.33 (s, 3 H), 3.29 (t, *J* = 8.0 Hz, 1 H), 3.02 (brs, 1 H), 2.22 (ddd, *J* = 14.4, 10.0, 2.8 Hz, 1 H), 2.08 (ddd, *J* = 13.2, 4.4, 2.0 Hz, 1 H), 1.82 (ddd, *J* = 14.4, 8.4, 2.4 Hz, 1 H), 1.71–1.44 (m, 9 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.1, 96.4, 76.2, 75.6, 71.3, 70.8, 70.0, 69.5, 68.0, 67.7, 55.2, 54.9, 39.3, 38.8, 37.2, 35.3, 29.6, 26.4, 26.2, 22.5, 18.4, 18.2, –2.7, –3.0, –3.8, –4.0; HRMS (ESI–TOF) calcd for $C_{30}H_{64}O_{10}Si_2Na$ $[M + Na]^+$ 663.3936, found 663.3934.

Candidate Compound 4h. To a solution of bis-TBS ether **66** (21.3 mg, 33.2 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 0.17 mL, 0.170 mmol) at room temperature. The mixture was stirred at the same temperature for 15 h. To the mixture was added TBAF (1.0 M in THF, 0.17 mL, 0.170 mmol) at room temperature. The mixture was stirred at the same temperature for 1 h. The mixture was filtered through short column chromatography (CH_2Cl_2/MeOH = 7:1). Concentration and column chromatography (EtOAc, EtOAc/MeOH = 5:1) gave candidate compound **4h** (9.7 mg, 71%): colorless oil; R_f = 0.48 (CH_2Cl_2/MeOH = 3:1); $[\alpha]_D^{23}$ +117 (*c* 0.34, CH_3OH); IR (neat) 3399, 2938 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 4.72 (d, *J* = 3.0 Hz, 1 H), 4.59 (s, 2 H), 4.11 (dt, *J* = 10.8, 2.4 Hz, 1 H), 3.90–3.87 (m, 1 H), 3.86–3.83 (m, 1 H), 3.79–3.76 (m, 1 H), 3.75–3.71 (m, 1 H), 3.53 (t, *J* = 6.6 Hz, 2 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.19 (dd, *J* = 7.8, 2.4 Hz, 1 H), 3.00 (t, *J* = 9.3 Hz, 1 H), 2.21 (ddd, *J* = 13.2, 10.8, 2.4 Hz, 1 H), 2.04 (dd, *J* = 12.6, 5.4 Hz, 1 H), 1.77 (ddd, *J* = 14.4, 10.2, 2.4 Hz, 1 H), 1.66–1.39 (m, 9 H); ^{13}C NMR (150 MHz, CD_3OD) δ 99.6, 97.4, 78.5, 77.5, 69.9, 69.6, 69.2, 68.8, 68.1, 55.4, 55.1, 41.8, 39.1, 39.0, 37.5, 30.8, 23.5; HRMS (ESI–TOF) calcd for $C_{18}H_{36}O_{10}Na$ $[M + Na]^+$

435.2206, found 435.2205.

Table S3. ^{1}H NMR chemical shifts of natural symbiodinolide (**1**) and the synthetic products **4a–4h**.[a]

Position	**1**[b]	**4a**[c]	**4b**[c]	**4c**[c]	**4d**[c]	**4e**[c]	**4f**[c]	**4g**[c]	**4h**[c]
75	3.89	3.98	3.98	3.86	3.89	3.89	3.90	4.10	4.11
76	3.18	3.36	3.31	3.40	3.41	3.22	3.19	3.18	3.19
77	3.95	3.93	3.97	3.86	3.93	4.06	4.11	3.80	3.88
79	3.84	3.80	3.82	3.85	3.84	3.78	3.81	3.85	3.84

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 3.30 ppm). [b] Data reported in reference 2. Recorded at 800 MHz. [c] Recorded at 600 MHz.

Table S4. ^{1}H NMR chemical shifts of natural symbiodinolide (**1**) and the synthetic products **4a–4h**.[a]

Position	**1**[b]	**4a**[c]	**4b**[c]	**4c**[c]	**4d**[c]	**4e**[c]	**4f**[c]	**4g**[c]	**4h**[c]
70a	1.64	1.62	1.61	1.62	1.63	1.59	1.59	1.59	1.62
70b	1.72	2.03	2.04	2.04	2.05	2.05	2.05	2.04	2.04
71	3.80	3.74	3.74	3.75	3.75	3.75	3.77	3.77	3.78
72	3.04	3.06	3.06	3.07	3.08	3.02	3.02	3.00	3.00
73	3.69	3.62	3.61	3.72	3.72	3.80	3.75	3.73	3.74

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 3.30 ppm). [b] Data reported in reference 2. Recorded at 800 MHz. [c] Recorded at 600 MHz.

Table S5. Deviations in the ^{1}H NMR chemical shifts of the synthetic products **4a–4h** ($\Delta\delta = \delta_{\mathbf{1}} - \delta_{\mathbf{4}}$) relative to those of natural symbiodinolide (**1**).

Position	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**
75	–0.09	–0.09	+0.03	0	0	–0.01	–0.21	–0.22
76	–0.18	–0.13	–0.22	–0.23	–0.04	–0.01	0	–0.01
77	+0.02	–0.02	+0.09	+0.02	–0.11	–0.16	+0.15	+0.07
79	+0.04	+0.02	–0.01	0	+0.06	+0.03	–0.01	0

Table S6. ^{13}C NMR chemical shifts of natural symbiodinolide (**1**) and the synthetic products **4a–4h**.[a]

Position	**1**[b]	**4a**[c]	**4b**[c]	**4c**[c]	**4d**[c]	**4e**[c]	**4f**[c]	**4g**[c]	**4h**[c]
75	69.6	71.9	71.7	73.1	73.2	69.3	69.6	67.8	68.1
76	78.5	75.9	76.8	78.2	78.5	77.5	78.6	78.4	78.5
77	70.5	72.9	70.8	73.0	70.6	70.4	68.6	72.3	69.9
79	70.3	71.0	69.0	71.5	69.1	71.0	69.2	71.8	69.2

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 49.0 ppm). [b] Data reported in reference 2. Recorded at 150 MHz. [c] Recorded at 150 MHz.

Table S7. ^{13}C NMR chemical shifts of natural symbiodinolide (**1**) and the synthetic products **4a–4h**.[a]

Position	**1**[b]	**4a**[c]	**4b**[c]	**4c**[c]	**4d**[c]	**4e**[c]	**4f**[c]	**4g**[c]	**4h**[c]
70	42.0	38.9	38.9	38.8	38.8	39.0	39.0	39.0	39.1
71	70.0	69.6	69.6	69.5	69.6	69.5	69.9	69.9	69.6
72	77.0	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
73	71.4	71.1	71.1	72.4	72.4	69.9	69.5	69.6	69.6

[a] Chemical shifts are reported in ppm with reference to the internal residual solvent (CD_3OD: 49.0 ppm). [b] Data reported in reference 2. Recorded at 150 MHz. [c] Recorded at 150 MHz.

Table S8. Deviations in the ^{13}C NMR chemical shifts of the synthetic products **4a–4h** ($\Delta\delta = \delta_1 - \delta_4$) relative to those of natural symbiodinolide (**1**).

Position	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**
75	–2.3	–2.1	–3.5	–3.6	+0.3	0	+1.8	+1.5
76	+2.6	+1.7	+0.3	0	+1.0	–0.1	+0.1	0
77	–2.4	–0.3	–2.5	–0.1	+0.1	+1.9	–1.8	+0.6
79	–0.7	+1.3	–1.2	+1.2	–0.7	+1.1	–1.5	+1.1

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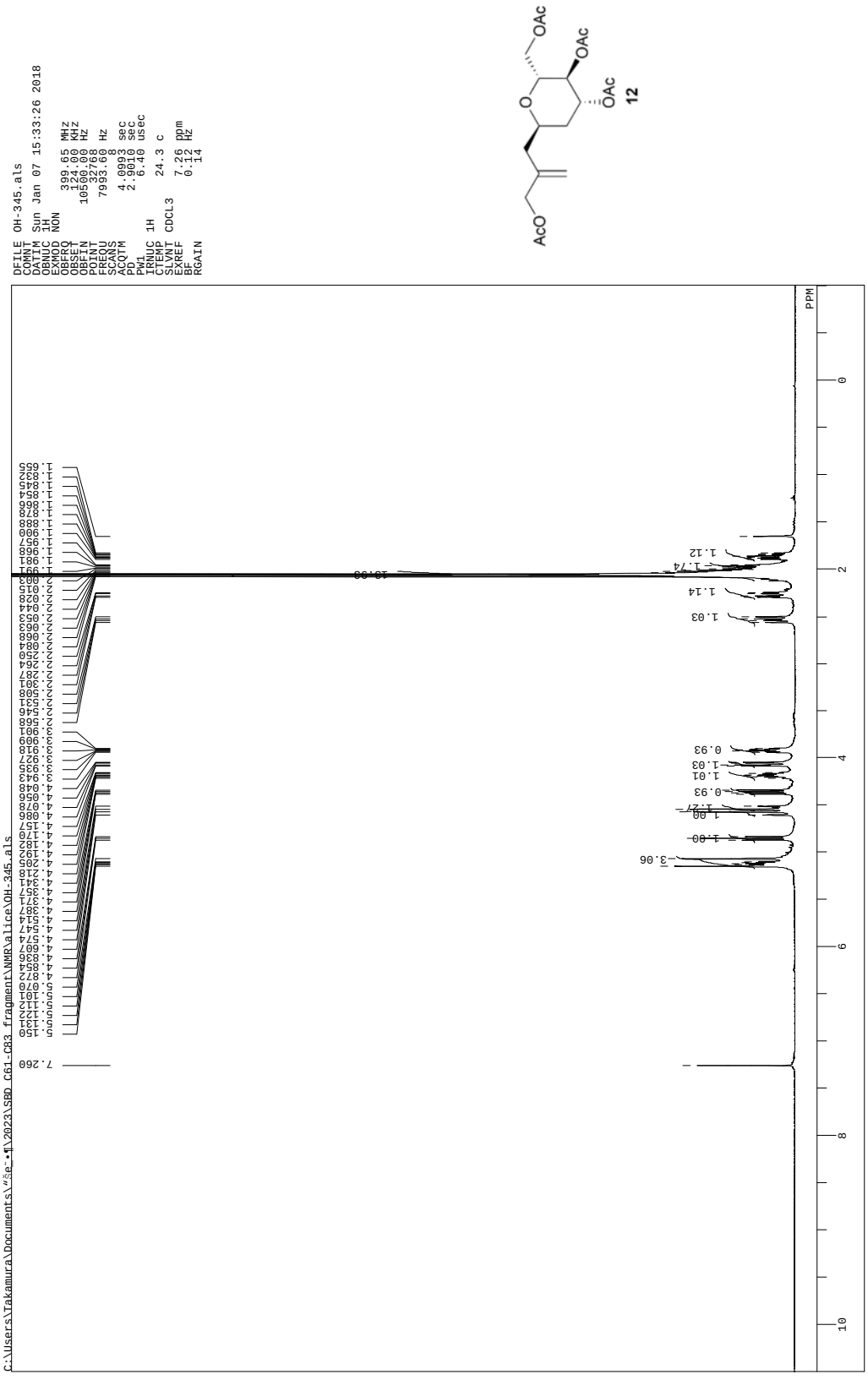
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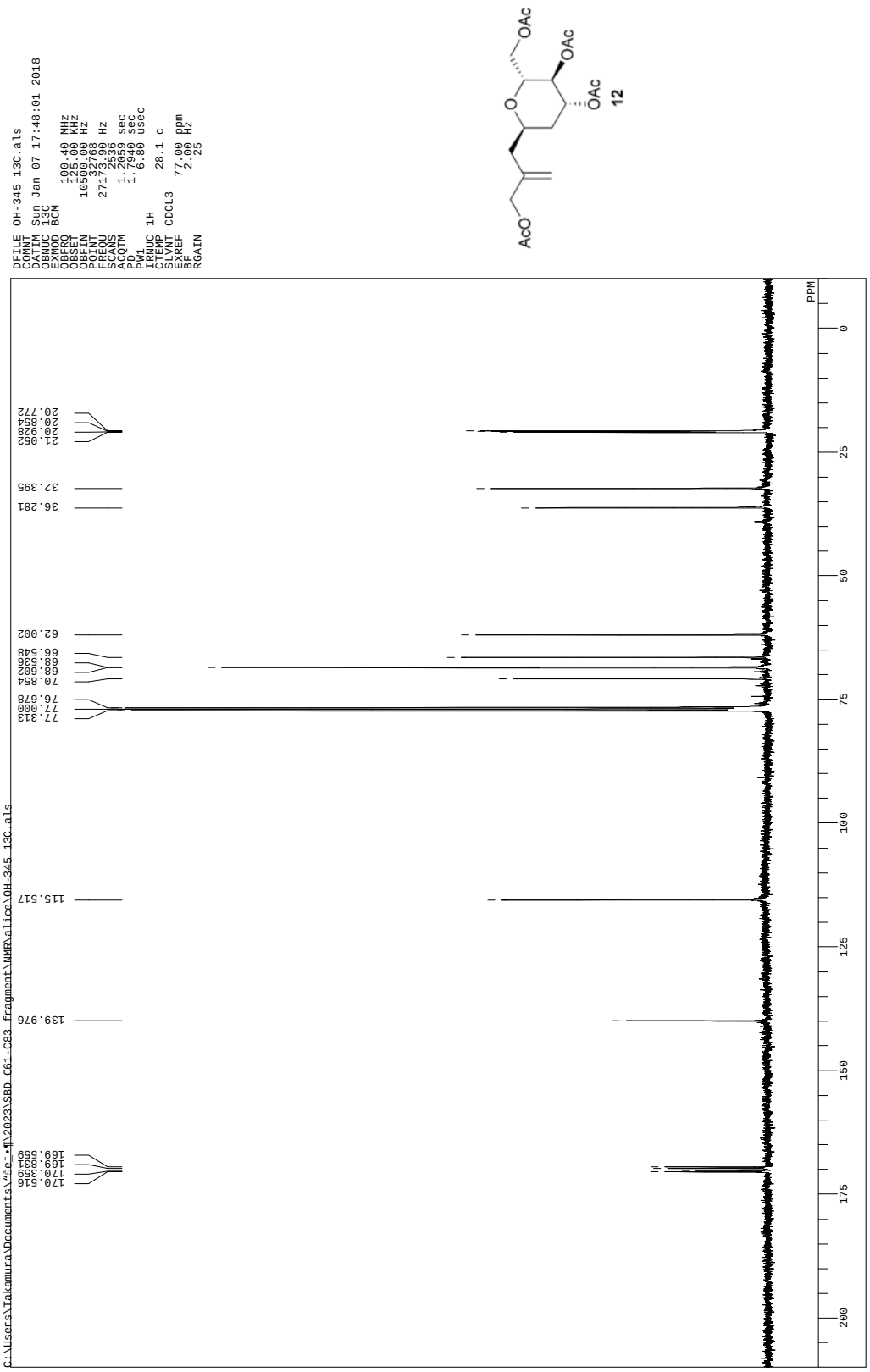
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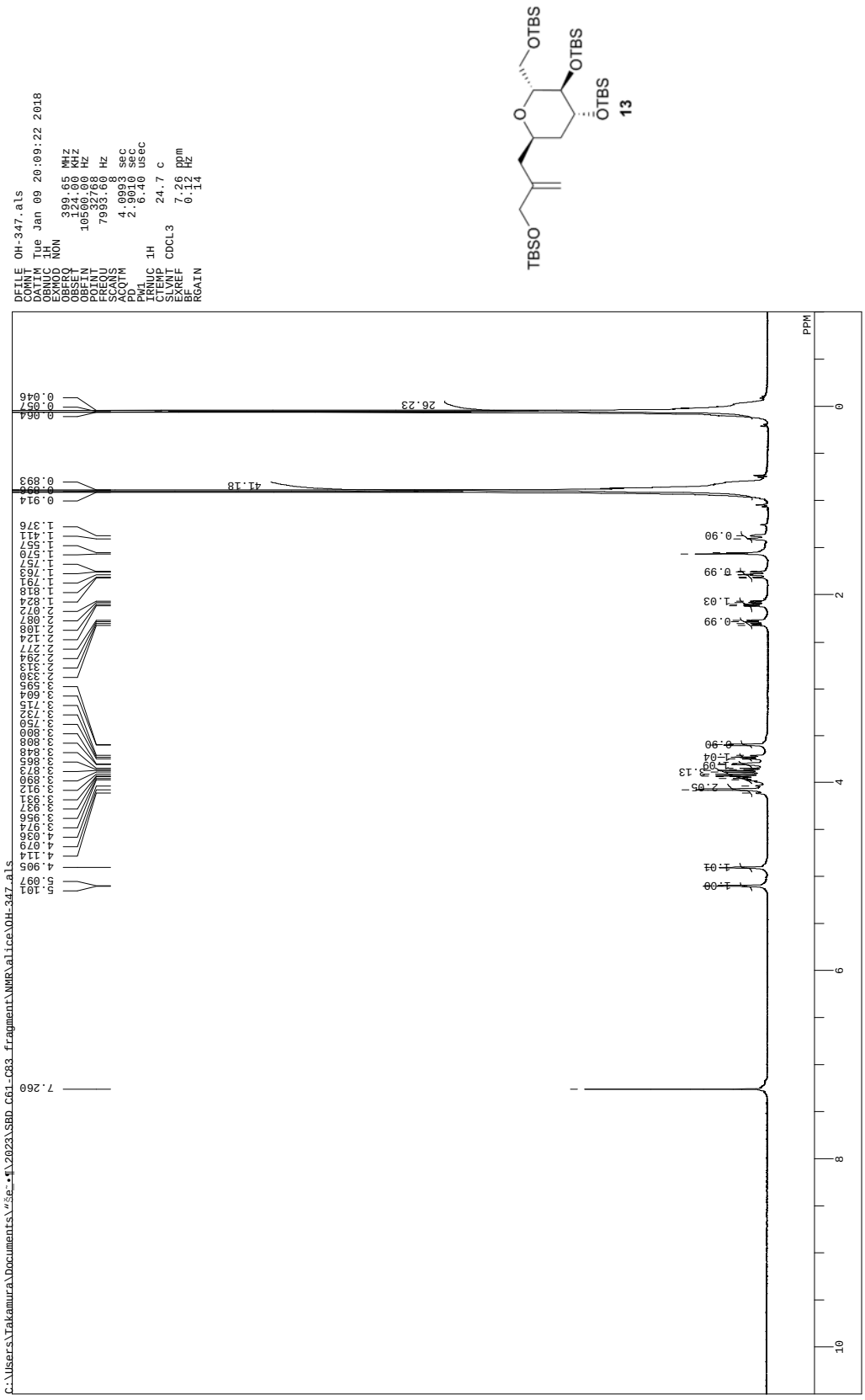
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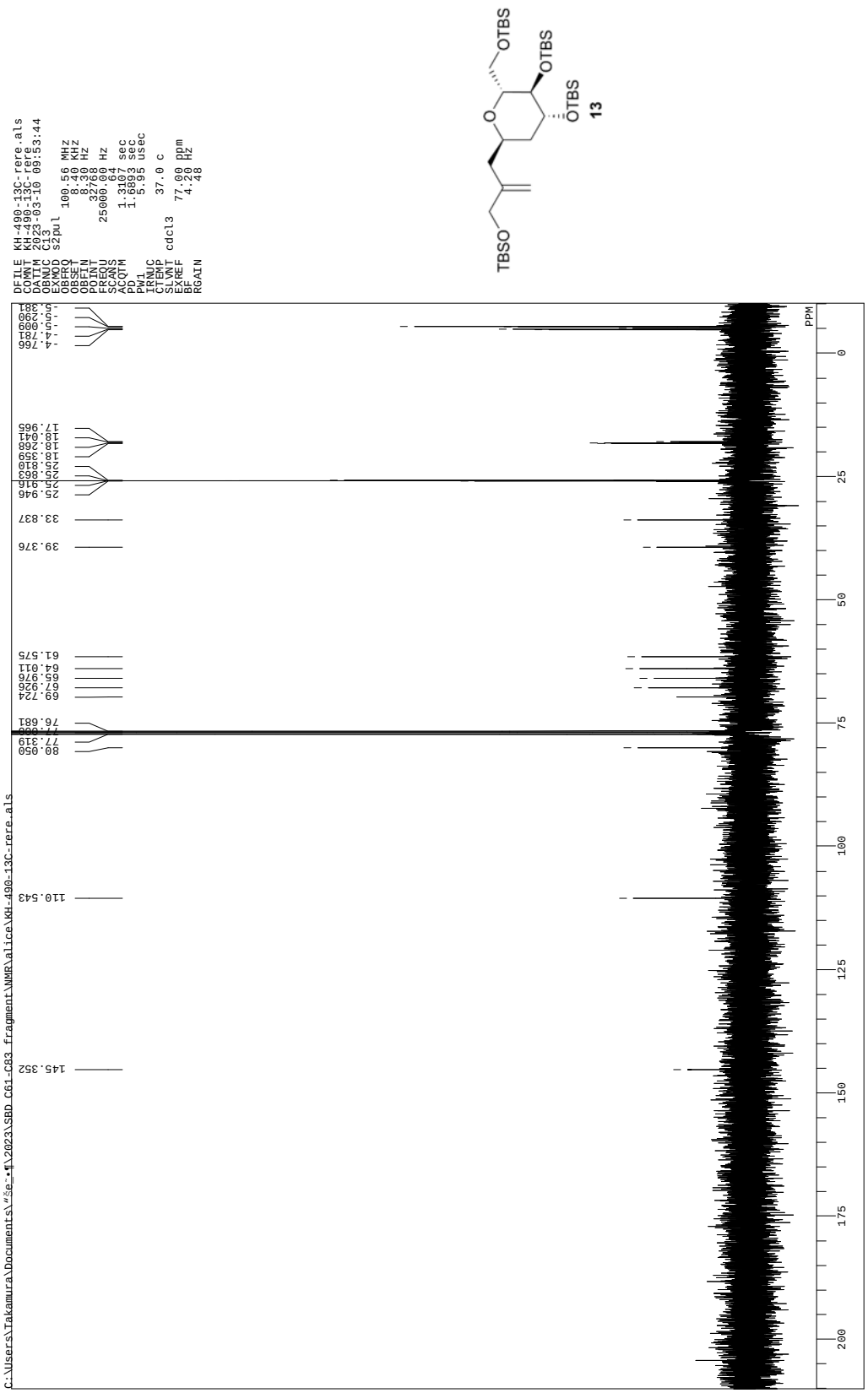
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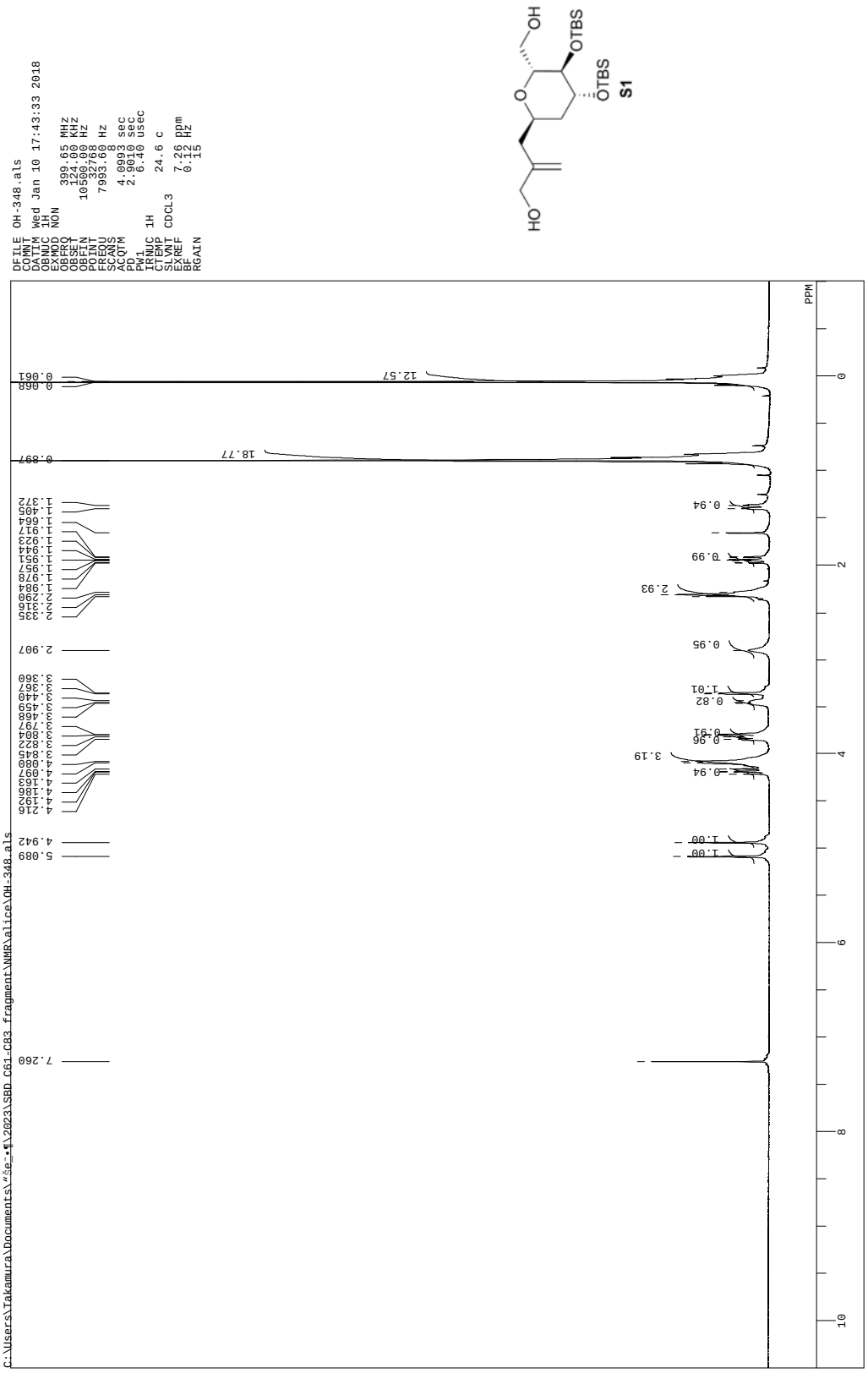
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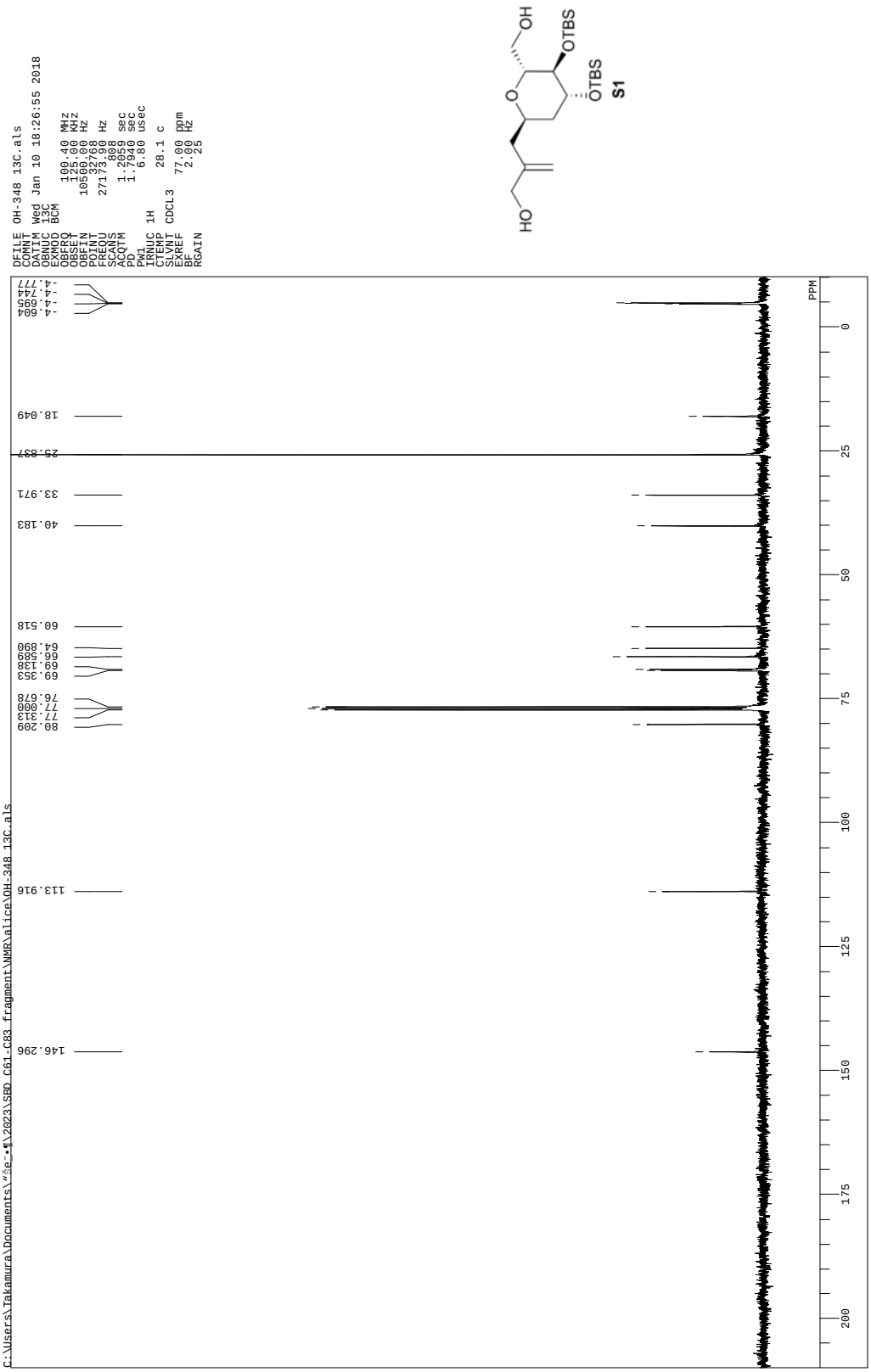
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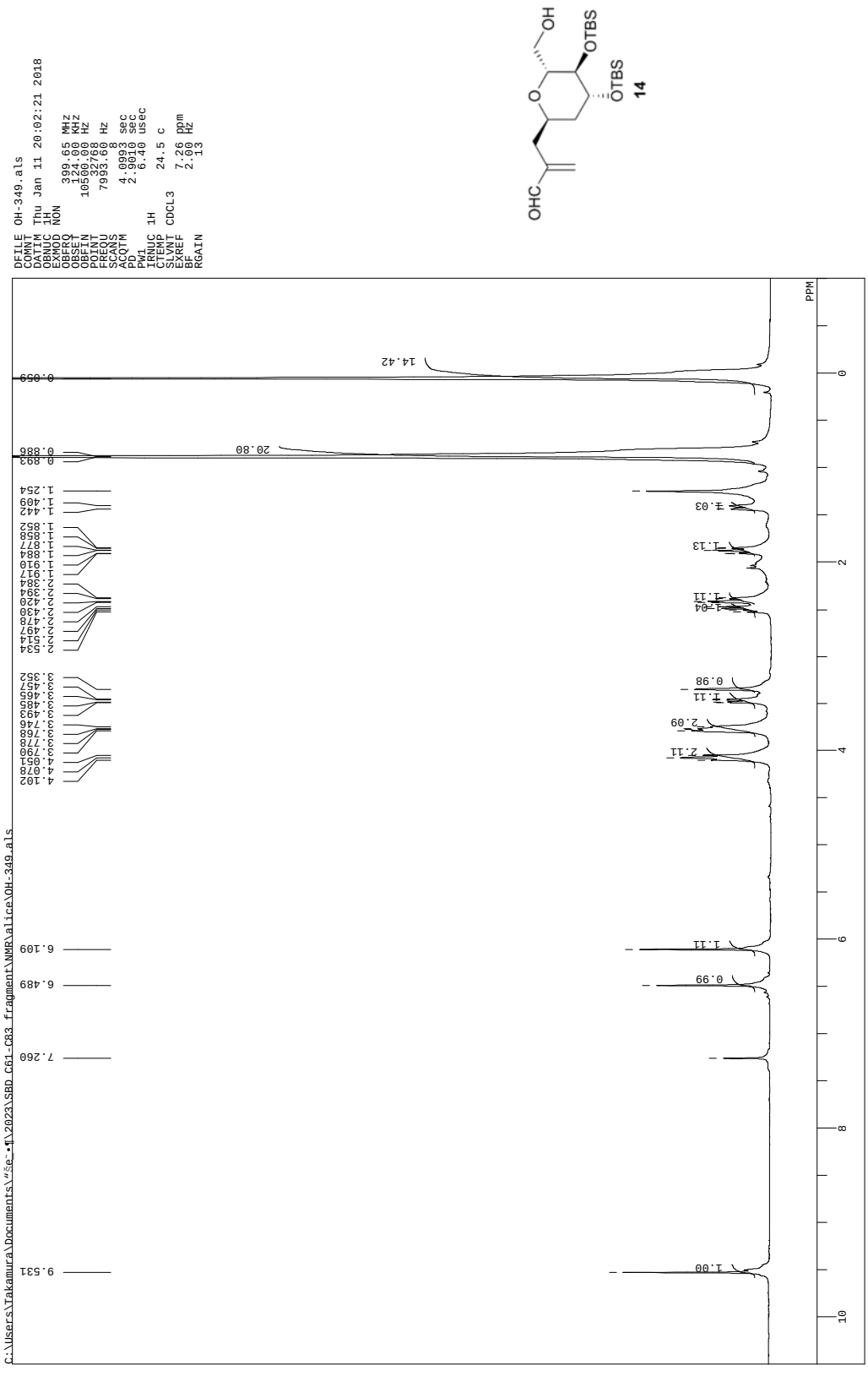
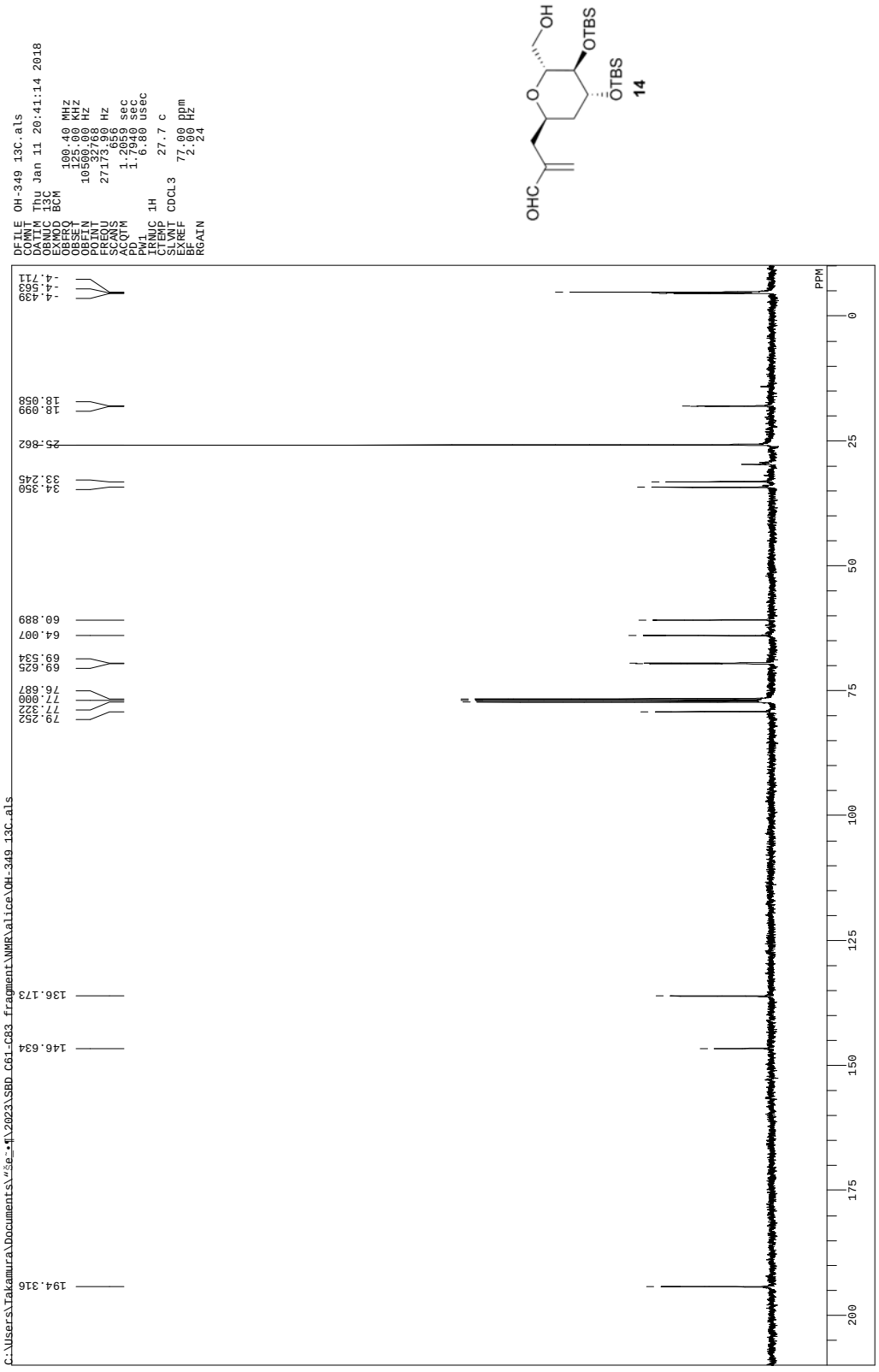
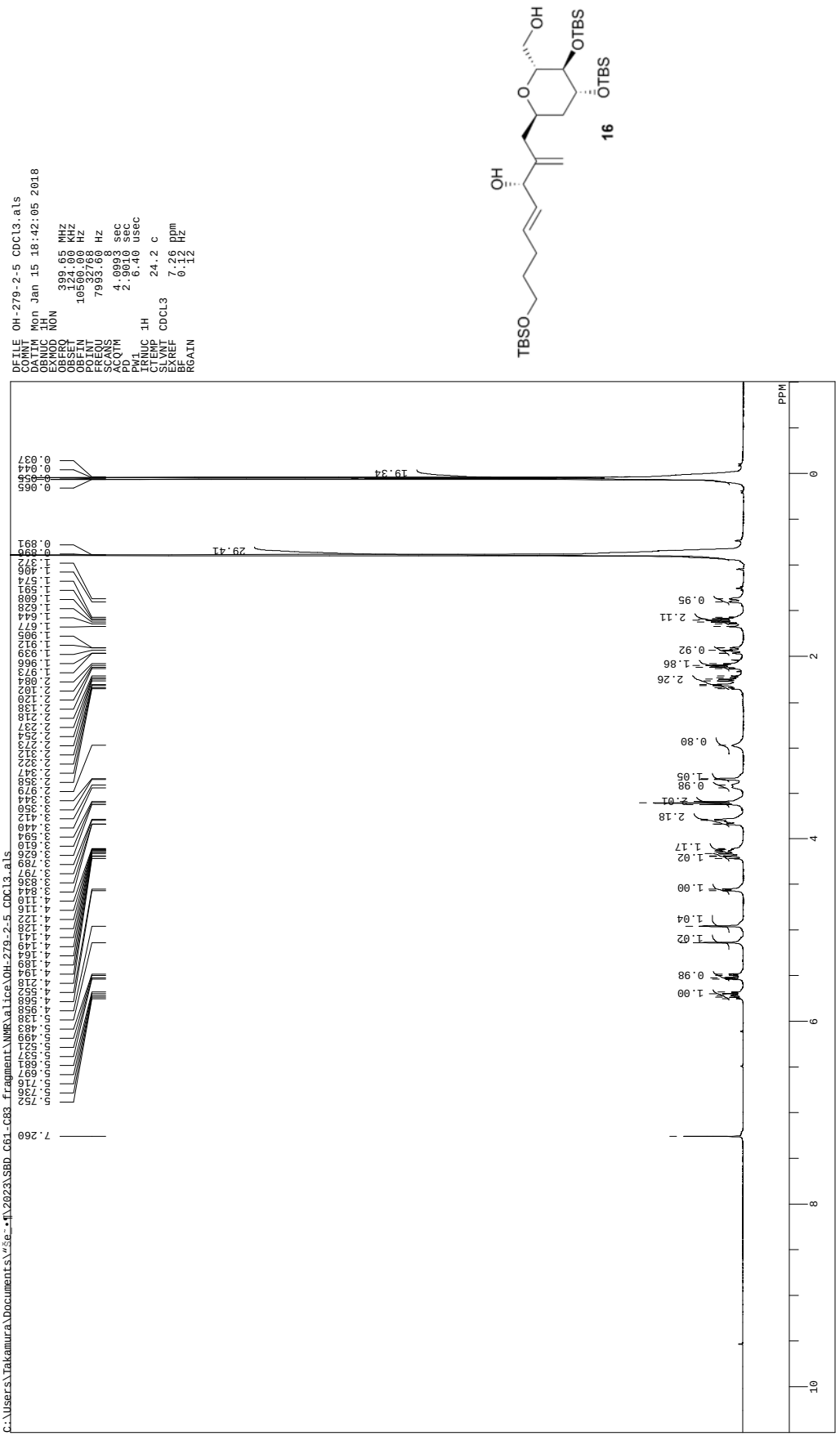
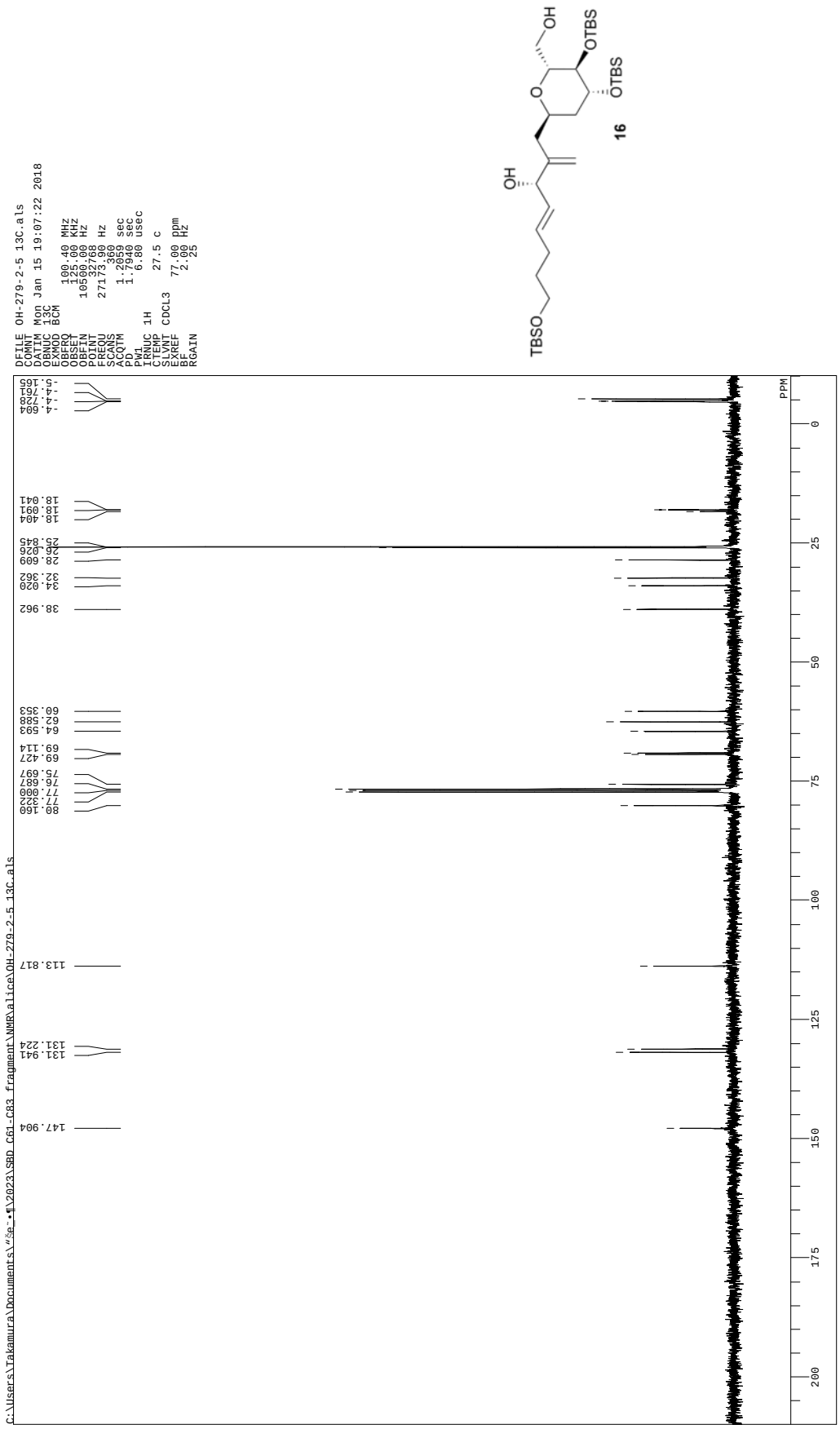
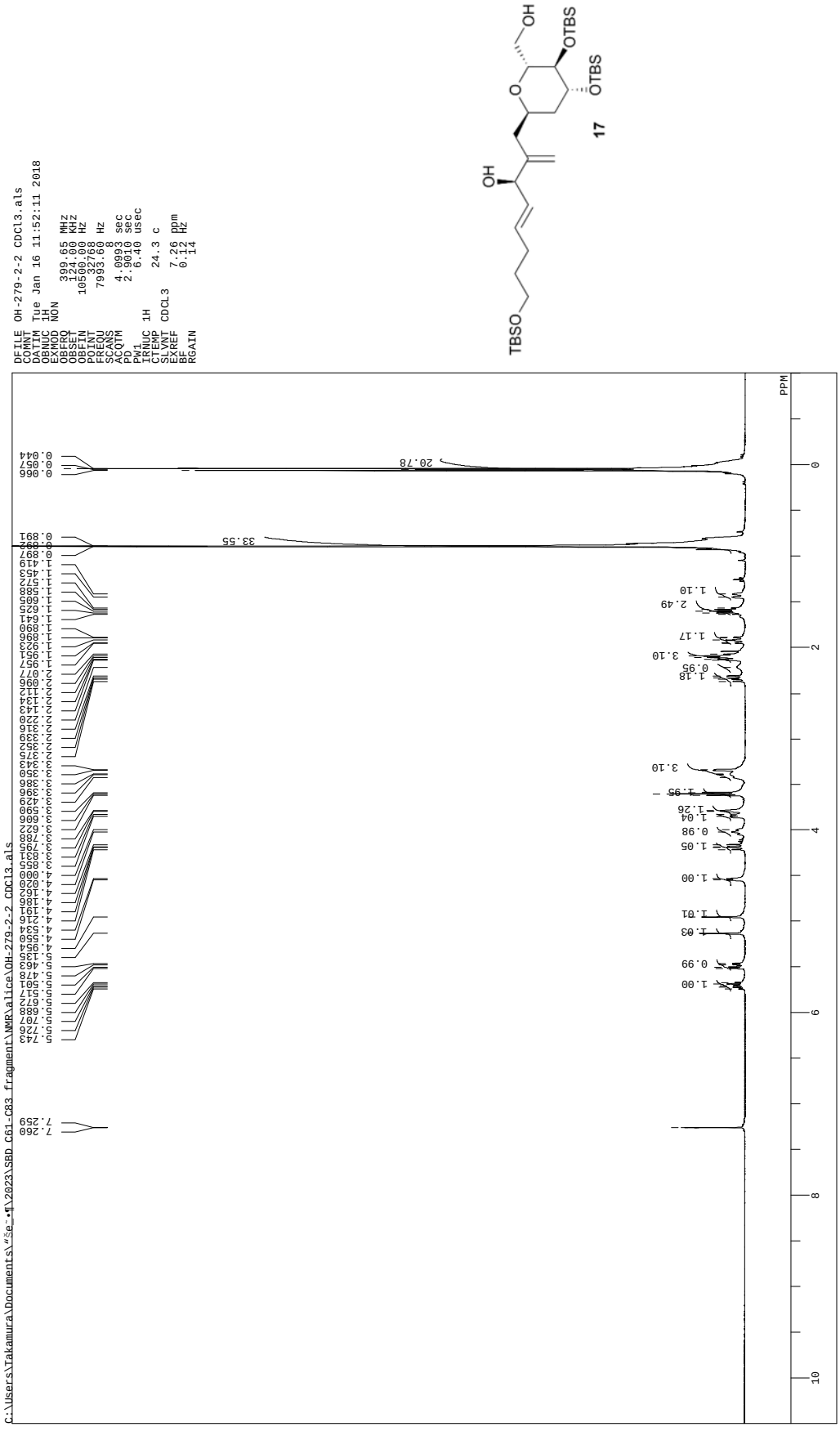
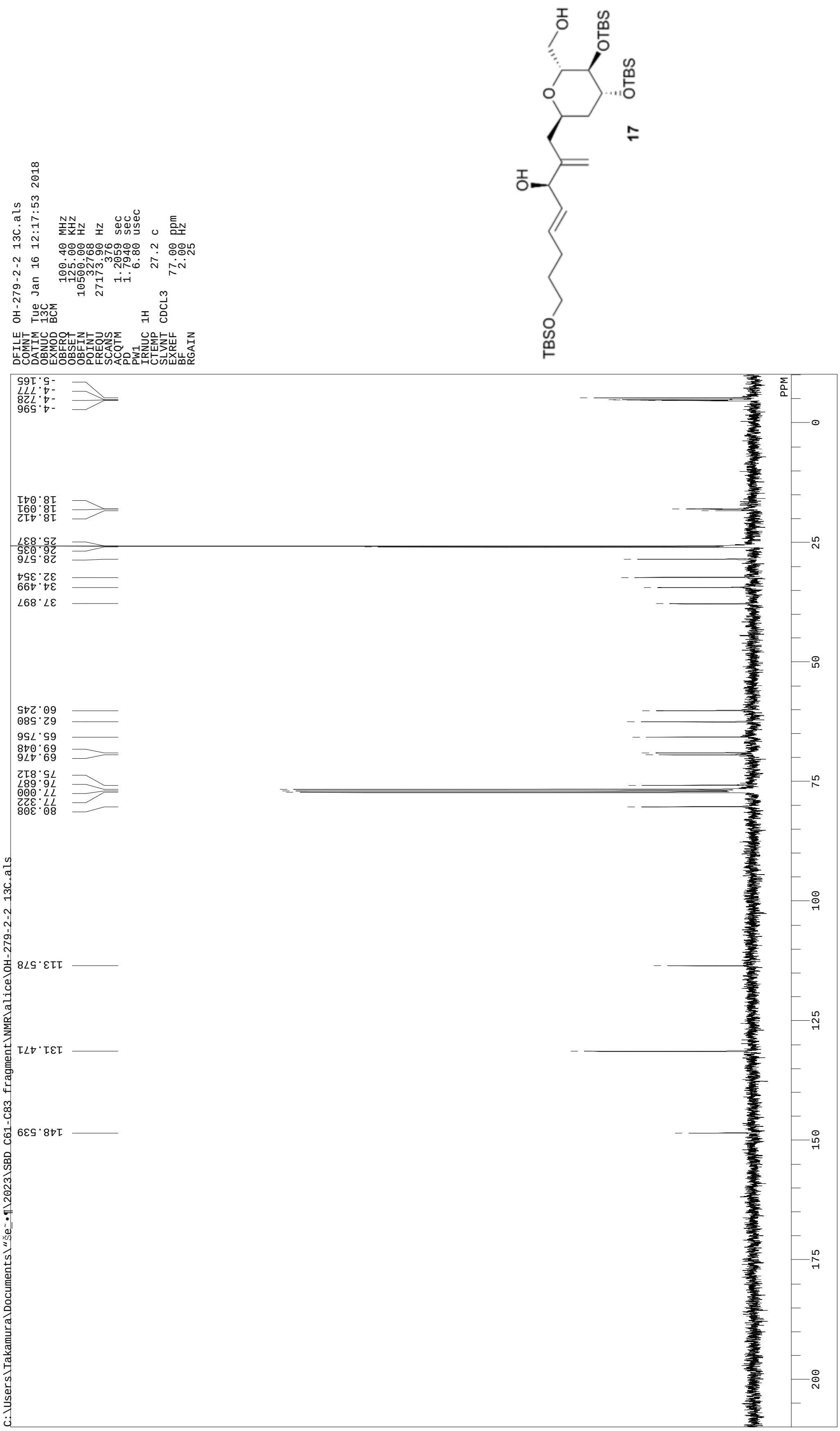

DFILE OH-349.als
COMNT
DATIM Thu Jan 11 20:02:21 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105907.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 400 MHz
RGAIN 13
OH
OTBS
OTBS
14
OHC
C:\Users\Takamura\Documents\"še-•¶\2023\SBD_C61-C83_fragment\NMR\alice\OH-349.als
PPM
14.42
20.80
4.03
1.13
1.11
1.04
1.11
0.98
2.09
2.11
1.11
0.99
1.00
9.531
7.260
6.489
6.109
4.102
4.078
4.051
3.790
3.778
3.768
3.746
3.493
3.485
3.465
3.457
3.352
2.534
2.514
2.497
2.478
2.430
2.420
2.394
2.384
1.917
1.910
1.884
1.877
1.858
1.852
1.442
1.409
1.254
0.893
0.886
0.059

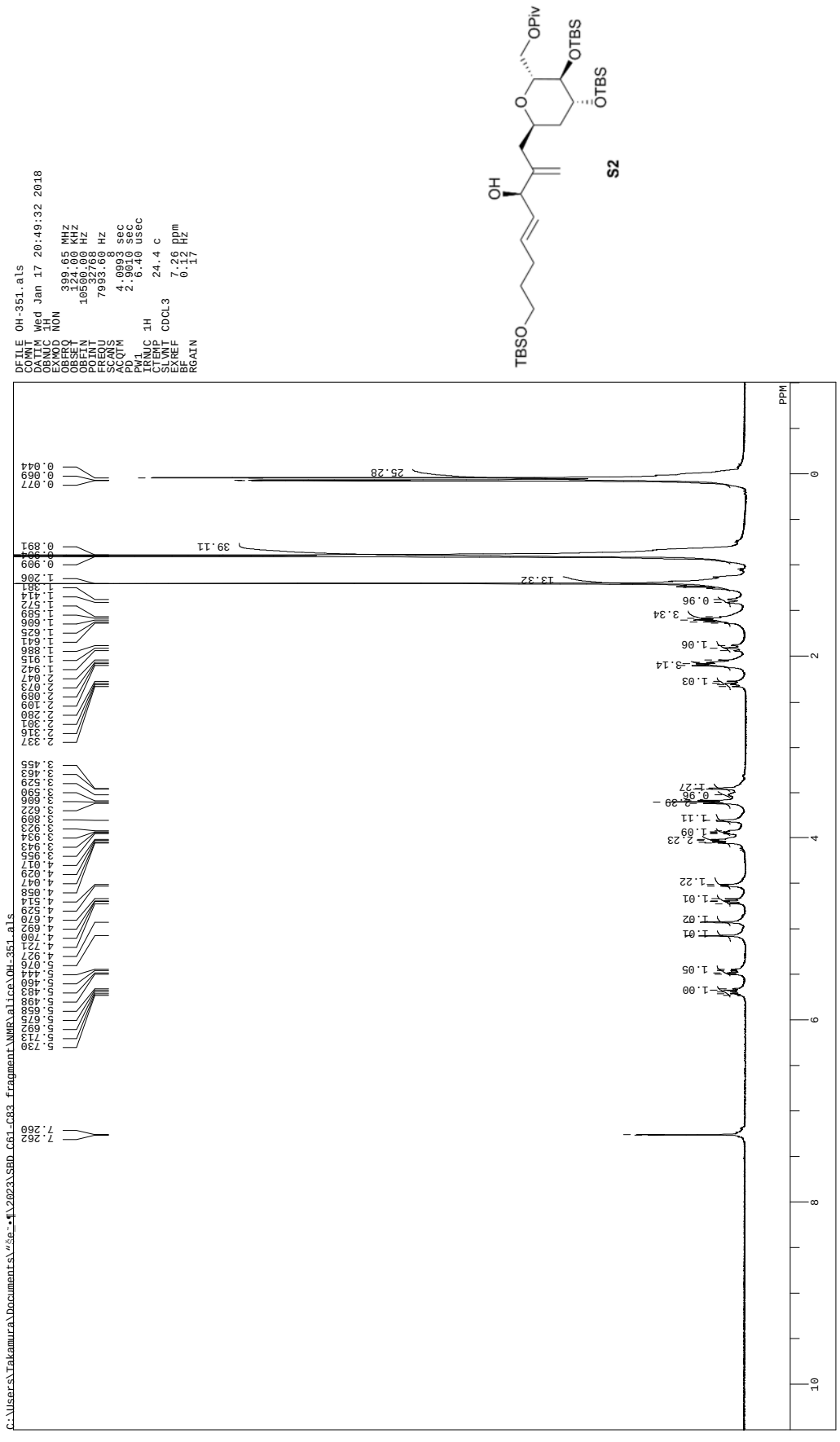

OH
OTBS
OTBS
O
OHC
14
PPM
0
25
50
75
100
125
150
175
200
-4.711
-4.563
-4.439
18.099
18.058
25.862
33.245
34.350
60.889
64.007
69.534
69.625
76.687
77.000
77.322
79.252
136.173
146.634
194.316

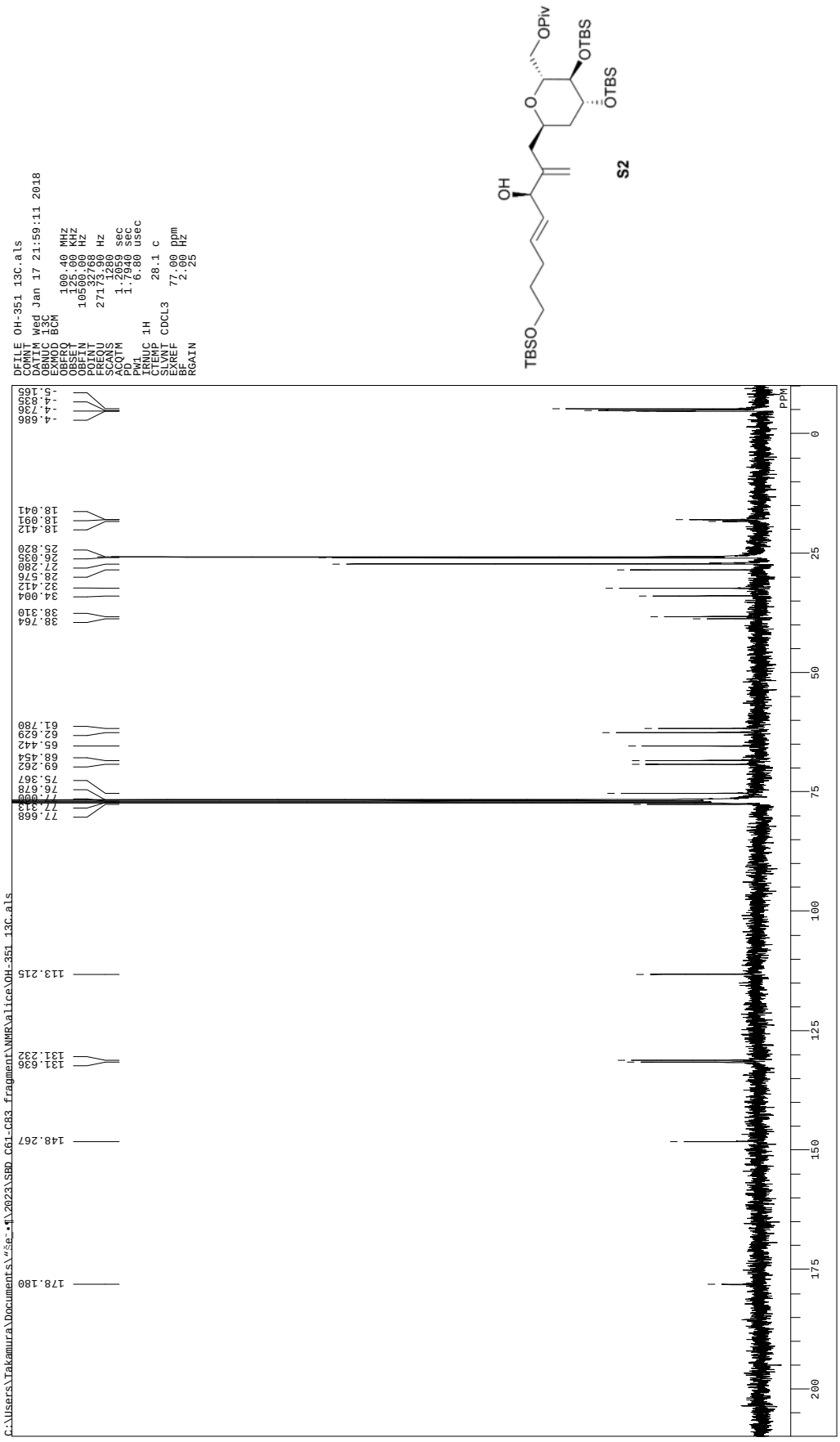

DFILE OH-279-2-5 CDCl3.als
COMNT
DATIM Mon Jan 15 18:42:05 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105907.00 Hz
POINT 27760
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.0010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BWIDTH 0.12
RGAIN
C:\Users\Takamura\Documents\"se-•¶\2023\SBD_G81-C83_fragment\NMR\alice\OH-279-2-5_CDCl3.als
PPM
TBSO
OH
OTBS
OTBS
16


OH
OTBS
O
OTBS
16
OH
TBSO
DFILE OH-279-2-5 13C.als
COMNT
DATIM Mon Jan 15 19:07:22 2018
OBNUC
EXMOD
OBSET 100.40 MHz
OBFIN 125.00 KHz
POINT 105600.000 Hz
FREQU 27173.768 Hz
SCANS 360
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.5 c
SLVNT CDCL3
EXREF 77.00 ppm
RGAIN 2.00
C:\Users\Takamura\Documents\Ÿšè¯•¶\2023\SBD_C61-C83_fragment\NMR\alice\OH-279-2-5_13C.als
PPM

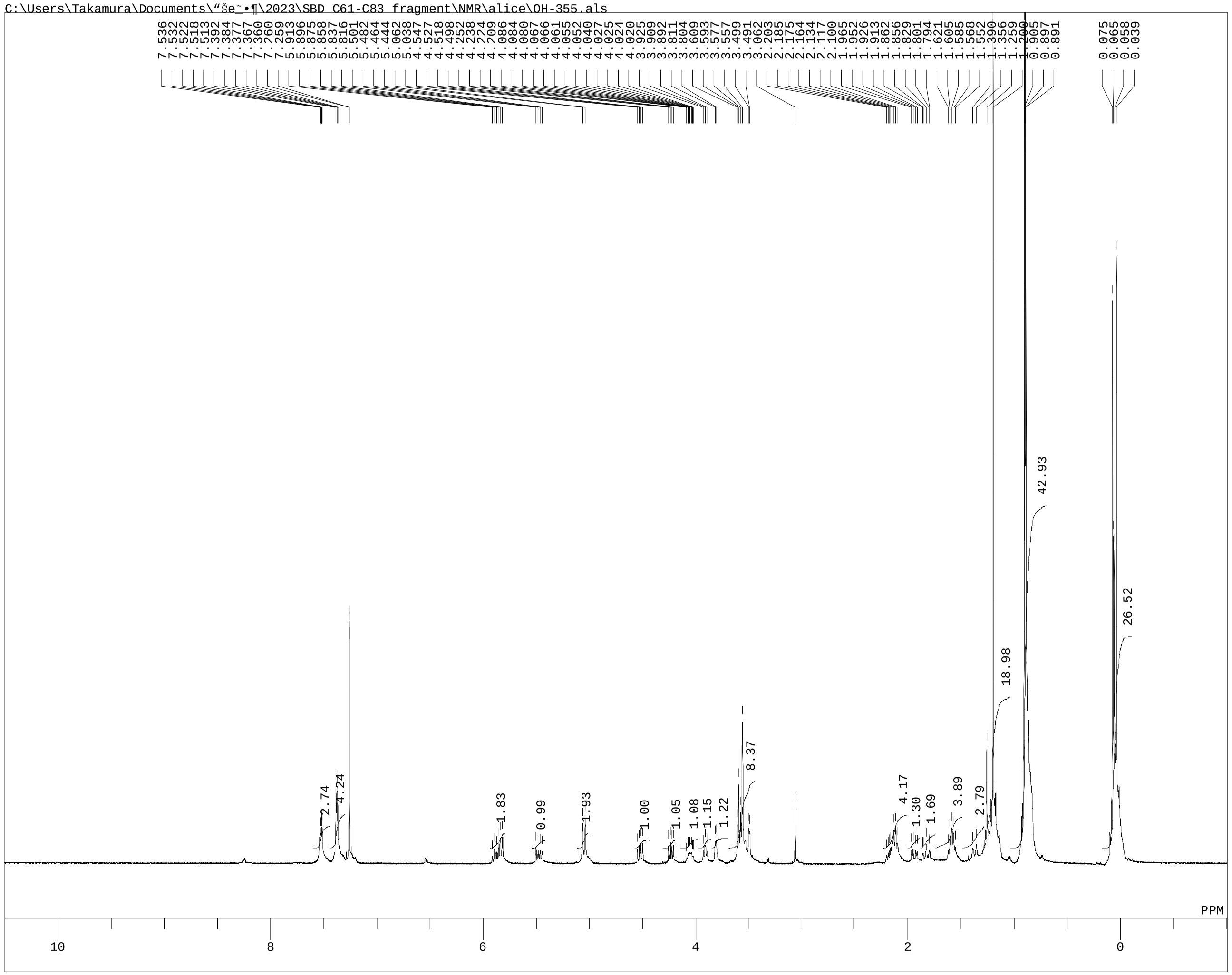

OH
OTBS
OTBS
17
TBSO
OH
DFILE OH-279-2-2 CDCl3.als
COMNT
DATIM Tue Jan 16 11:52:11 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10560.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.3 c
SOLVENT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN
C:\Users\Takamura\Documents\"Se-•¶\2023\SBD_C61_C83_fragment\NMR\alice\OH-279-2-2_CDCl3.als
PPM


C:\Users\Takamura\Documents\“ŠŠe”•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-279-2-2 13C.als
DFILE OH-279-2-2 13C.als
COMNT
DATIM Tue Jan 16 12:17:53 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 376
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25
-5.165
-4.777
-4.728
-4.596
18.041
18.091
18.412
25.837
26.035
28.576
32.354
34.499
37.897
60.245
62.580
65.756
69.048
69.476
75.812
76.687
77.000
77.322
80.308
113.578
131.471
148.539
PPM
0
25
50
75
100
125
150
175
200
TBSO
OH
O
OTBS
OTBS
OH
17

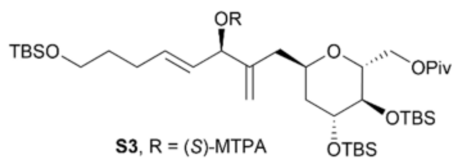

OPiv
OTBS
OTBS
OH
TBSO
S2
C:\Users\Takamura\Documents\"Se-•ft\2022\SBD_C61_C83_fragment\NMR\alice\OH-351.als
PPM


OPiv
OTBS
OTBS
O
OH
TBSO
S2
DFILE OH-351 13C.als
COMNT Wed Jan 17 21:59:11 2018
DATIM
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 105007.68 Hz
POINT 227207
FREQU 27173.90 Hz
SCANS 1280
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
TRNUC 1H
CTEMP 28.1 c
SLVNT CDCl3
EXREF 77.00 ppm
RGAIN 2.25
C:\Users\Takamura\Documents\ﾏｽﾀｰ･ﾃﾞｰﾀ\2023\SBD_C61-C83_fragment\NMR\Alice\OH-351_13C.als
PPM

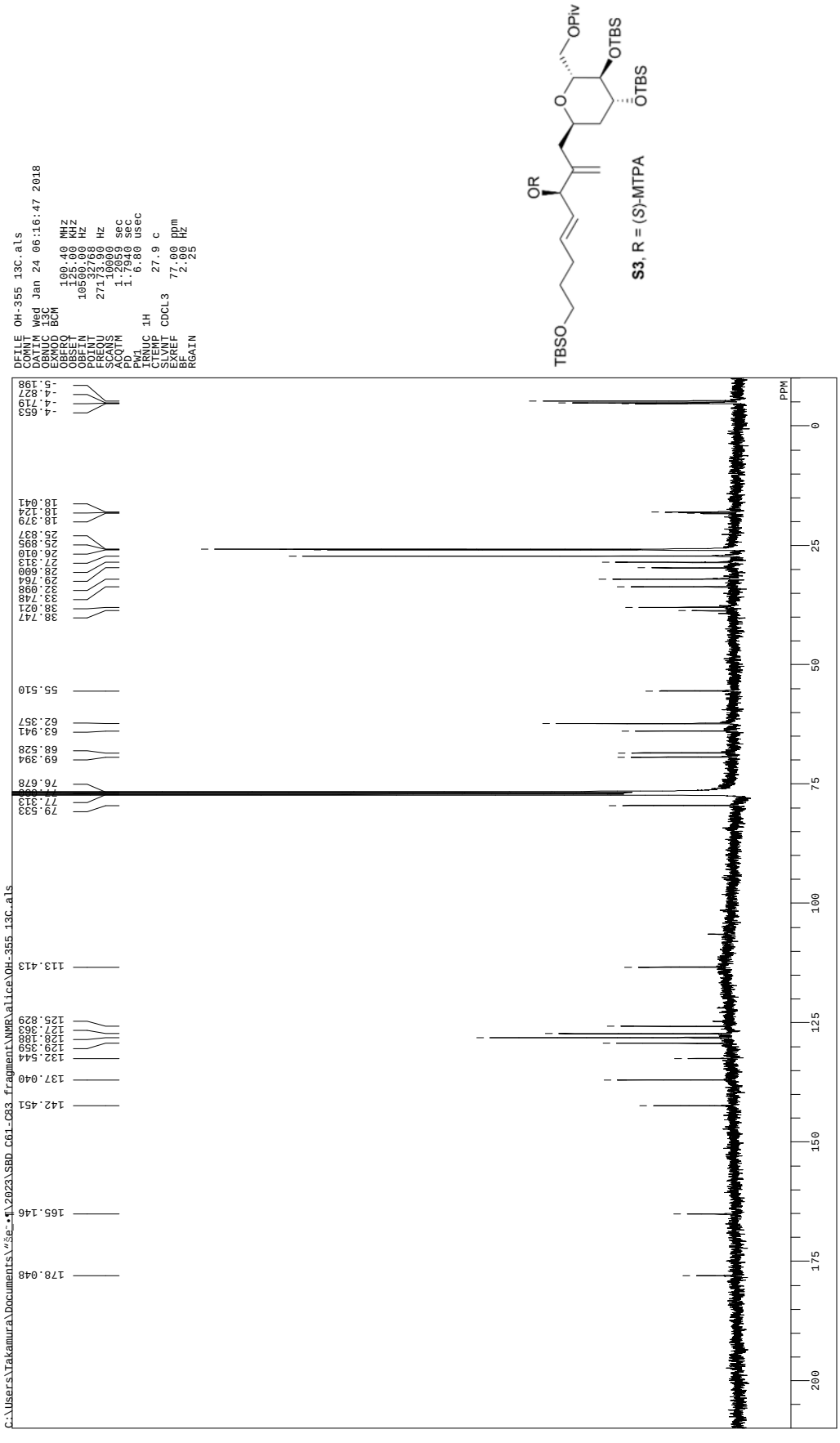
C:\Users\Takamura\Documents\“še¨•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-355.als

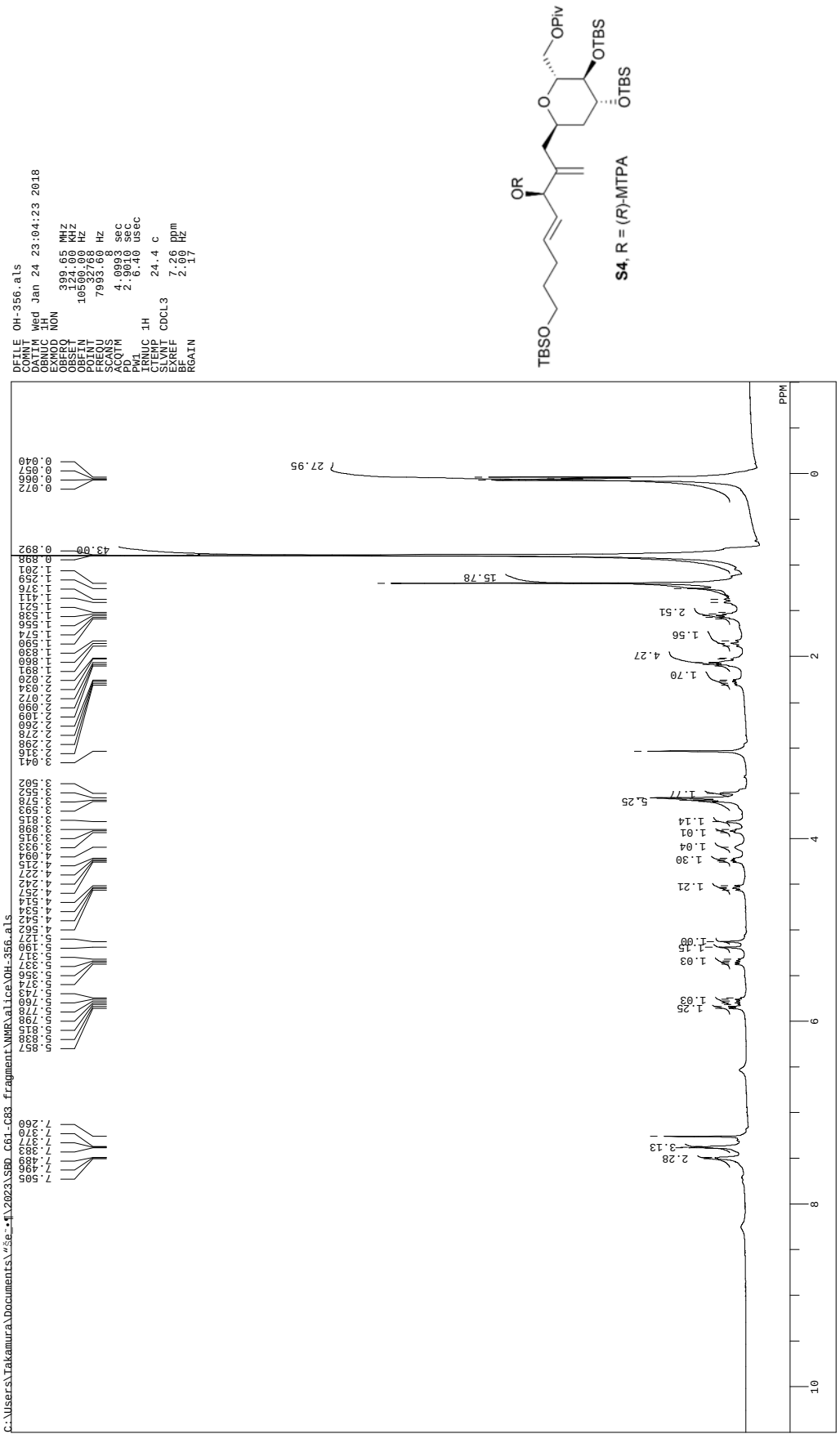


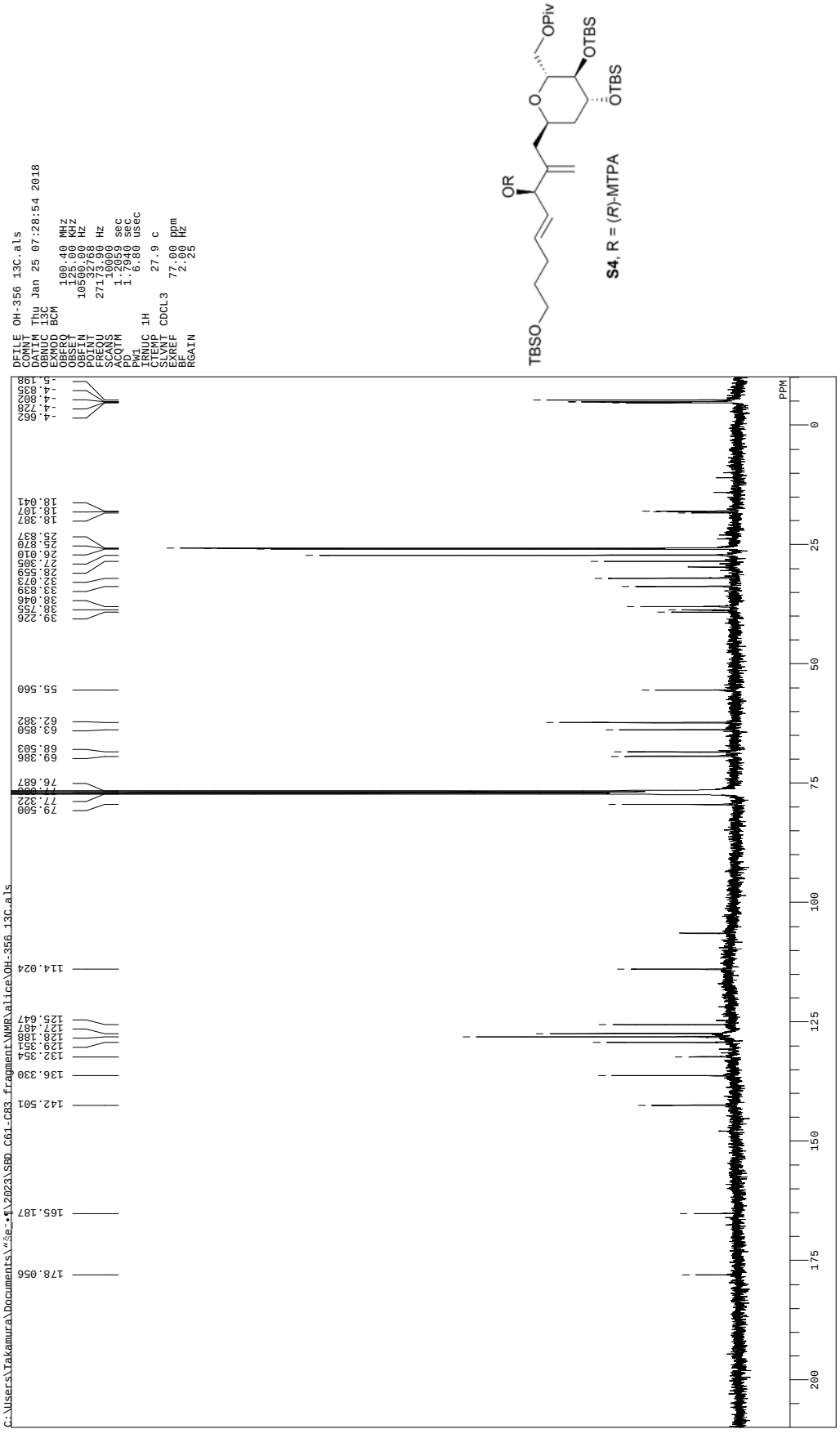

```
DFILE  OH-355.als
COMNT
DATIM  Tue Jan 23 19:49:46 2018
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7993.60 Hz
SCANS             8
ACQTM        4.0993 sec
PD           2.9010 sec
PW1            6.40 usec
IRNUC  1H
CTEMP          24.7 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            17
```

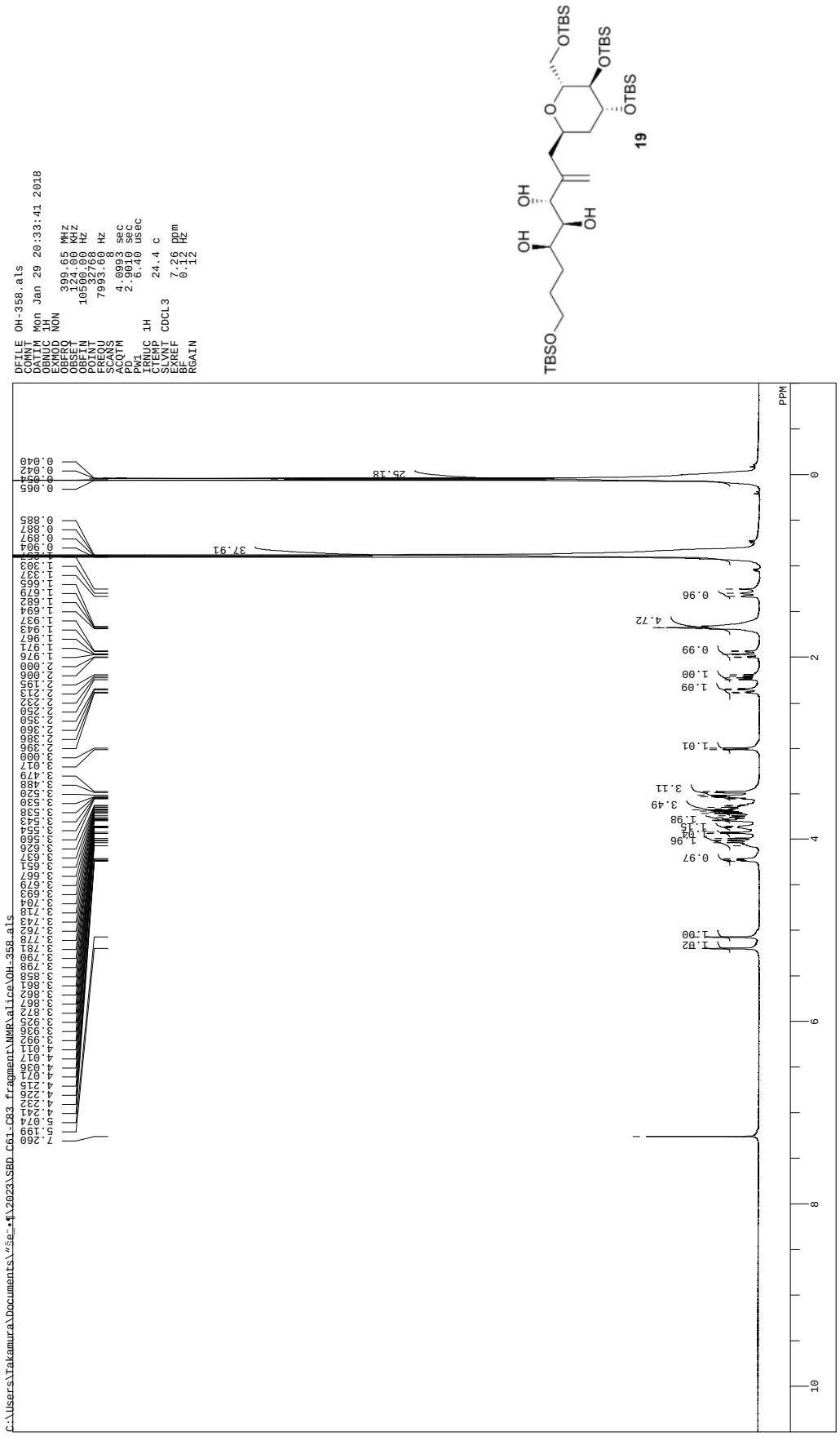


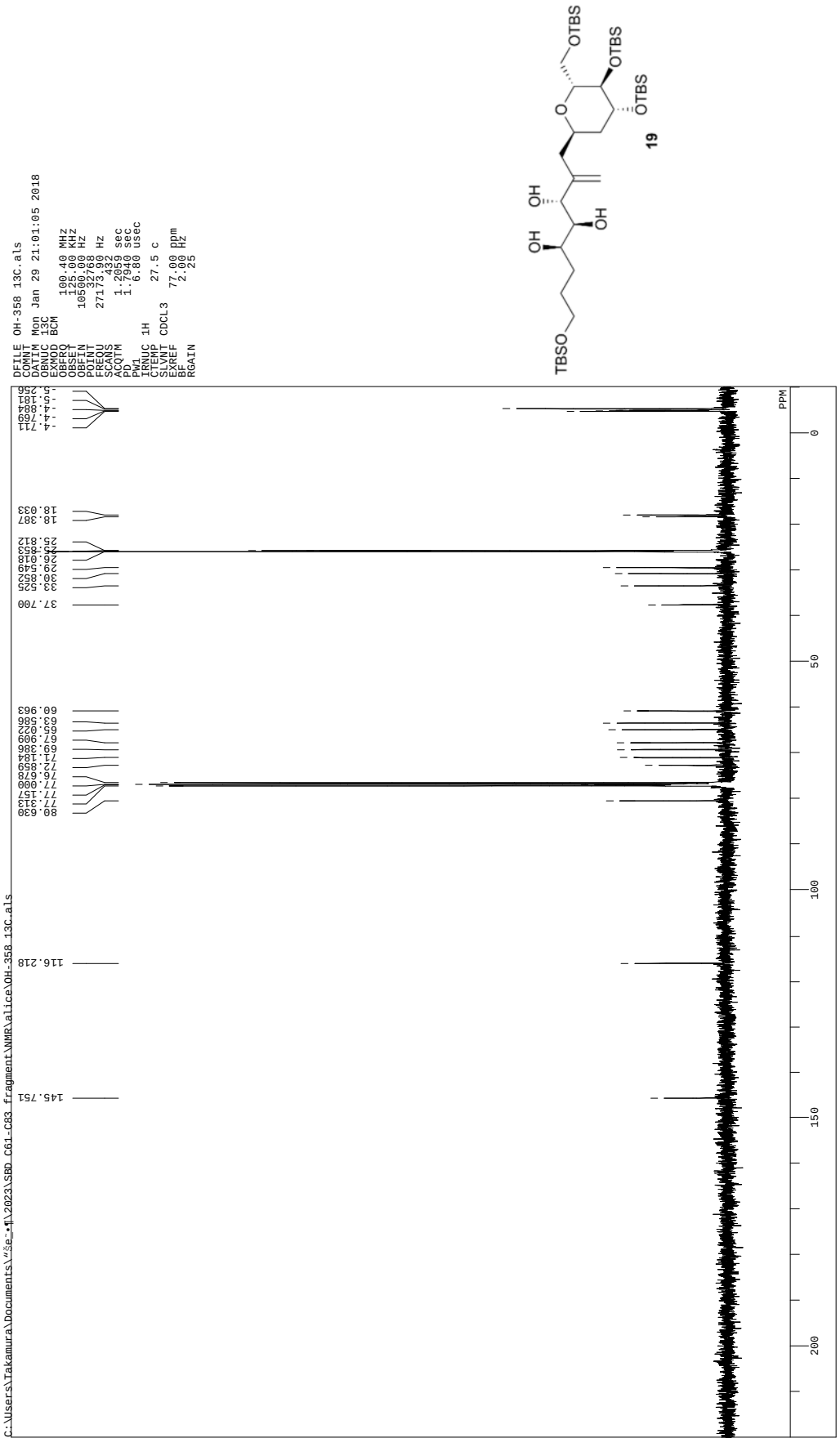
S3, R = (*S*)-MTPA

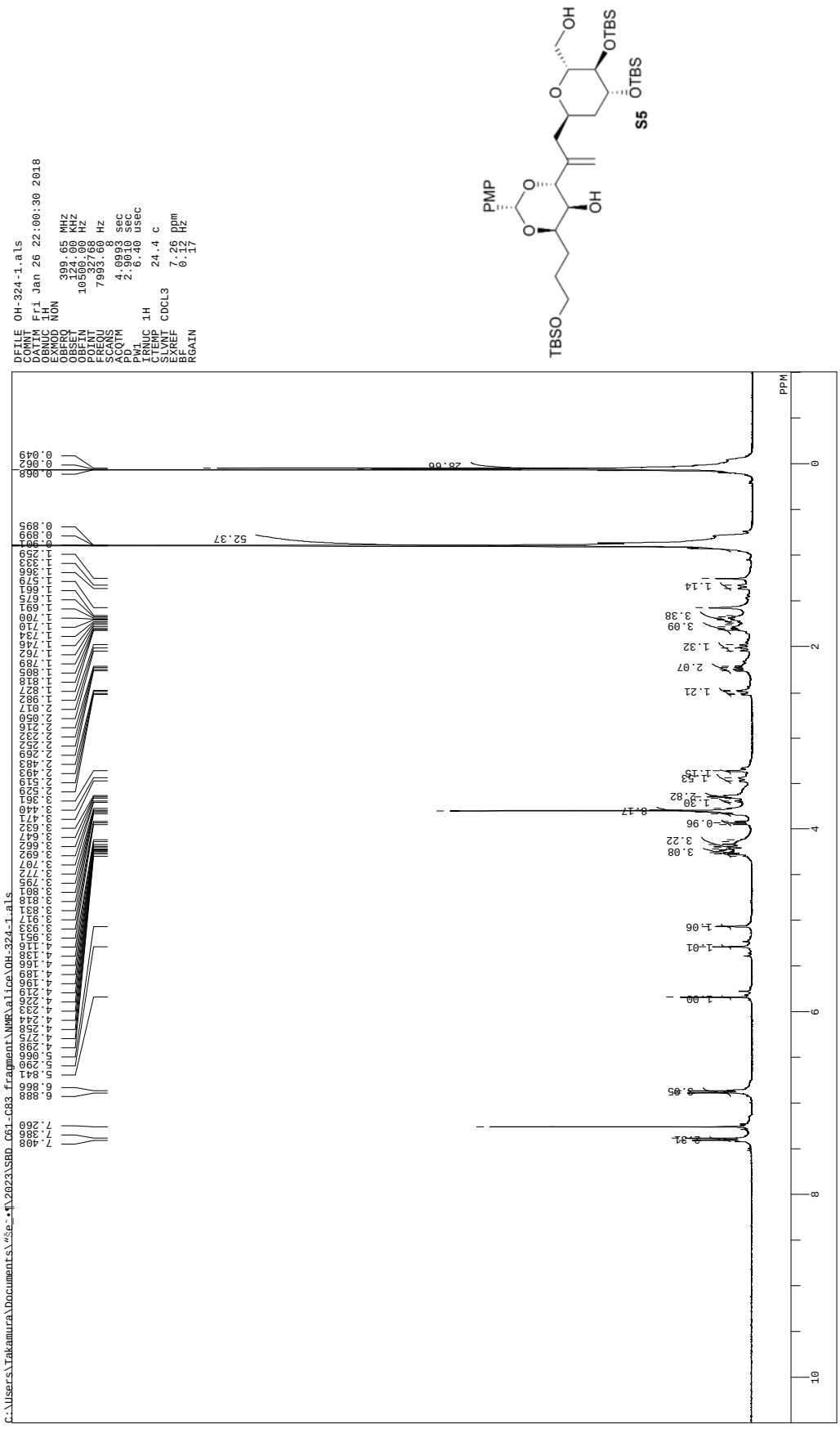

OPiv
OTBS
OTBS
OR
TBSO
S3, R = (S)-MTPA
PPM

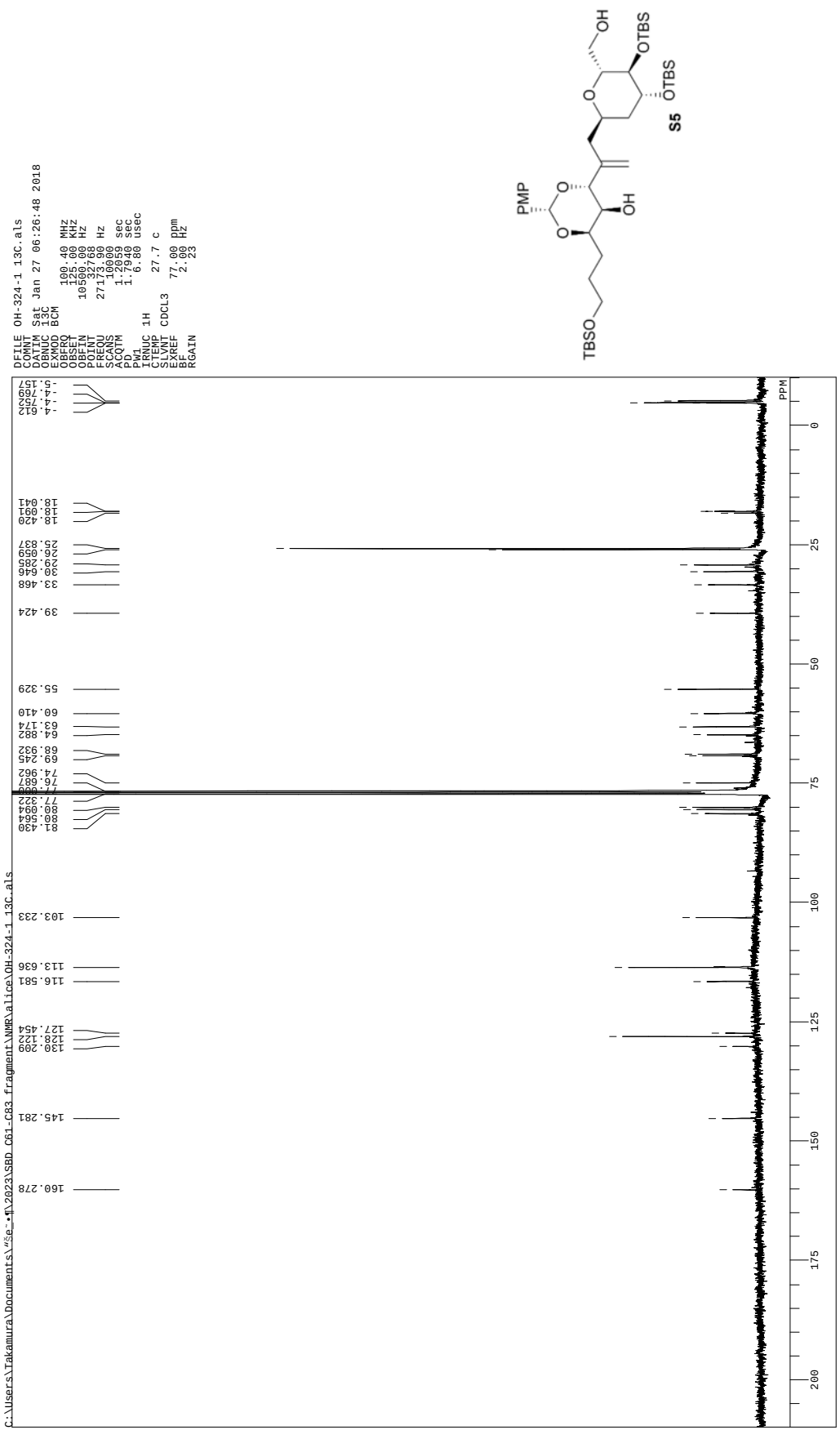

C:\Users\Takamura\Documents\データ_1\2023\SBD_C61-C83_fragment\NMR\alice\OH-356.als
DFILE OH-356.als
COMNT
DATIM Wed Jan 24 23:04:23 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105007.68 Hz
POINT 32768 Hz
FREQU 7993.6 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TNUC 1H
CTEMP 24.4 c
SLVNT CDCl3 7.26 ppm
EXREF 77.0 Hz
RGAIN 2.17
OR
OPiv
OTBS
OTBS
TBSO
S4, R = (R)-MTPA
PPM

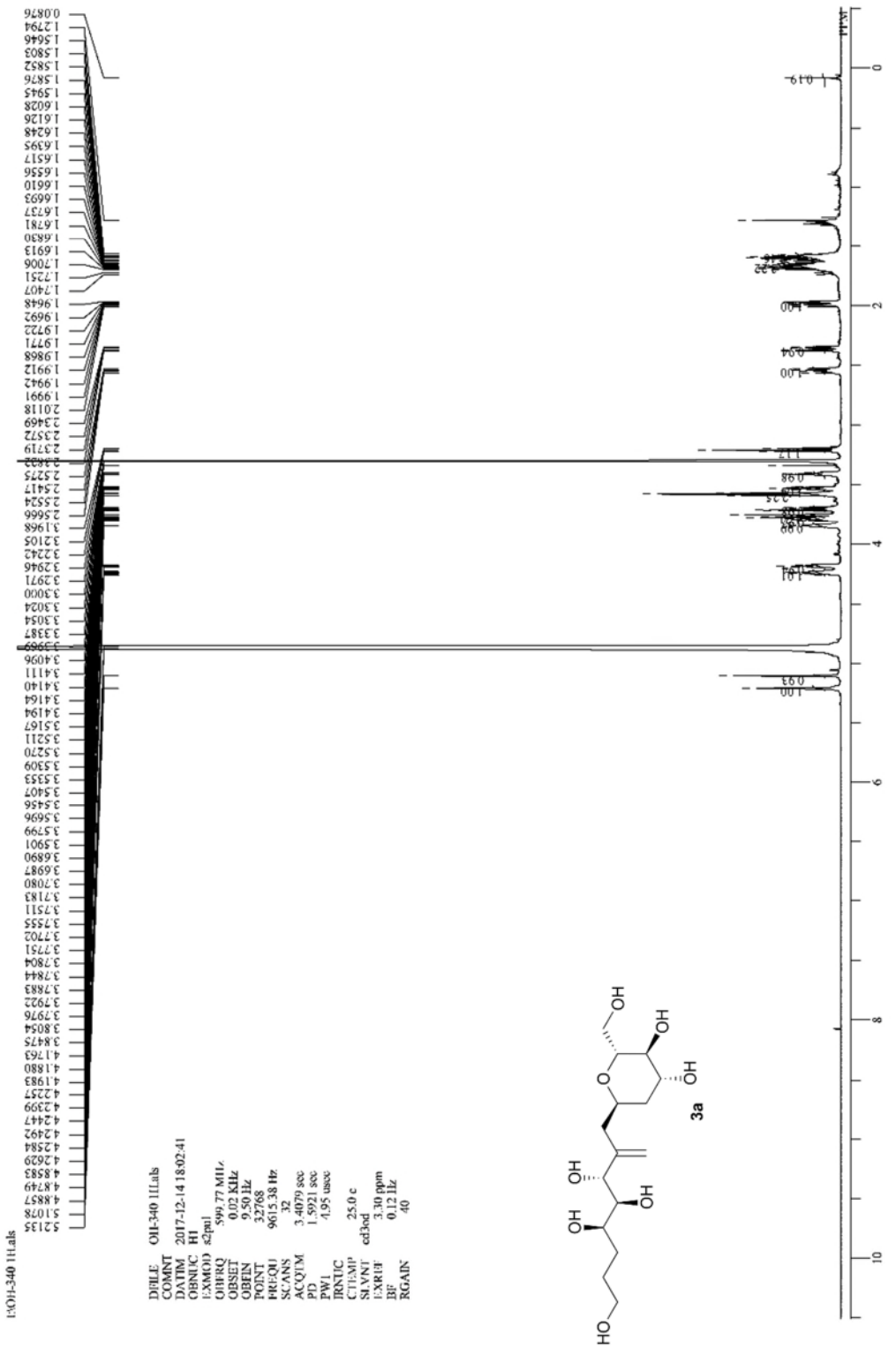

OPiv
OTBS
OTBS
OR
TBSO
S4, R = (R)-MTPA
PPM

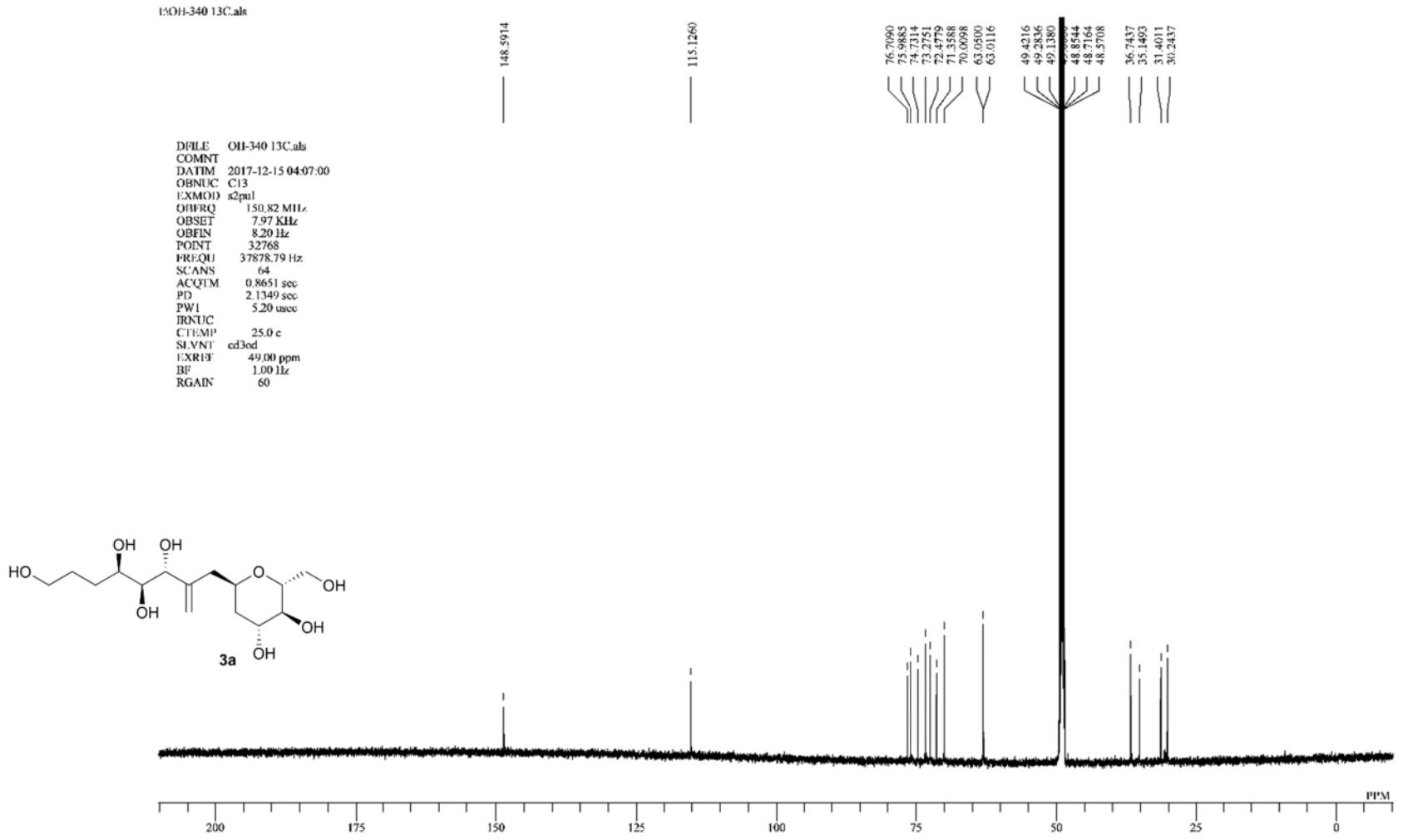

DFILE OH-358.als
COMNT
DATIM Mon Jan 29 20:33:41 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
SWEEP 124.00 KHz
OBSET 10500.00 Hz
OBFIN 32768 Hz
POINT 7993.60 Hz
FREQU
SCANS 4.0993 sec
ACQTM 2.9010 sec
PD 6.40 usec
PW1
INUC 1H
CTEMP 24.4 c
SLVNT CDCL3 7.26 ppm
EXREF 0.12 Hz
BF
RGAIN
C:\Users\Takamura\Documents\ﾏｽﾀｰ\2023\SBD_C61_C83_fragment\NMR\alice\OH-358.als
PPM
TBSO
OTBS
OTBS
OTBS
OH
OH
OH
19


OTBS
OTBS
OTBS
O
OH
OH
OH
TBSO
19
DFILE OH-358 13C.als
COMNT
DATIM Mon Jan 29 21:01:05 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 105500.000 Hz
POINT 32768
FREQU 27173.439 Hz
SCANS 432
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25
C:\Users\Takamura\Documents\"še~ą\2023\SBD_C61-C83_fragment\NMR\alice\OH-358_13C.als
PPM
0
50
100
150
200


C:\Users\Takamura\Documents\Vše...\2023\SBD_061-C83_fragment\NMR\alice\OH-324-1.als
DFILE OH-324-1.als
COMNT
DATIM Fri Jan 26 22:00:30 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 17
PMP
OH
TBSO
OTBS
OTBS
S5
PPM


DFILE OH-324-1 13C.als
COMNT
DATIM Sat Jan 27 06:26:48 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.000 KHz
OBFIN 105609.768 Hz
POINT 32768
FREQU 27173.691 Hz
SCANS 100000
ACQTM 1.20059 sec
PD 1.79400 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 23
C:\Users\Takamura\Documents\ゼミ_卒研\2023\SBD C61-C83 fragment\NMR\alice\OH-324-1 13C.als
PPM
PMP
OH
TBSO
OTBS
OTBS
OH
S5

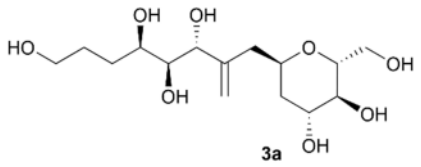

OH-340 1H.als
DATA
DFILE OH-340 1H.als
COMNT
DATIM 2017-12-14 18:02:41
OBNUC H1
EXMOD s2pul
OBFRQ 599.77 MHz
OBSET 0.02 KHz
OBFIN 9.50 Hz
POINT 32768
FREQU 9015.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 4.95 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 40
3a


OH-340 13C.als
148.5914
115.1260
76.7090
75.9885
74.7314
73.2751
72.4779
71.3588
70.0098
63.0500
63.0116
49.4216
49.2836
49.1380
48.8544
48.7164
48.5708
36.7437
35.1493
31.4011
30.2437
DFILE OH-340 13C.als
COMNT
DATIM 2017-12-15 04:07:00
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.97 KHz
OBFIN 8.20 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.20 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 1.00 Hz
RGAIN 60
HO
OH
OH
OH
O
OH
OH
OH
3a
PPM
200
175
150
125
100
75
50
25
0

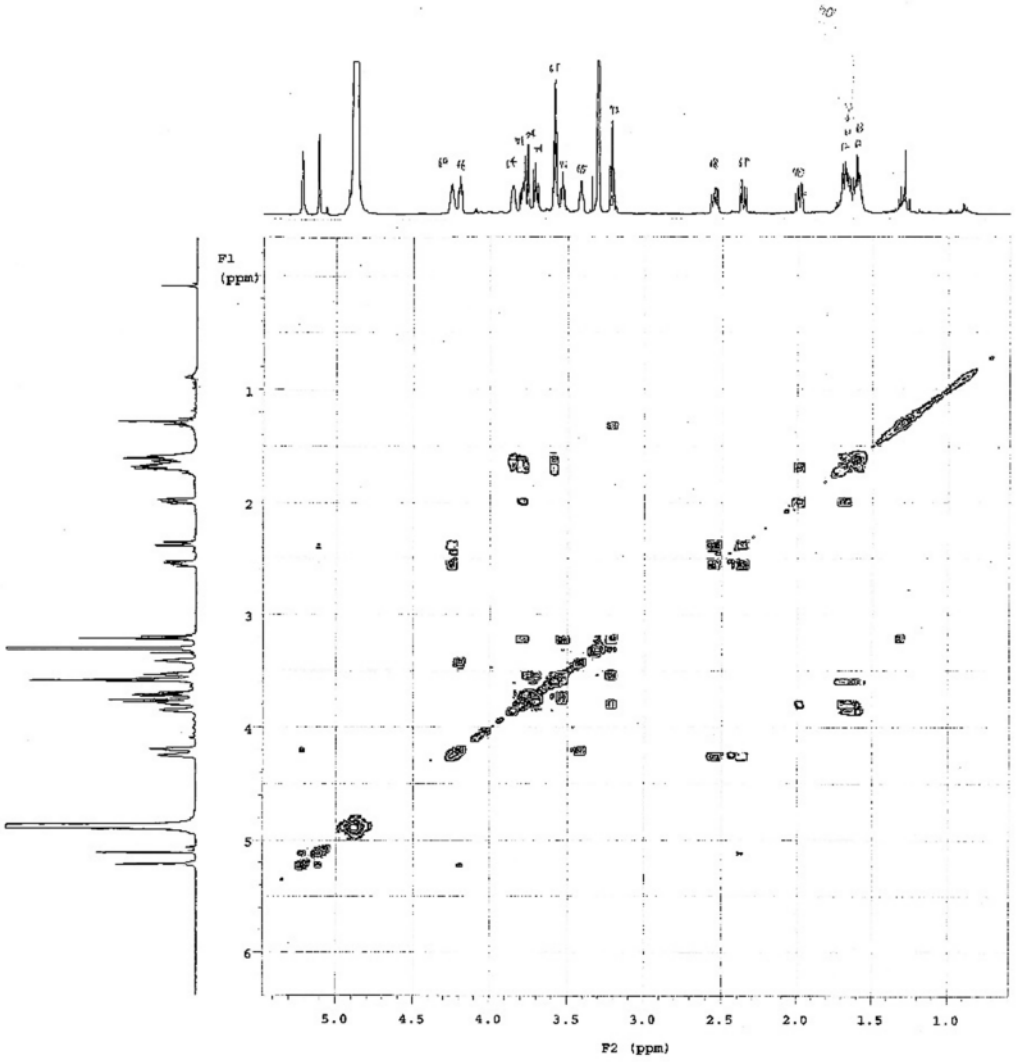
exp3 gCOSY

SAMPLE		FLAGS	
date	Dec 14 2017	ho	nn
solvent	cd3od	nopul	y
sample		hsglvl	6408
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	46
np	2884	spin	0
fb	4900	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	8	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.027
ni	256	sbs1	not used
d2	0	procl	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	354.4
TRANSMITTER		wp	3928.0
tn	H1	sp1	-204.3
sfrq	599.770	wp1	4033.0
tof	599.8	rf1	1209.6
tpwr	59	rfp	0
pw	9.900	rf11	1209.6
GRADIENTS		rfp1	0
gzlvl2	5347	PLOT	
gt2	0.001000	wc	198.0
EDratio	1.000	sc	0
gstab	0.000500	wc2	198.0
DECOUPLER		sc2	0
dn	C13	vs	191
dm	nnn	th	2
		ai cdc sv	

^{1}H–^{1}H COSY (600 MHz, CD_3OD)

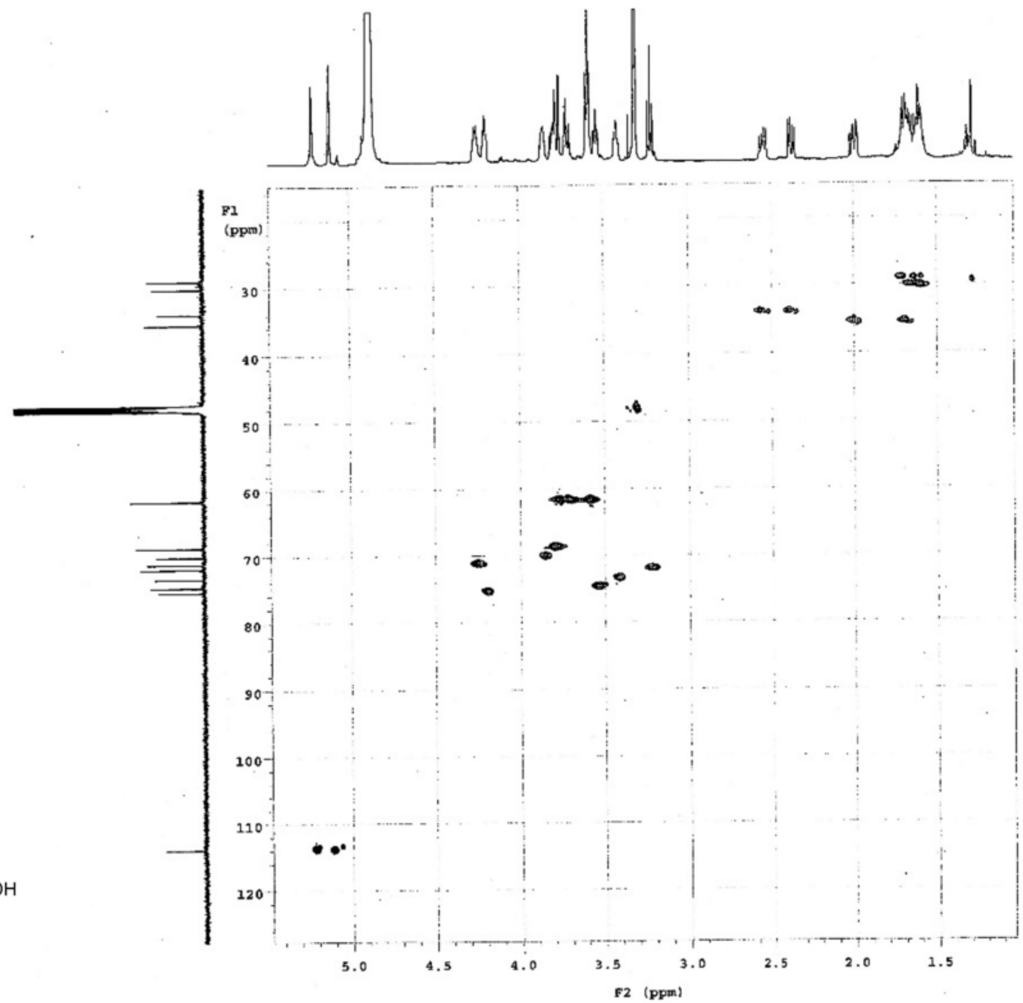


3a

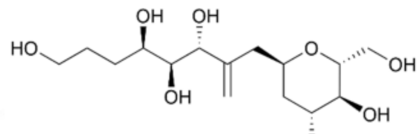


exp3 gHMQC

SAMPLE		FLAGS		ACQUISITION ARRAYS	
date	Dec 14 2017	hs	nn	array	phase
solvent	cd3od	sspul	y	arraydim	512
sample		PFGflg	y		
ACQUISITION		hsglvl	6408	i	phase
sw	9615.4	SPECIAL		1	1
at	0.150	temp	not used	2	2
np	2884	gain	60		
fb	4000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlvlE	5347		
nt	32	gtE	0.002000		
2D ACQUISITION		EDratio	3.977		
sw1	34692.1	gstab	0.000500		
ni	256	F2 PROCESSING			
phase	arrayed	gf	0.069		
PRESATURATION		gfs	not used		
satmode	n	fn	4096		
wet	n	F1 PROCESSING			
TRANSMITTER		gf1	0.007		
tn	H1	gfs1	not used		
sfrq	599.770	proc1	lp		
tof	599.8	fn1	2048		
tpwr	59	DISPLAY			
pw	9.900	sp	617.3		
DECOUPLER		wp	2662.1		
dn	C13	sp1	2248.9		
dof	1541.6	wp1	17007.3		
dm	nny	rfl	1209.0		
decwave W40_onenmr		rfp	0		
dmf	35088	rfl1	1511.6		
dpwr	40	rfp1	0		
pwxlvl	59	PLOT			
pwx	8.900	wc	198.0		
HMQC		sc	0		
j1xh	146.0	wc2	198.0		
nullflg	y	sc2	0		
mult	2	vs	191		
		th	2		
		ai cdc ph			



HMQC (600 MHz, CD_3OD)

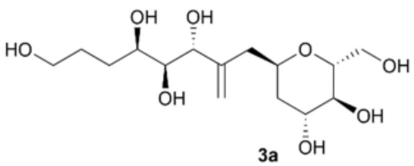


3a

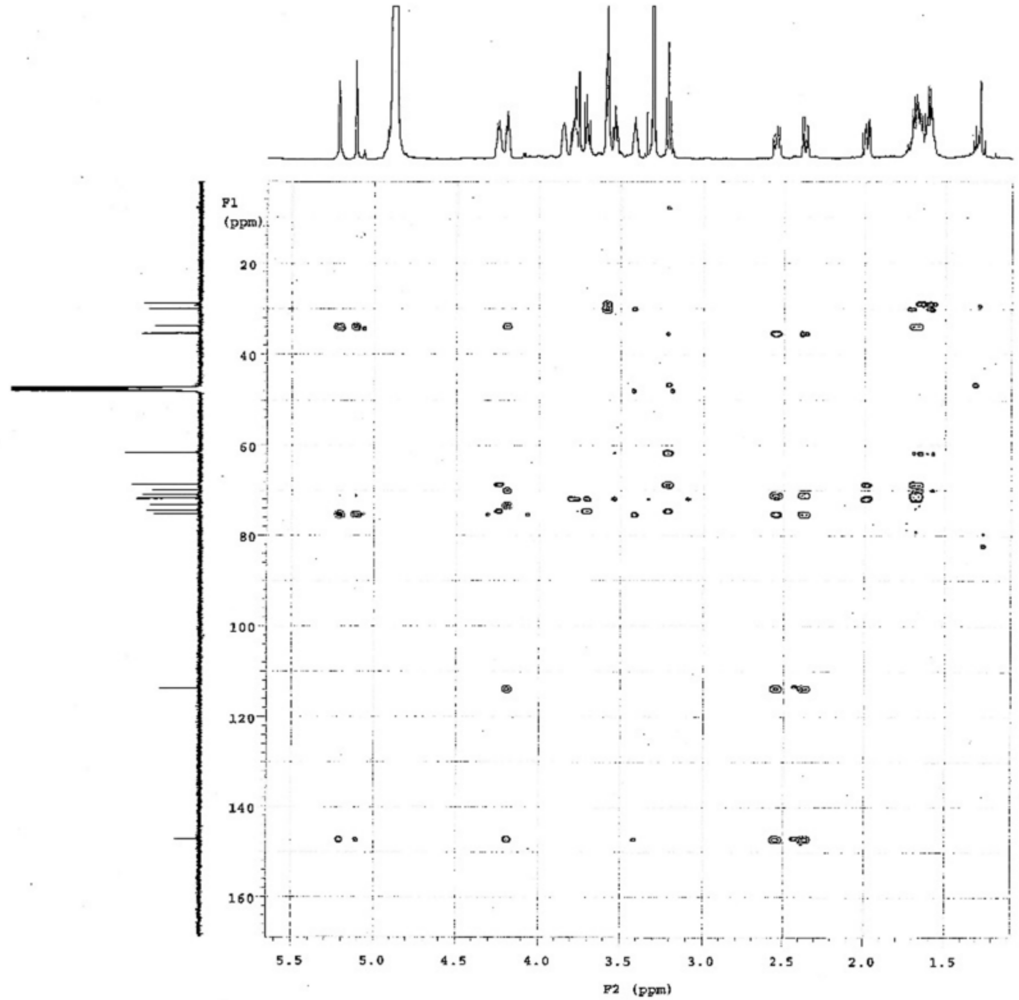
```
exp3  gHMBCAD

     SAMPLE                  FLAGS            ACQUISITION ARRAYS
date   Dec 14 2017  hs                 nn     array       phase
solvent      cd3od  sspul               y     arraydim      400
sample              PFGflg              y
  ACQUISITION       hsglvl           6408      i          phase
sw          9615.4       SPECIAL               1              1
at           0.150  temp         not used      2              2
np            2884  gain               60
fb            4000  spin                0
ns              32      GRADIENTS
d1           1.000  gzlvl1            500
nt              32  gt1          0.001000
  2D ACQUISITION    gzlvl3           1500
sw1        36199.1  gt3          0.001000
ni             200  gstab        0.000500
phase      arrayed    F2 PROCESSING
  PRESATURATION     sb             -0.075
satmode          n  sbs          not used
wet              n  fn               4096
   TRANSMITTER        F1 PROCESSING
tn              H1  gf1             0.005
sfrq       599.770  gfs1         not used
tof          599.8  procl              lp
tpwr            59  fn1              2048
pw           9.900        DISPLAY
   DECOUPLER        sp              650.2
dn             C13  wp             2737.2
dof         1542.4  sp1             316.3
dm             nnn  wp1           25134.3
decwave W40_onenmr  rfl            1209.0
dmf          35088  rfp                 0
dpwr            40  rfl1           2264.3
pwxlvl          59  rfp1                0
pwx          8.900          PLOT
      HMBC          wc              198.0
j1xh         146.0  sc                  0
jnxh           8.0  wc2             198.0
   ADIABATCIC       sc2                 0
pwx180ad onenmr_ad- vs                228
               300  th                  4
pwxlvl180       54  ai   cdc   av
pwx180       400.0
```

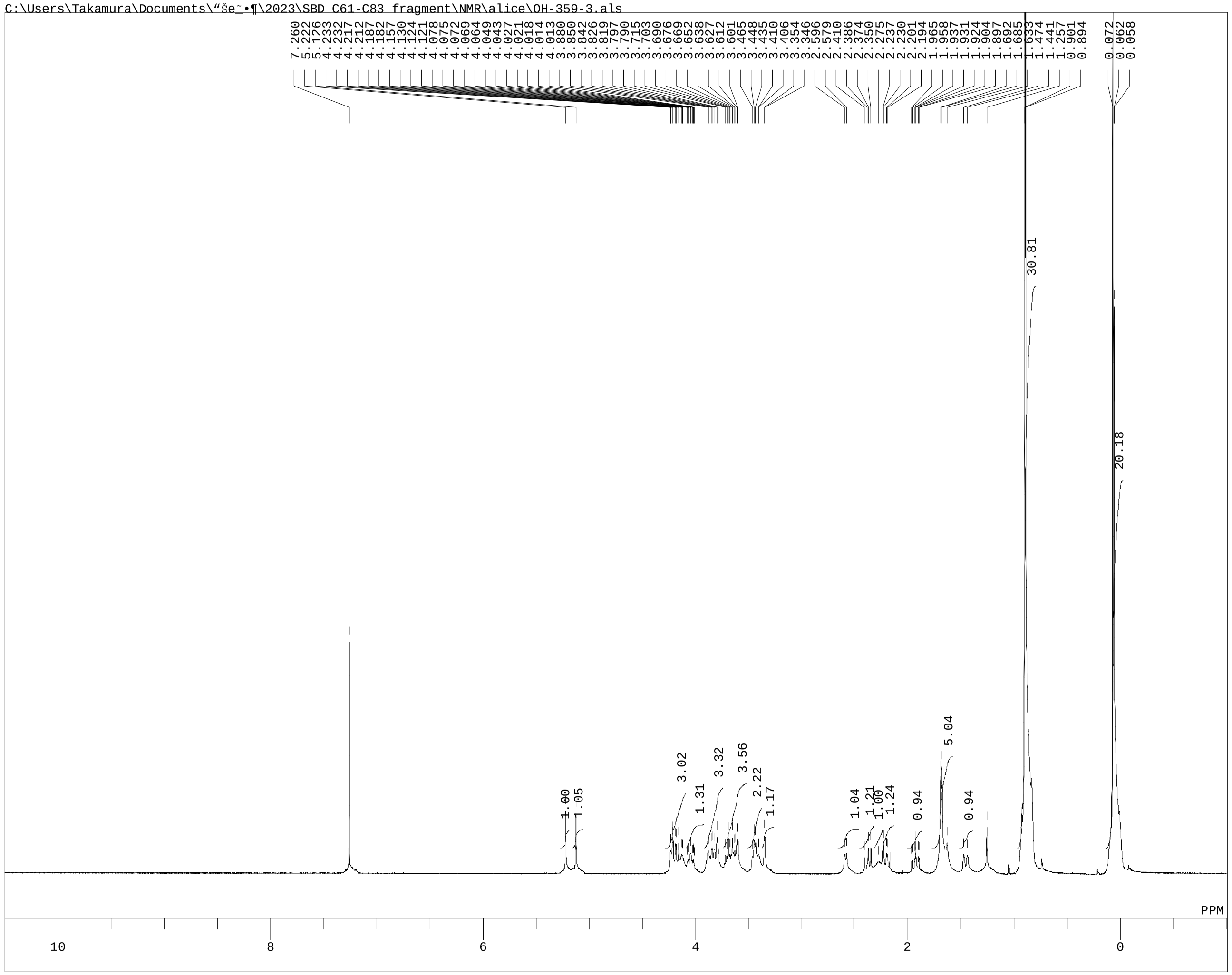
HMBC (600 MHz, CD_3OD)



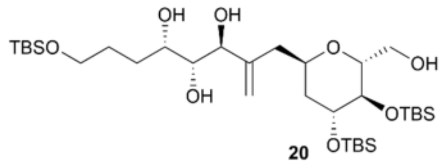
3a



C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-359-3.als



DFILE OH-359-3.als
COMNT
DATIM Tue Jan 30 22:11:20 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14



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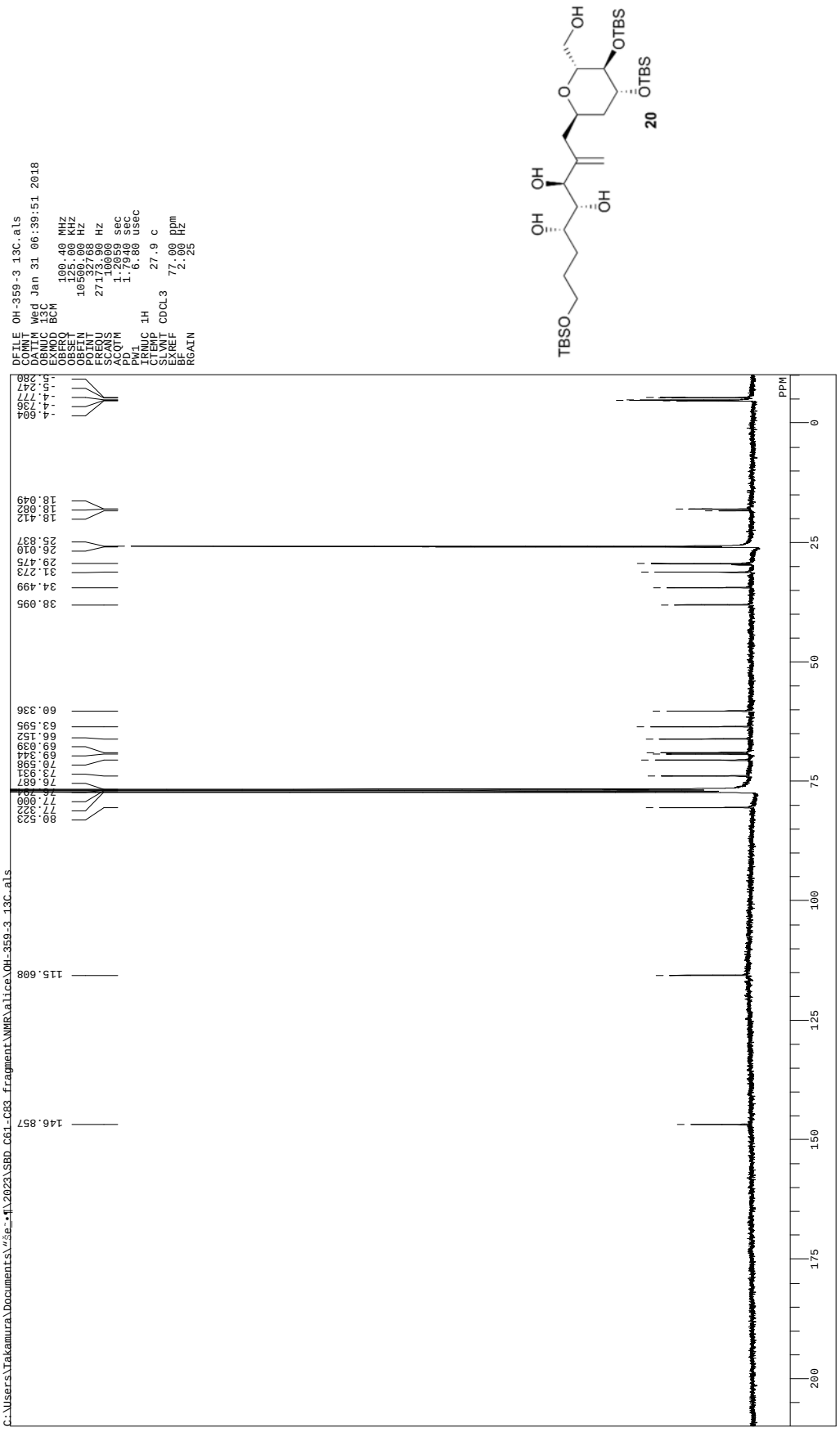
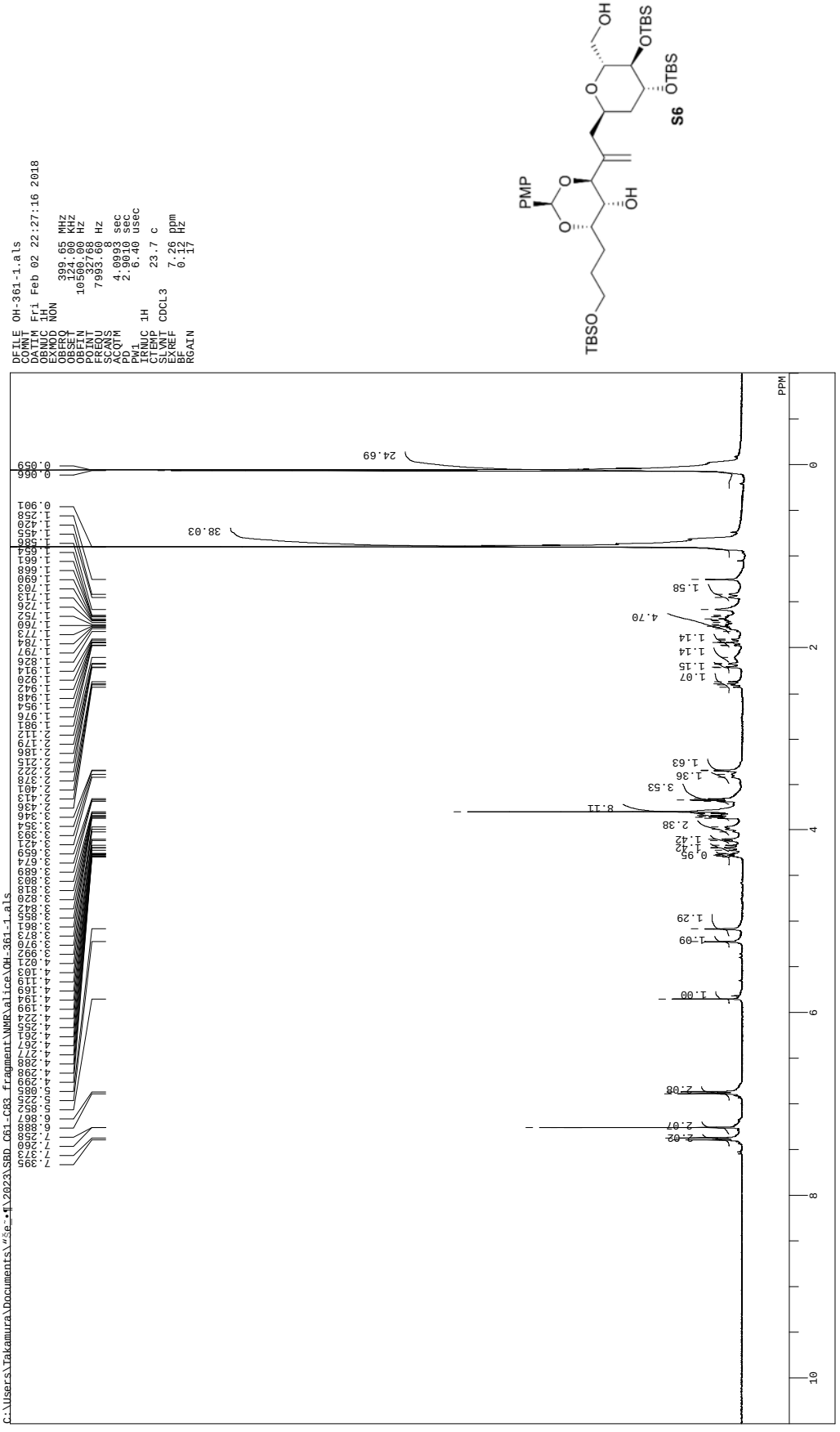
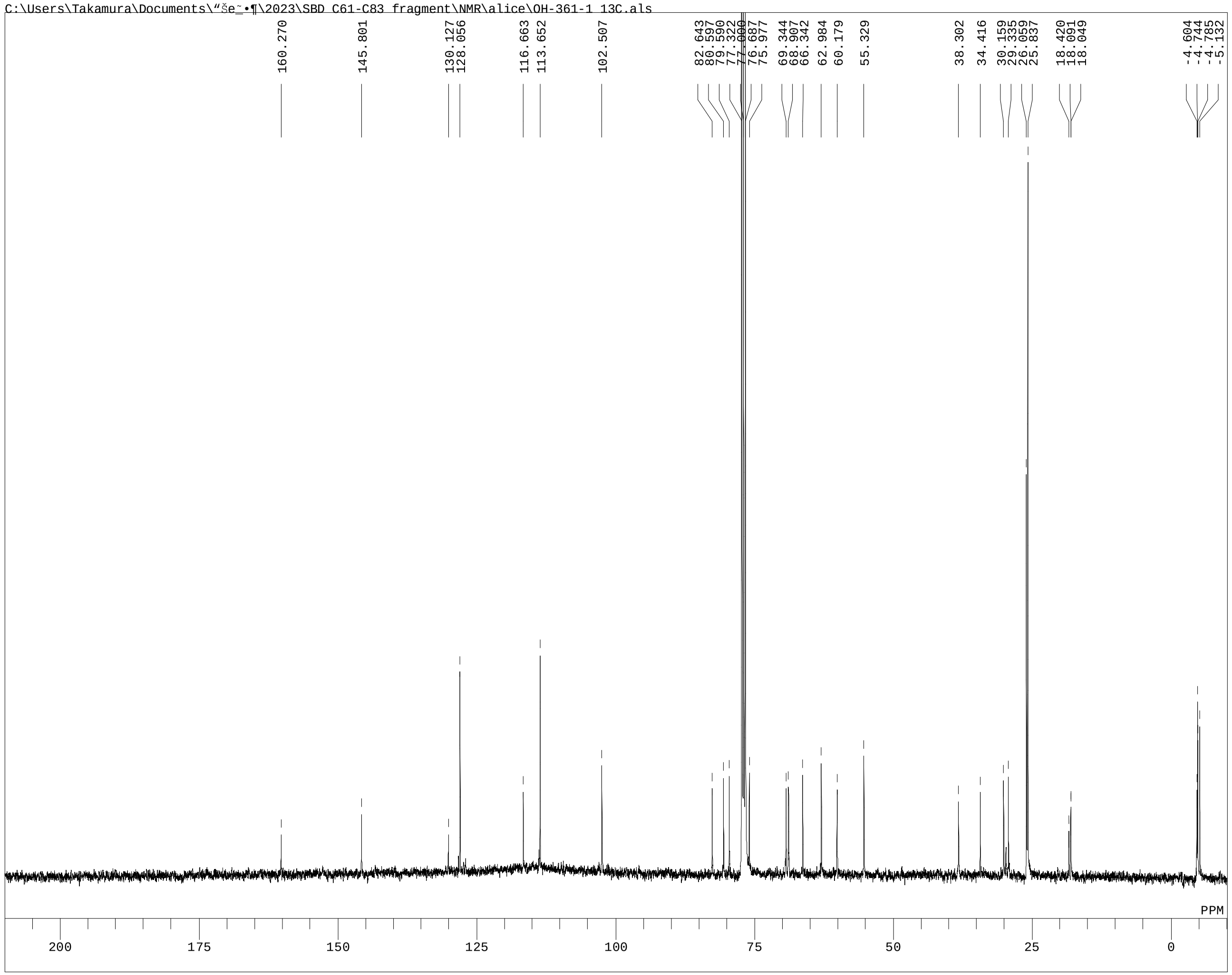
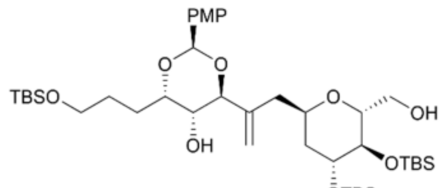

C:\Users\Takamura\Documents\"$e_•¶\2023\SBD_CG1_C83_fragment\NMR\alice\OH-359-3_13C.als
DFILE OH-359-3 13C.als
COMNT
DATIM Wed Jan 31 06:39:51 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 105603.7 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 1000 sec
ACQTM 1.2949 sec
PD 6.80 usec
PW1
IRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 HZ
RGAIN 25
-5.280
-5.247
-4.777
-4.736
-4.604
18.049
18.082
18.412
25.837
26.010
29.475
31.273
34.499
38.095
60.336
63.595
66.152
69.039
69.244
70.598
73.931
76.687
77.000
77.323
80.523
115.608
146.857
PPM
0
25
50
75
100
125
150
175
200
TBSO
OH
OH
OH
OTBS
OTBS
O
20

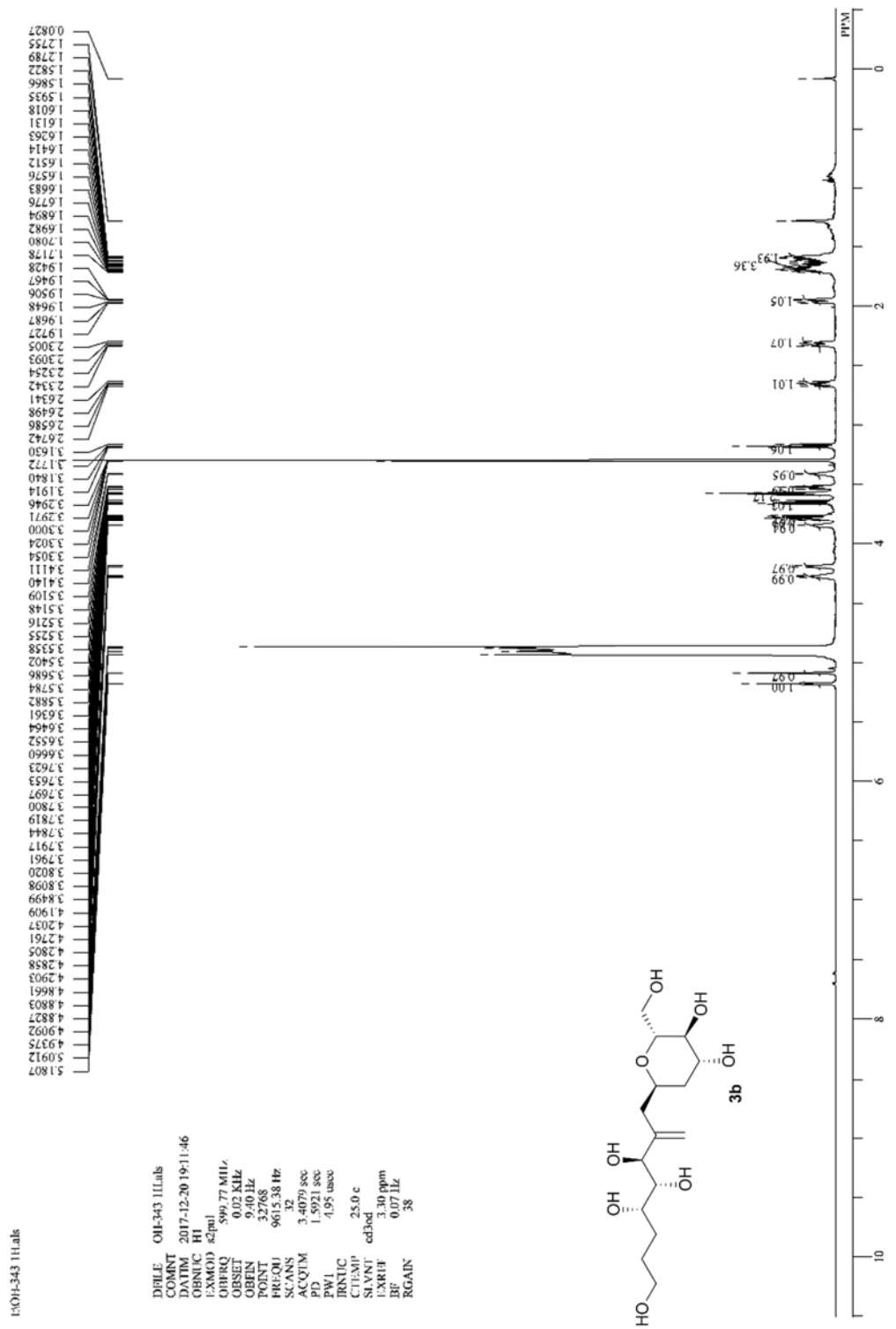

DFILE OH-361-1.als
COMNT
DATIM Fri Feb 02 22:27:16 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105907.60 Hz
POINT 7993.60 Hz
FREQU 8
SCANS 4.0993 sec
ACQTM 2.9010 sec
PD 0.540 usec
PW1
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3 7.26 ppm
EXREF 0.12 HZ
RGAIN 0.17
C:\Users\Takamura\Documents\ﾍﾟｰｼﾞ_1\2023\SBD_C61-C83_fragment\NMR\alice\OH-361-1.als
PPM
TBSO
PMP
OH
OTBS
OTBS
OH
S6

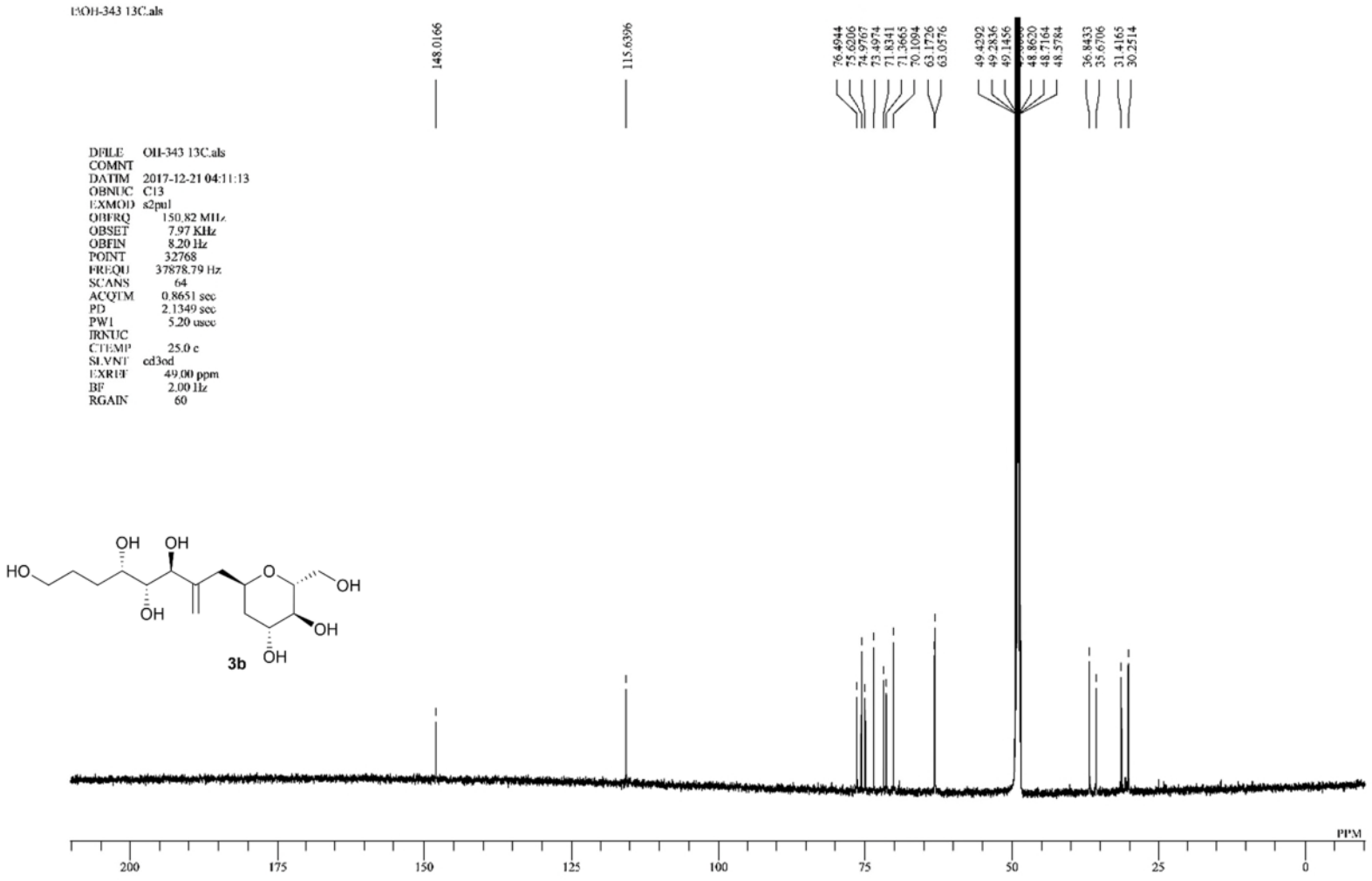


DFILE OH-361-1 13C.als
COMNT
DATIM Sat Feb 03 06:52:00 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 10000
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25

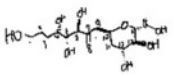


S6


EOH-343 1H.als
DATE OH-343 1H.als
COMNT
DATIM 2017-12-20 19:11:46
OBNUC H1
EXMOD s2pul
OBFRQ 599.77 MHz
OBSET 0.02 KHz
OBFIN 9.40 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 4.95 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.07 Hz
RGAIN 38
3b
PPM


OH-343 13C.als
148.0166
115.6396
76.4944
75.6206
74.9767
73.4974
71.8341
71.3665
70.1094
63.1726
63.0576
49.4292
49.2836
49.1456
48.8620
48.7164
48.5784
36.8433
35.6706
31.4165
30.2514
DFILE OH-343 13C.als
COMNT
DATIM 2017-12-21 04:11:13
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.97 KHz
OBFIN 8.20 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.20 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 2.00 Hz
RGAIN 60
HO
OH
OH
OH
O
OH
OH
OH
3b
PPM
200
175
150
125
100
75
50
25
0

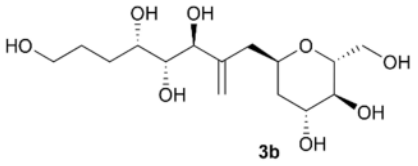
COSY



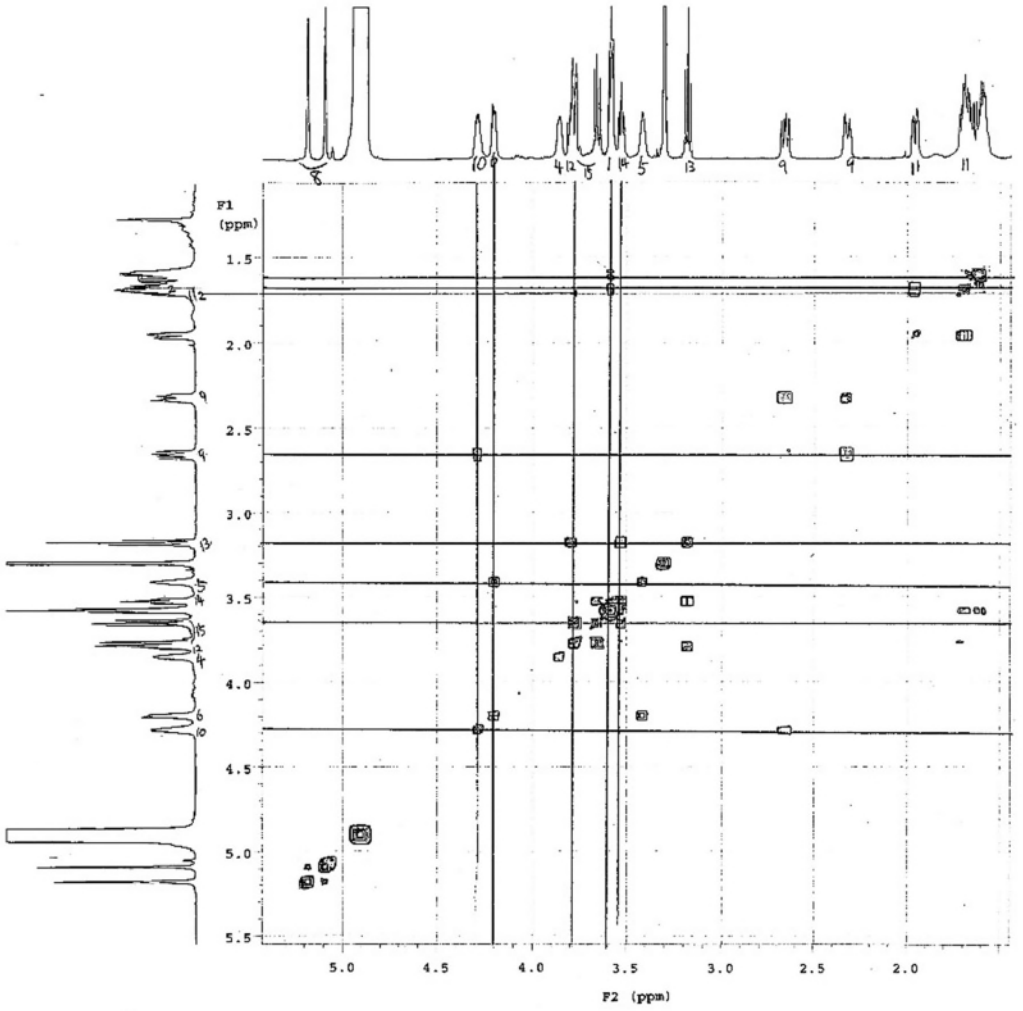
exp3 gCOSY

SAMPLE		FLAGS	
date	Dec 20 2017	hs	nn
solvent	cdjod	sspul	y
sample		hsglvl	6408
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	38
np	2884	spin	0
fb	4096	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.090	sbs	not used
nt	16	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.621
ni	200	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	864.1
TRANSMITTER		wp	2385.1
tn	H1	spl	637.6
sfrq	599.770	wp1	2690.2
tof	599.7	rf1	3196.4
tpwr	59	rfp	1979.3
pw	9.900	rf11	3196.2
GRADIENTS		rfp1	1979.3
grlvl2	5347	PLOT	
gt2	0.001000	wc	198.0
EDratio	1.000	sc	0
gstab	0.000500	wc2	198.0
DECOUPLER		sc2	0
dn	C13	vs	282
dm	nnn	th	2
		ai cdc av	

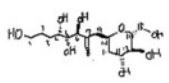
$^{1}H–^{1}H$ COSY (600 MHz, CD_3OD)



3b

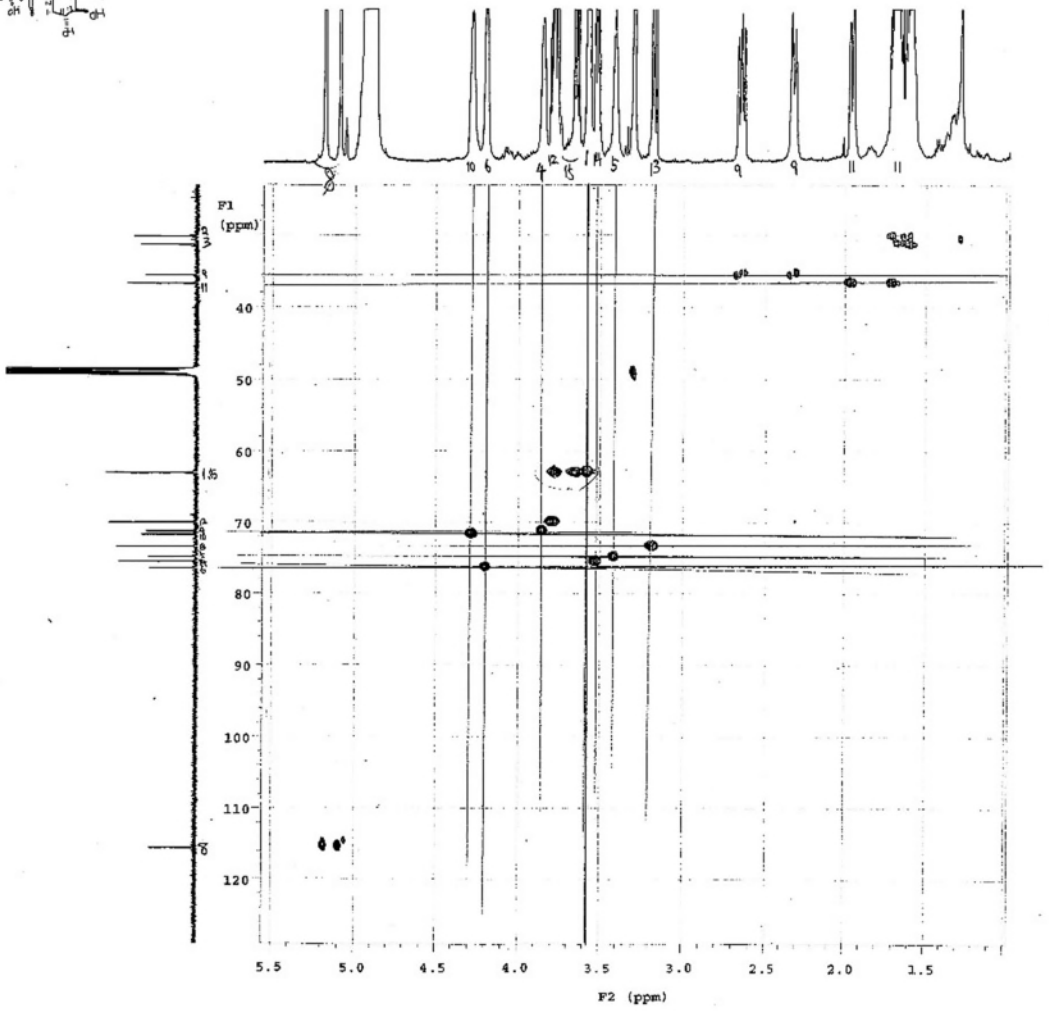


HMQC

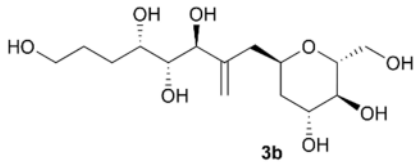


exp1 gHMQC

SAMPLE		FLAGS		ACQUISITION ARRAYS	
date	Dec 20 2017	hs	nn	array	phase
solvent	cd3od	sspul	y	arrayelem	400
sample		PFGflg	y		
ACQUISITION		hsglvl	5408	i	phase
sw	9615.4	SPECIAL		1	1
at	0.150	temp	not used	2	2
np	2884	gain	60		
fb	4000	spin	0		
ns	32	GRADIENTS			
d1	1.000	gslvlE	5347		
nt	32	gtE	0.602000		
2D ACQUISITION		EDratio	3.977		
sw1	36199.1	gstab	0.600500		
ni	200	F2 PROCESSING			
phase	arrayed	gf	0.069		
PRESATURATION		gfs	not used		
satmode	n	fn	4096		
wat	n	F1 PROCESSING			
TRANSMITTER		gf1	0.065		
tn	H1	gfs1	not used		
sfrq	599.770	proc1	lp		
tof	599.7	fn1	2048		
tpwr	59	DISPLAY			
pw	9.800	sp	584.8		
DECOUPLER		wp	2746.6		
dn	C13	spl	3475.7		
dof	789.1	wp1	15978.5		
dm	any	rf1	3188.0		
dmm	waltz16	rfp	1979.3		
dmf	35088	rfl1	10241.9		
dpwr	40	rfp1	7389.8		
pwxlvl	59	PLOT			
pwx	9.900	wc	198.0		
HMQC		sc	0		
jlxh	146.0	wc2	198.0		
nullflg	y	sc2	0		
mult	2	vs	282		
		th	2		
		al cdc ph			

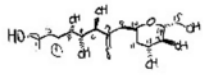


HMQC (600 MHz, CD_3OD)



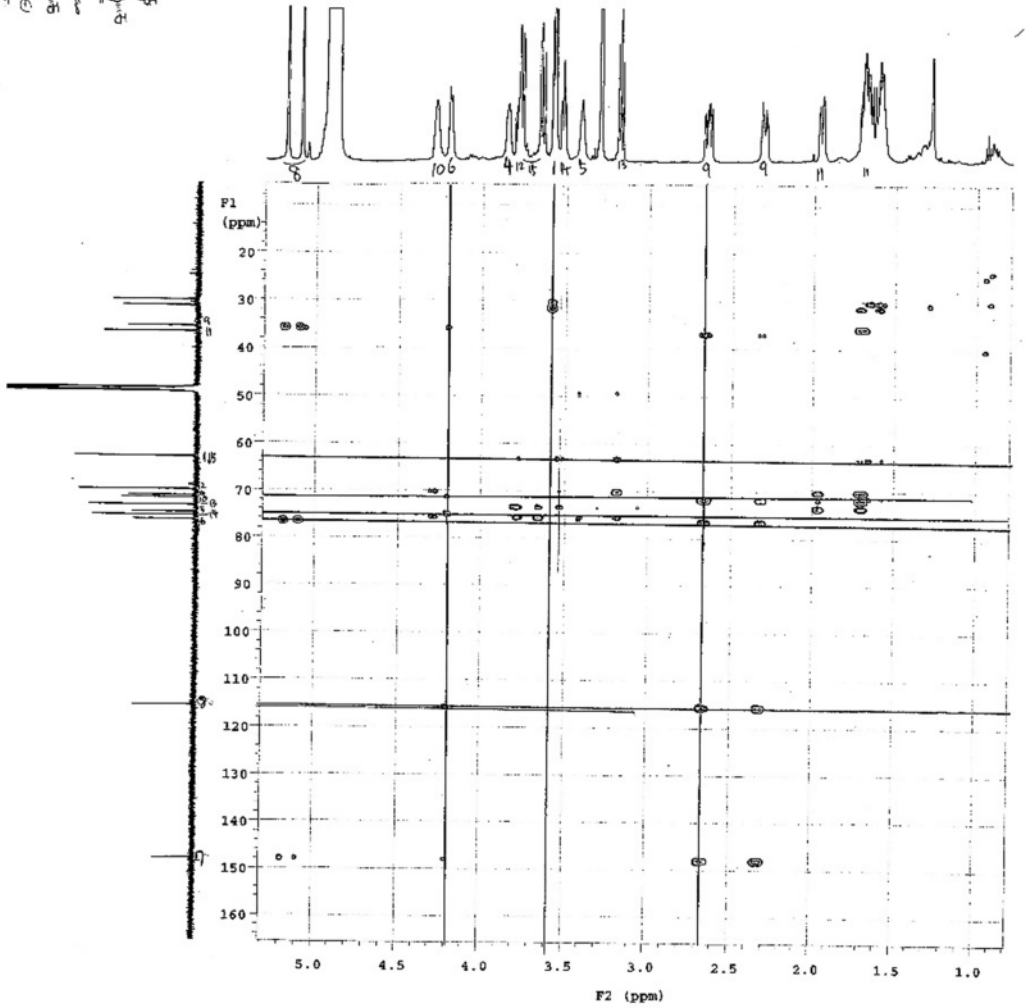
3b

HMBC

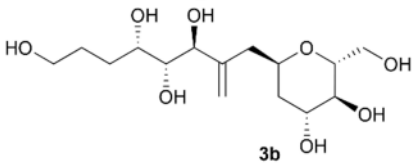


exp3 SHMBCAD

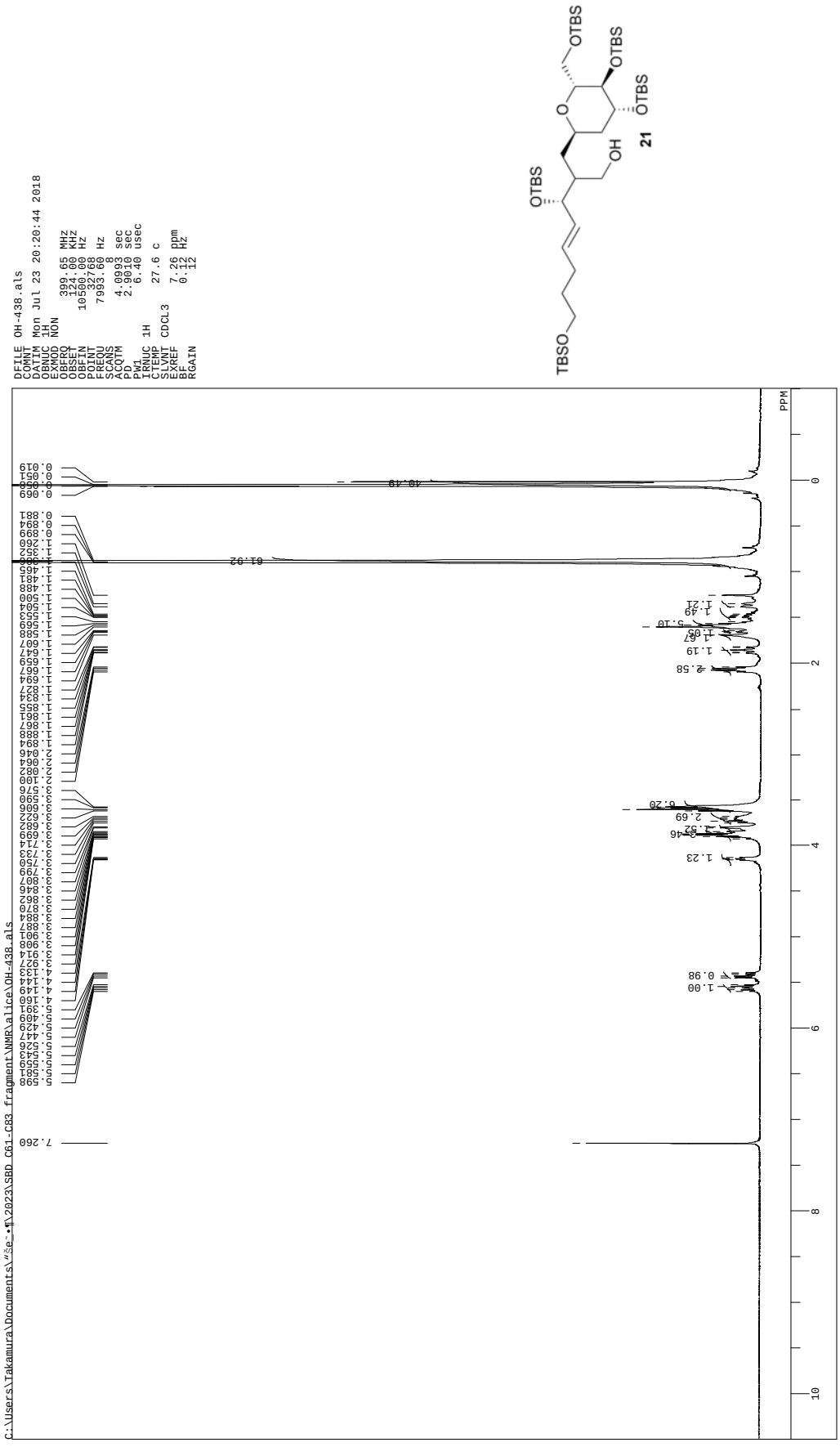
SAMPLE		FLAGS		ACQUISITION ARRAYS	
date Dec 20 2017		hs	nn	array	phase
solvent cd3od		sspul	y	arraydim	400
sample		PFGflg	y		
ACQUISITION		hsglvl	6408	1	phase
sw	9615.4	SPECIAL		1	1
at	0.150	temp	not used	2	2
np	2884	gain	60		
fb	4000	spin	0		
ss	32	GRADIENTS			
d1	1.000	gzlvl1	500		
nt	32	gt1	0.001000		
2D ACQUISITION		gzlvl3	1500		
sw1	36199.1	gt3	0.001000		
ni	200	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
PRESATURATION		sb	-0.075		
satmode	n	sbs	not used		
wet	n	fn	4096		
TRANSMITTER		F1 PROCESSING			
tn	H1	gf1	0.005		
sfrq	599.770	gfs1	not used		
tof	599.7	proc1	lp		
tpwr	55	fn1	2048		
pw	9.500	DISPLAY			
DECOUPLER		sp	472.1		
dn	C13	wp	2713.7		
dof	1542.4	sp1	847.0		
dm	nnn	wp1	24109.2		
decwave	W40_onesmx	rf1	3187.9		
dmf	35088	rfp	1979.2		
dpwr	40	rfl1	9441.5		
pwx1vl	59	rfp1	7389.8		
pwx	8.900	PLOT			
HMBC		wc	198.0		
j1xh	146.6	sc	0		
jnxh	8.0	wc2	198.0		
ADIABATICIC		sc2	0		
pwx180ad	chomsx_ad-	vs	1343		
	300	th	4		
pwx1vl180	54	ai cdc av			
pwx180	400.0				



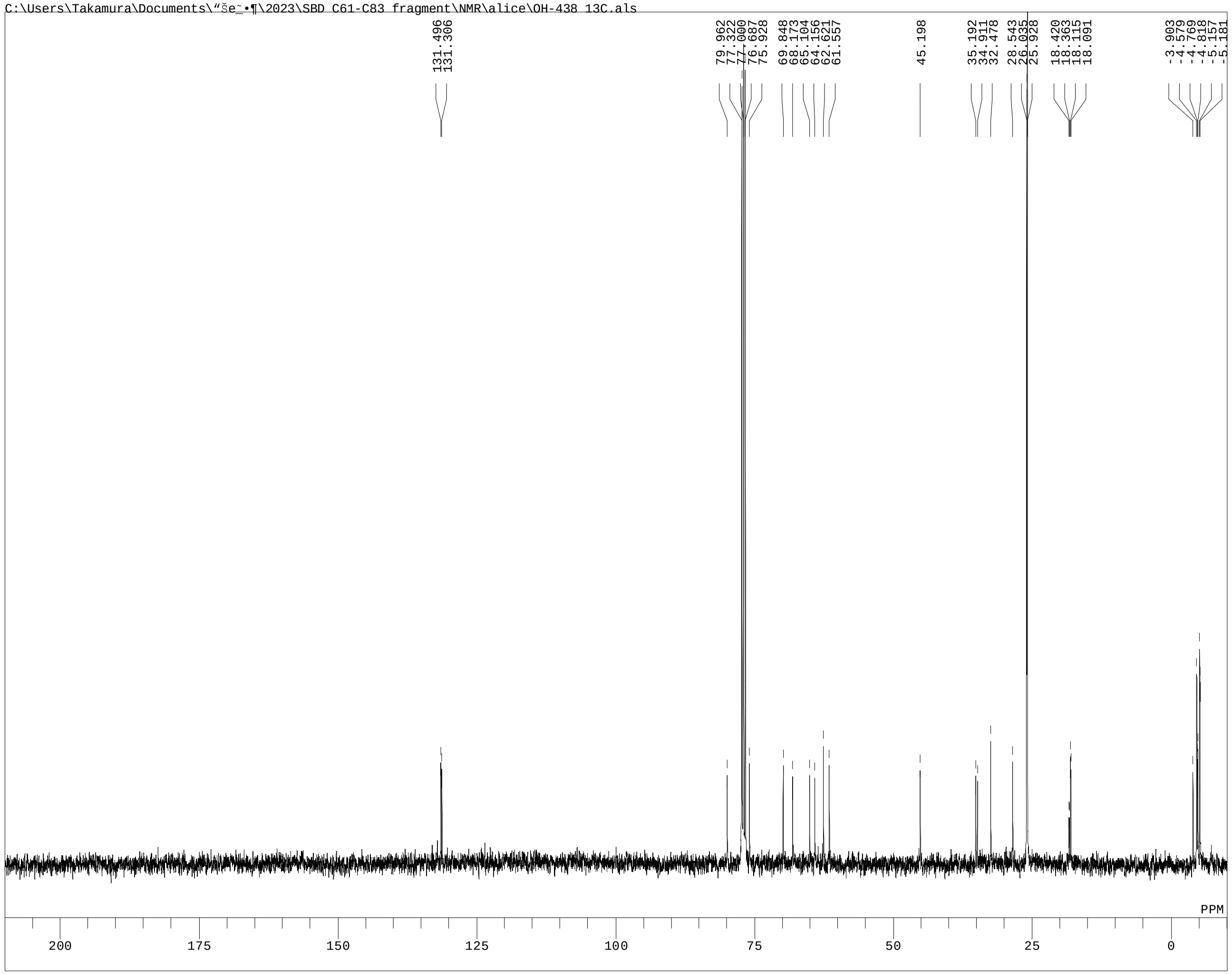
HMBC (600 MHz, CD_3OD)



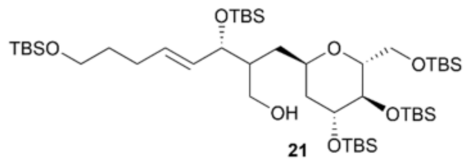
3b


DFILE OH-438.als
COMNT
DATIM Mon Jul 23 20:20:44 2018
OBNUC 1H
EXMOD NON
OBSET 399.65 MHz
OBFIN 124.00 KHz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TRNUC 1H
STEMP 27.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN
C:\Users\Takamura\Documents\ﾍﾟｰｽﾄ\2023\SBD_C61-C83_fragment\NMR\alice\OH-438.als
PPM
TBSO
OTBS
OH
OTBS
OTBS
21

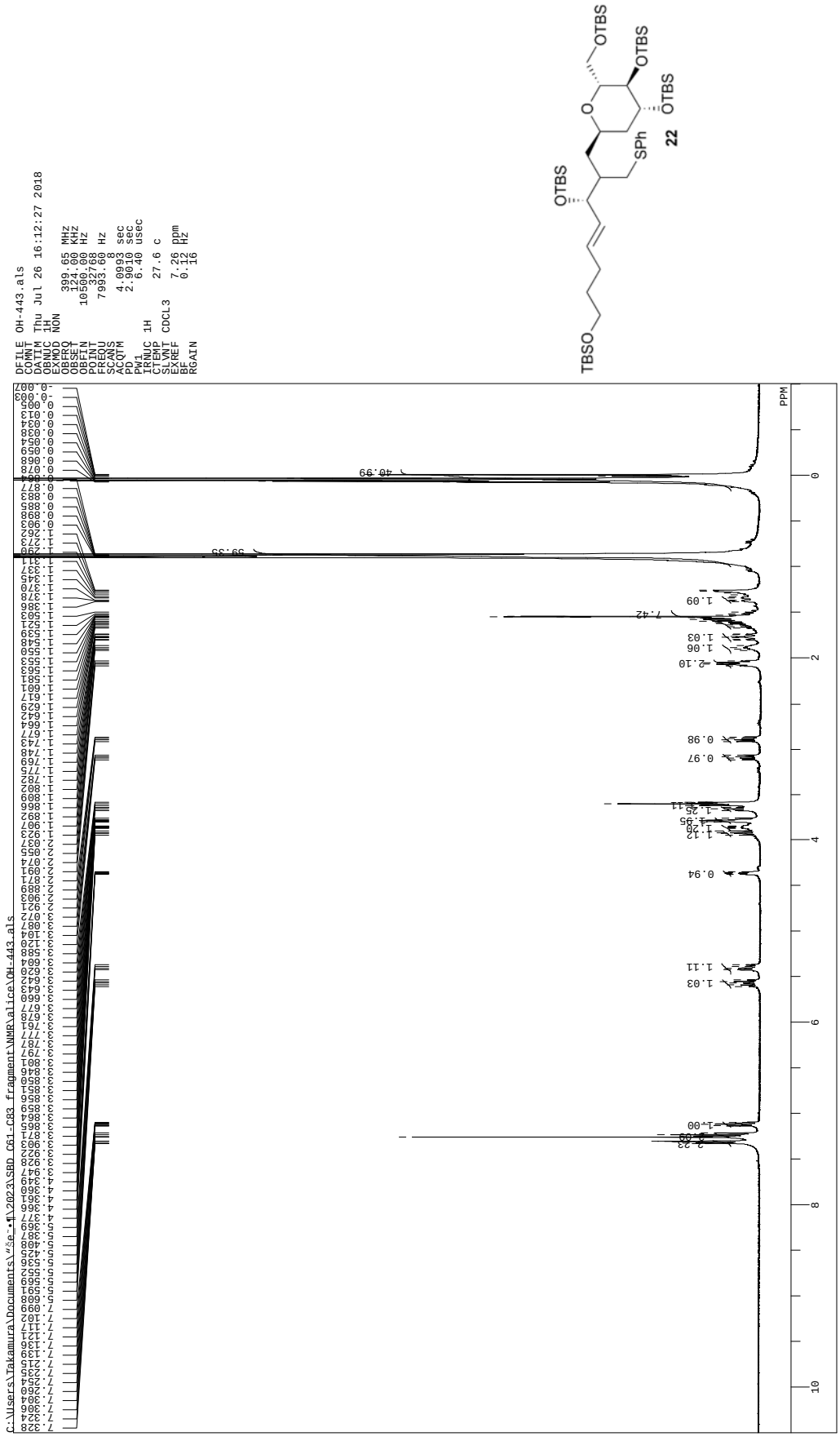
C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-438 13C.als

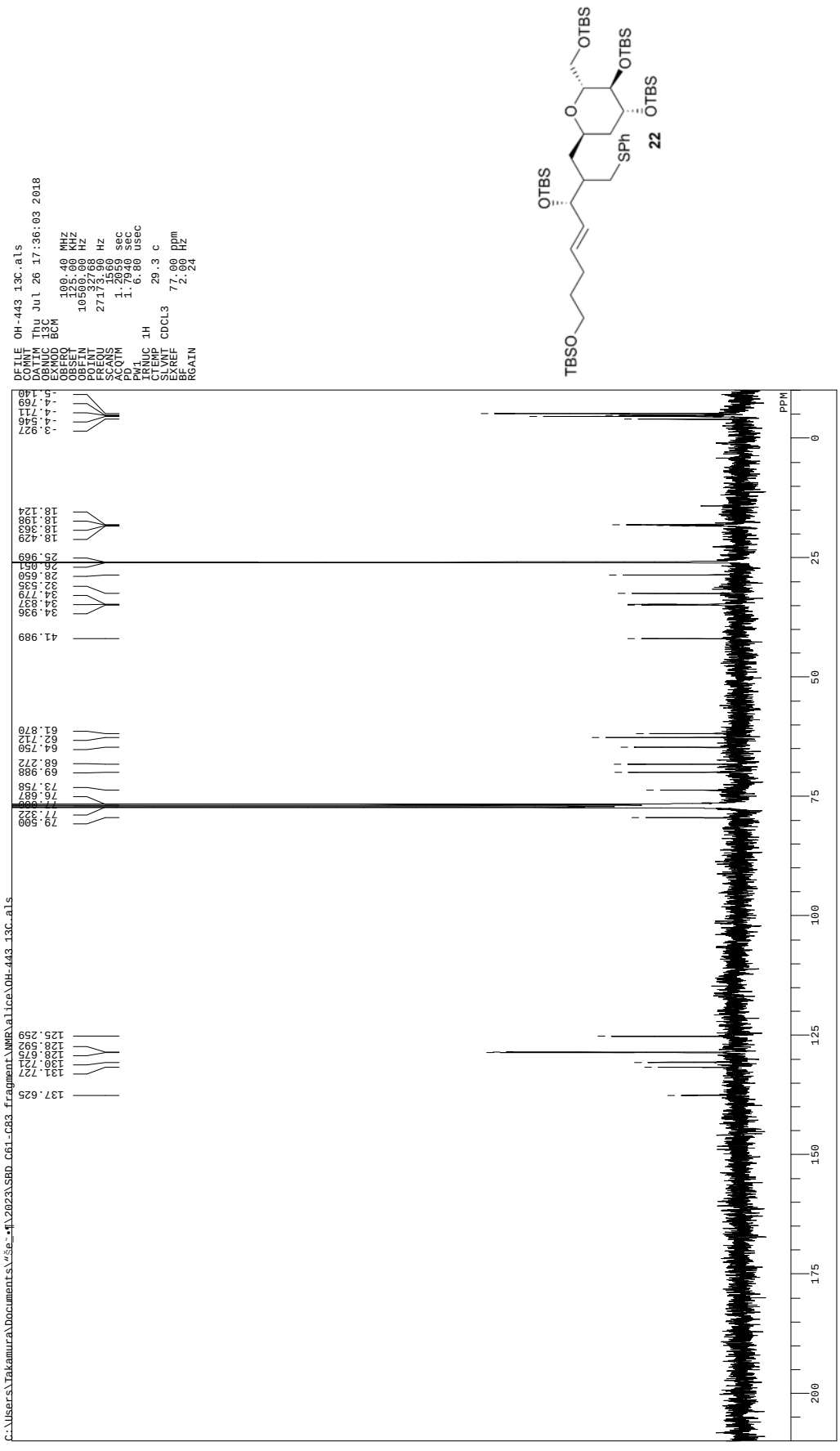


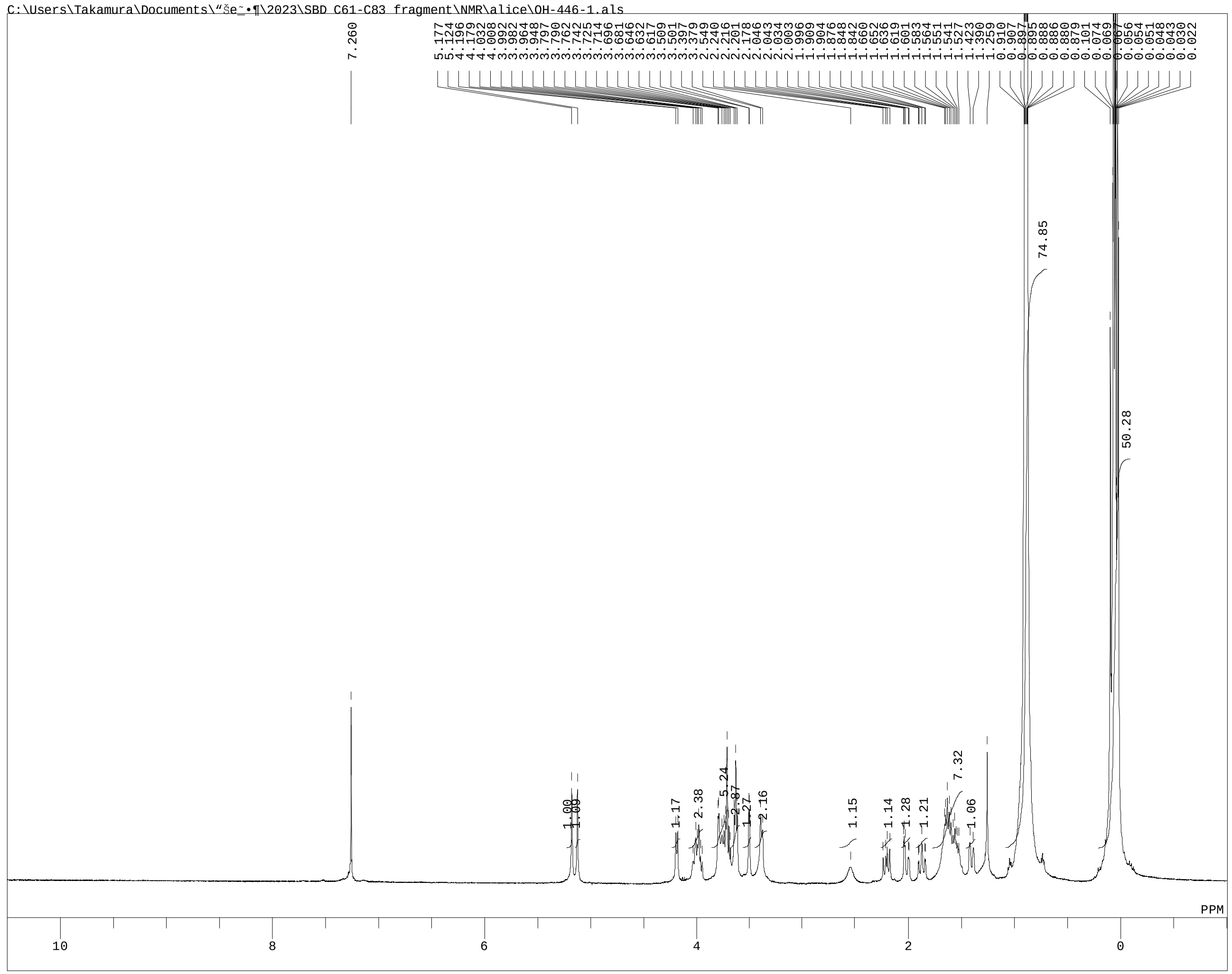
DFILE OH-438 13C.als
COMNT
DATIM Mon Jul 23 20:54:16 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 560
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24



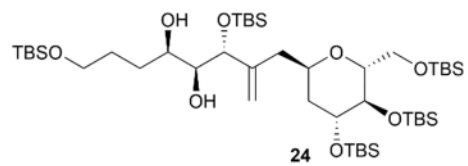
21


OTBS
OTBS
OTBS
O
SPh
TBSO
22

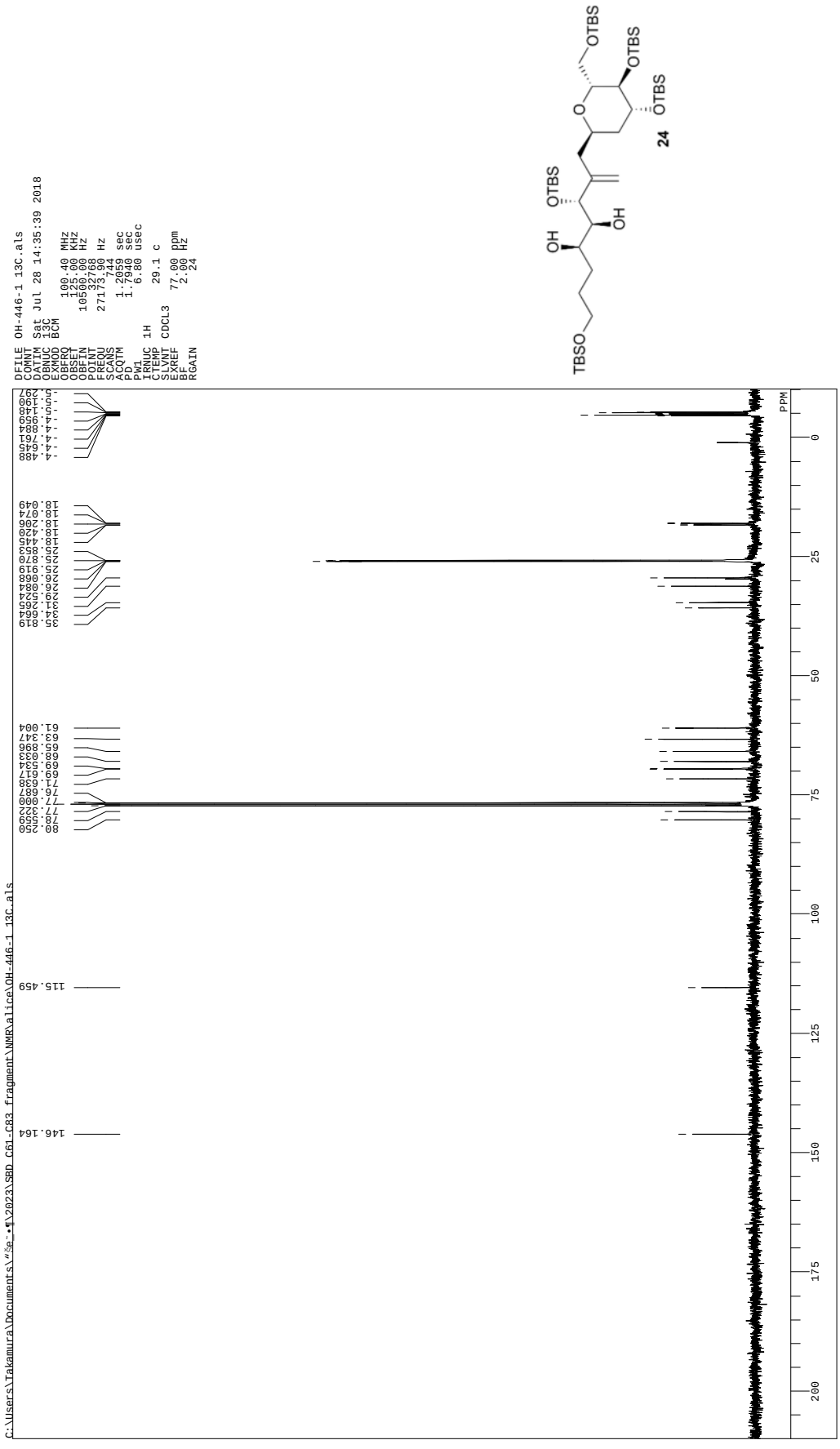

OTBS
OTBS
OTBS
O
SPh
TBSO
22
DFILE OH-443 13C.als
COMNT
DATIM Thu Jul 26 17:36:03 2018
OBNUC 13C
EXMOD BCM
OBSET 100.40 MHz
OBFIN 105600.000 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 256
ACQTM 1.7940 sec
PD 1.0000 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.3 c
SLVNT CDCL3 77.00 ppm
EXREF 2.000 Hz
BF 2.24
RGAIN
C:\Users\Takamura\Documents\マウス・¶\202X\SBD_C61-C83_fragment\NMR\alice\OH-443_13C.als
PPM

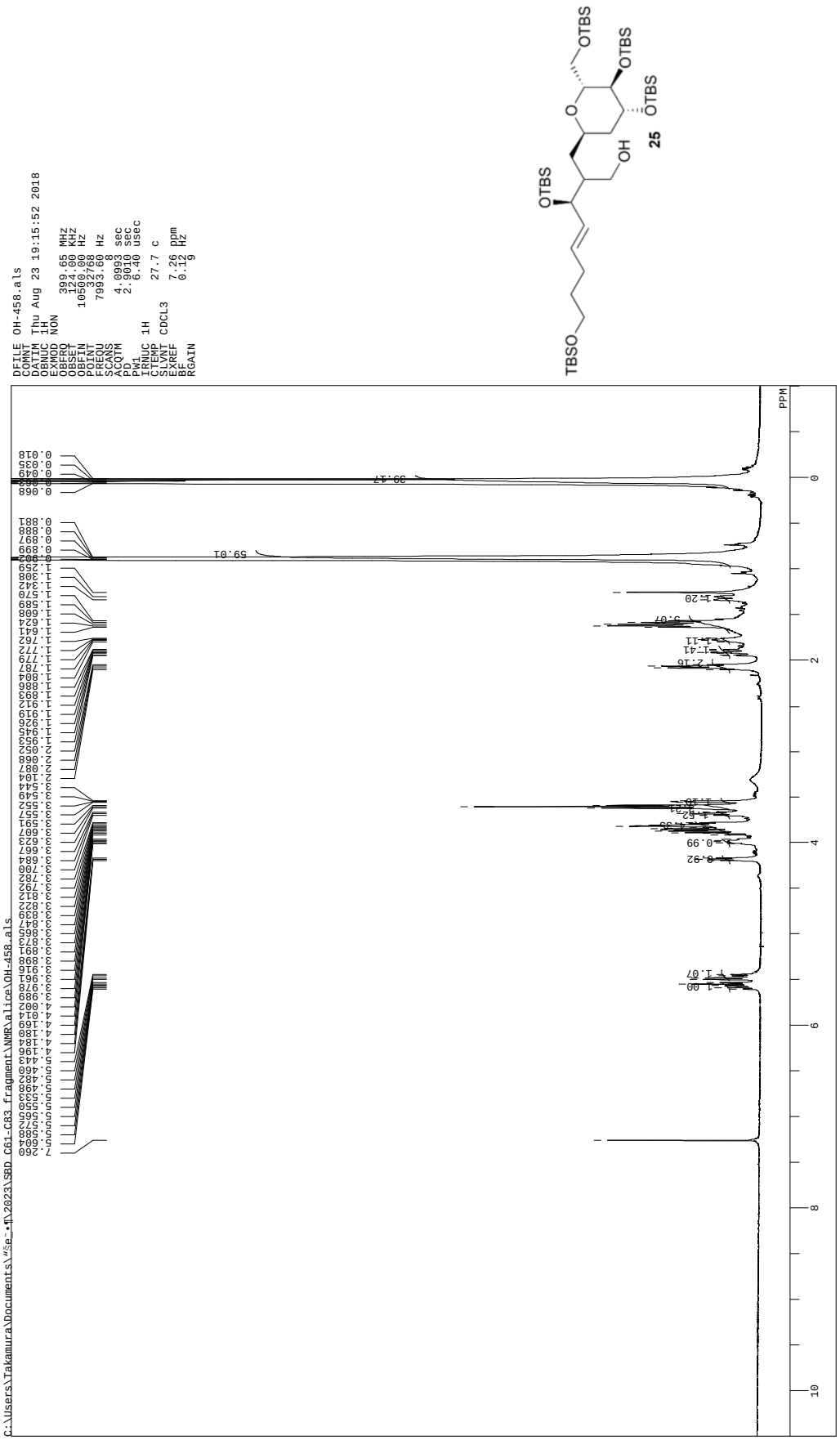


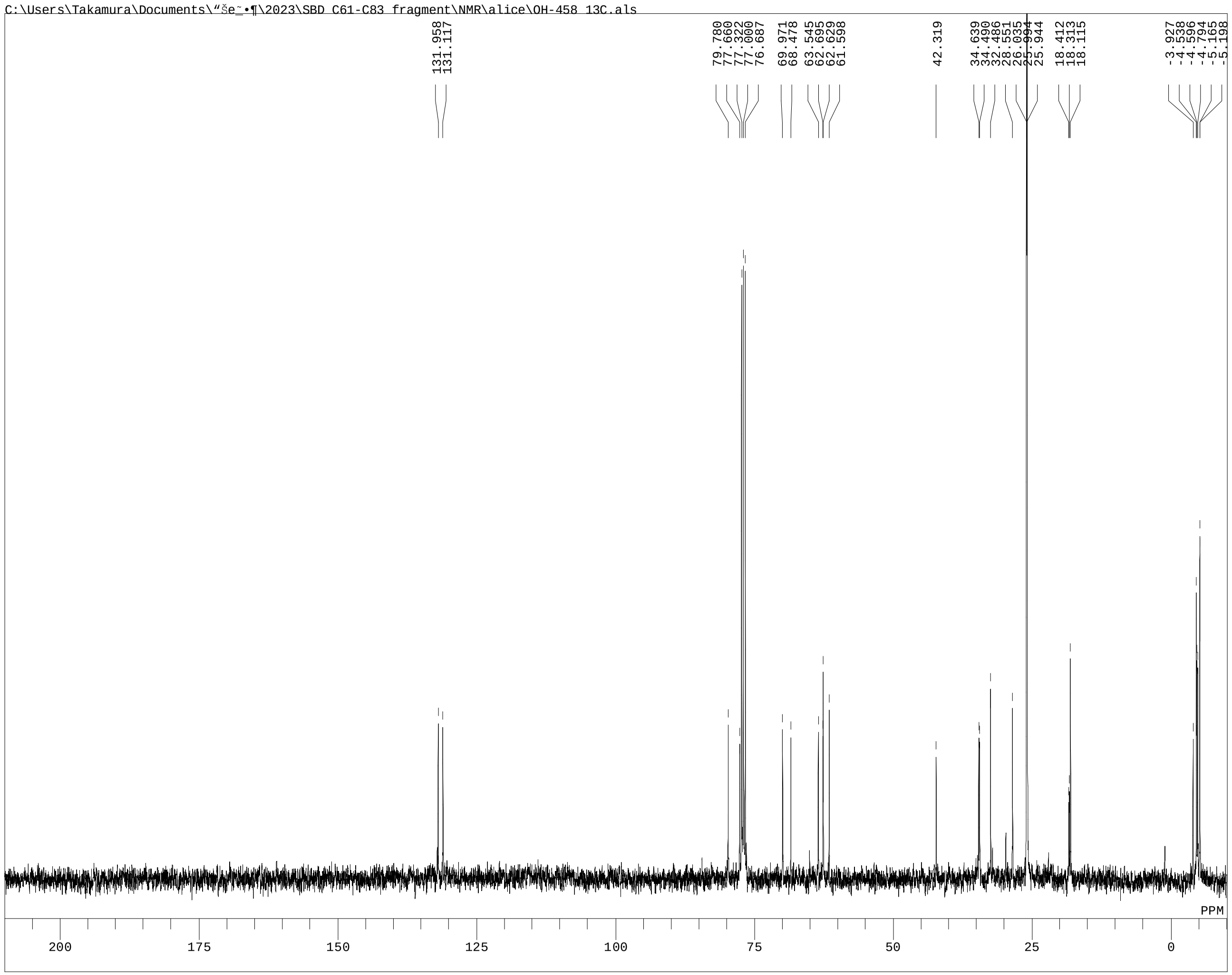
DFILE OH-446-1.als
COMNT
DATIM Sat Jul 28 13:38:24 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 12

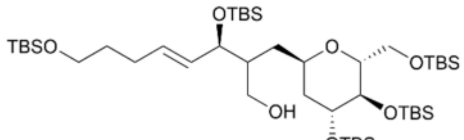


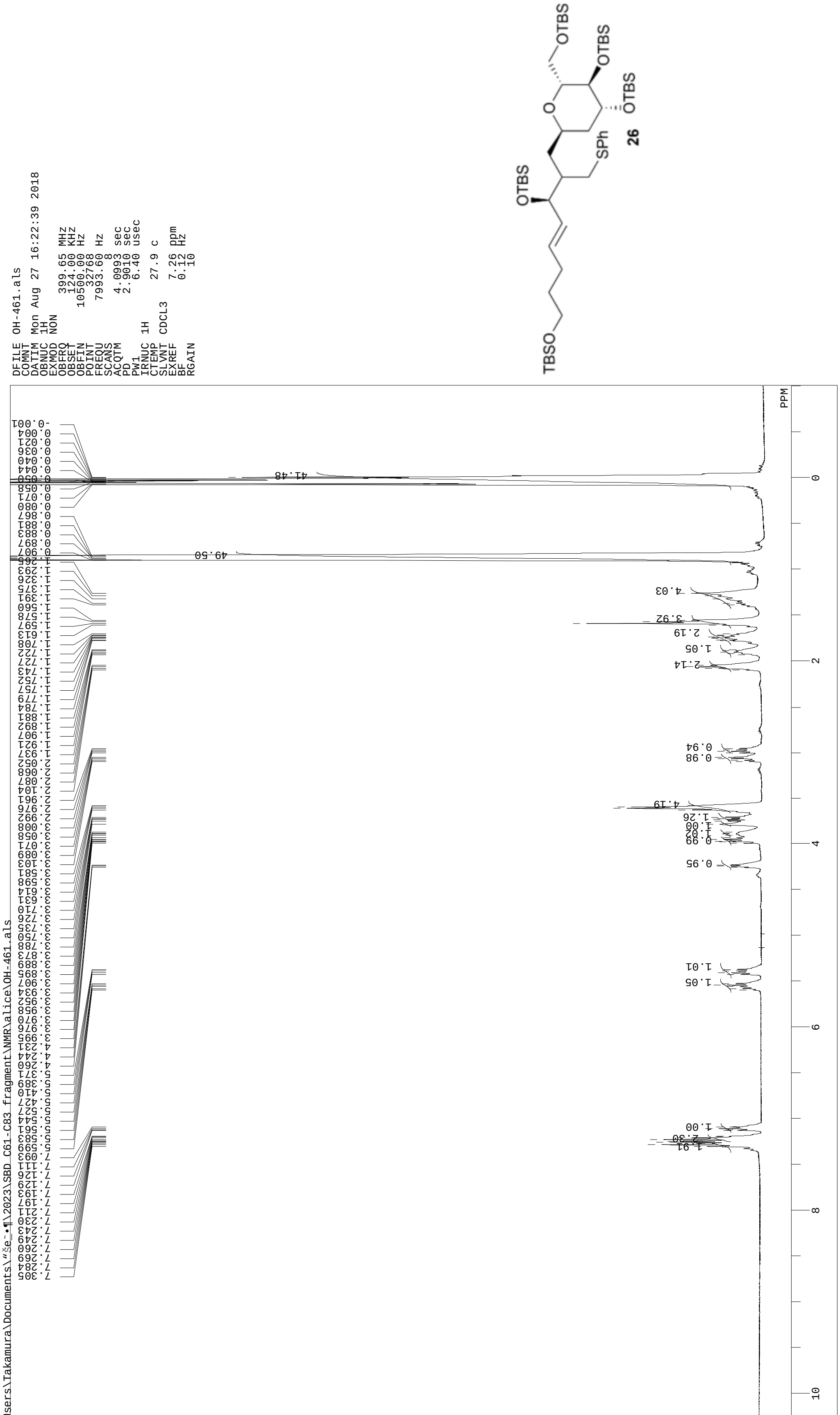
24

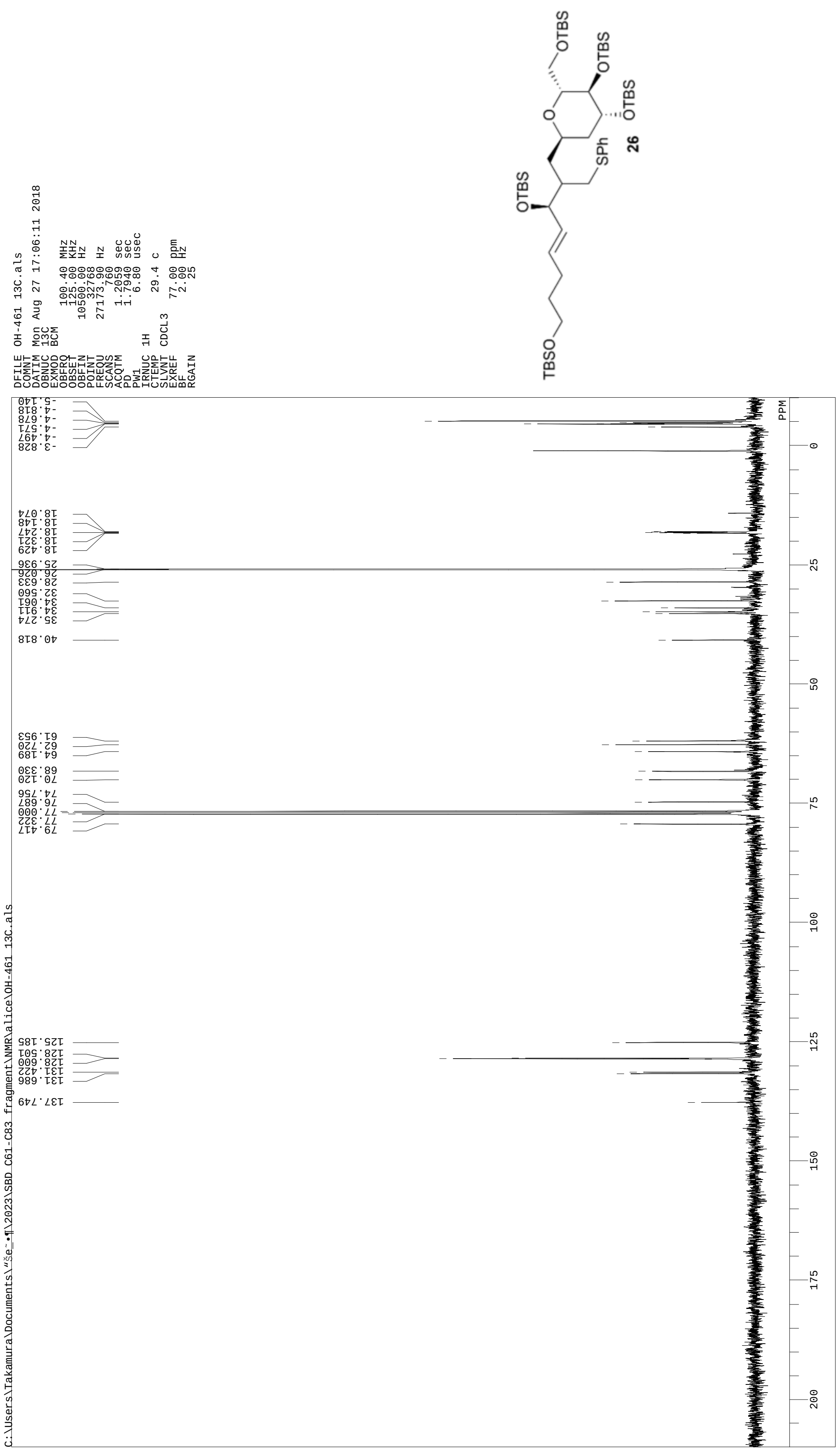

DFILE OH-446-1 13C.als
COMNT
DATIM Sat Jul 28 14:35:39 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.000 KHz
OBFIN 105500.000 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 44
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.1 c
SLVNT CDCL3 77.00 ppm
EXREF 2.00 Hz
BF 24
RGAIN
C:\Users\Takamura\Documents\ベータ\2023\SBD_C61-C83_fragment\NMR\alice\OH-446-1 13C.als
PPM
OTBS
OTBS
OTBS
O
OH
OTBS
OH
TBSO
24


OTBS
OTBS
OTBS
O
OH
TBSO
25
DFILE OH-458.als
COMNT
DATIM Thu Aug 23 19:15:52 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105000.00 Hz
POINT 32768
FREQU 7993.61 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.0010 sec
PW1 6.40 usec
TEMP 27.7 c
SLVNT CDCL3
EXREF 7.26 ppm
RGAIN 0.12
C:\Users\Takamura\Documents\NMR\alice\OH-458.als
PPM


C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-458 13C.als
131.958
131.117
79.780
77.660
77.322
77.000
76.687
69.971
68.478
63.545
62.695
62.629
61.598
42.319
34.639
34.490
32.486
28.551
26.035
25.994
25.944
18.412
18.313
18.115
-3.927
-4.538
-4.596
-4.794
-5.165
-5.198
DFILE OH-458 13C.als
COMNT
DATIM Thu Aug 23 19:31:18 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 240
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25
PPM
200
175
150
125
100
75
50
25
0


TBSO
OTBS
OH
OTBS
OTBS
OTBS
25


TBSO
OTBS
OTBS
OTBS
OTBS
SPh
26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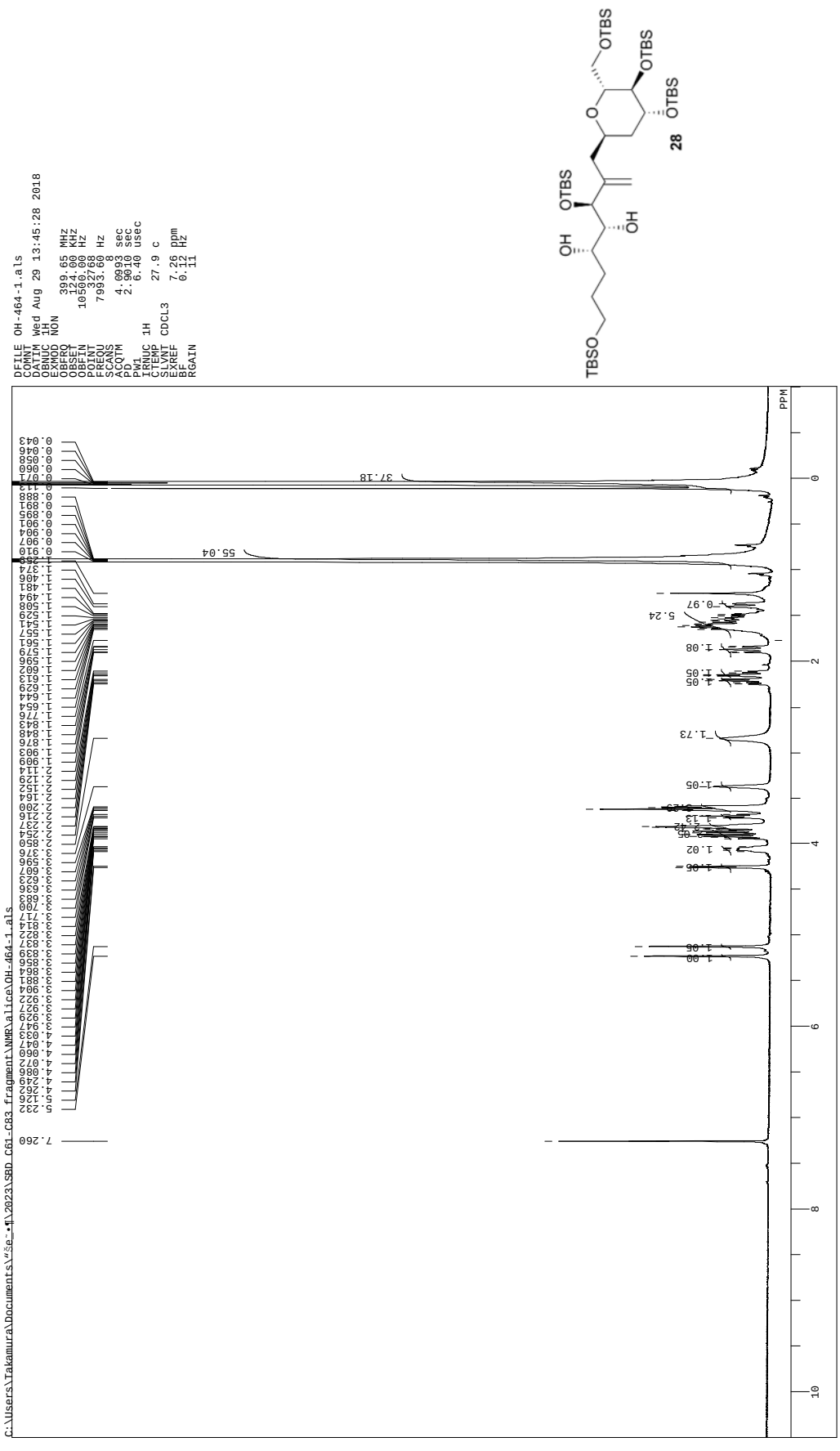
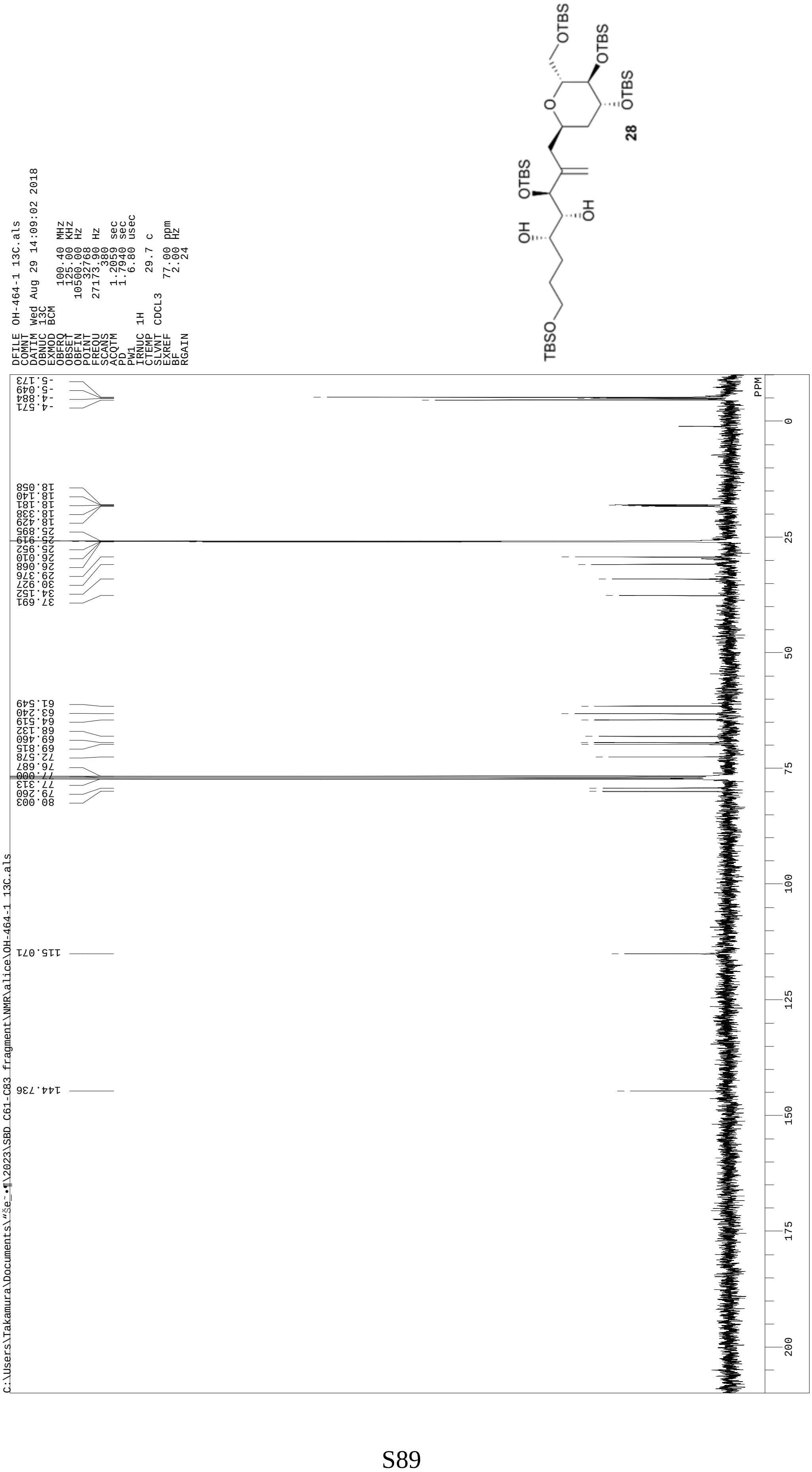
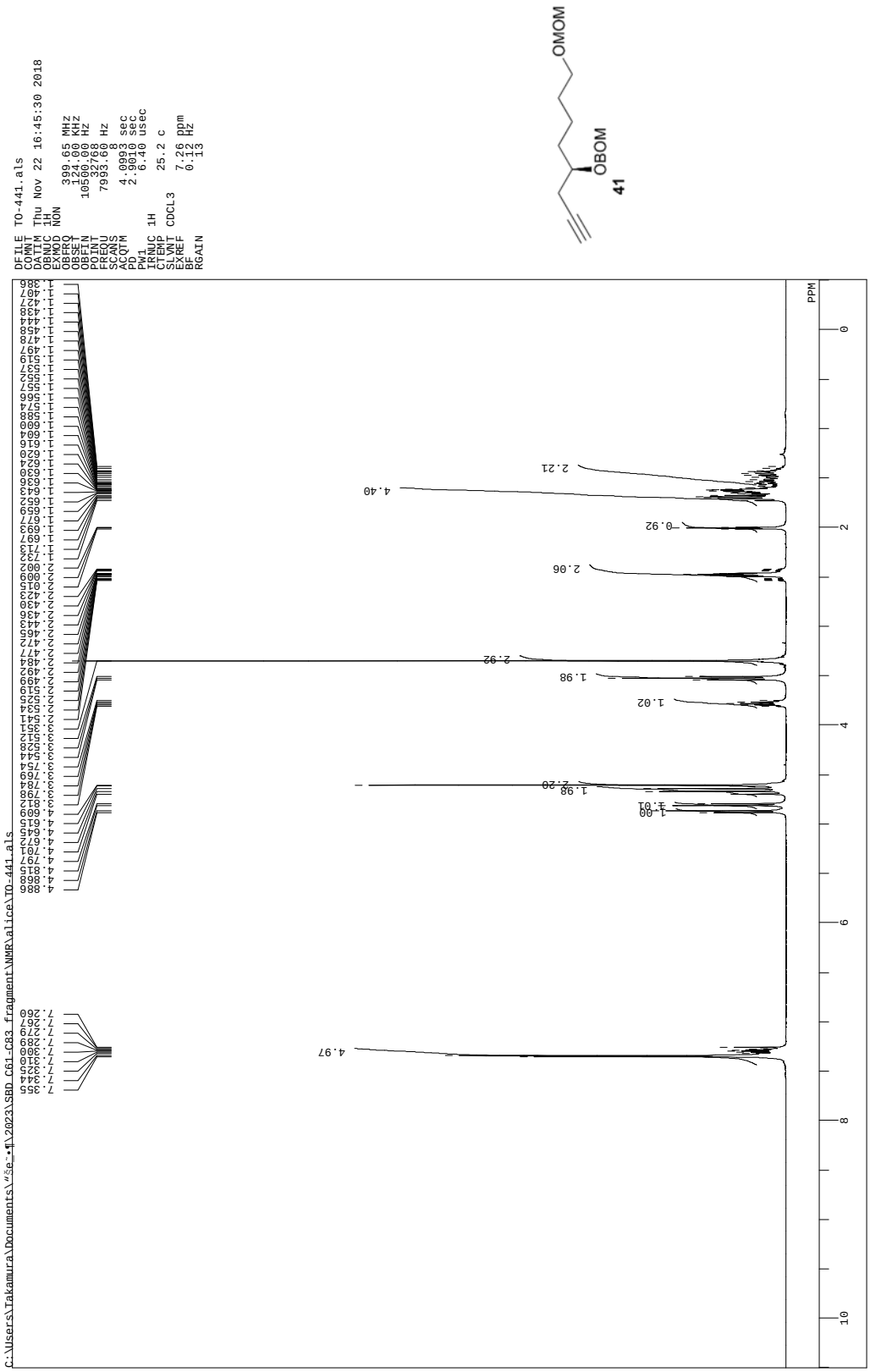
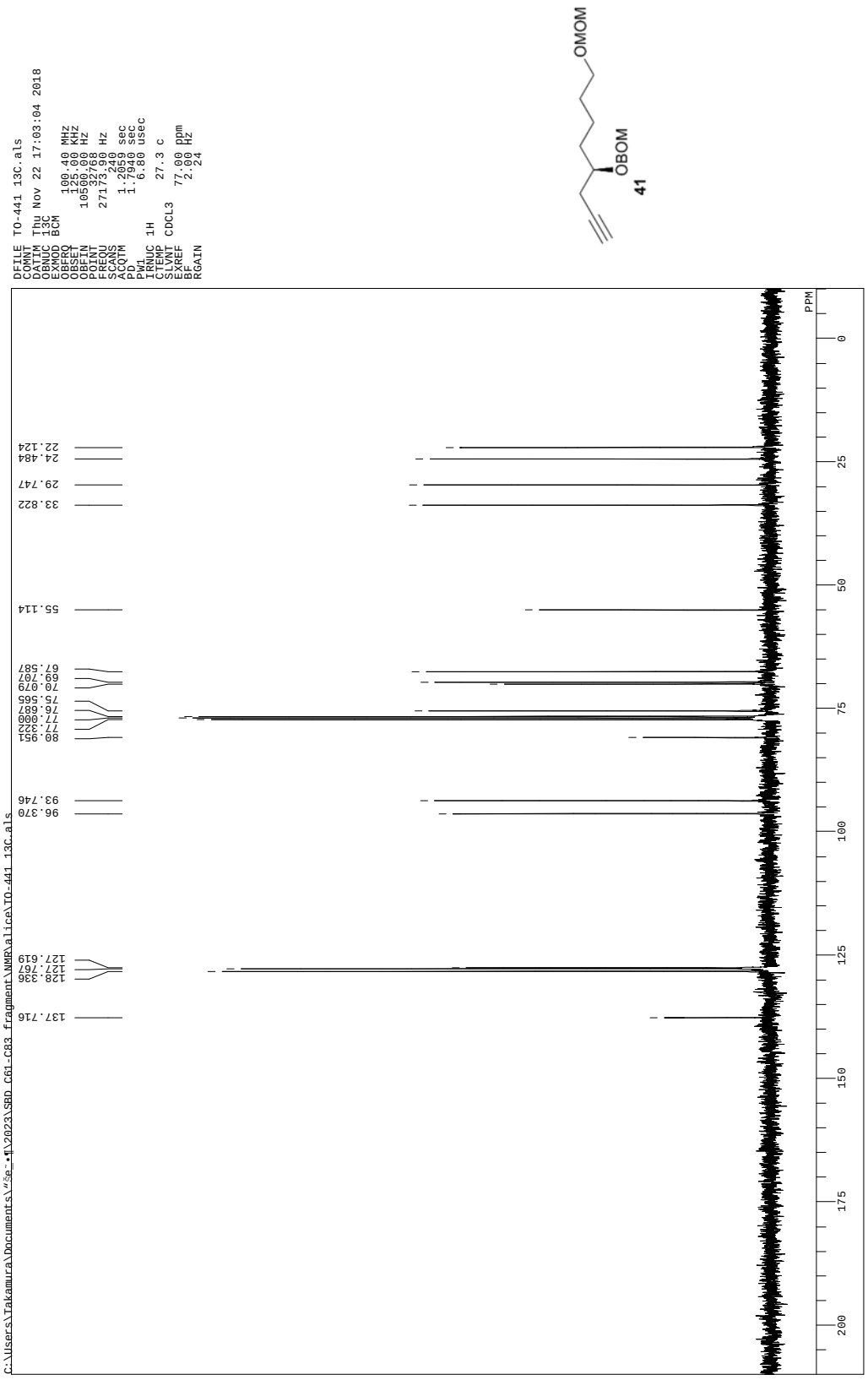
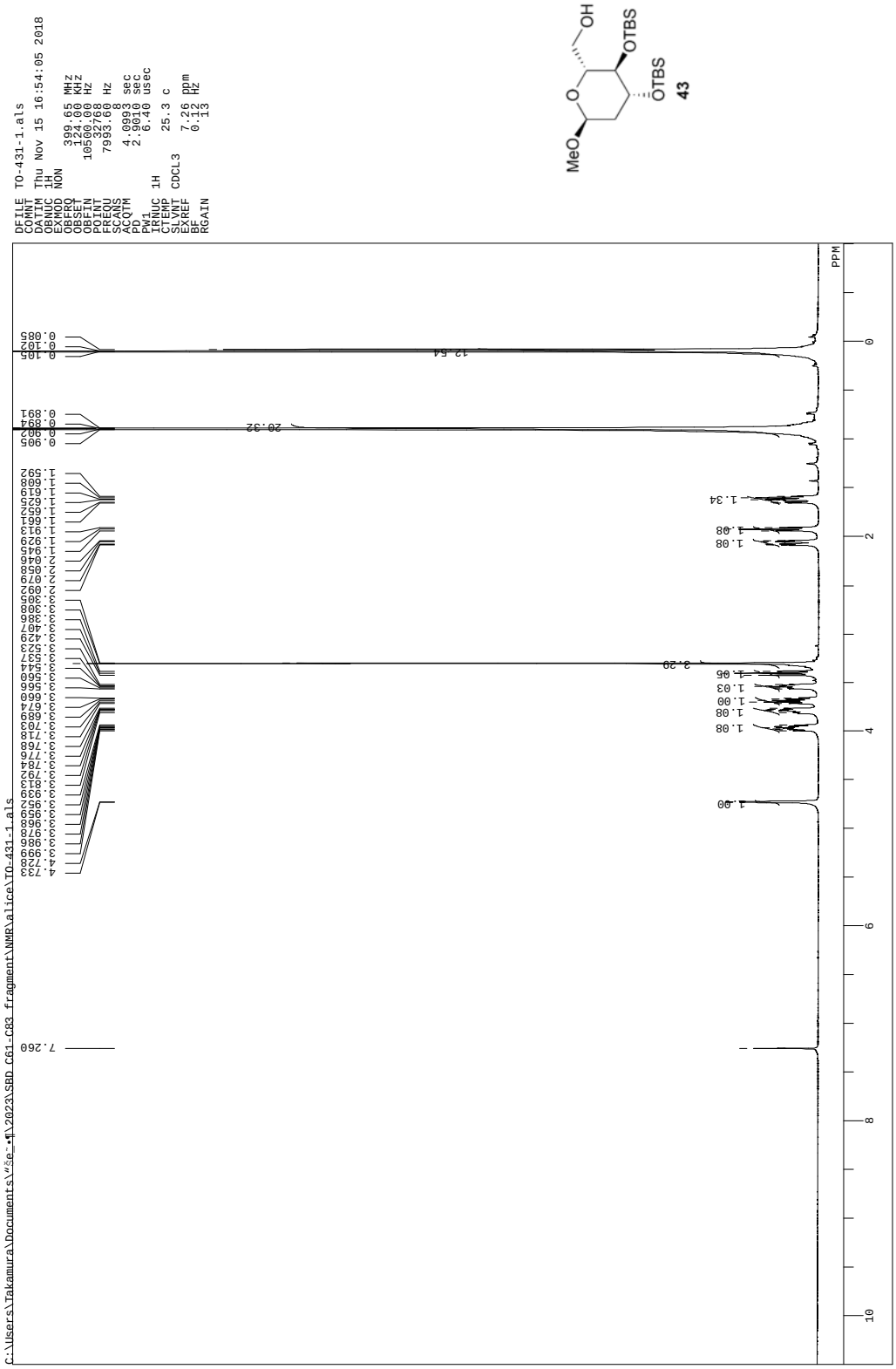
COMNT
DATIM Mon Aug 27 17:06:11 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 760
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25
-5.140
-4.818
-4.678
-4.571
-4.497
-3.828
18.074
18.148
18.247
18.321
18.429
25.936
26.026
28.633
32.560
34.061
34.911
35.274
40.818
61.953
62.720
64.189
68.330
70.120
74.756
76.687
77.000
77.322
79.417
125.185
128.501
128.600
131.422
131.686
137.749
PPM
TBSO
OTBS
SPh
OTBS
OTBS
OTBS
26

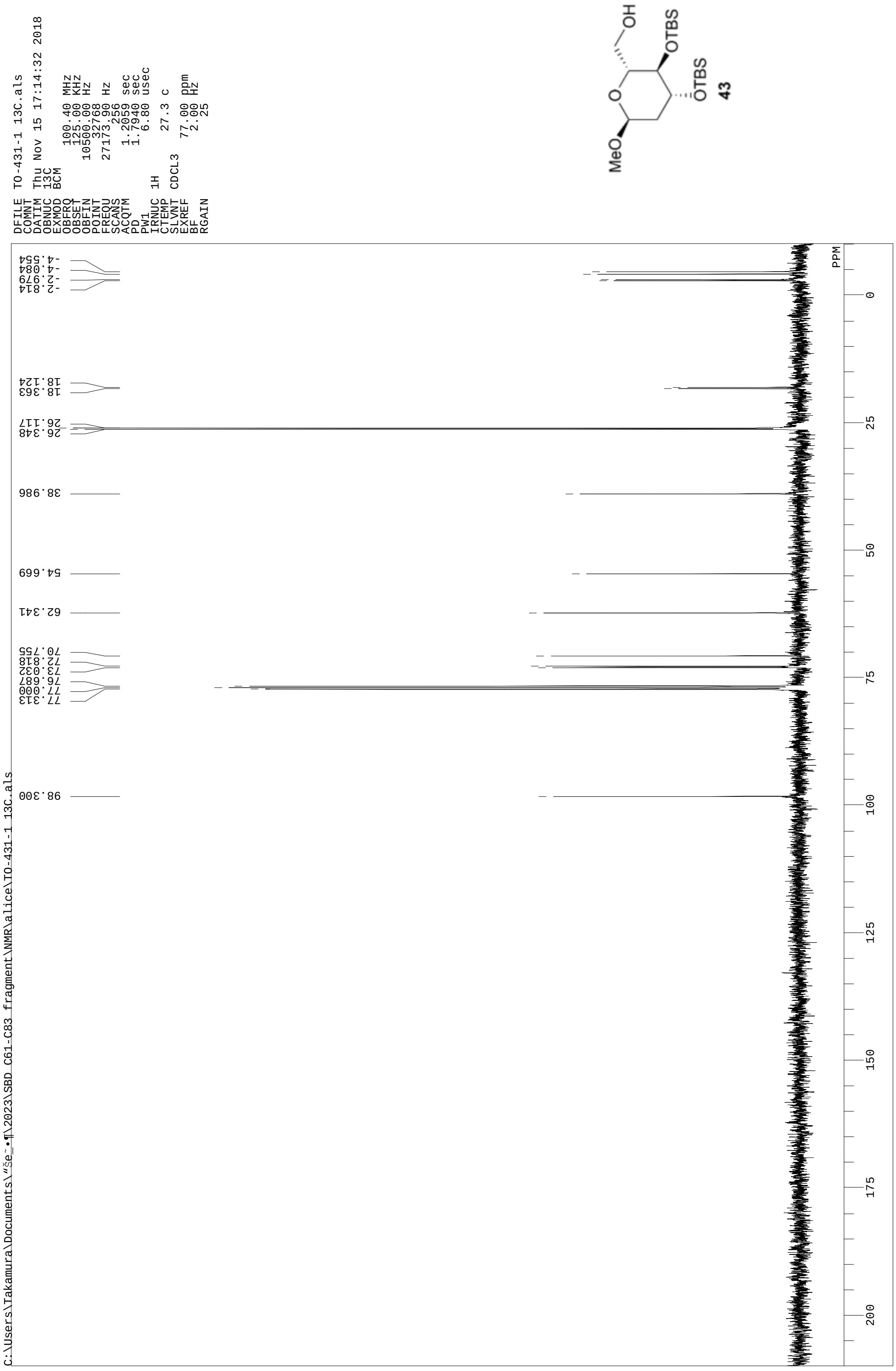

DFILE OH-464-1.als
COMNT
DATIM Wed Aug 29 13:45:28 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10560.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 11
C:\Users\Takamura\Documents\ﾊﾟﾗﾒｰﾀ\2023\SBD_C61-C83_fragment\NMR\alice\OH-464-1.als
PPM
TBSO
OH
OTBS
OH
OTBS
OTBS
O
28


C:\Users\Takamura\Documents\...\2023\SBD C61-C83 fragment\NMR\alice\OH-464-1 13C.als
DFILE OH-464-1 13C.als
COMNT
DATIM Wed Aug 29 14:09:02 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 380
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 29.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
-5.173
-5.049
-4.884
-4.571
18.058
18.140
18.181
18.338
18.429
25.895
25.919
25.952
26.010
26.068
29.376
30.927
34.152
37.691
61.549
63.240
64.519
68.132
69.460
69.815
72.578
76.687
77.000
77.313
79.260
80.003
115.071
144.736
PPM
0
25
50
75
100
125
150
175
200
TBSO
OH
OTBS
OH
O
OTBS
OTBS
OTBS
28

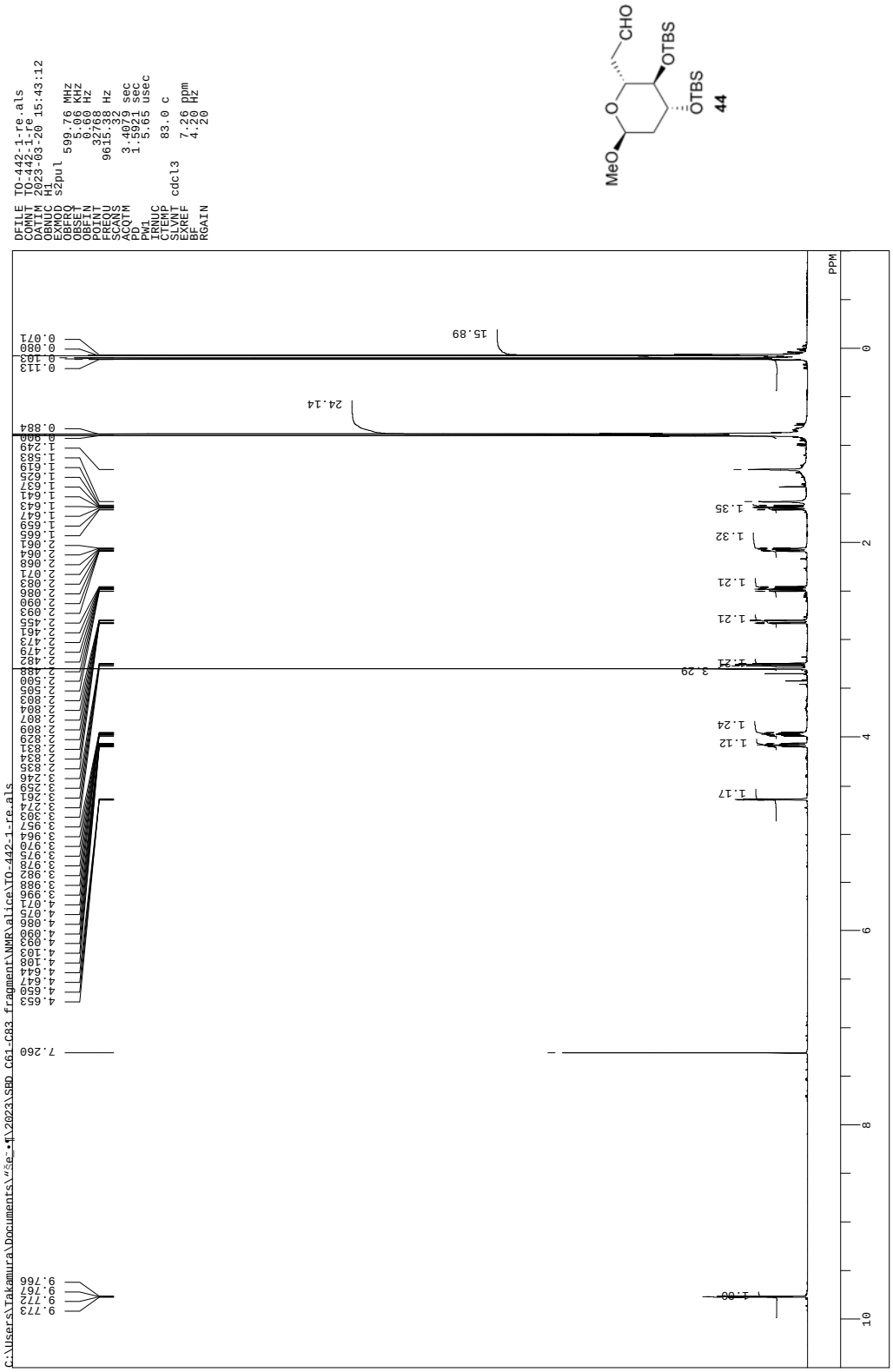

OMOM
OBOM
41
DFILE TO-441.als
COMNT
DATIM Thu Nov 22 16:45:30 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFTN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 13
C:\Users\Takamura\Documents\ﾏｽﾀｰ･1\2023\SBD_C61-C83_fragment\NMR\alice\TO-441.als
PPM
0
2
4
6
8
10
4.40
2.21
0.92
2.06
2.92
1.98
1.02
1.98
2.20
1.00
3.01
4.97

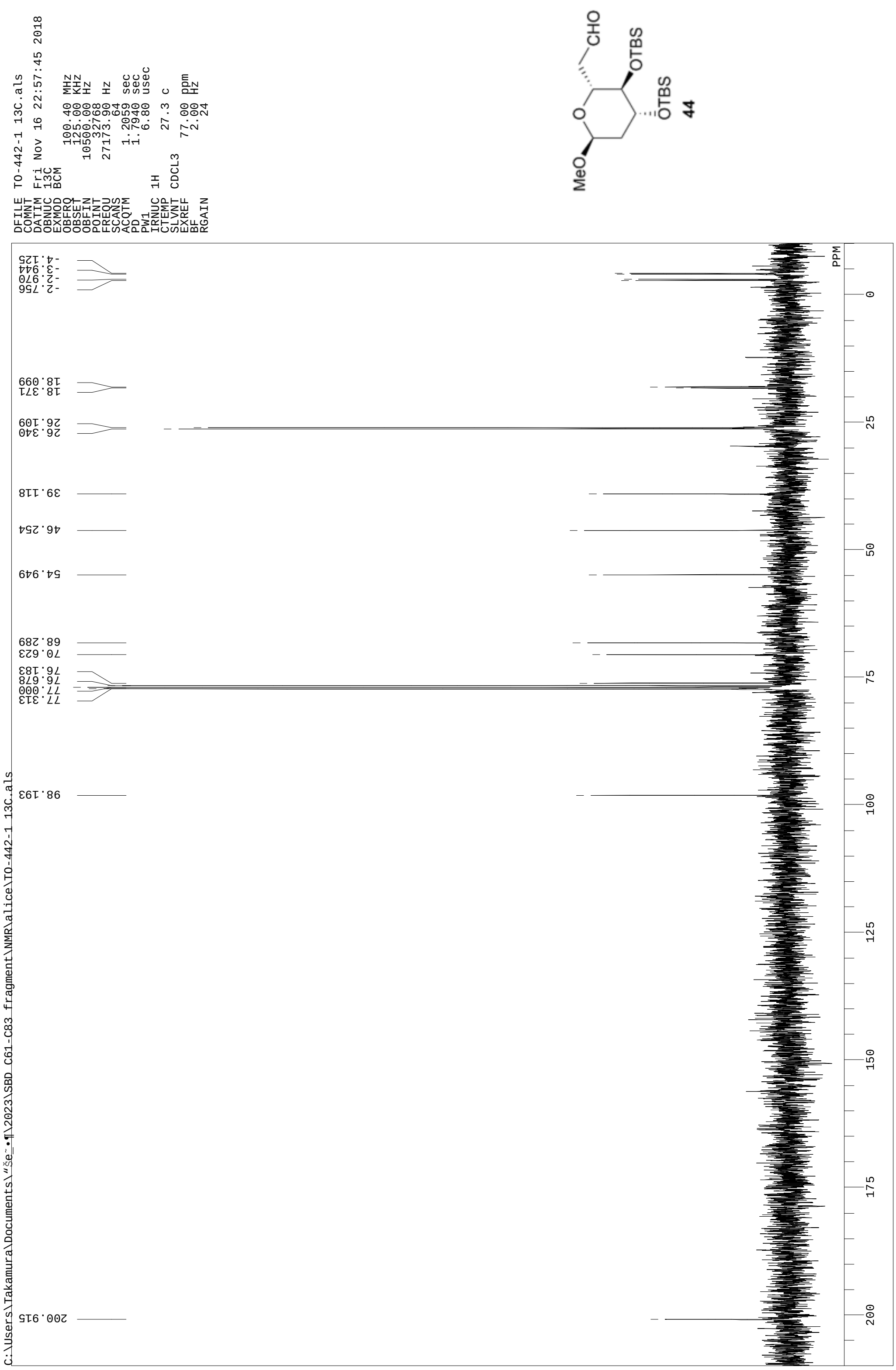

OMOM
OBOM
41
DFILE TO-441 13C.als
COMNT
DATIM Thu Nov 22 17:03:04 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 15.00 KHz
OBFIN 10560.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 240
ACQTM 1.2060 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 HZ
RGAIN 24
C:\Users\Takamura\Documents\%e-•¶\2023\SBD_C61-C83_fragment\NMR\alice\TO-441_13C.als
22.124
24.484
29.747
33.822
55.114
67.587
69.707
70.079
75.565
76.687
77.000
77.322
80.951
93.746
96.370
127.619
127.767
128.336
137.716
PPM
0
25
50
75
100
125
150
175
200

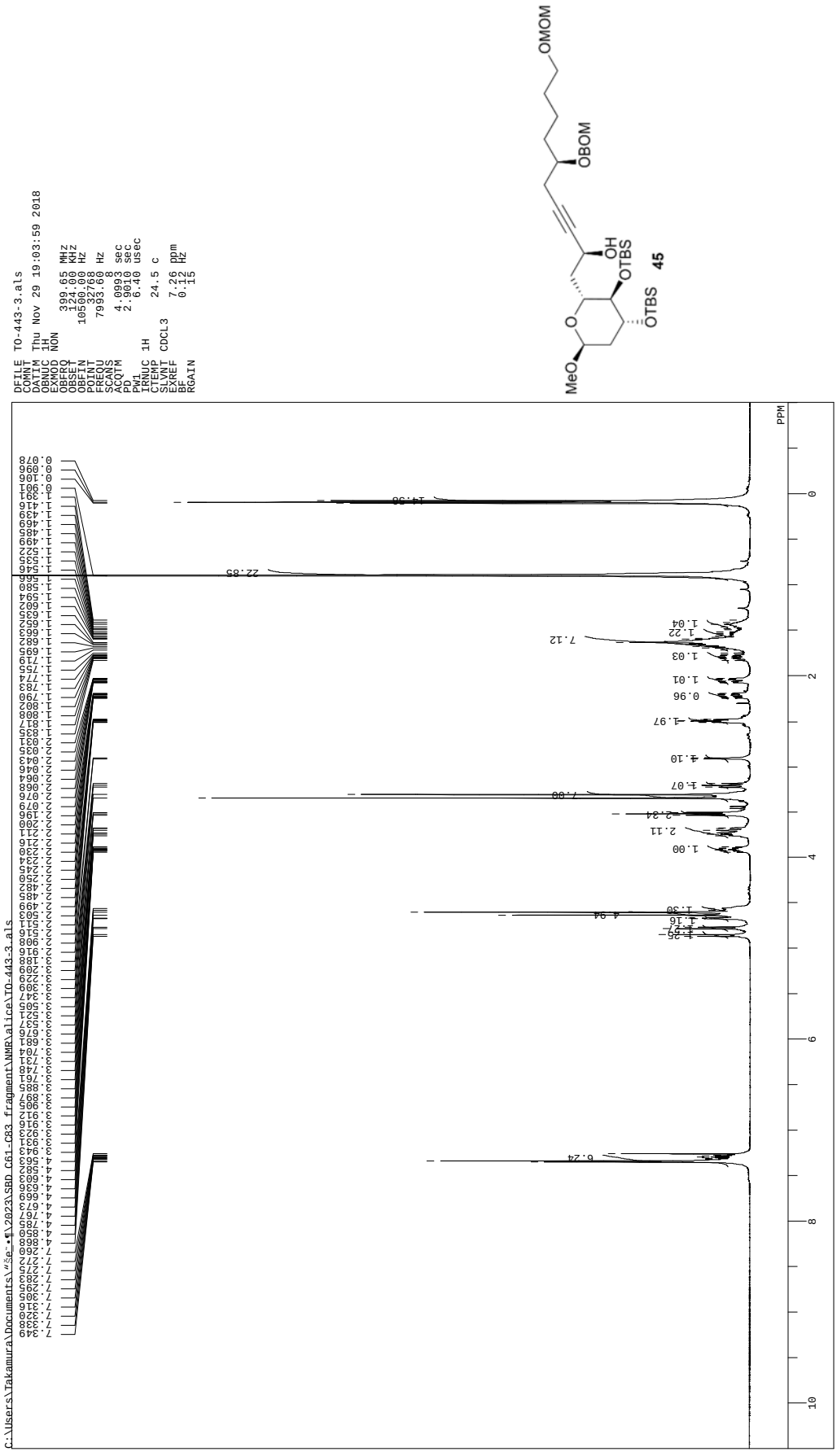

DFILE TO-431-1.als
COMNT
DATIM Thu Nov 15 16:54:05 2018
OBNUC 1H
EXMOD NON
OBSFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10560.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 13
OH
OTBS
OTBS
O
MeO
43
PPM
0
2
4
6
8
10
c:\Users\Takamura\Documents\ﾌﾟﾗｲﾍﾞｰﾄ\2023\SBD C61-c83 fragment\NMR\alice\TO-431-1.als

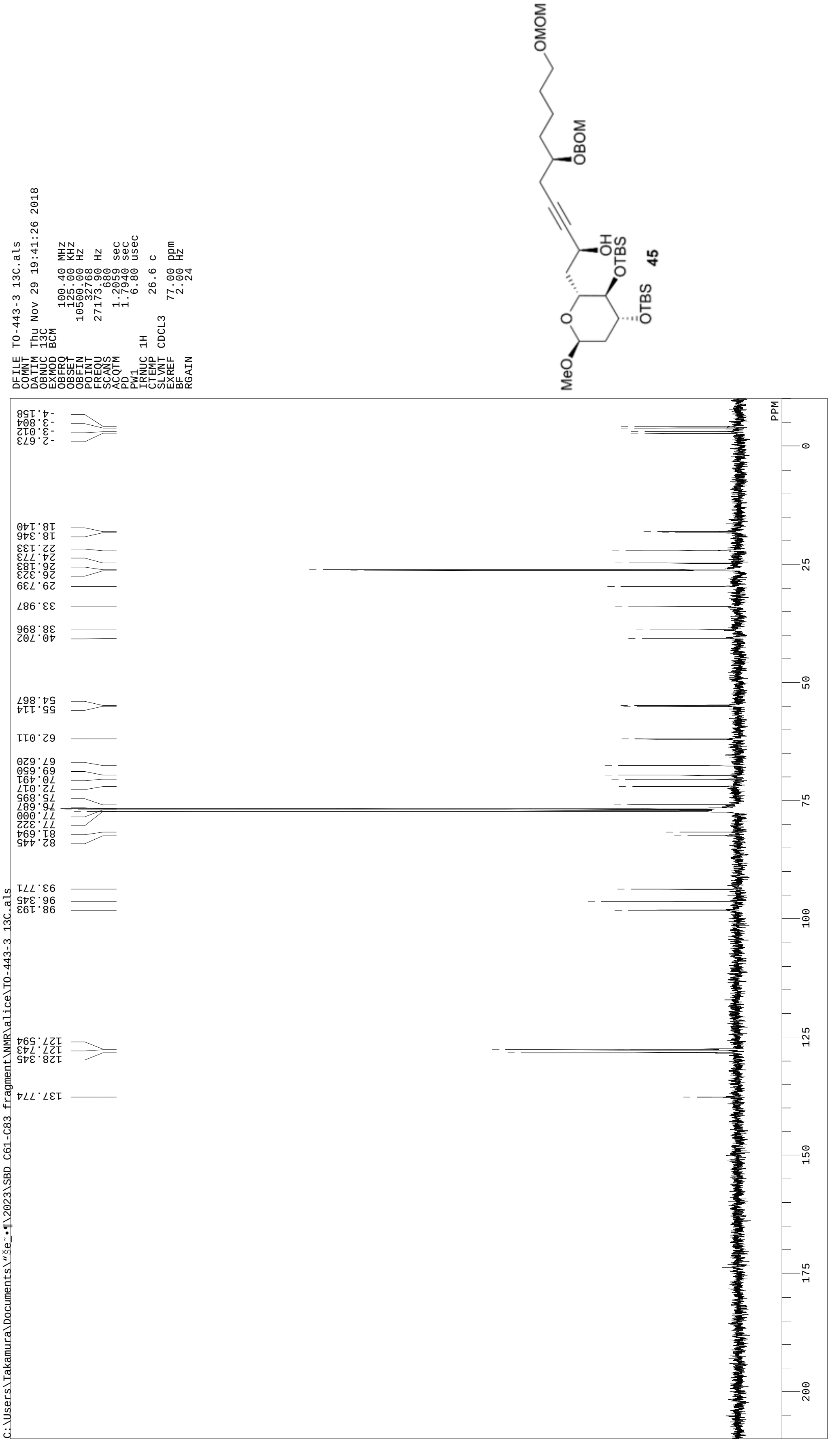

DFILE TO-431-1 13C.als
COMNT
DATIM Thu Nov 15 17:14:32 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 256
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25
-4.554
-4.084
-2.979
-2.814
18.124
18.363
26.117
26.348
38.986
54.669
62.341
70.755
72.818
73.032
76.687
77.000
77.313
98.300
PPM
0
25
50
75
100
125
150
175
200
2023\SBD C61-C83 fragment\NMR\alice\TO-431-1 13C.als
MeO
O
OH
OTBS
OTBS

43

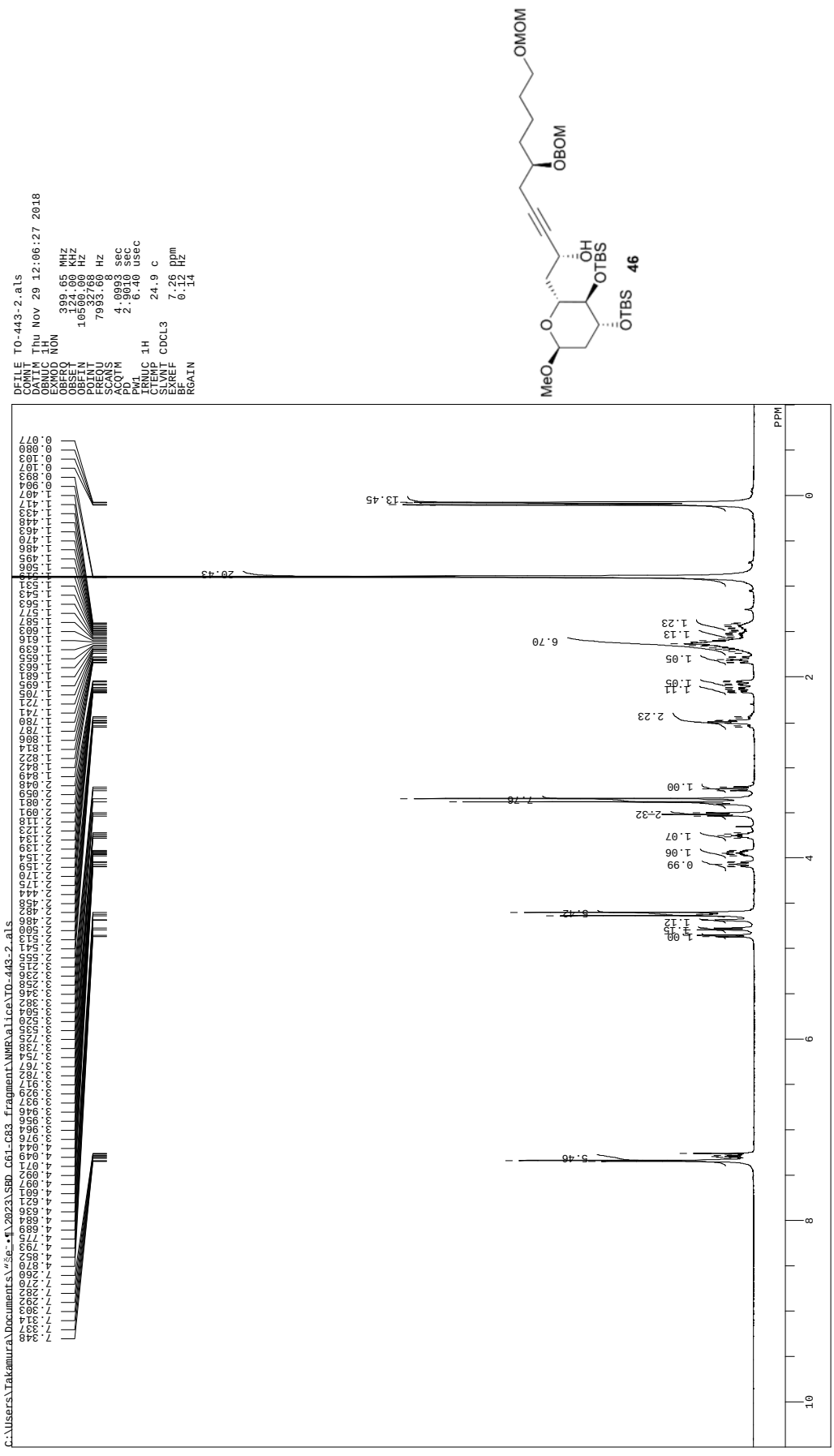

DFILE TO-442-1-re.als
COMNT TO-442-1-re
DATIM 2023-03-20 15:43:12
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 5.06 KHz
OBFIN 3768 Hz
POINT 96315.38 Hz
FREQU 32
SCANS 3.4079 sec
ACQTM 1.5971 sec
PW1 5.65 usec
IRNUC
CTEMP 83.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF1 4.20
RGAIN
CHO
OTBS
OTBS
MeO
44
C:\Users\Takamura\Documents\データ\2023\SBD_C61-C83_fragment\NMR\alice\TO-442-1-re.als
PPM

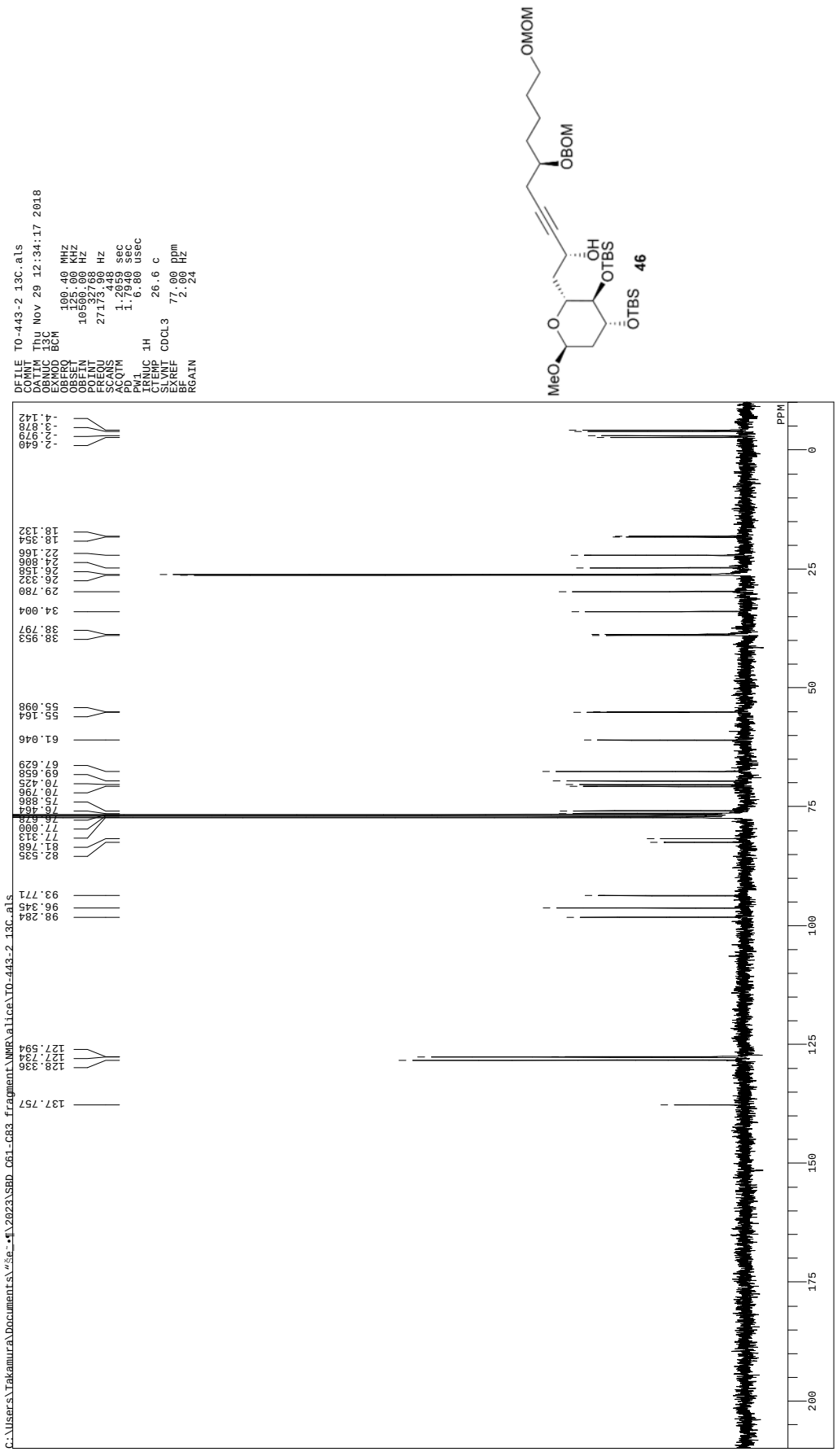

DFILE TO-442-1 13C.als
COMNT
DATIM Fri Nov 16 22:57:45 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 64
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
-4.125
-3.944
-2.970
-2.756
18.099
18.371
26.109
26.340
39.118
46.254
54.949
68.289
70.623
76.183
76.678
77.000
77.313
98.193
200.915
C:\Users\Takamura\Documents\\2023\SBD C61-C83 fragment\NMR\alice\TO-442-1 13C.als
PPM
0
25
50
75
100
125
150
175
200
MeO
O
CHO
OTBS
OTBS
44

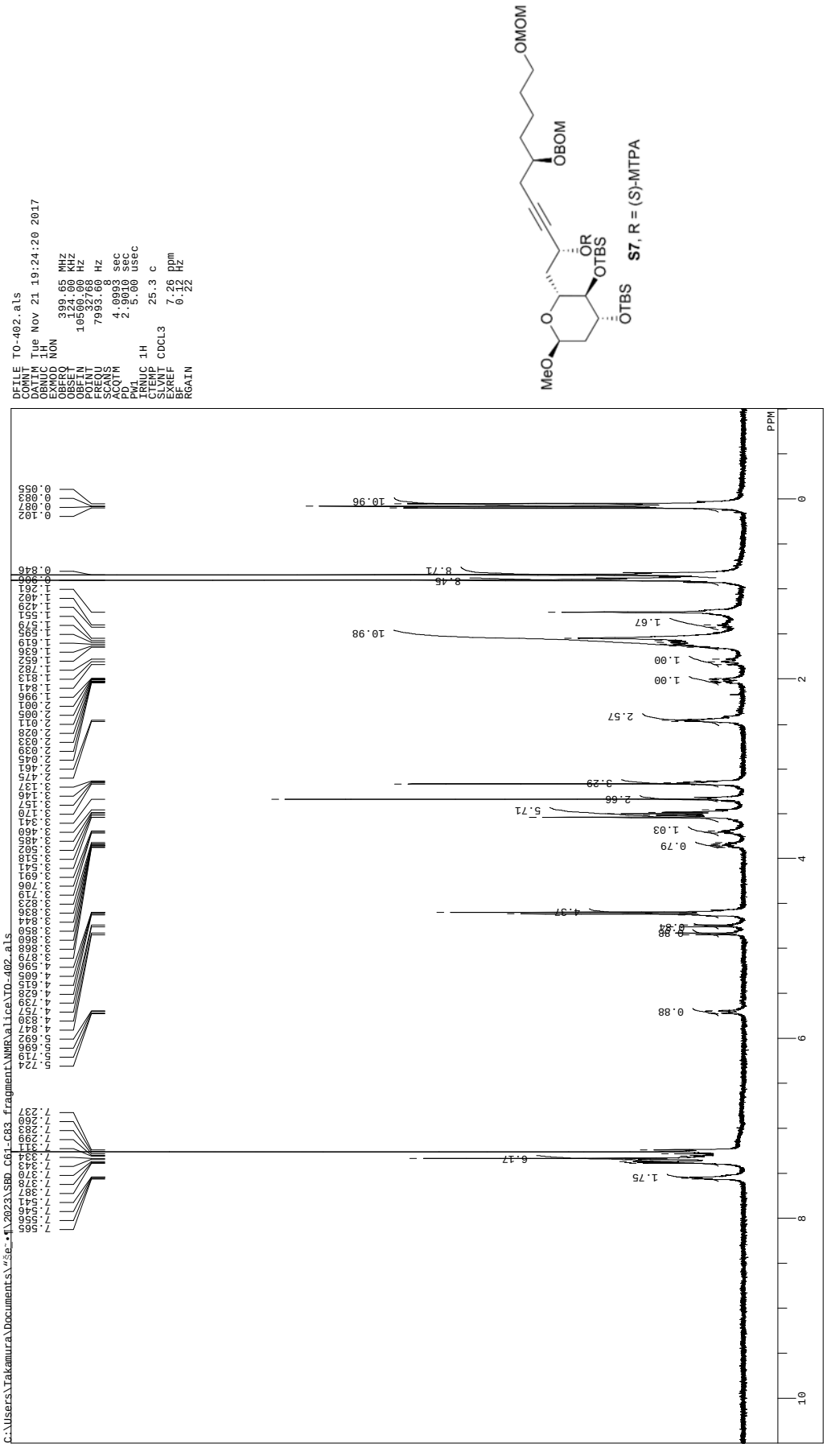

DFILE TO-443-3.als
COMNT
DATIM Thu Nov 29 19:03:59 2018
OBNUC 1H
EXMOD NON
OBSFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 15
c:\Users\Takamura\Documents\ACD\SBD_C61_C83_fragment\NMR\alice\TO-443-3.als
PPM
MeO
O
OTBS
OH
OBOM
OMOM
45

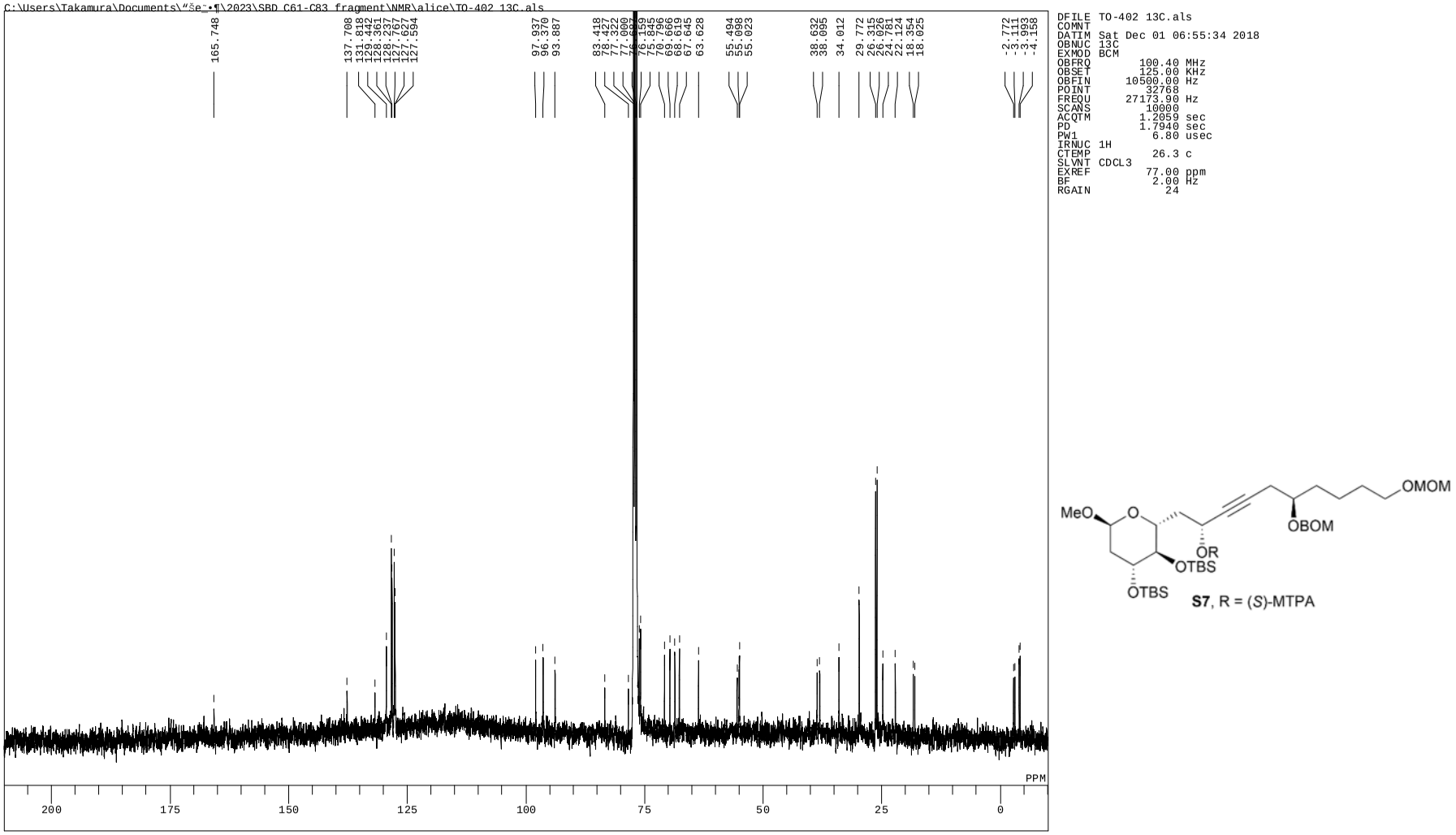


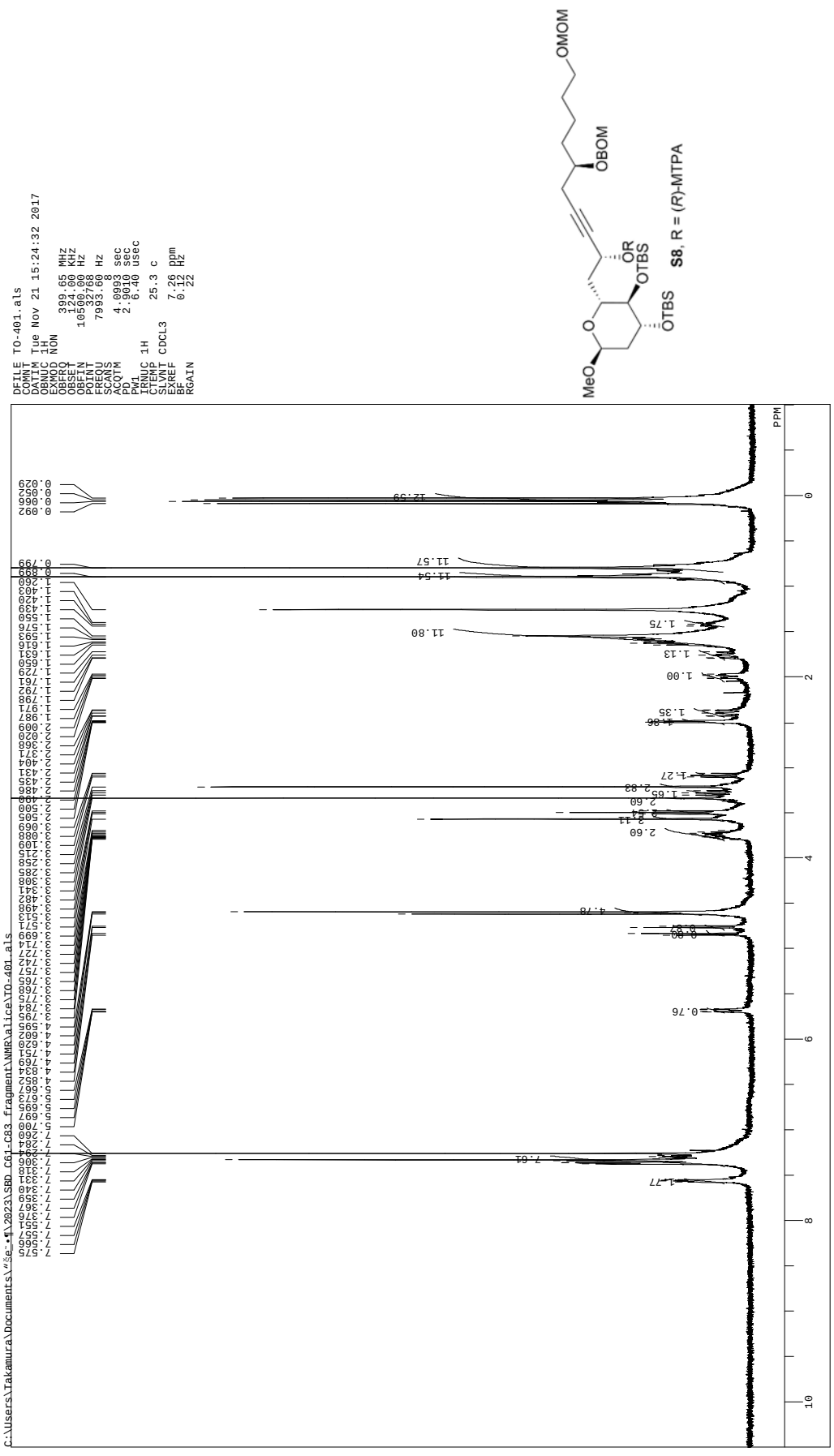
DFILE TO-443-3 13C.als
COMNT
DATIM Thu Nov 29 19:41:26 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 680
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
C:\Users\Takamura\Documents\"še_•¶\2023\SBD_C61-C83_fragment\NMR\alice\TO-443-3_13C.als
-4.158
-3.804
-3.012
-2.673
18.140
18.346
22.133
24.773
26.183
26.323
29.739
33.987
38.896
40.702
54.867
55.114
62.011
67.620
69.650
70.491
72.017
75.895
76.687
77.000
77.322
81.694
82.445
93.771
96.345
98.193
127.594
127.743
128.345
137.774
PPM
0
25
50
75
100
125
150
175
200
OMOM
OBOM
OH
OTBS
OTBS
MeO
O
45

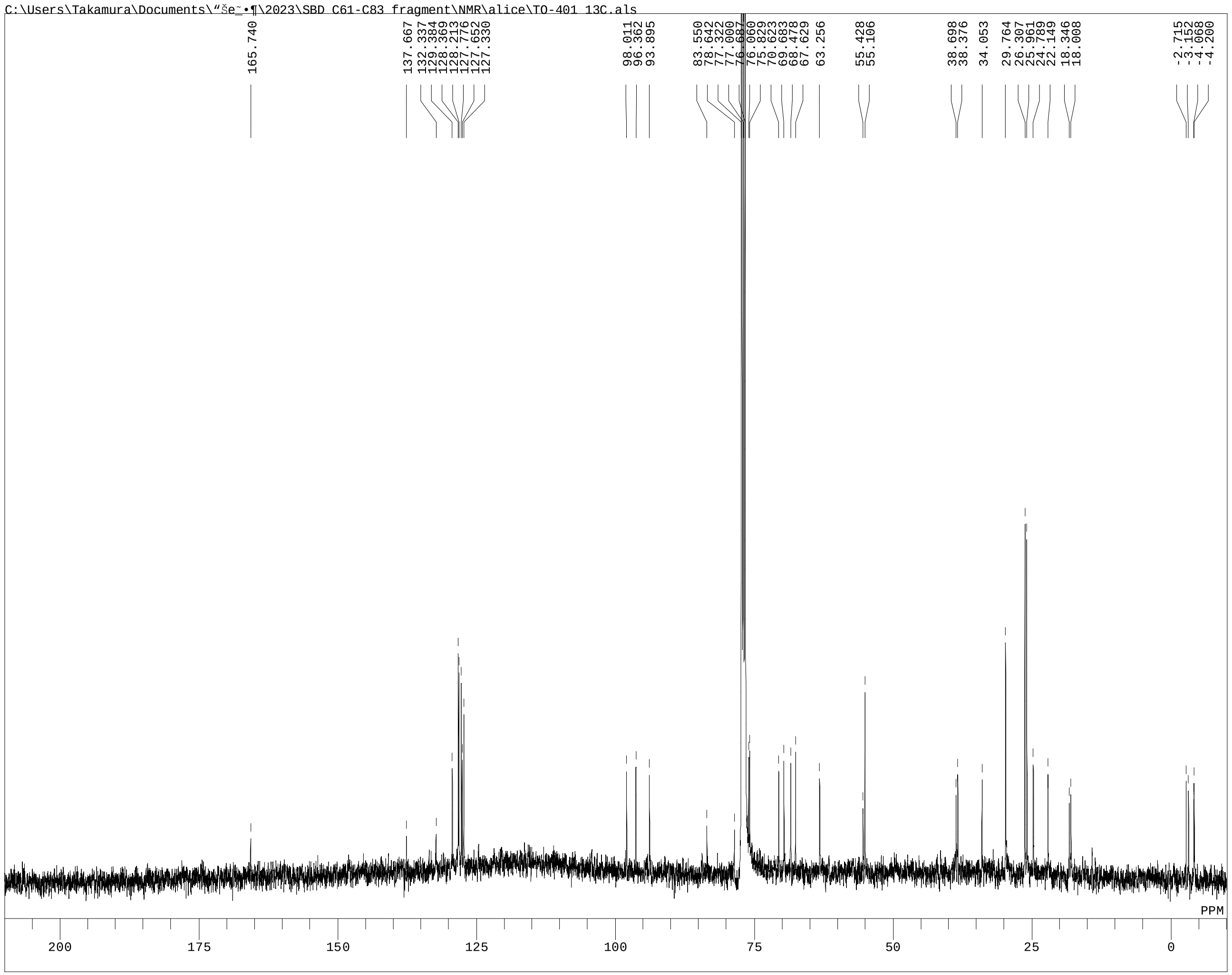

OMOM
OBOM
OH
OTBS
OTBS
46
MeO
O
DFILE TO-443-2.als
COMNT
DATIM Thu Nov 29 12:06:27 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TEMP 24.9 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14
C:\Users\Takamura\Documents\ﾏｽﾀｰ･1\2023\SBD_CG1-C83_fragment\NMR\alice\TO-443-2.als
PPM


DFILE TO-443-2 13C.als
COMNT
DATIM Thu Nov 29 12:34:17 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSWD 125.00 KHz
OBSET 10500.00 Hz
OBFIN 32768 Hz
POINT 27173.90 Hz
FREQU 0.49 sec
SCANS 1.2059 sec
ACQTM 1.79940 sec
PD 6.80 usec
PW1
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
C:\Users\Takamura\Documents\ﾍﾟｰﾊﾟｰ\2023\SBD_C61-C83_fragment\NMR\alice\TO-443-2 13C.als
PPM
OMOM
OBOM
OH
OTBS
OTBS
46
MeO
O


OMOM
OBOM
OR
OTBS
OTBS
MeO
O
S7, R = (S)-MTPA
PPM
0
2
4
6
8
10


C:\Users\Takamura\Documents\"šeˆ•¶\2023\SBD C61-C83 fragment\NMR\alice\TO-402 13C.als
165.748
137.708
131.818
131.442
128.361
128.237
127.767
127.667
127.594
97.937
96.370
93.887
83.418
78.427
77.322
77.000
76.159
75.845
70.796
69.666
68.619
67.645
63.628
55.494
55.098
55.023
38.632
38.095
34.012
29.772
26.315
26.030
24.781
22.124
18.354
18.025
-2.772
-3.111
-3.993
-4.158
PPM
200
175
150
125
100
75
50
25
0
DFILE TO-402 13C.als
COMNT
DATIM Sat Dec 01 06:55:34 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 10000
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
MeO
O
OMOM
OBOM
OR
OTBS
OTBS
S7, R = (S)-MTPA


OMOM
OBOM
OR
OTBS
OTBS
MeO
O
S8, R = (R)-MTPA
DFILE TO-401.als
COMNT
DATIM Tue Nov 21 15:24:32 2017
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768 Hz
FREQU 7993.60 Hz
SCANS 4
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
INUC 1H
CTEMP 25.3 c
SLVNT CDCL3 7.26 ppm
EXREF 0.12 Hz
BF 22
RGAIN
C:\Users\Takamura\Documents\ﾍﾟｰｽﾄ\2023\SBD_C61-C83_fragment\NMR\alice\TO-401.als
PPM

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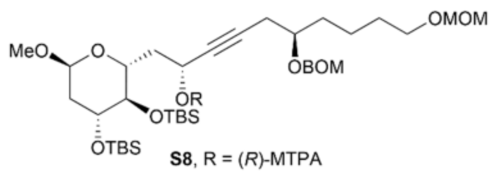
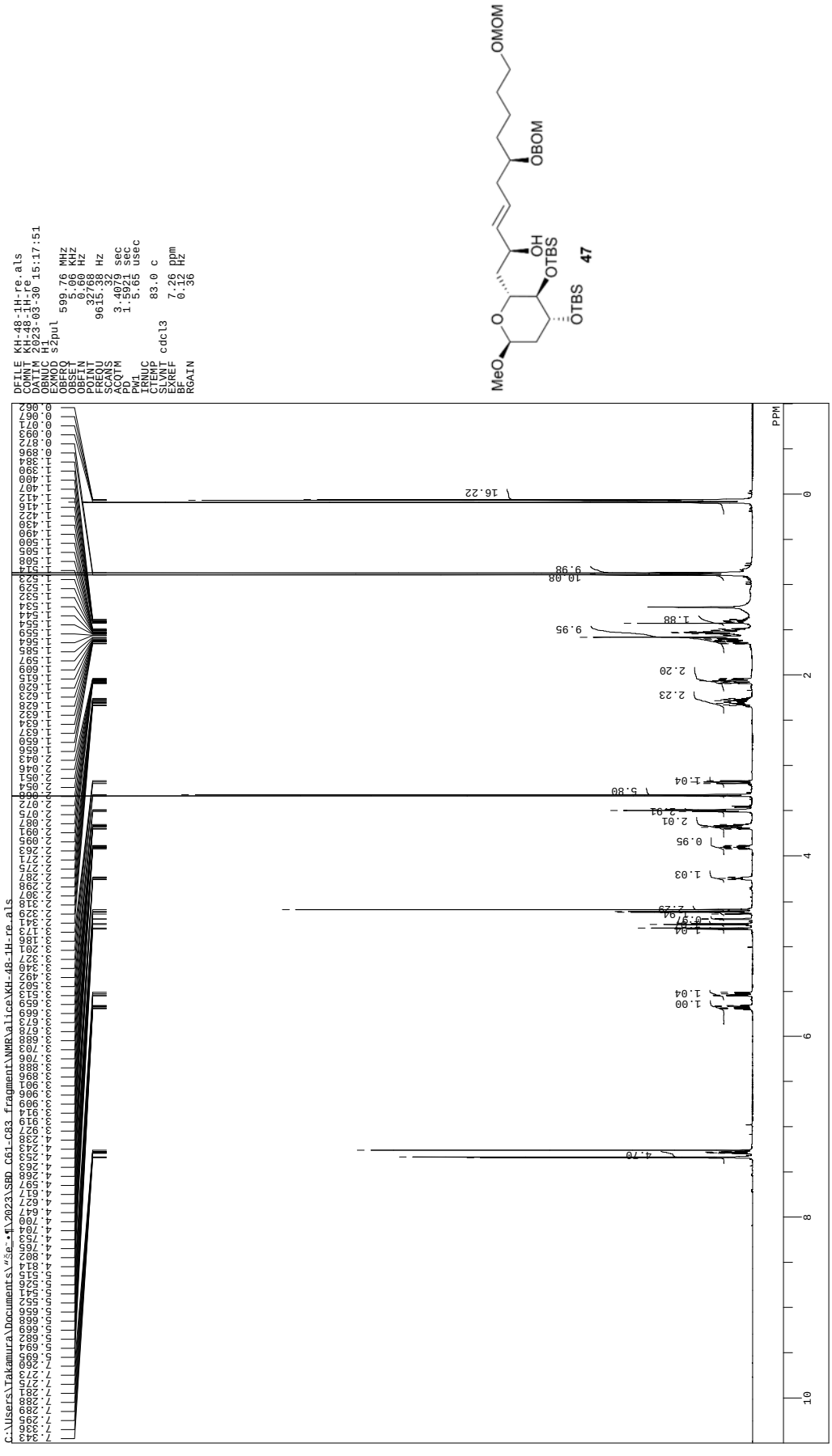
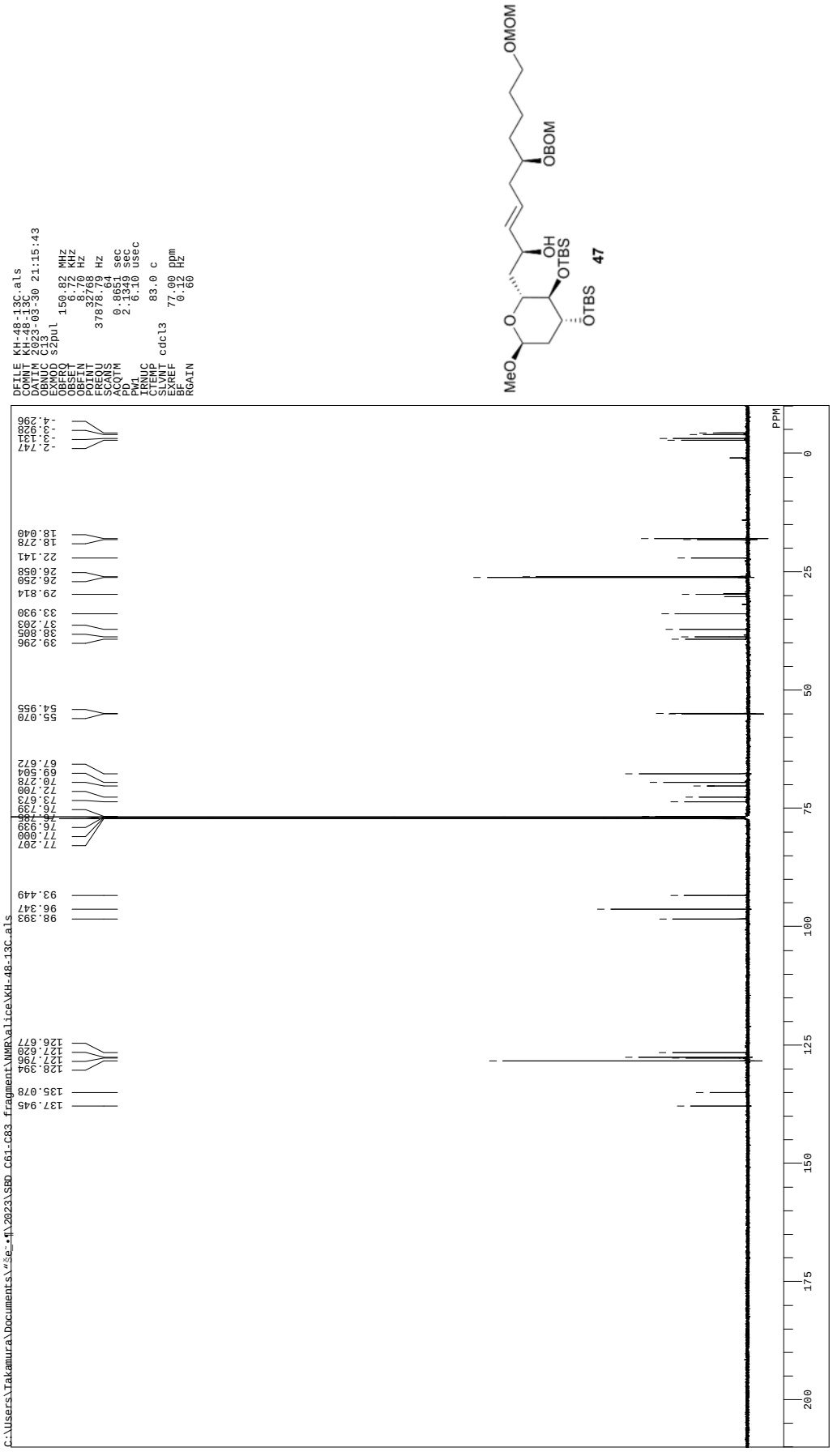
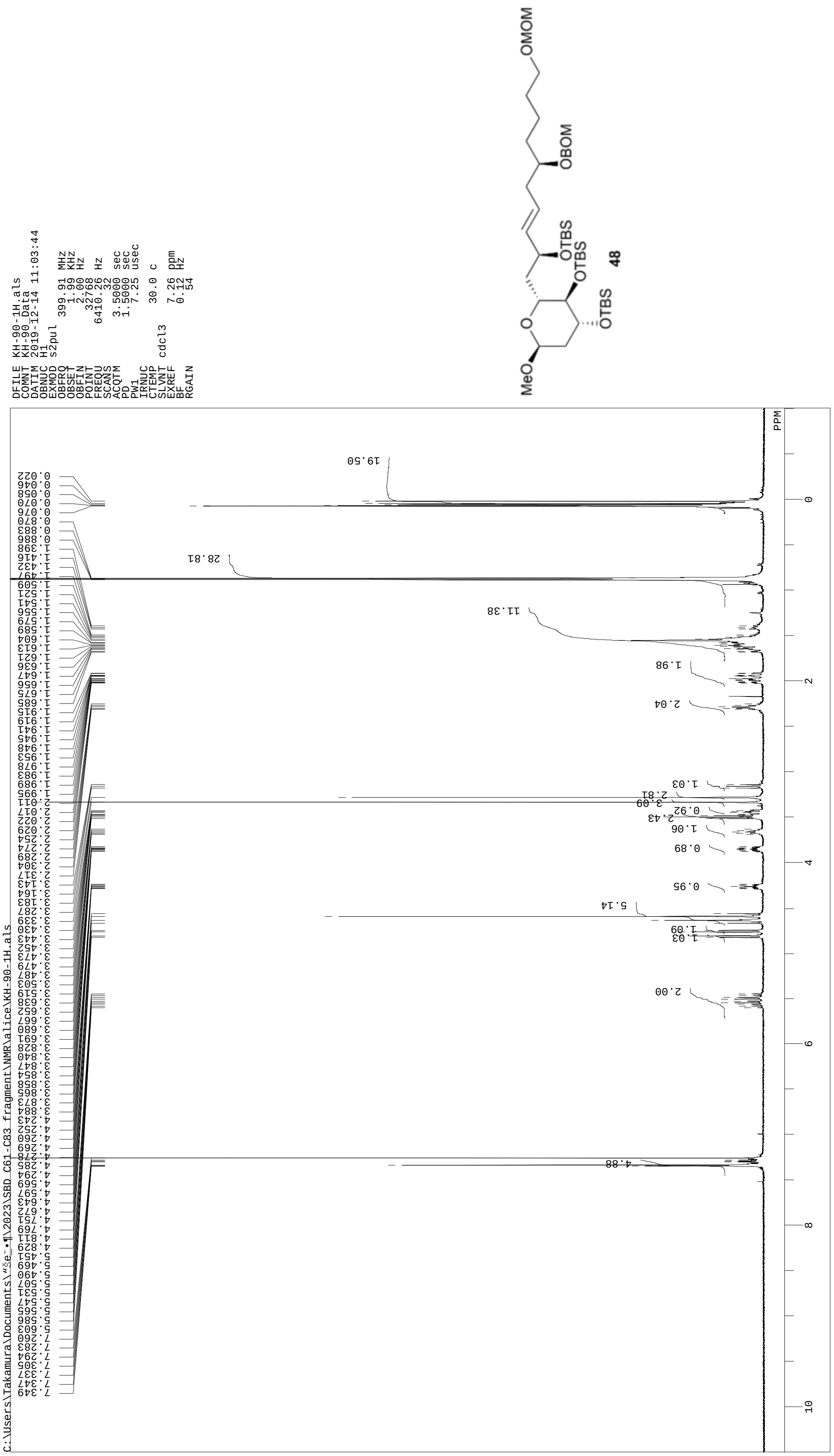
DFILE  TO-401 13C.als
COMNT
DATIM  Fri Nov 30 06:26:00 2018
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU     27173.90 Hz
SCANS        10000
ACQTM       1.2059 sec
PD          1.7940 sec
PW1           6.80 usec
IRNUC  1H
CTEMP         26.2 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```

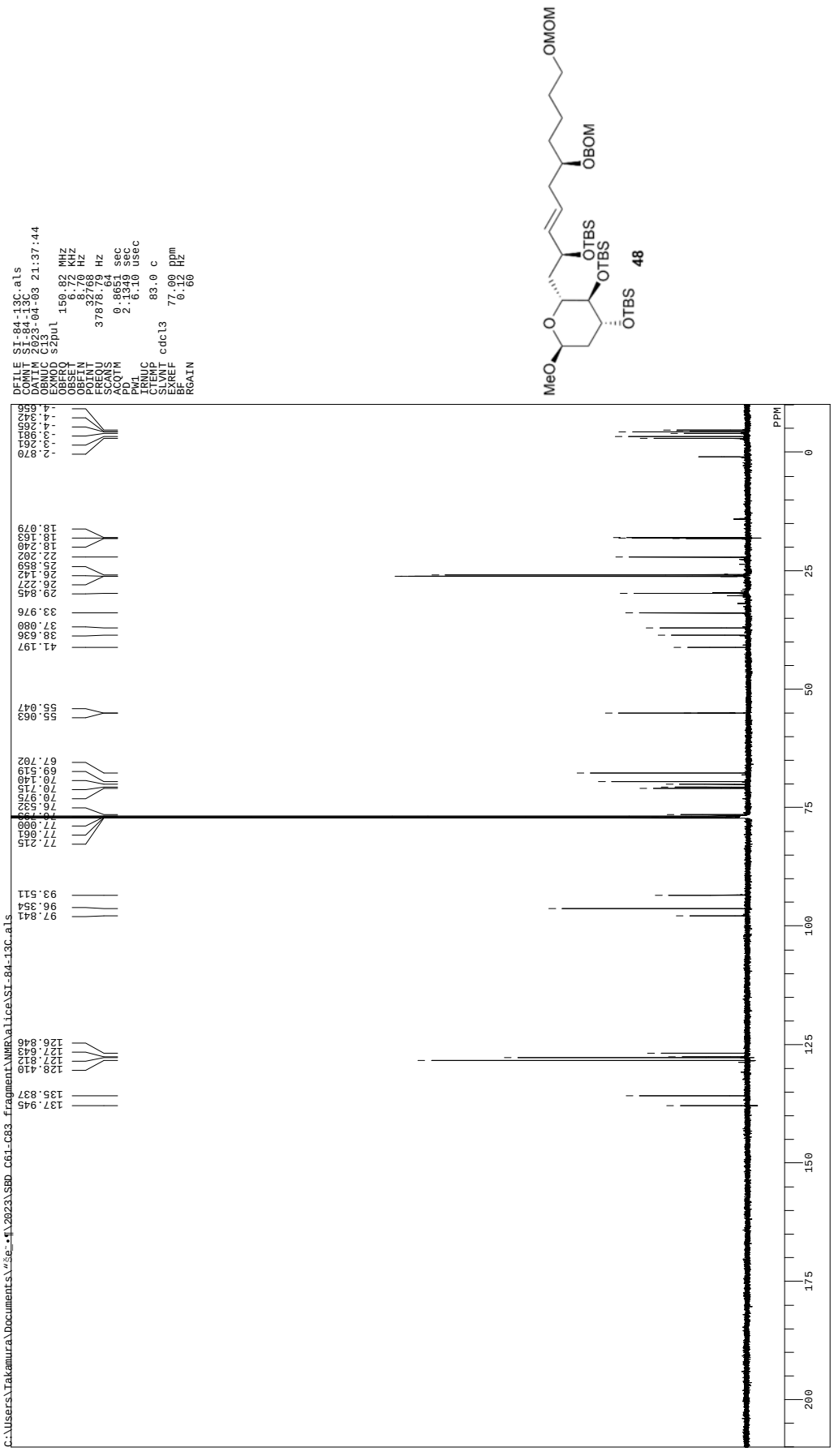


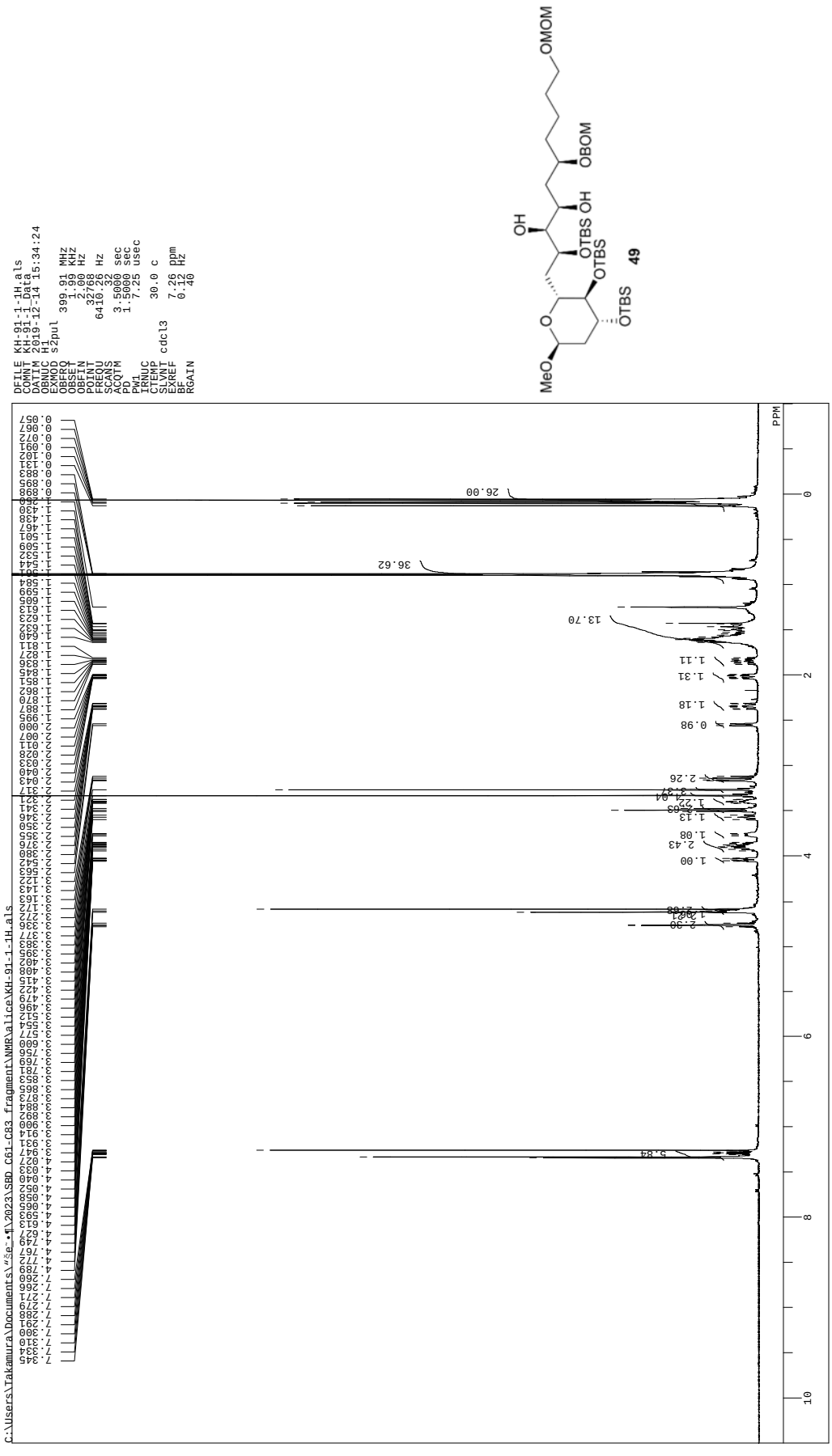
S8, R = (*R*)-MTPA

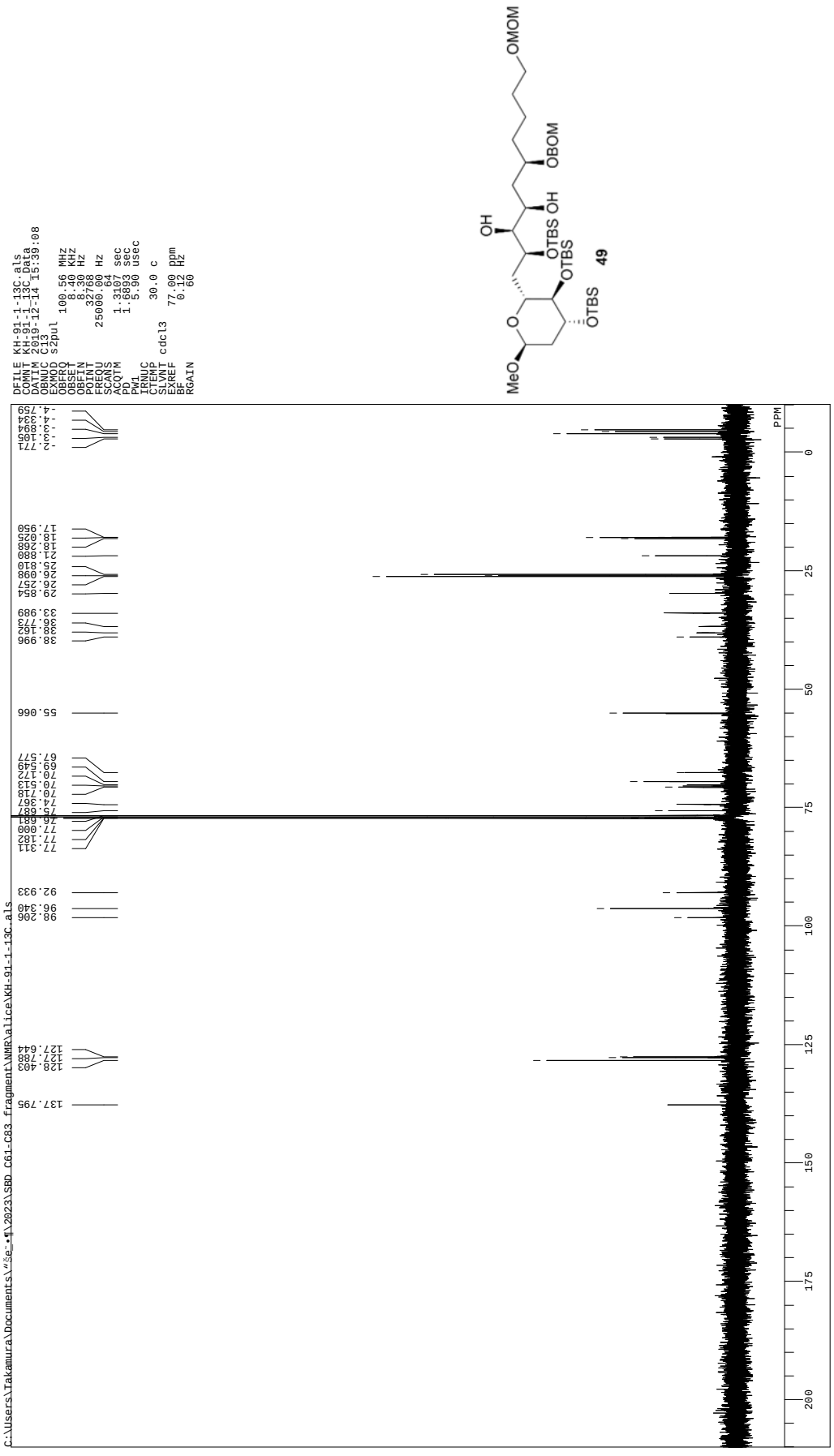

DFILE KH-48-1H-re.als
COMNT KH-48-1H-re 15:17:51
DATIM 2023-03-30
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 5.06 KHz
OBFIN 0.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 2
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.65 usec
TEMP 83.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 36
C:\Users\Takamura\Documents\アセテート\2023\SBD_CG1-C83_fragment\NMR\alice\KH-48-1H-re.als
OMOM
OBOM
OH
OTBS
OTBS
47
MeO
O
16.22
9.98
10.08
9.95
1.88
2.20
2.23
1.04
5.80
2.01
2.01
0.95
1.03
2.29
1.04
1.00
1.04
4.70
PPM


DFILE KH-48-13C.als
COMNT KH-48-13C
DATIM 2023-03-30 21:15:43
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 6.72 KHz
OBFIN 8.70 Hz
POINT 32768
FREQU 37878.74 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 6.10 usec
CTEMP 83.0 c
SLVNT cdcl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
C:\Users\Takamura\Documents\ﾏｸﾛ･ﾏｸﾛ\2023\SBD_C61-C83_fragment\NMR\alice\KH-48-13C.als
PPM
MeO
O
OTBS
OH
OBOM
OMOM
47

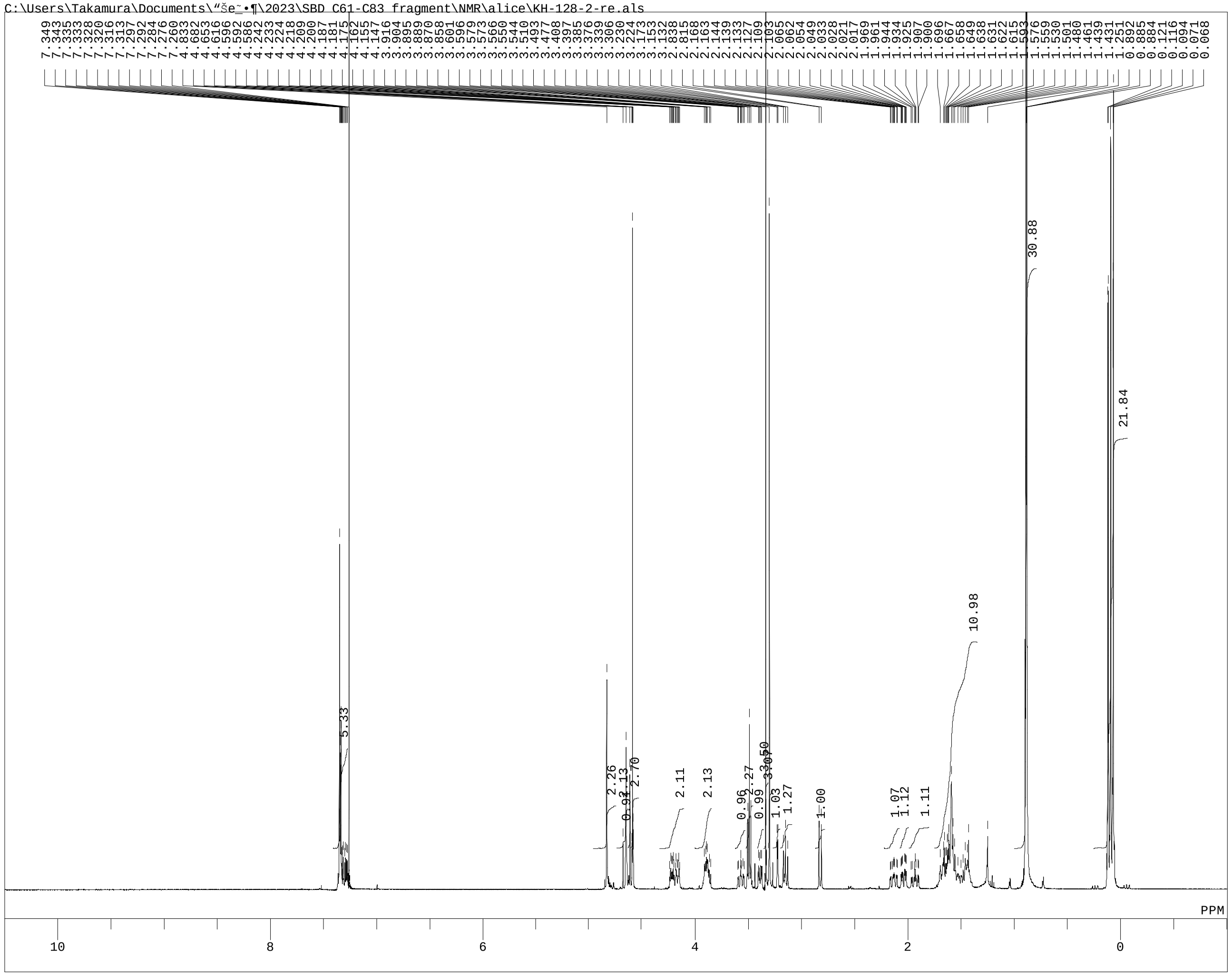

DFILE KH-90-1H.als
COMNT KH-90 Data
DATIM 2019-12-14 11:03:44
OBNUC 1H
EXMOD s2pul
OBFRQ 399.91 MHz
OBSET 1.99 KHz
OBFIN 2.90 Hz
POINT 32768
FREQU 6410.26 Hz
SCANS 32
ACQTM 3.5000 sec
PD 1.5000 sec
PW1 7.25 usec
IRNUC
CTEMP 30.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 54
MeO
OTBS
OTBS
OTBS
OBOM
OMOM
48
PPM


OMOM
OBOM
OTBS
OTBS
OTBS
MeO
O
48
PPM

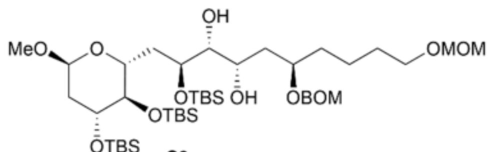

C:\Users\Takamura\Documents\マイ ドキュメント\2023\SBD_CG1-C83_fragment\NMR\alice\KH-91-1-1H.als
PPM
MeO
OTBS
OTBS
OTBS
OH
OH
OBOM
OMOM
49


OMOM
OBOM
OH
OTBS OH
OTBS
OTBS
MeO
O
49
DFILE KH-91-1-13C.als
COMNT KH-91-1-13C.data
DATIM 13-12-14 15:59.08
OBNUC C13
EXMOD s2pul
OBFRQ 100.56 MHz
OBSET 8.40 KHz
OBFIN 8.30 Hz
POINT 32768
FREQU 25000.00 Hz
SCANS 64
ACQTM 1.3107 sec
PD 1.6000 sec
PW1 5.90 usec
IRNUC
CTEMP 30.0 c
SLVNT cdcl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
C:\Users\Takamura\Documents\ﾏｽﾀｰ･ﾃﾞｰﾀ\2023\SBD_C61-C83_fragment\NMR\alice\KH-91-1-13C.als
PPM

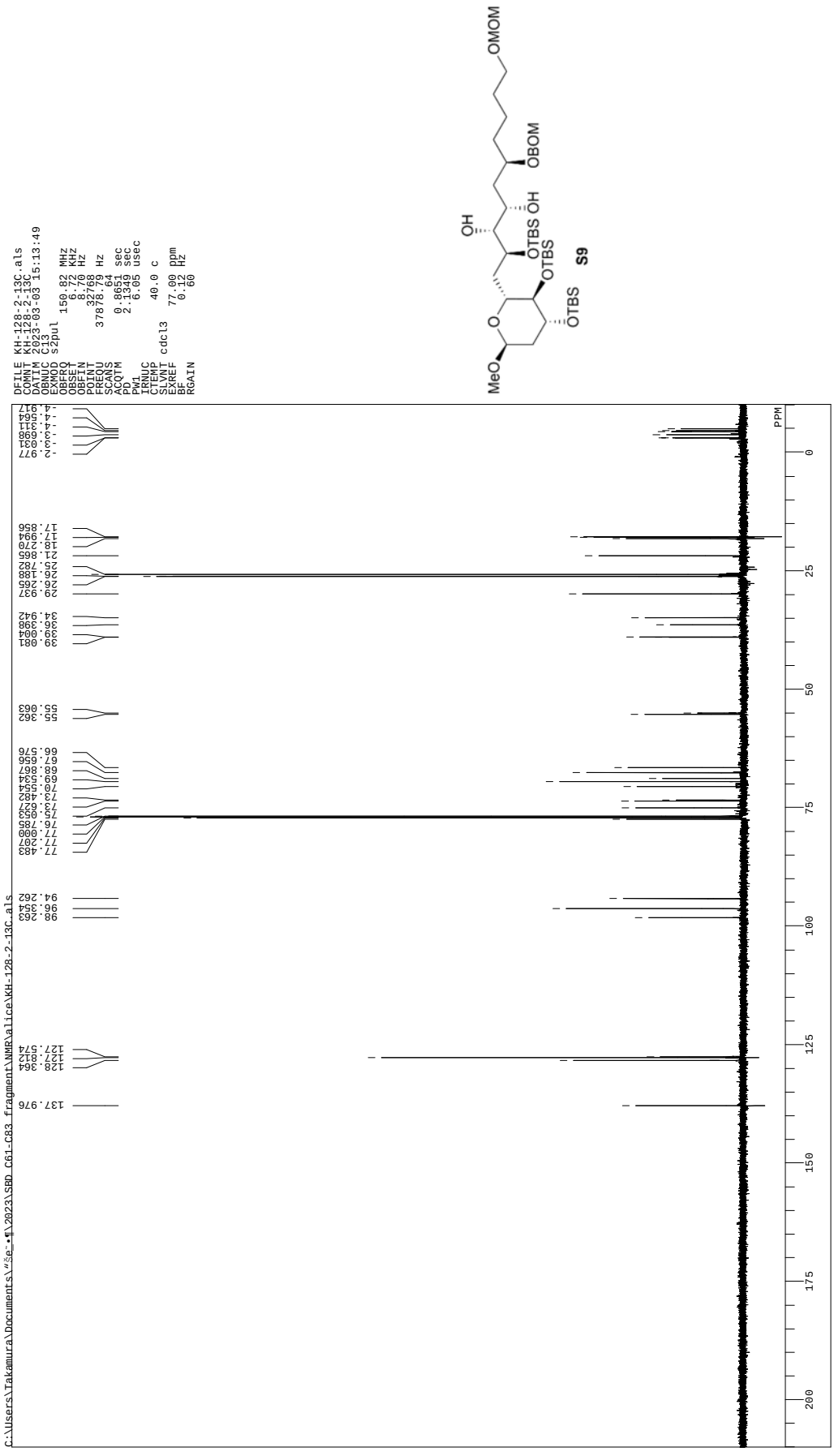
C:\Users\Takamura\Documents\“še¨•¶\2023\SBD C61-C83 fragment\NMR\alice\KH-128-2-re.als

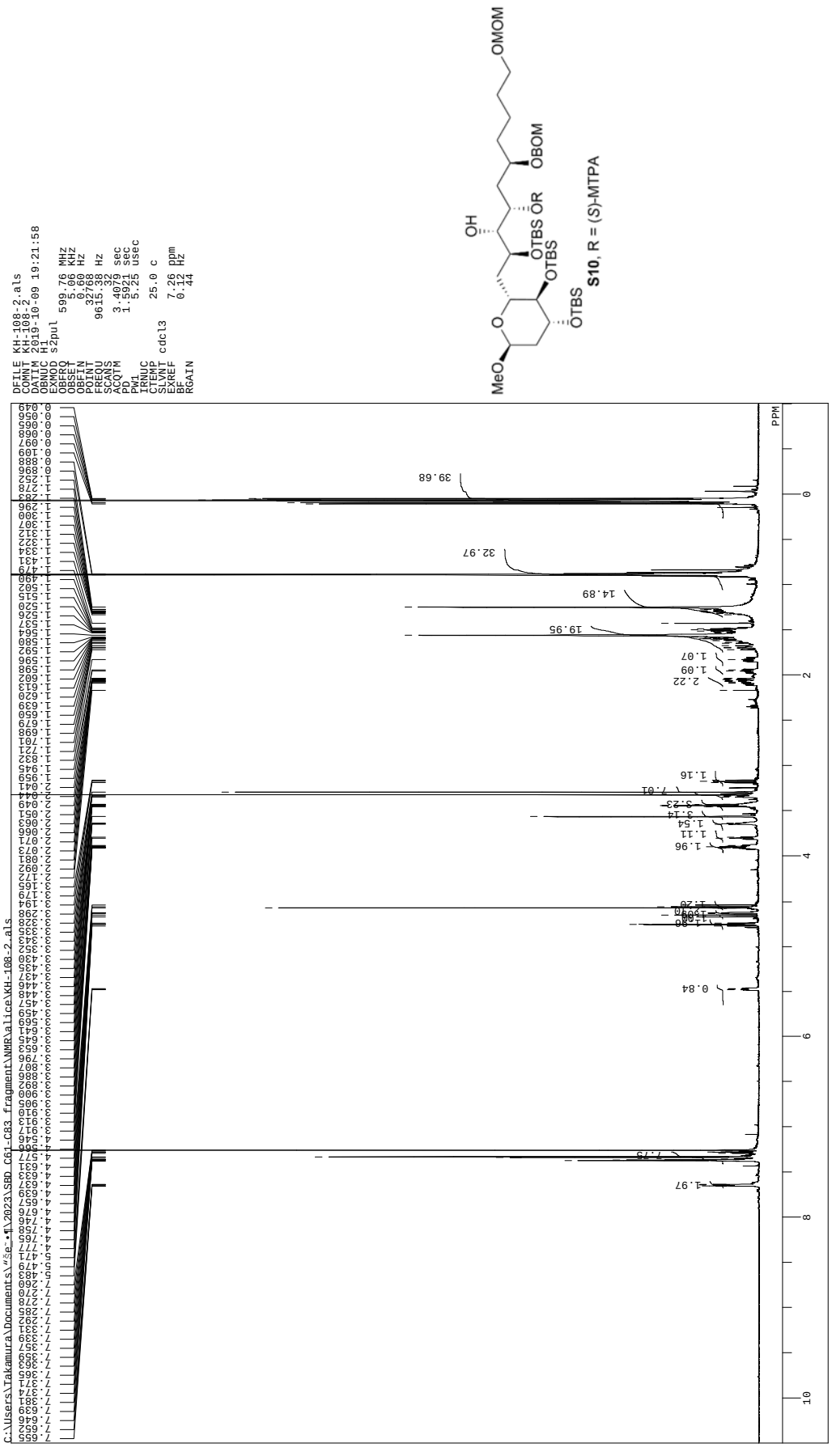


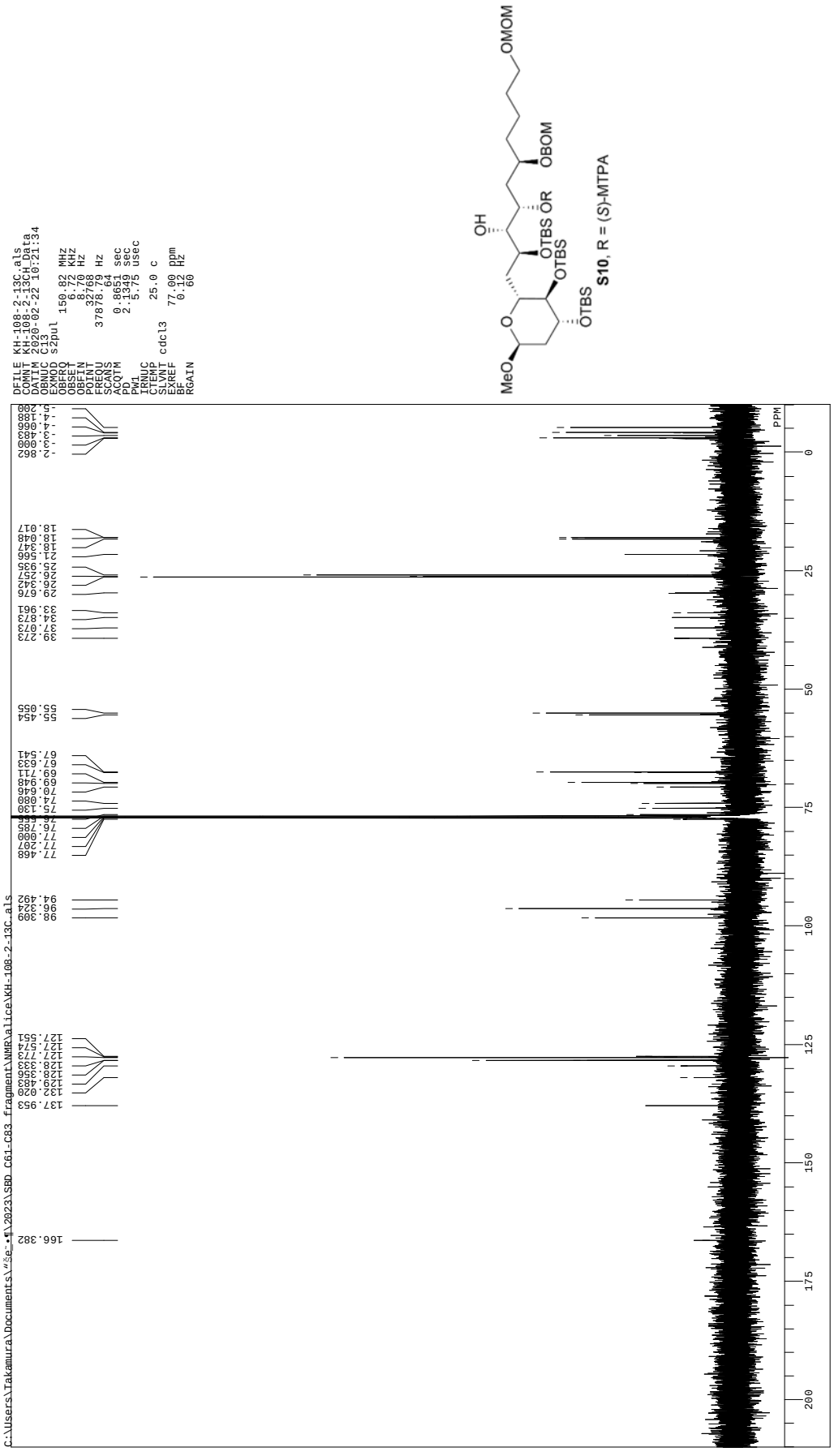
DFILE KH-128-2-re.als
COMNT KH-128-2-re
DATIM 2023-03-06 11:37:43
OBNUC H1
EXMOD s2pul
OBFRQ 399.91 MHz
OBSET 1.99 KHz
OBFIN 2.00 Hz
POINT 32768
FREQU 6410.26 Hz
SCANS 32
ACQTM 3.5000 sec
PD 1.5000 sec
PW1 7.15 usec
IRNUC
CTEMP 37.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF 4.20 Hz
RGAIN 42

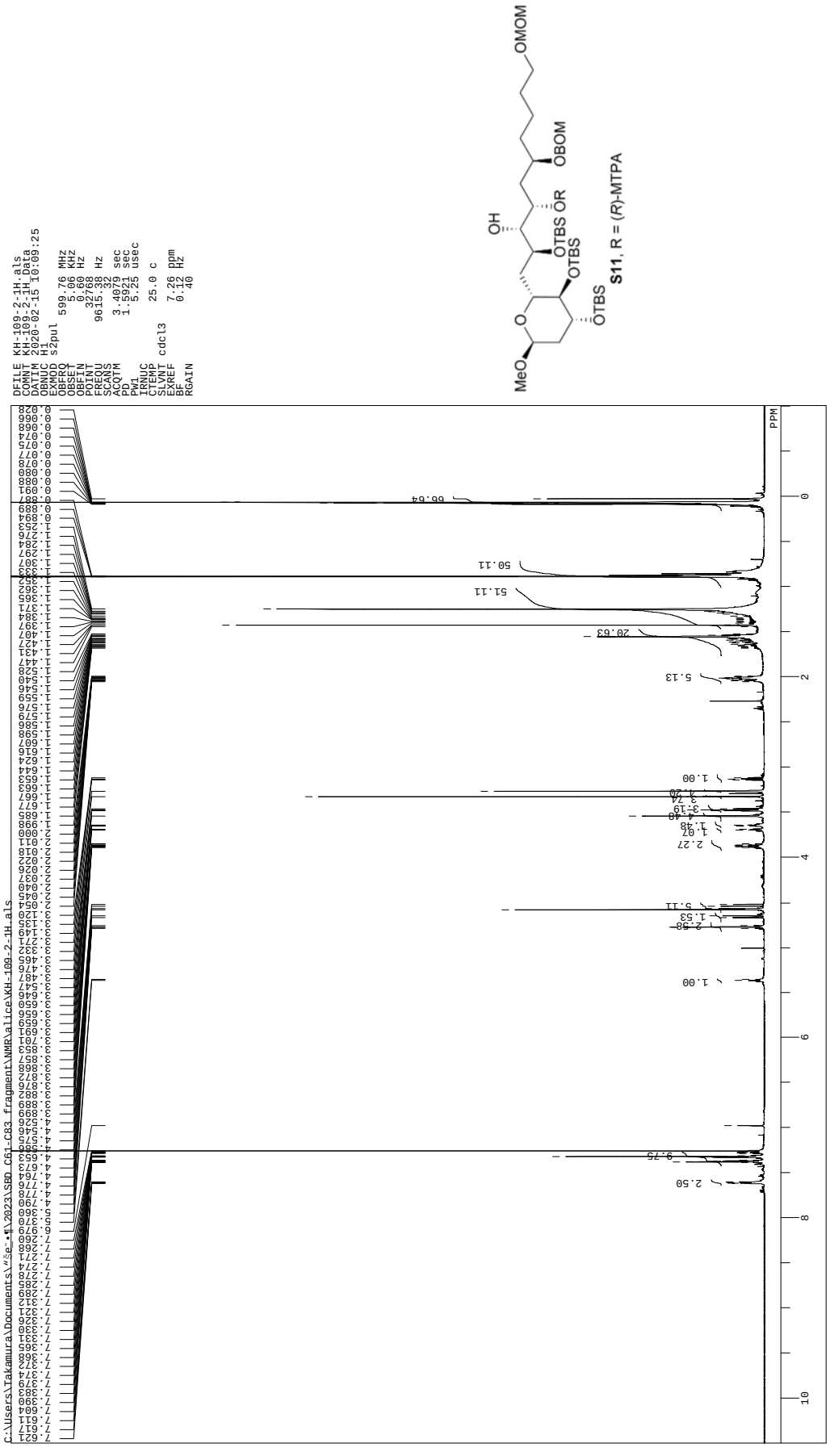


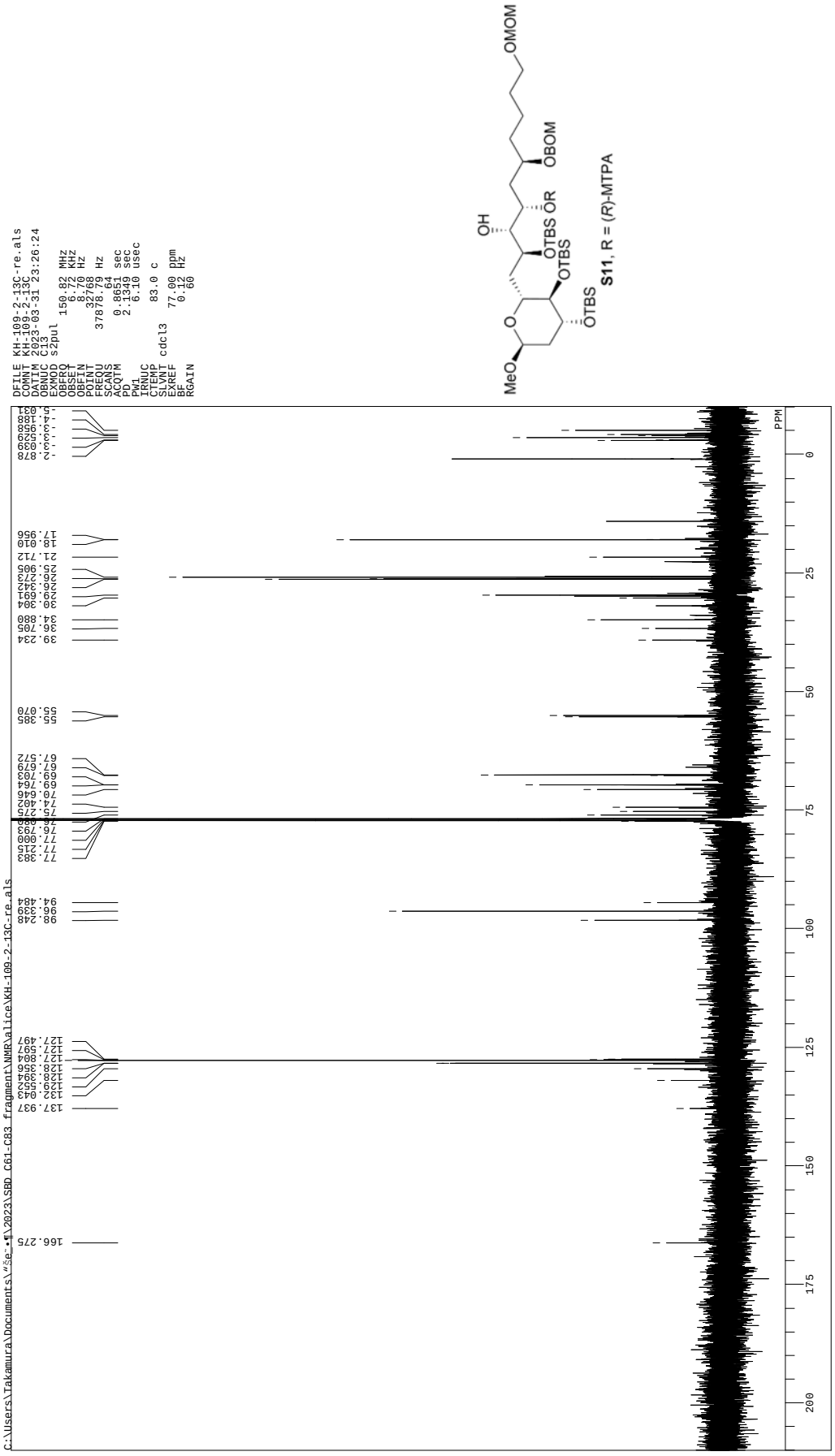
S9


C:\Users\Takamura\Documents\Case-1\2023\SBD_C61-C83_fragment\NMR\alice\KH-128-2-13C.als
DFILE KH-128-2-13C.als
COMNT KH-128-2-13C
DATIM 2023-03-03 15:13:49
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 6.72 KHz
OBFIN 8.70 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 6.05 usec
TEMP 40.0 c
SLVNT cdcl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
MeO
OTBS
OTBS
OTBS OH
OH
OBOM
OMOM
S9
PPM

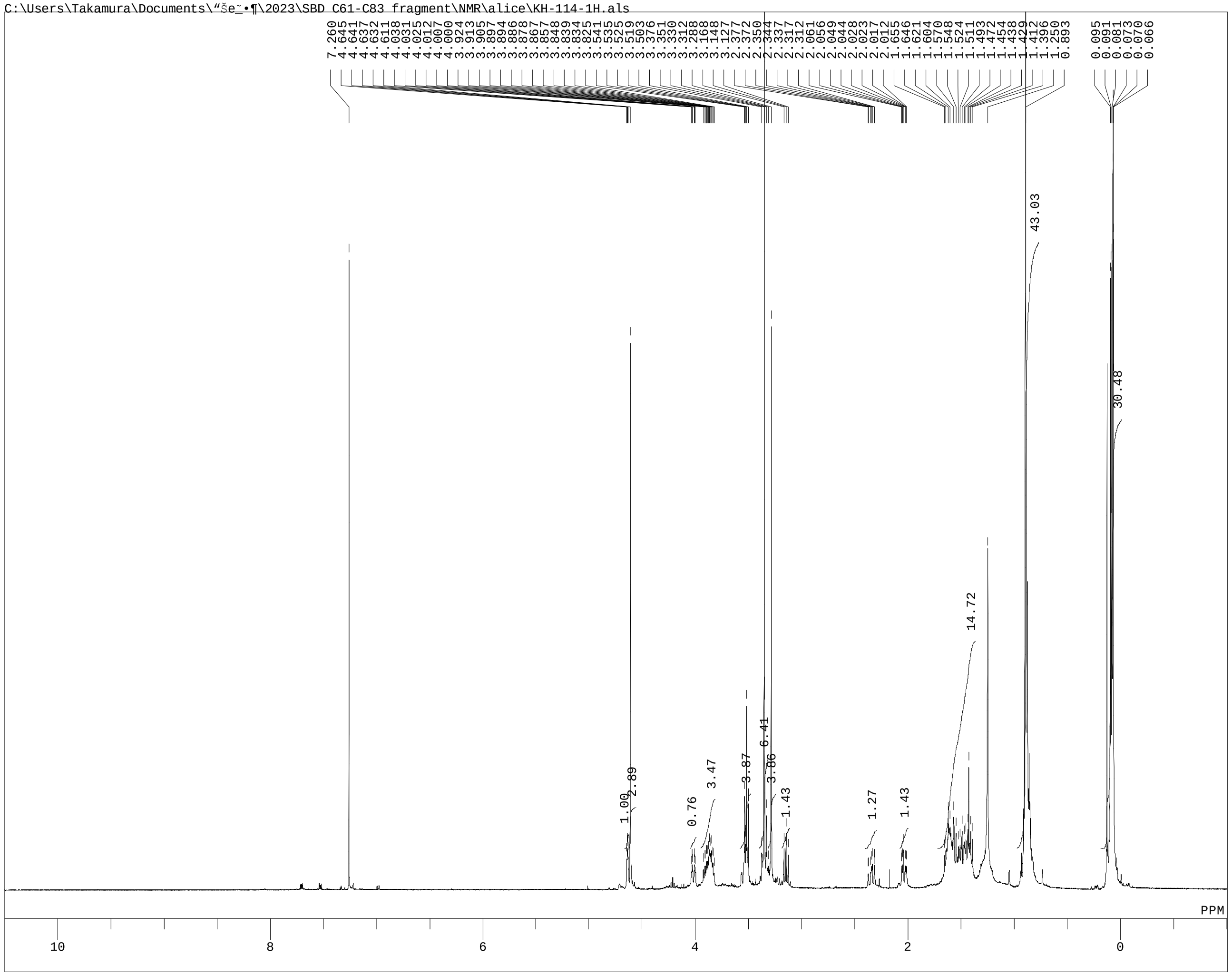

DFILE KH-108-2.als
COMNT KH-108-2
DATIM 2019-10-09 19:21:58
OBNUC H2
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 5.06 KHz
OBFIN 0.60 Hz
POINT 32768 Hz
FREQU 9615.32 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
TEMP 25.0 c
SLVNT cdcl3 7.26 ppm
EXREF 0.12 Hz
RGAIN 44
OMOM
OBOM
OH
OTBS OR
OTBS
OTBS
MeO
S10, R = (S)-MTPA
C:\Users\Takamura\Documents\ﾏｽﾀｰ\2023\SBD_CG1-C83_fragment\NMR\alice\KH-108-2.als
PPM
39.68
32.97
14.89
19.95
1.07
1.09
2.22
1.16
7.01
1.96
1.11
1.54
0.84
7.19
4.97


OMOM
OBOM
OH
OTBS
OR
OTBS
OTBS
MeO
O
S10, R = (S)-MTPA

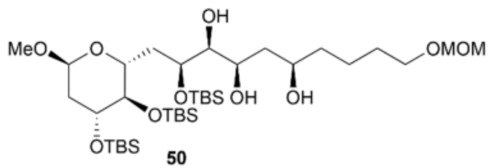

DFILE KH-109-2-1H.als
COMNT KH-109-2-1H data
DATIM KH-20-02-15 10:09:25
ONUC H1
OBFRQ 599.76 MHz
OBSET 5.06 KHz
OBFIN 8.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PW1 1.5925 usec
IRNUC
CTEMP 25.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 40
OMOM
OBOM
OH
OTBS OR
OTBS
OTBS
MeO
S11, R = (R)-MTPA
C:\Users\Takamura\Documents\ﾏｽﾀｰ･ﾅﾋﾞ\2023\SBD_CG1-C83_fragment\NMR\alice\KH-109-2-1H.als
PPM


C:\Users\Takamura\Documents\データ\2023\SBD_G01-C83_fragment\NMR\alice\KH-109-2-13C-re.als
DFILE KH-109-2-13C-re.als
CMNT KH-109-2-13C
DATIM 2023/03/31 23:26:24
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 67.70 KHz
OBFIN 32768 Hz
POINT 37878.79 Hz
FREQU 64
SCANS 0.8051 sec
ACQTM 2.1943 sec
PD 6.10 usec
PW1
IRNUC 83.0 c
CTEMP
SOLVENT cdcl3 77.00 ppm
EXREF 0.12 Hz
BF 60
RGAIN
OMOM
OBOM
OH
OTBS OR
OTBS
OTBS
MeO
S11, R = (R)-MTPA
PPM

C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\KH-114-1H.als

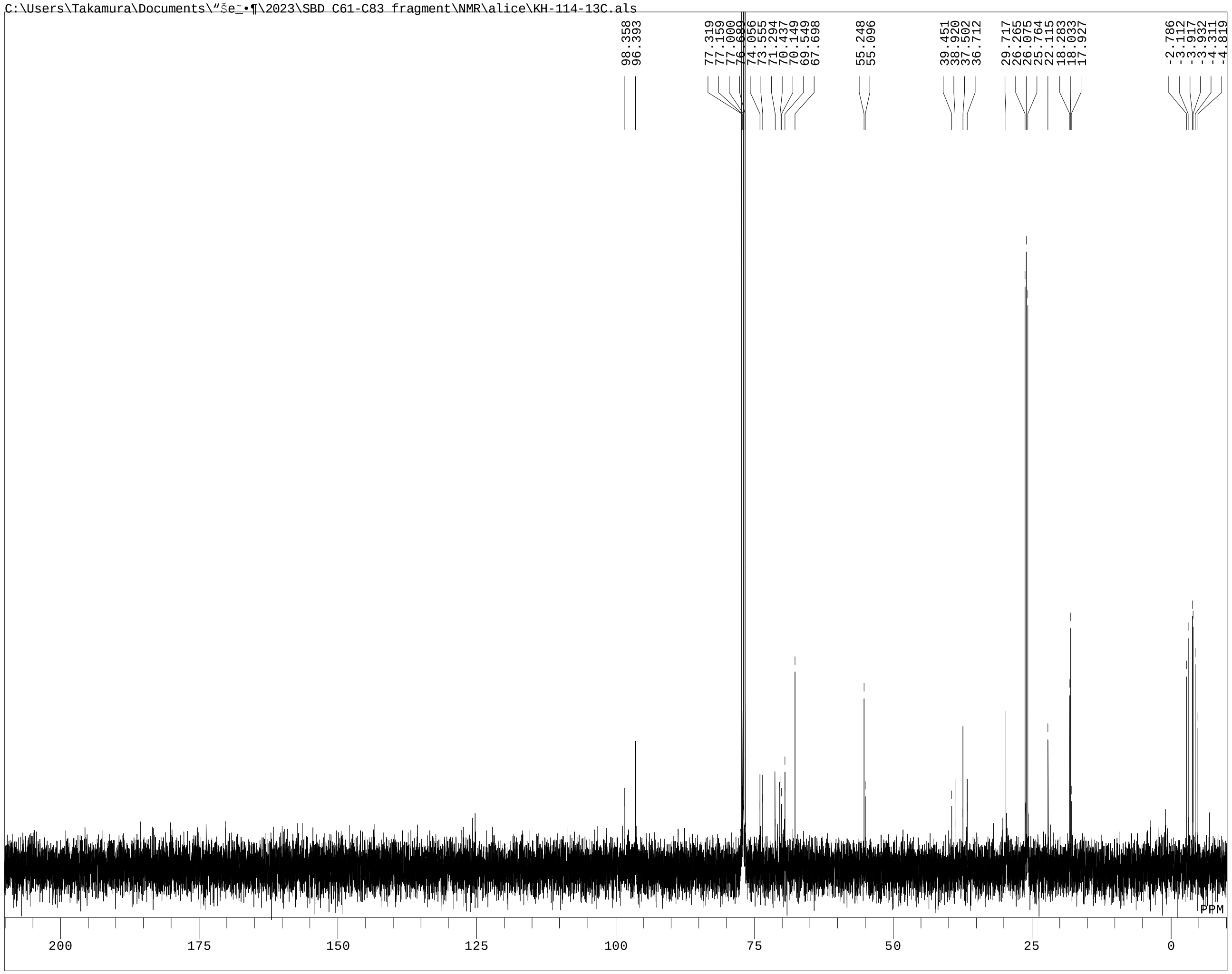


DFILE KH-114-1H.als
COMNT KH-114_data
DATIM 2019-12-13 12:13:28
OBNUC H1
EXMOD s2pul
OBFRQ 399.91 MHz
OBSET 1.99 KHz
OBFIN 2.00 Hz
POINT 32768
FREQU 6410.26 Hz
SCANS 32
ACQTM 3.5000 sec
PD 1.5000 sec
PW1 7.25 usec
IRNUC
CTEMP 30.0 c
SLVNT cdcl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 42

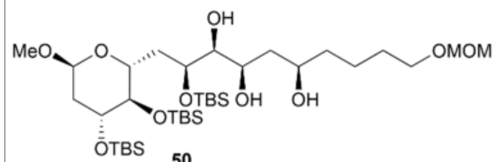


50

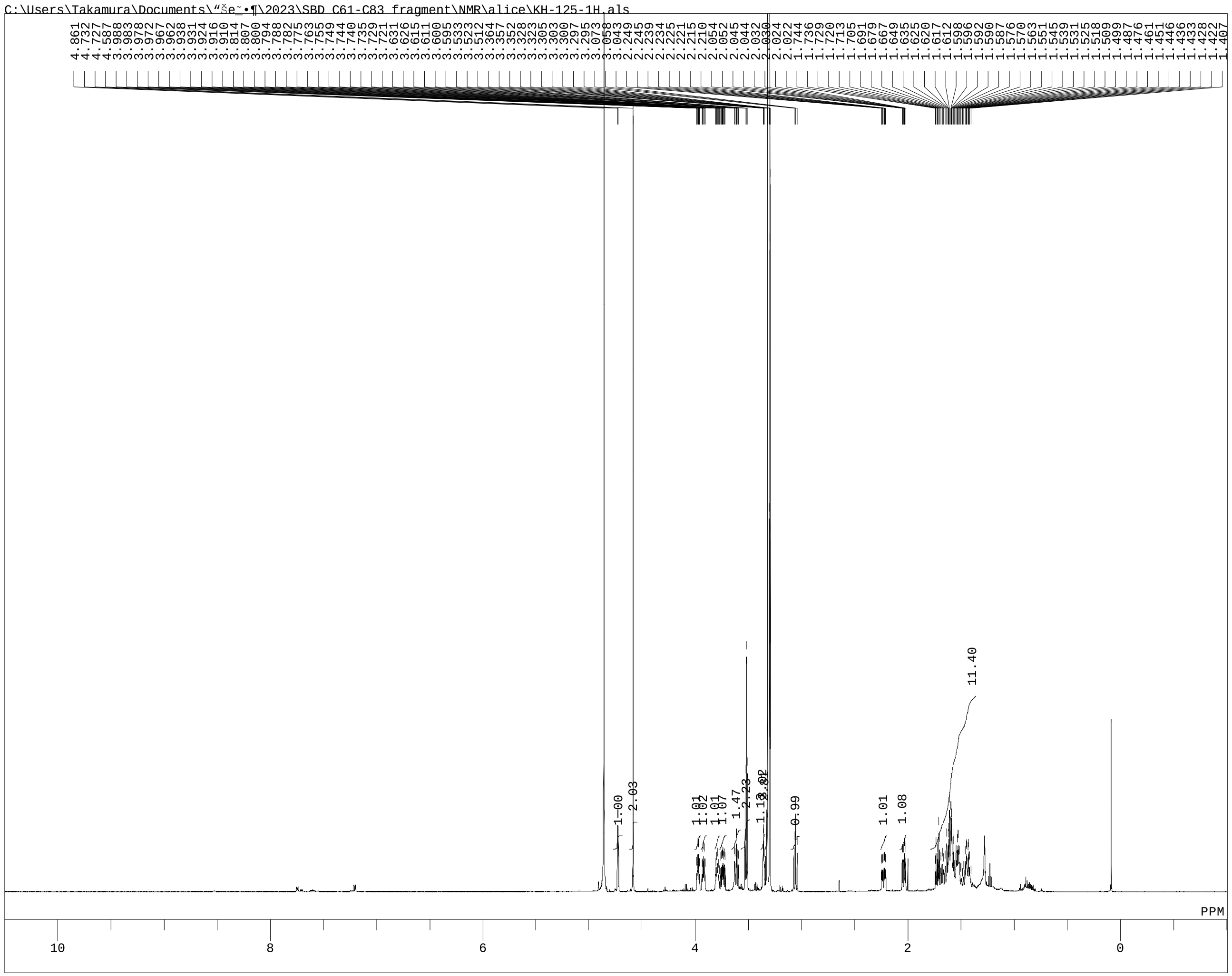
C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\KH-114-13C.als



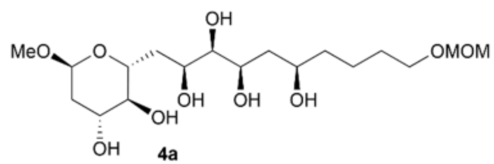

```
DFILE  KH-114-13C.als
COMNT  KH-114-13C_data
DATIM  2019-12-13 12:21:49
OBNUC  C13
EXMOD  s2pul
OBFRQ       100.56 MHz
OBSET         8.40 KHz
OBFIN         8.30 Hz
POINT        32768
FREQU     25000.00 Hz
SCANS           64
ACQTM       1.3107 sec
PD          1.6893 sec
PW1           5.90 usec
IRNUC
CTEMP         30.0 c
SLVNT  cdcl3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           54
```



50

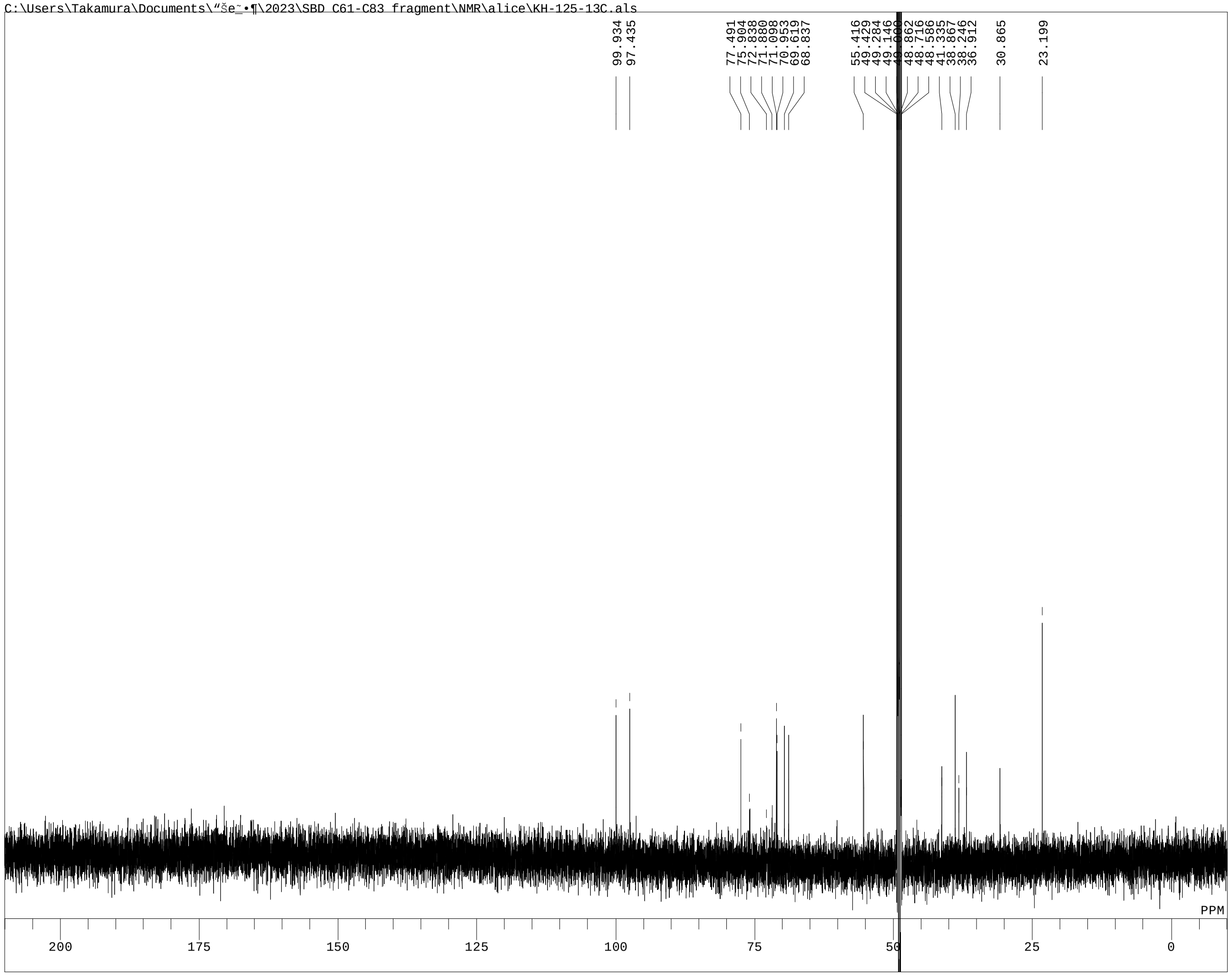


DFILE KH-125-1H.als
COMNT KH-125_Data
DATIM 2020-01-27 20:56:43
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 7.42 KHz
OBFIN 3.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 42

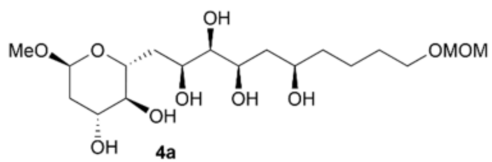


4a

C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\KH-125-13C.als




```
DFILE  KH-125-13C.als
COMNT  KH-125_13C_Data
DATIM  2020-01-27 21:01:44
OBNUC  C13
EXMOD  s2pul
OBFRQ       150.82 MHz
OBSET         7.32 KHz
OBFIN         3.00 Hz
POINT        32768
FREQU     37878.79 Hz
SCANS           64
ACQTM       0.8651 sec
PD          2.1349 sec
PW1           5.75 usec
IRNUC
CTEMP         25.0 c
SLVNT  cd3od
EXREF        49.00 ppm
BF            0.12 Hz
RGAIN           60
```

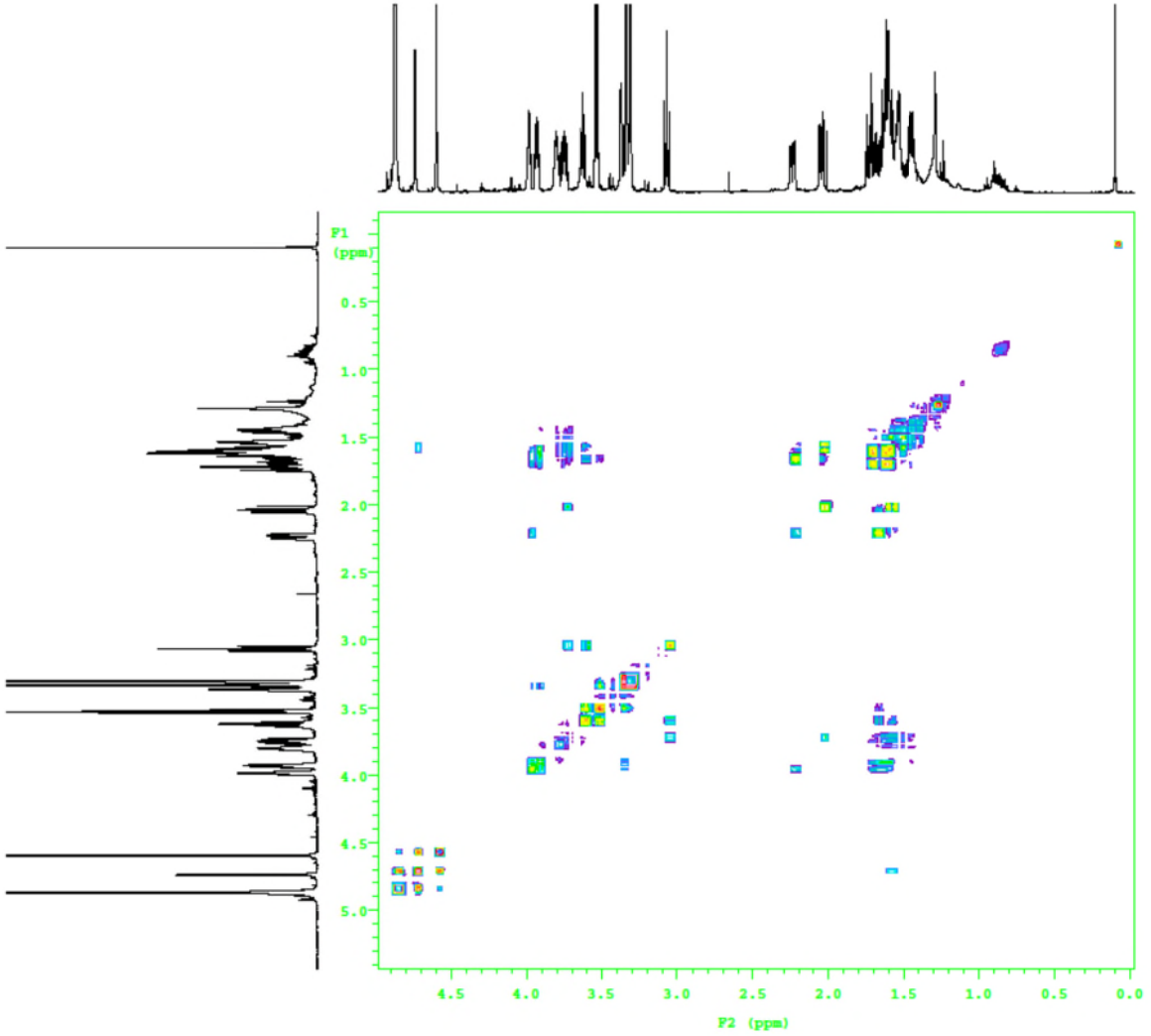


4a

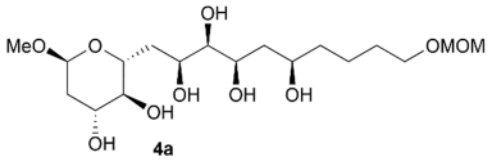
KH-125_Data

exp3 gCOSY

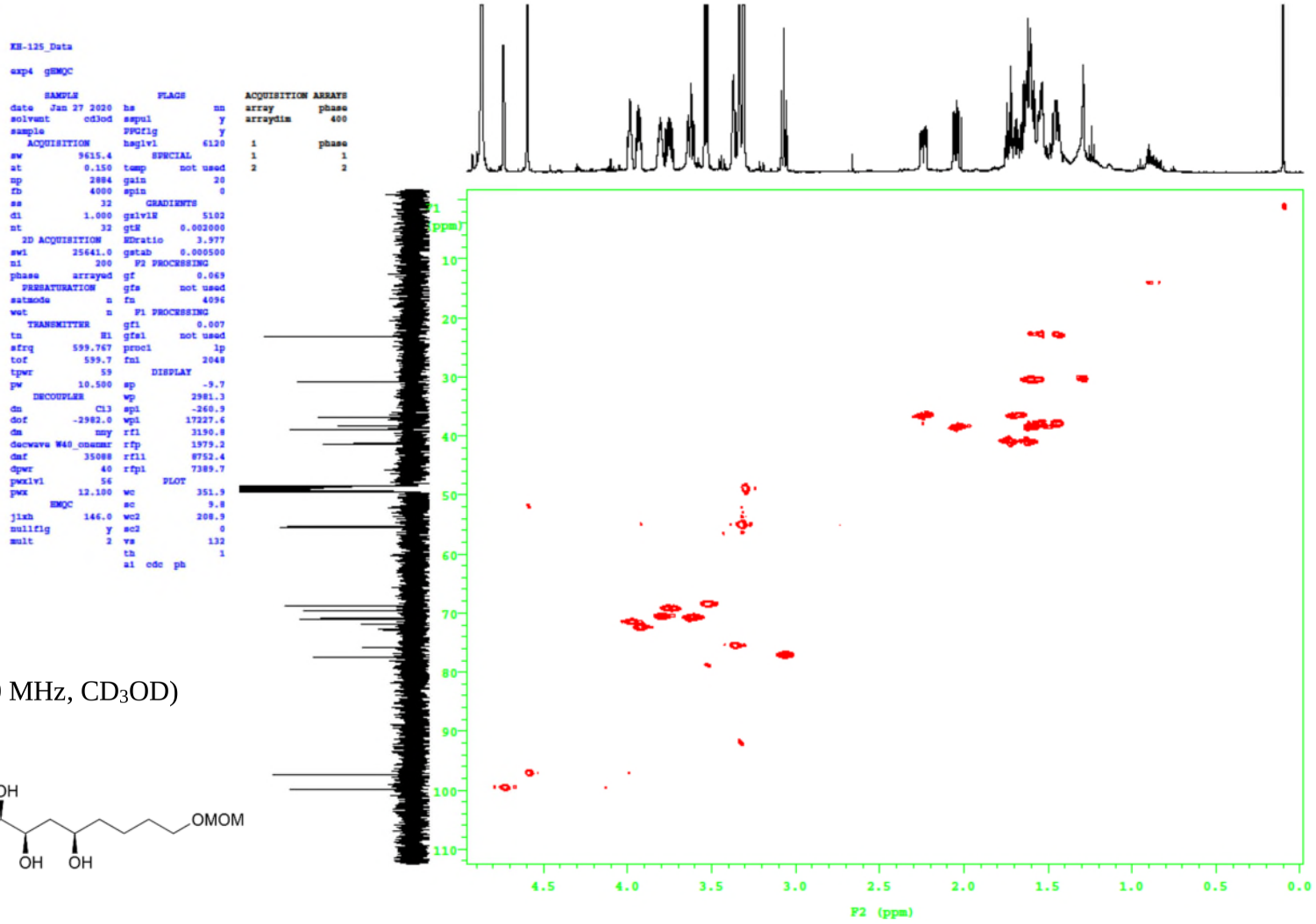
SAMPLE		FLAGS	
date	Jan 27 2020	hs	nn
solvent	cd3od	aspul	y
sample		hsglvl	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	42
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	16	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.007
ni	256	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-14.1
TRANSMITTER		wp	3000.1
tn	H1	sp1	-97.8
sfrq	599.767	wp1	3356.9
tof	599.7	rf1	3199.9
tpwr	59	rfp	1979.2
pw	10.500	rf11	3208.5
GRADIENTS		rfp1	1979.2
gzlvlE	5102	PLOT	
gtE	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	445
dm	nnn	th	4
		al cdc av	



^{1}H–^{1}H COSY (600 MHz, CD_3OD)

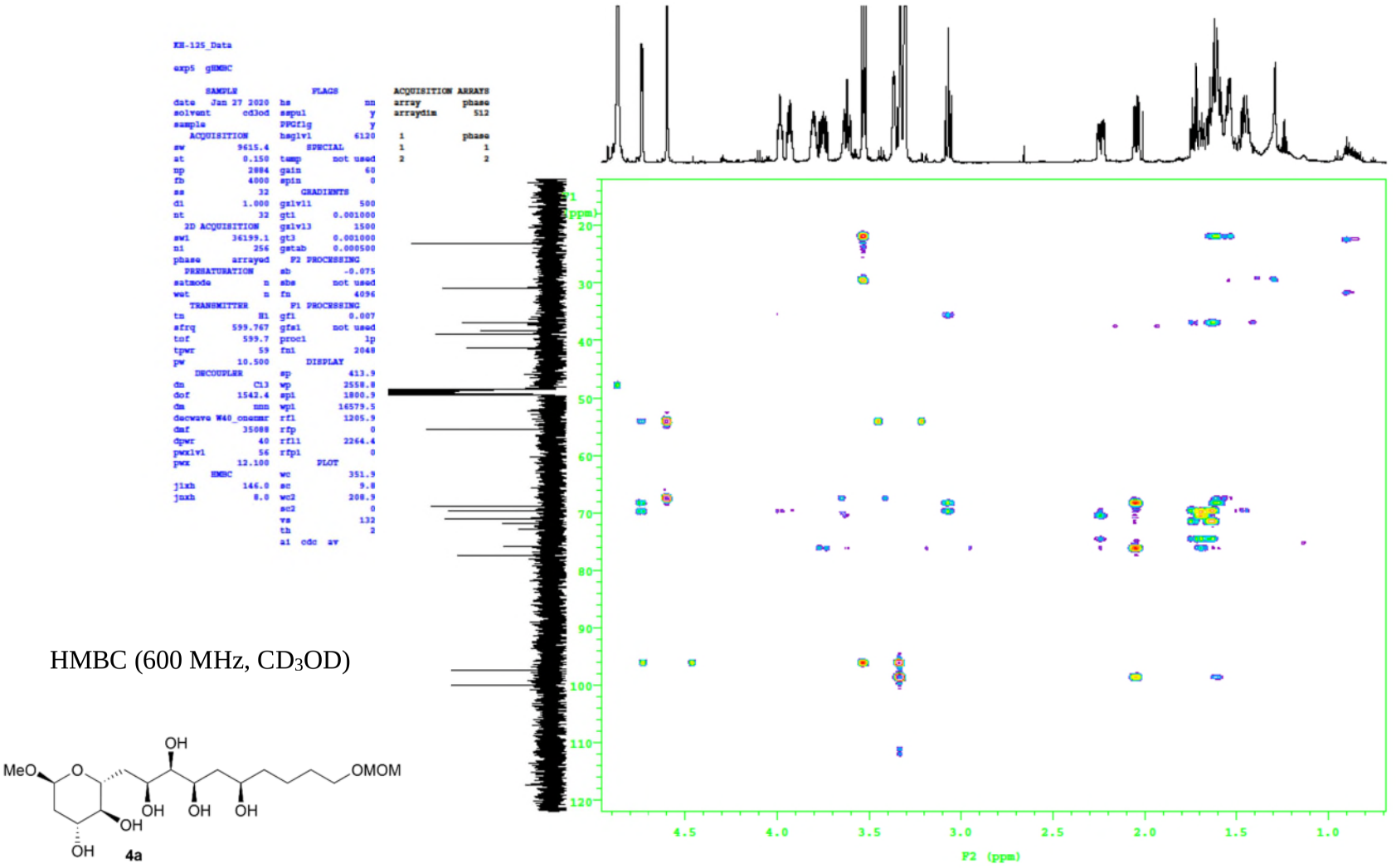


4a



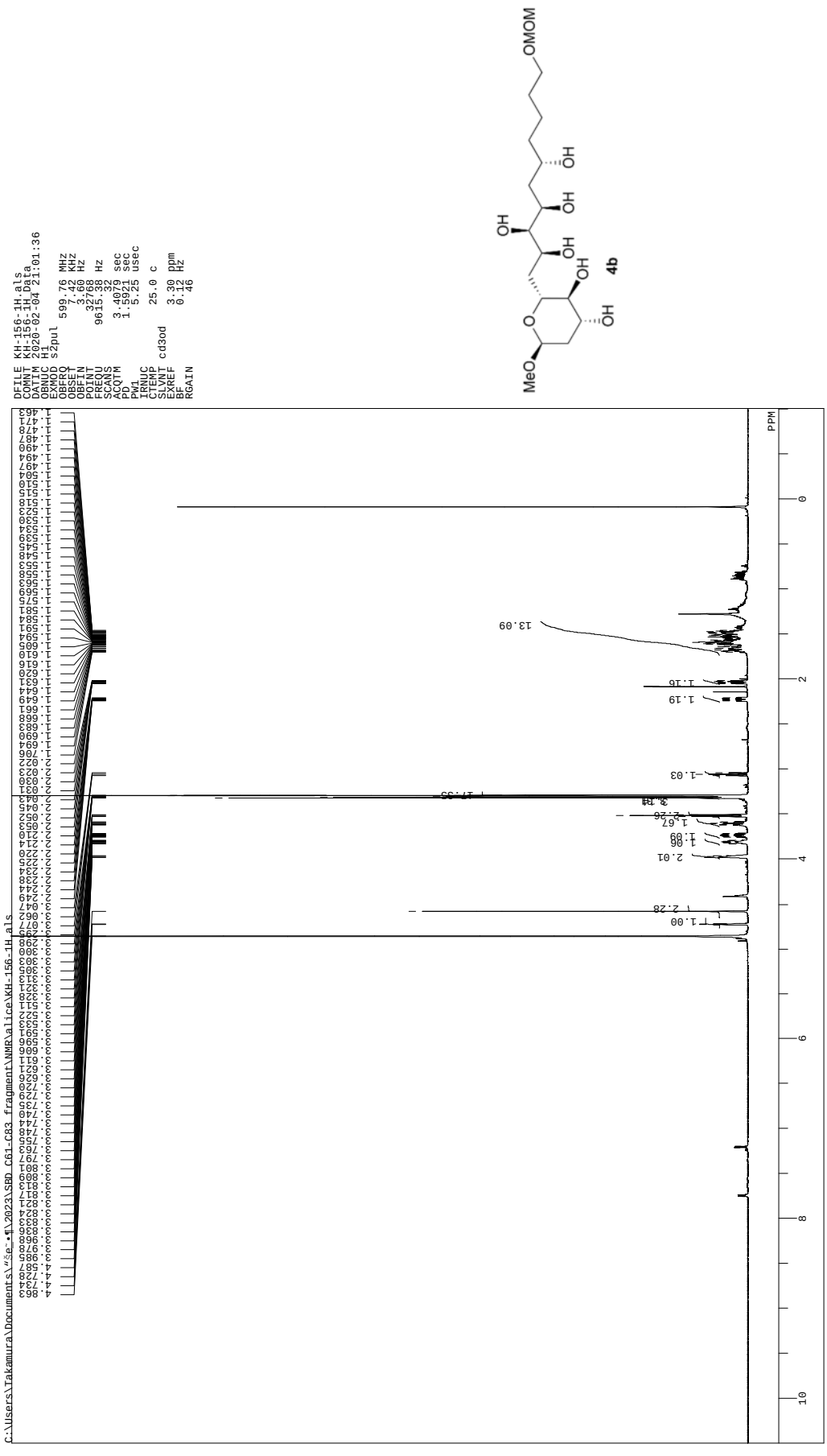
HMQC (600 MHz, CD_3OD)

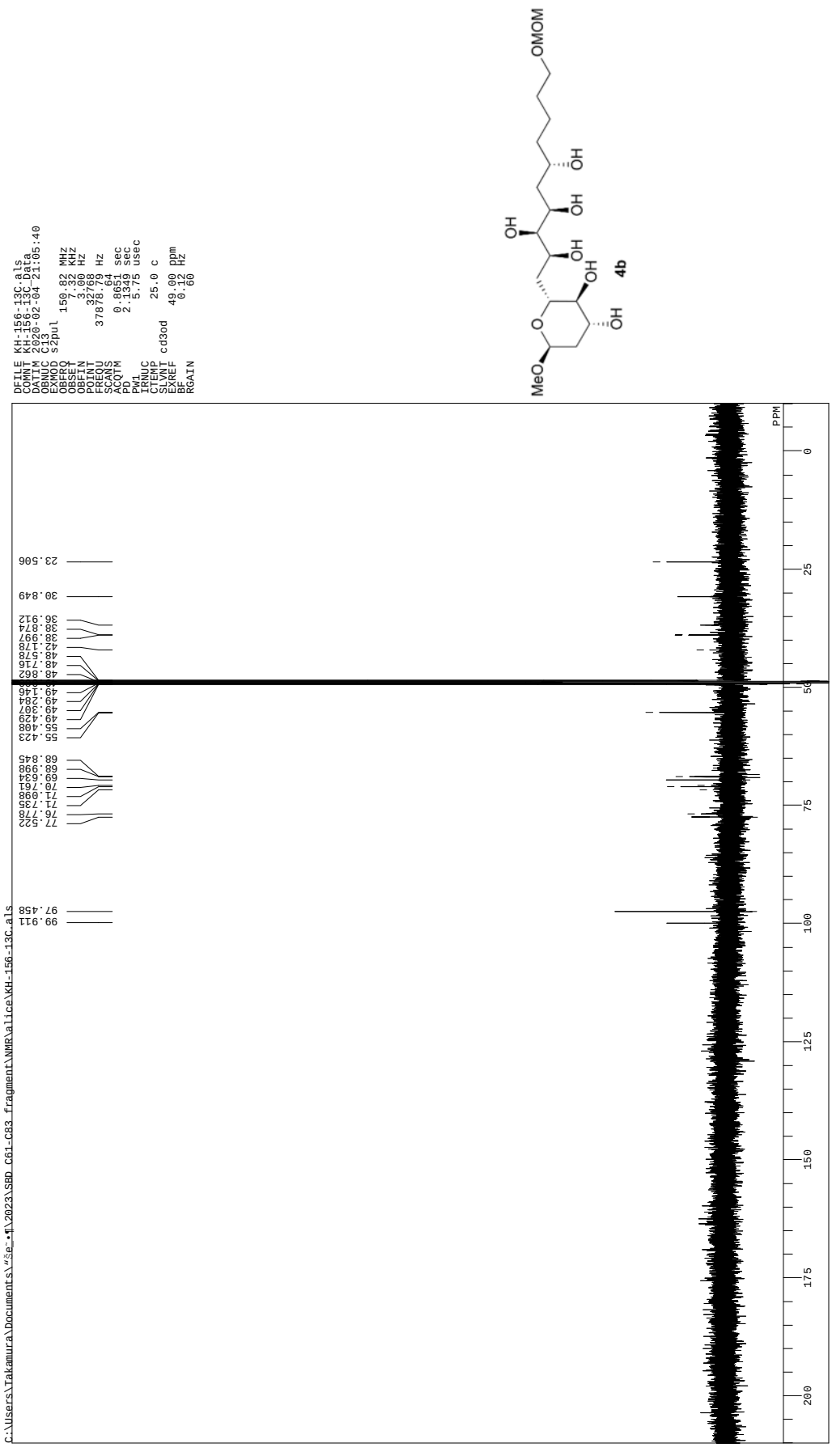
4a



HMBC (600 MHz, CD_3OD)

4a

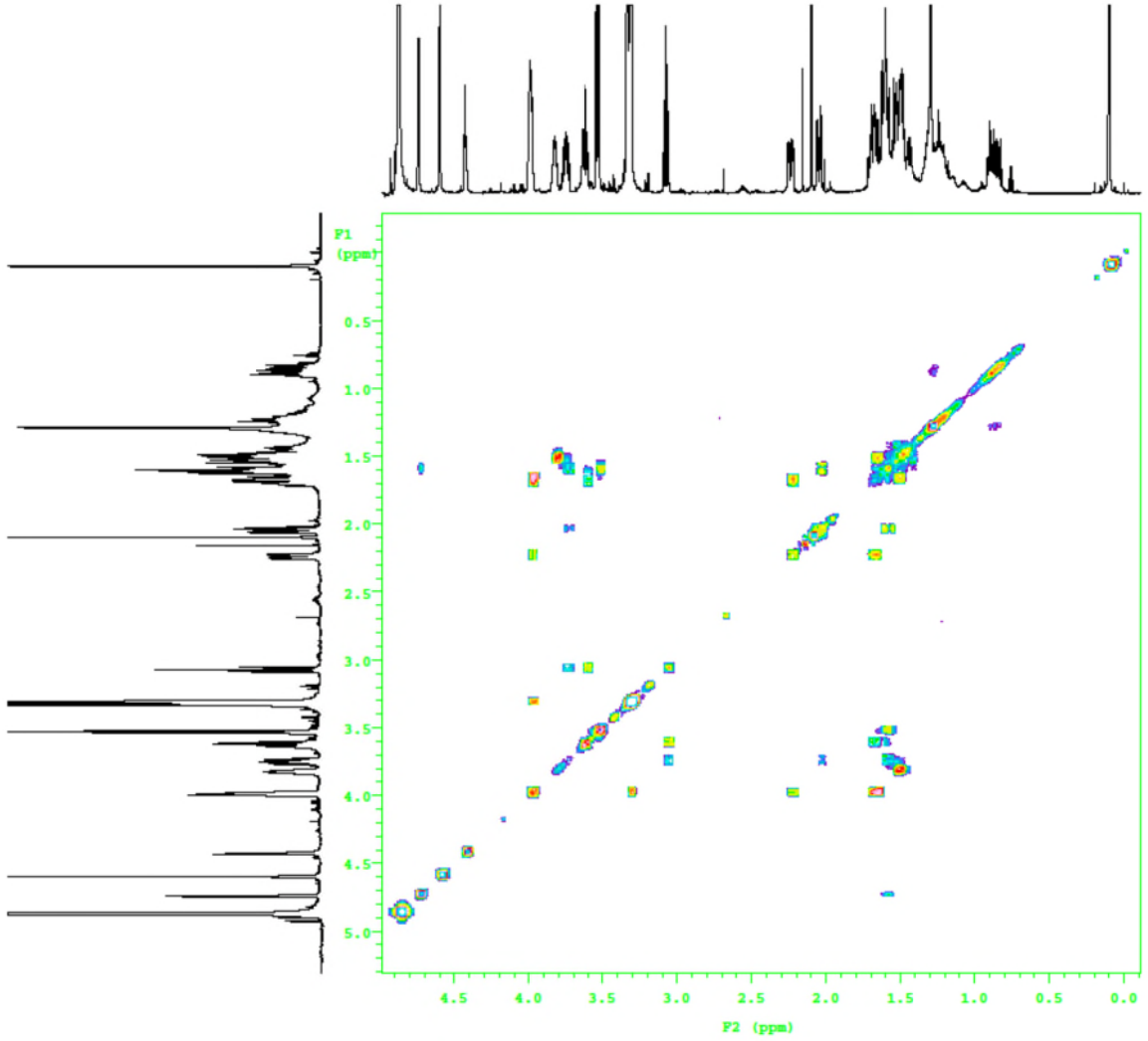

OMOM
OH
OH
OH
OH
OH
OH
O
MeO
4b
PPM
13.09
1.16
1.19
1.03
17.35
3.11
2.26
1.67
1.09
1.06
2.01
1.00
2.28


OMOM
OH
OH
OH
OH
OH
OH
O
MeO
4b
DFILE KH-156-13C.als
COMNT KH-156-13C.fid.a
DATIM 2020-02-04 21:05:40
OBNUC
EXMOD s2pul
OBSET 150.82 MHz
OBFIN 7.32 KHz
POINT 3.00 Hz
FREQU 32768
SCANS 37878.79 Hz
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
C:\Users\Takamura\Documents\マスター\2023\SBD_GG1-C83_fragment\NMR\alice\KH-156-13C.als
23.506
30.849
36.912
38.874
38.997
42.178
48.578
48.716
48.862
49.146
49.284
49.397
49.429
55.408
55.423
68.845
68.998
69.634
70.761
71.098
71.735
76.778
77.522
97.458
99.911
PPM
0
25
50
75
100
125
150
175
200

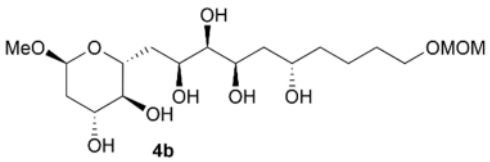
KH-156-1H_Data

exp3 gCOSY

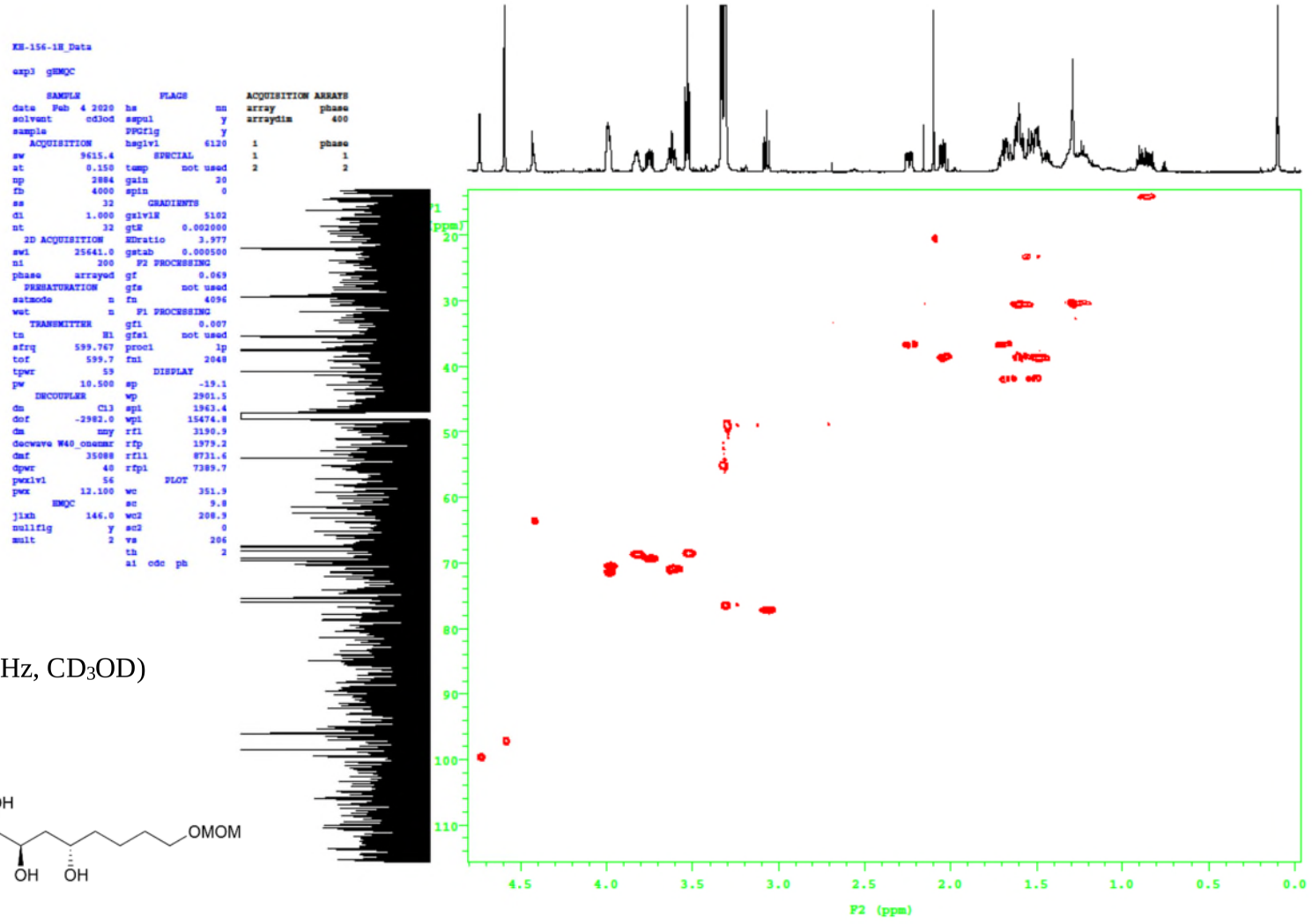
SAMPLE		FLAGS	
date	Feb 4 2020	hs	nn
solvent	cd3od	sspul	y
sample		hsglv1	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	46
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	16	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.027
n1	256	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-63.9
TRANSMITTER		wp	3051.8
tn	H1	sp1	-173.9
sfrq	599.767	wp1	3356.9
tof	599.7	rf1	3198.1
tpwr	59	rfp	1979.2
pw	10.500	rf11	3200.1
GRADIENTS		rfp1	1979.2
gzlvlE	5102	PLOT	
gtE	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	206
dm	nnn	th	4
		ai	cdc av



^{1}H–^{1}H COSY (600 MHz, CD_3OD)

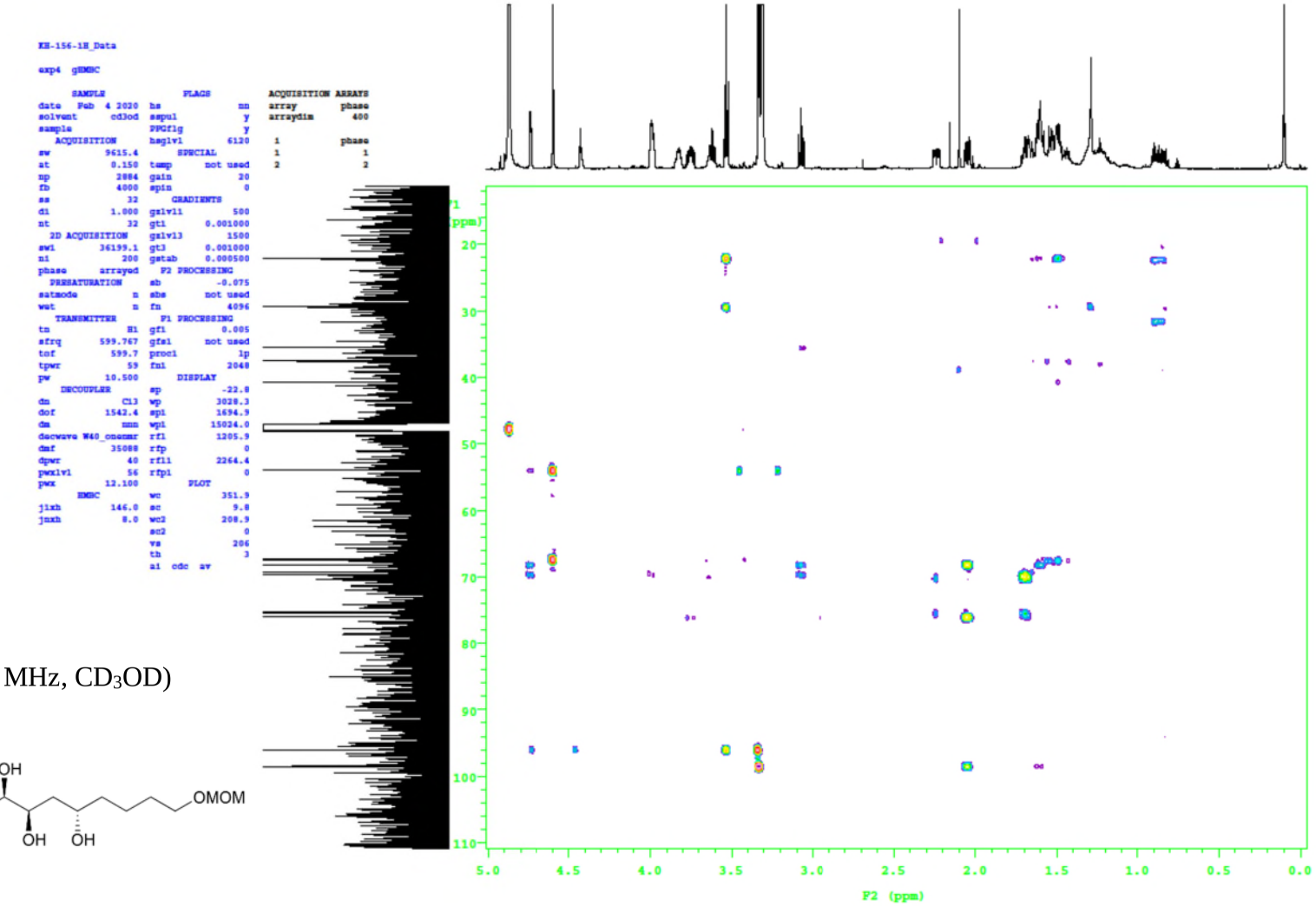


4b



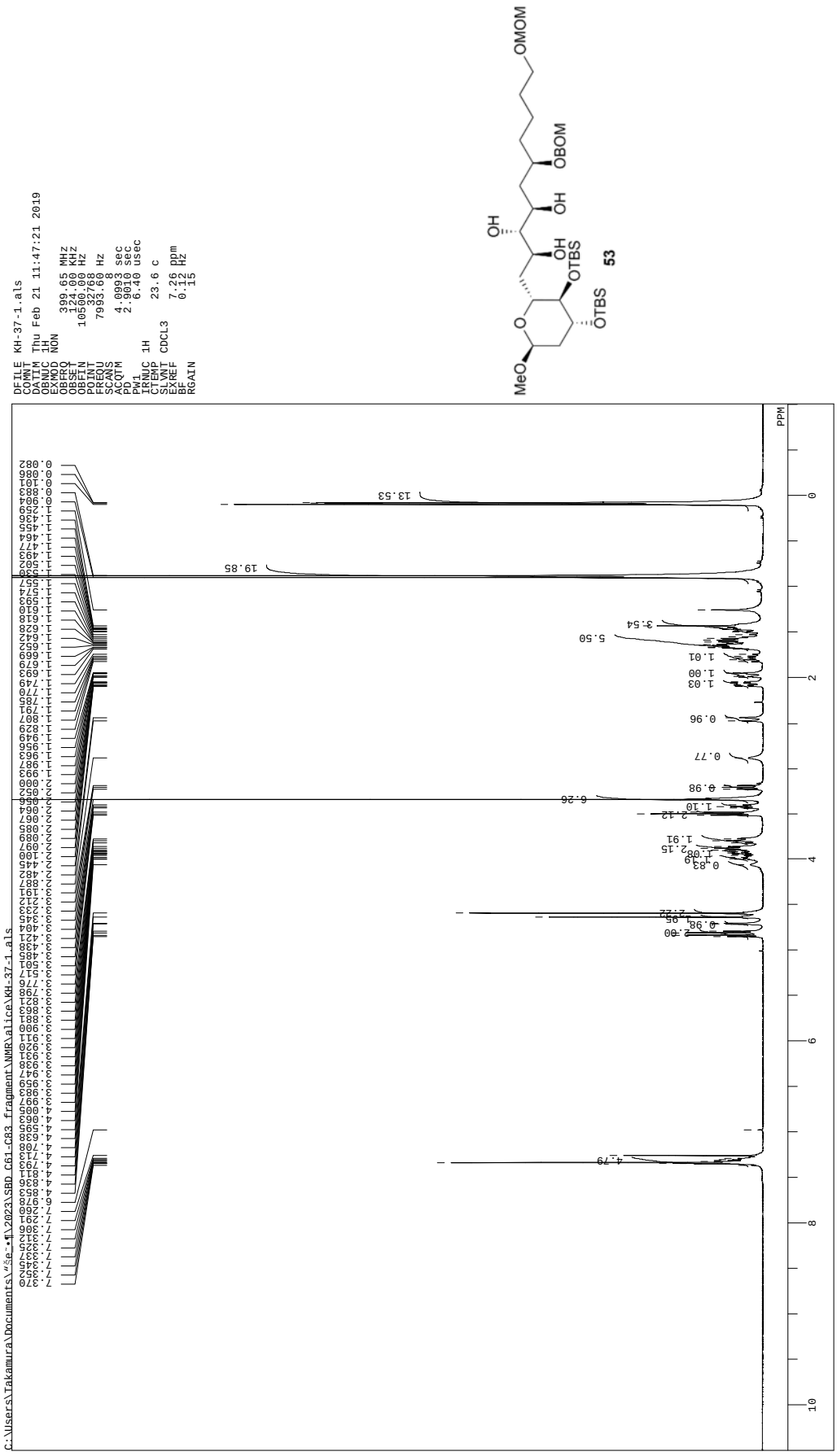
HMQC (600 MHz, CD_3OD)

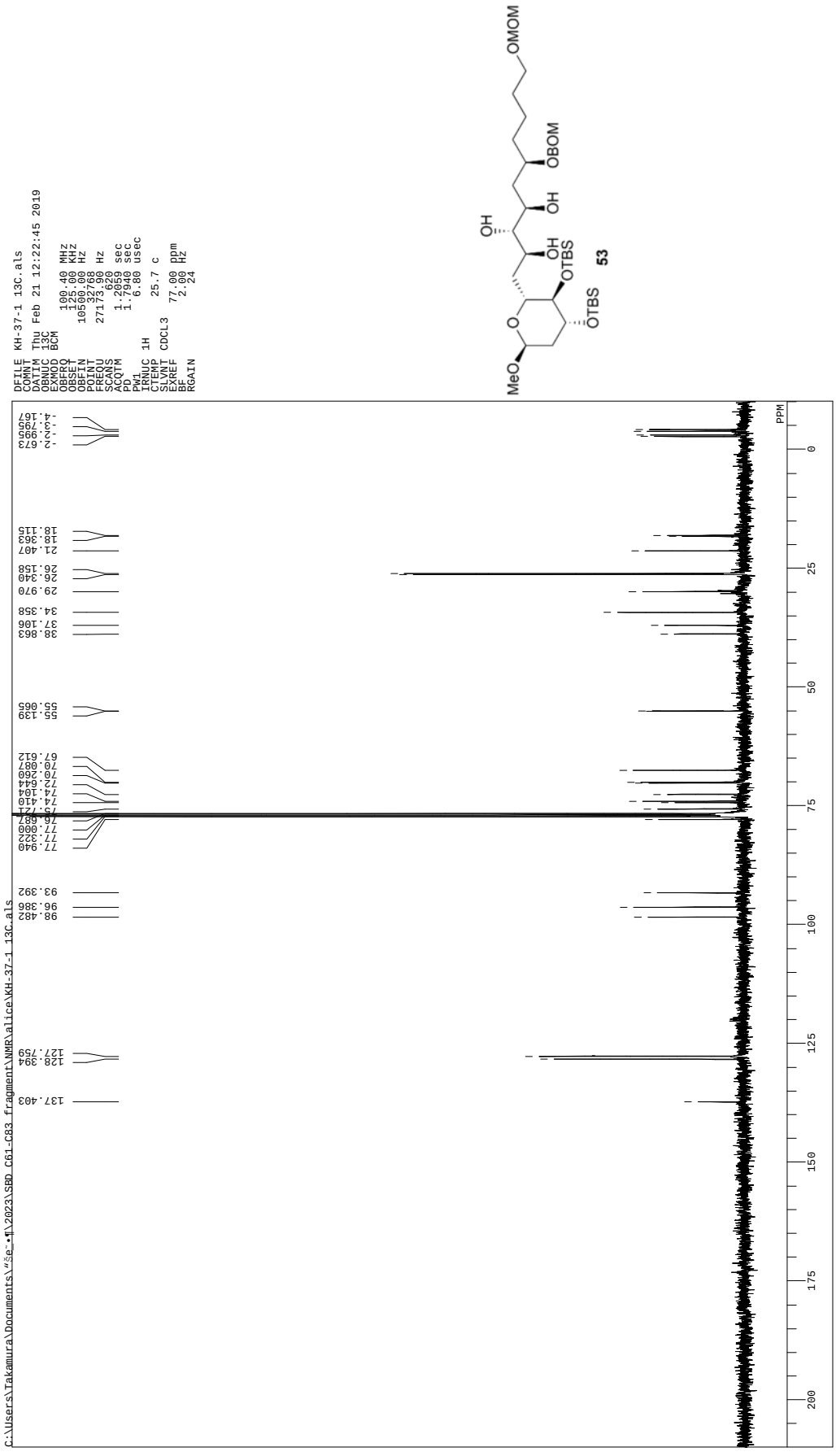
4b

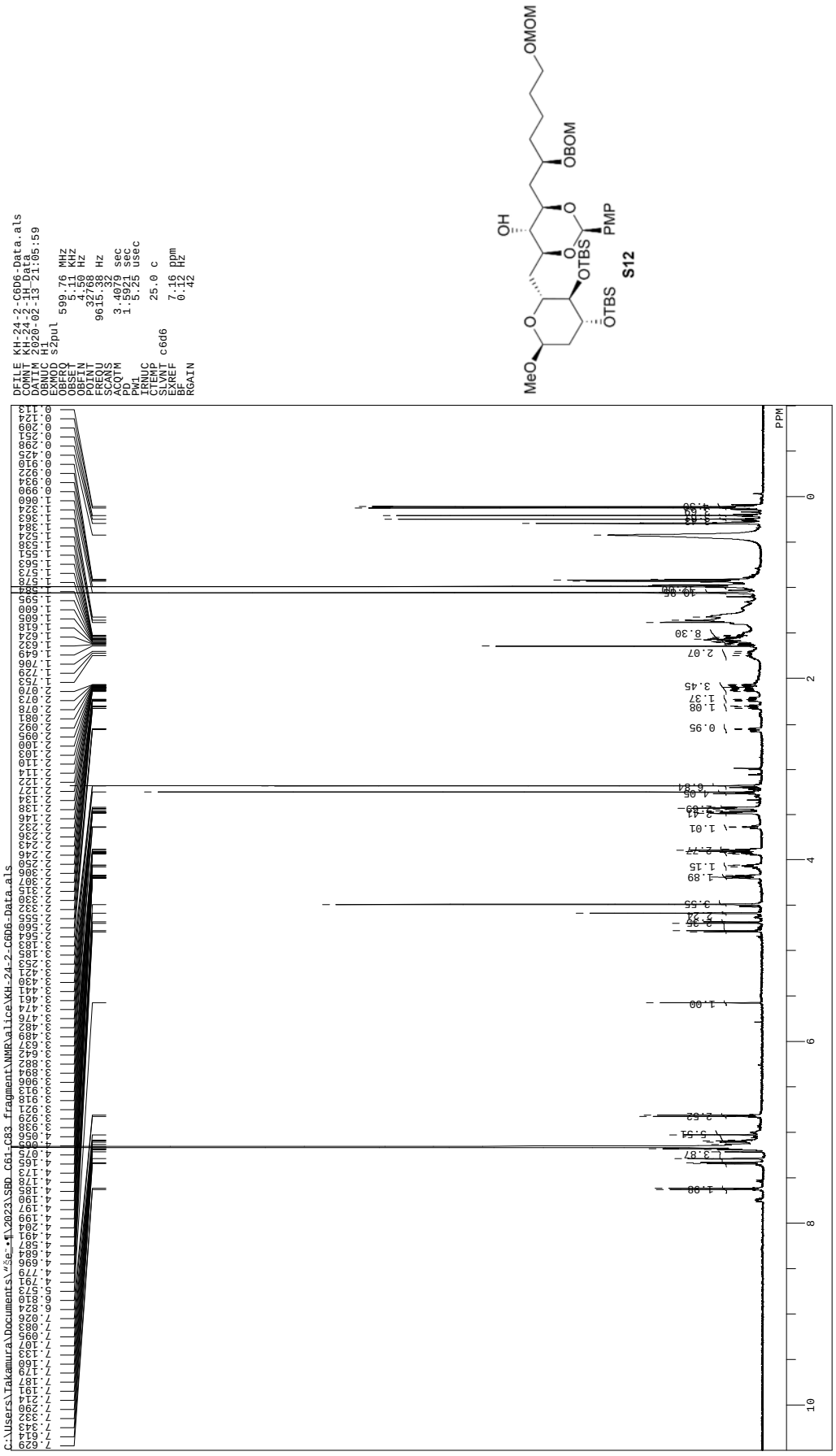


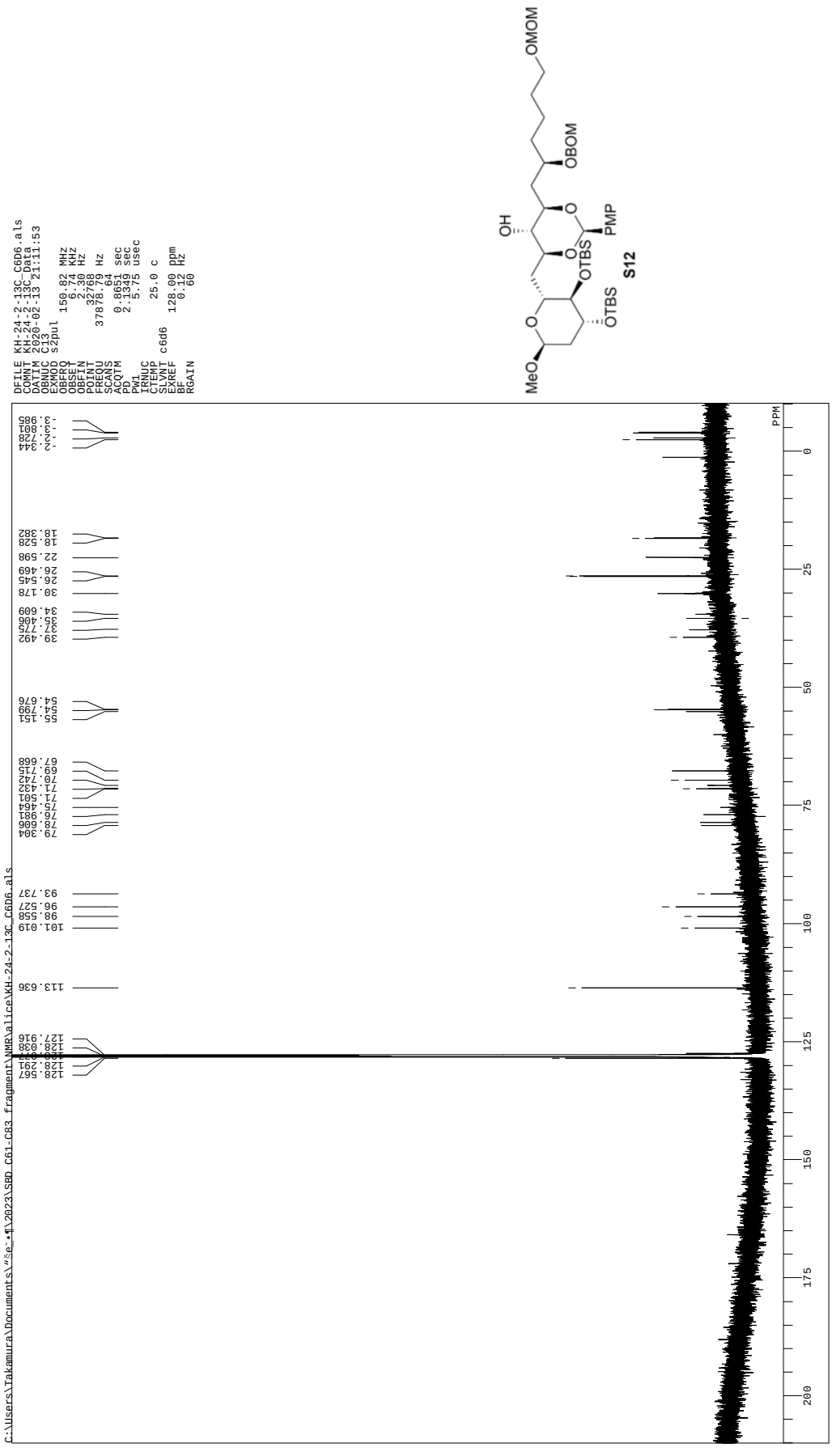
HMBC (600 MHz, CD_3OD)

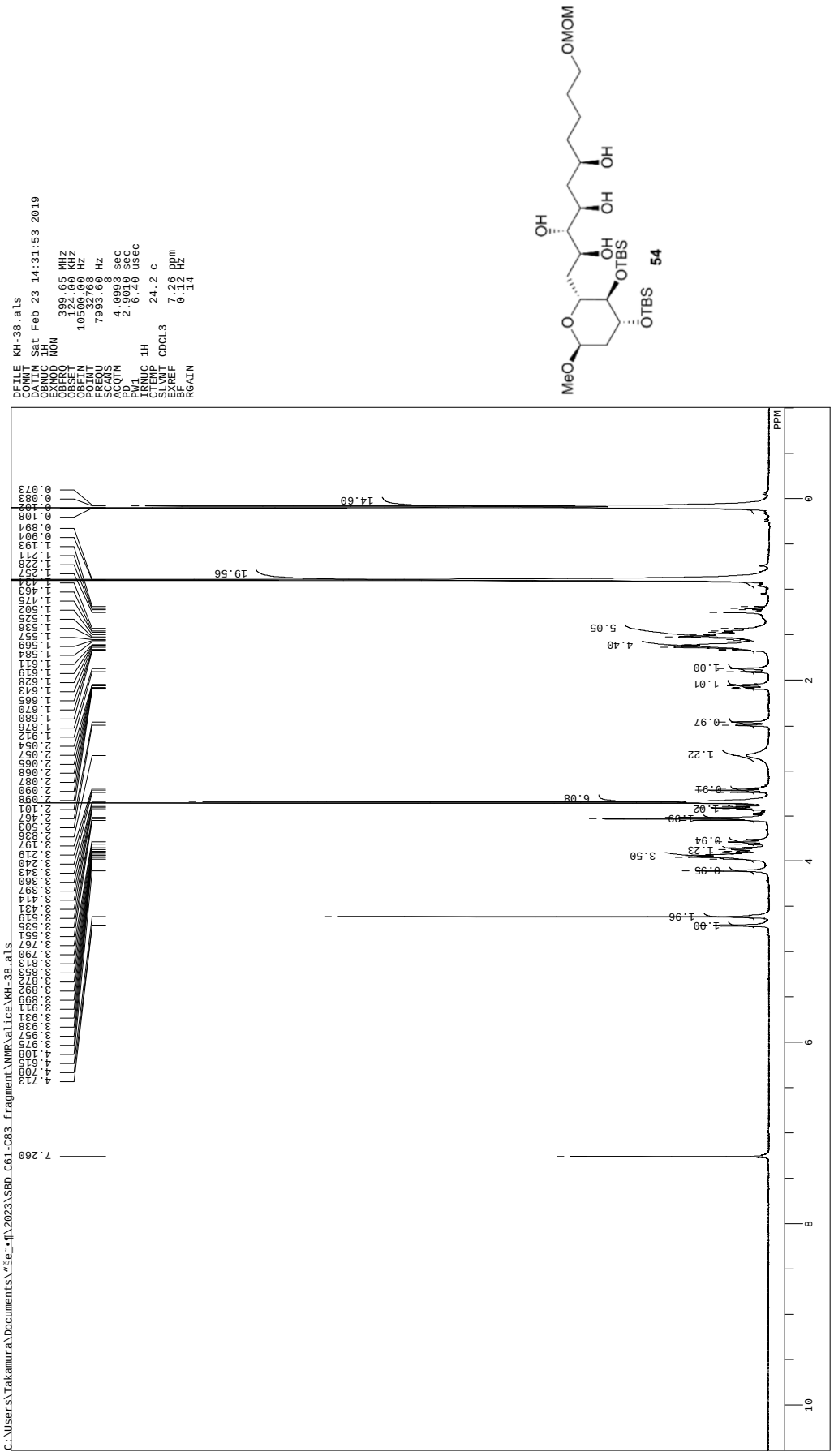
4b

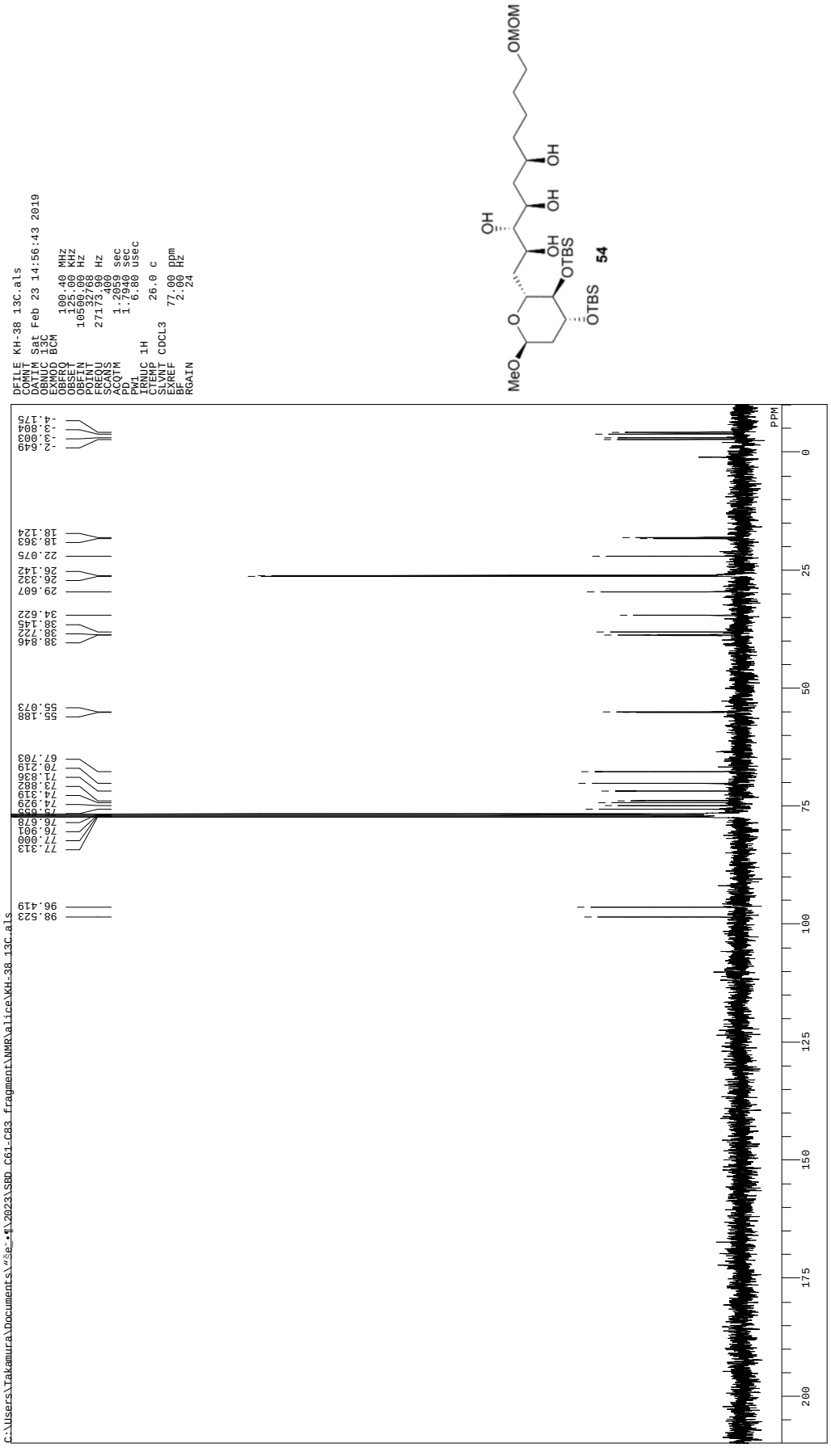

OMOM
OBOM
OH
OH
OH
OTBS
OTBS
MeO
53
DFILE KH-37-1.als
COMNT
DATIM Thu Feb 21 11:47:21 2019
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IN1
DE 23.6 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 15
C:\Users\Takamura\Documents\NMR\2023\SBD_C61_C83_fragment\NMR\alice\KH-37-1.als
PPM
13.53
19.85
6.26
4.79
5.50
3.54
1.01
1.00
1.03
0.96
0.77
0.98
1.10
2.12
1.91
1.02
2.15
0.83
1.19
2.82
1.95
0.98
2.00

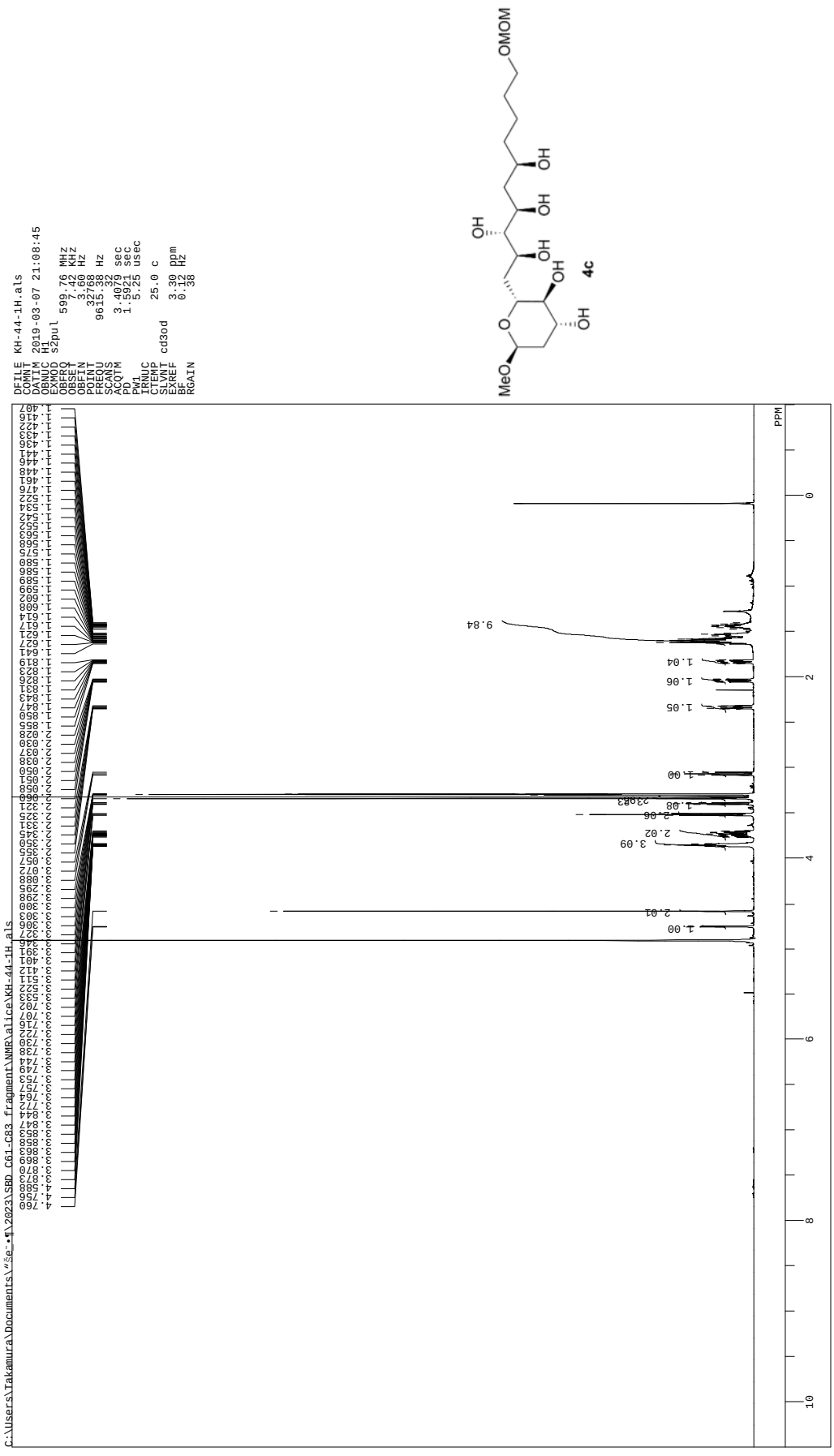

OMOM
OBOM
OH
OH
OH
OTBS
OTBS
MeO
O
53
PPM
0
25
50
75
100
125
150
175
200

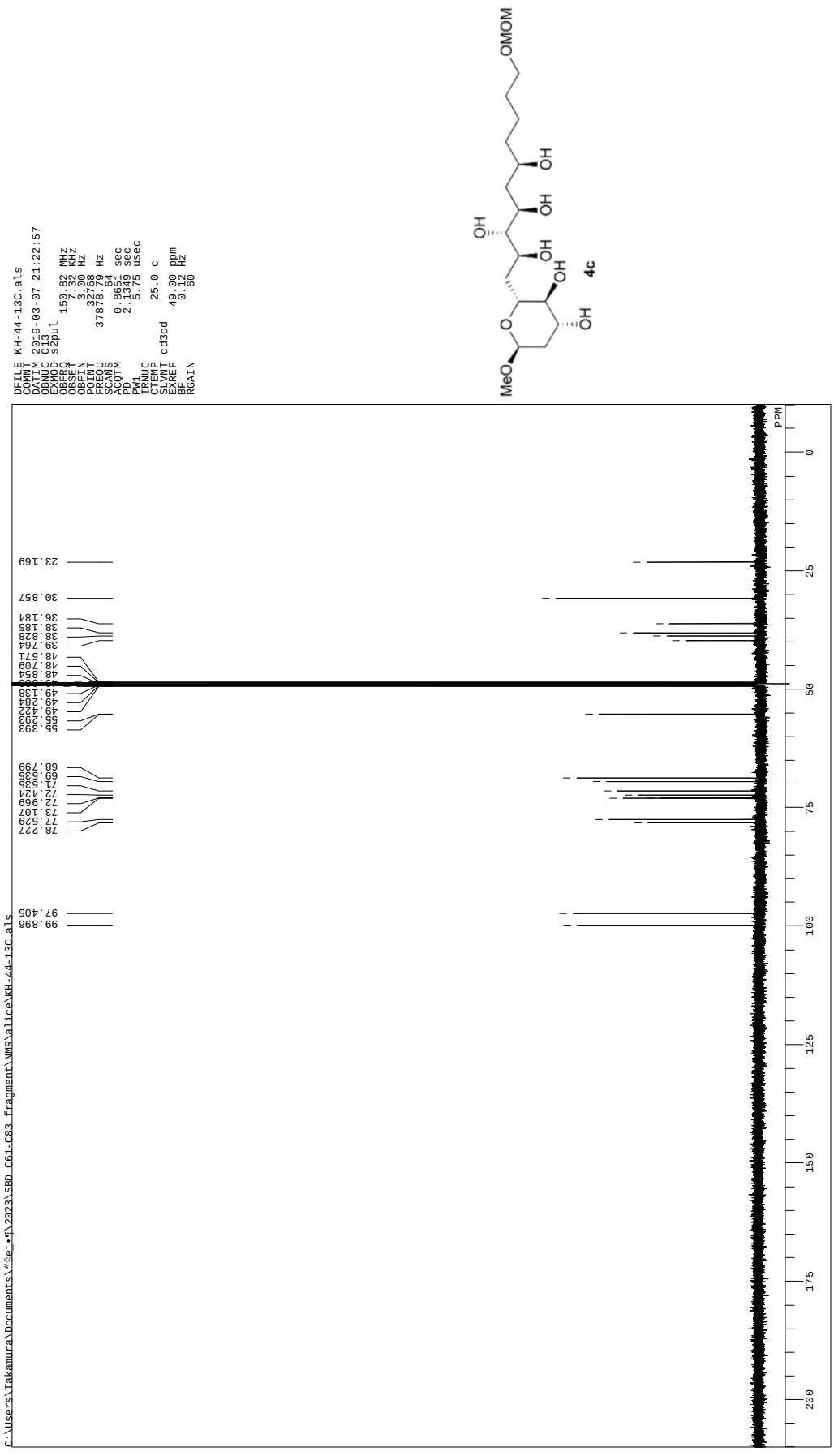

DFILE KH-24-2-C6D6-Data.als
COMNT KH-24-2-1H_Data
DATIM 2023-02-13 21:05:59
ONUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 5.11 KHz
OBFIN 4.57 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PW1 1.5225 usec
IRNUC
CTEMP 25.0 c
SLVNT c6d6
EXREF 7.16 ppm
BF 0.12 Hz
RGAIN 42
C:\Users\Takamura\Documents\ﾏｽﾀｰ\2023\SBD_C61_C83_fragment\NMR\alice\KH-24-2_C6D6-Data.als
PPM
MeO
OTBS
OTBS
OH
OTBS
PMP
OBOM
OMOM
S12


DFILE KH-24-2-13C_C6D6.als
COMNT KH-24-2-13C_data
DATIM 2020-02-13 21:11:53
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 6.74 KHz
OBFIN 2.30 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
TEMP 25.0 c
SLVNT c6d6
EXREF 128.00 ppm
BF 0.12 Hz
RGAIN 60
C:\Users\Takamura\Documents\ﾏｽﾀｰ･1\2023\SBD_G61-C83_fragment\NMR\alice\KH-24-2-13C_C6D6.als
PPM
OMOM
OBOM
OH
PMP
OTBS
OTBS
MeO
S12


DFILE KH-38.als
COMNT
DATIM Sat Feb 23 14:31:53 2019
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105290.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14
C:\Users\Takamura\Documents\ぜe-•¶\2023\SBD_G61-G83_fragment\NMR\alice\KH-38.als
PPM
MeO
OTBS
OTBS
OMOM
54


DFILE KH-38 13C.als
COMNT
DATIM Sat Feb 23 14:56:43 2019
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.91 Hz
SCANS 400
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
PRNUC 1H
CTEMP 26.0 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
C:\Users\Takamura\Documents\ﾏｽﾀｰﾃﾞｰﾀ\2023\SBD_C61-C83_fragment\NMR\alice\KH-38_13C.als
PPM
MeO
OTBS
OTBS
OH
OH
OH
OH
OMOM
54

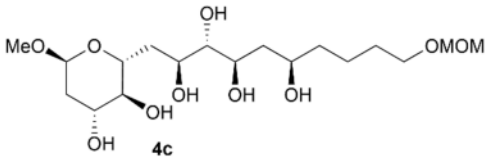

OMOM
OH
OH
OH
OH
OH
OH
O
MeO
4c
PPM
0
2
4
6
8
10
9.84
1.04
1.06
1.05
4.00
1.08
2.06
2.02
3.09
2.01
1.00


DFILE KH-44-13C.als
COMNT
DATIM 2019-03-07 21:22:57
OBNUC C13
EXMOD s2pul
OBSET 150.82 MHz
OBFIN 37878.79 Hz
POINT 32768
FREQU 3.00 KHz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
OMOM
OH
OH
OH
OH
OH
OH
MeO
O
4c
C:\Users\Takamura\Documents\データ\2023\SBD_CG1-C83_fragment\NMR\alice\KH-44-13C.als
23.169
30.857
36.184
38.185
38.828
39.764
48.571
48.709
48.854
49.138
49.284
49.429
55.293
55.393
68.799
69.535
71.535
72.424
72.969
73.107
77.529
78.227
97.405
99.896
PPM
0
25
50
75
100
125
150
175
200

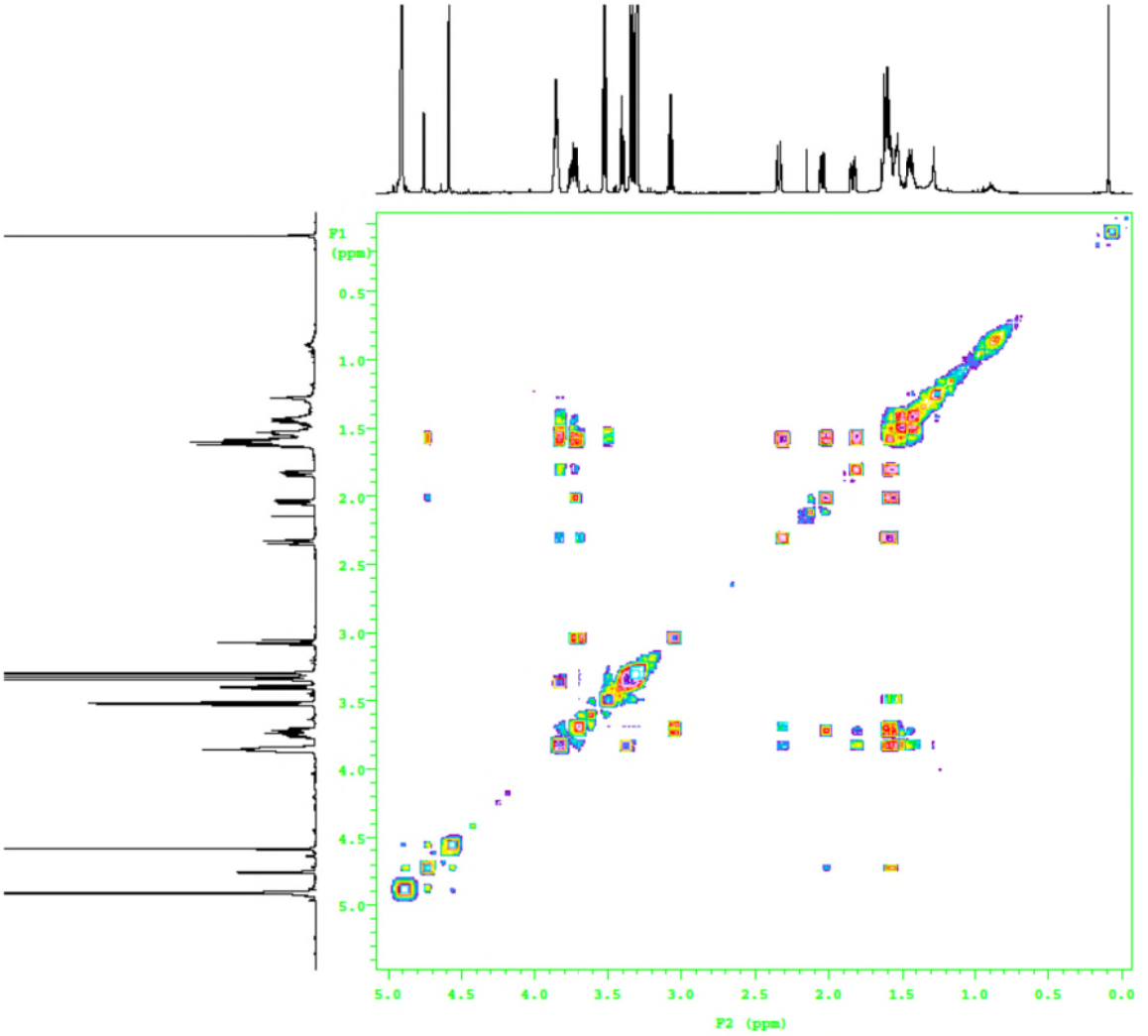
```
exp3  gCOSY

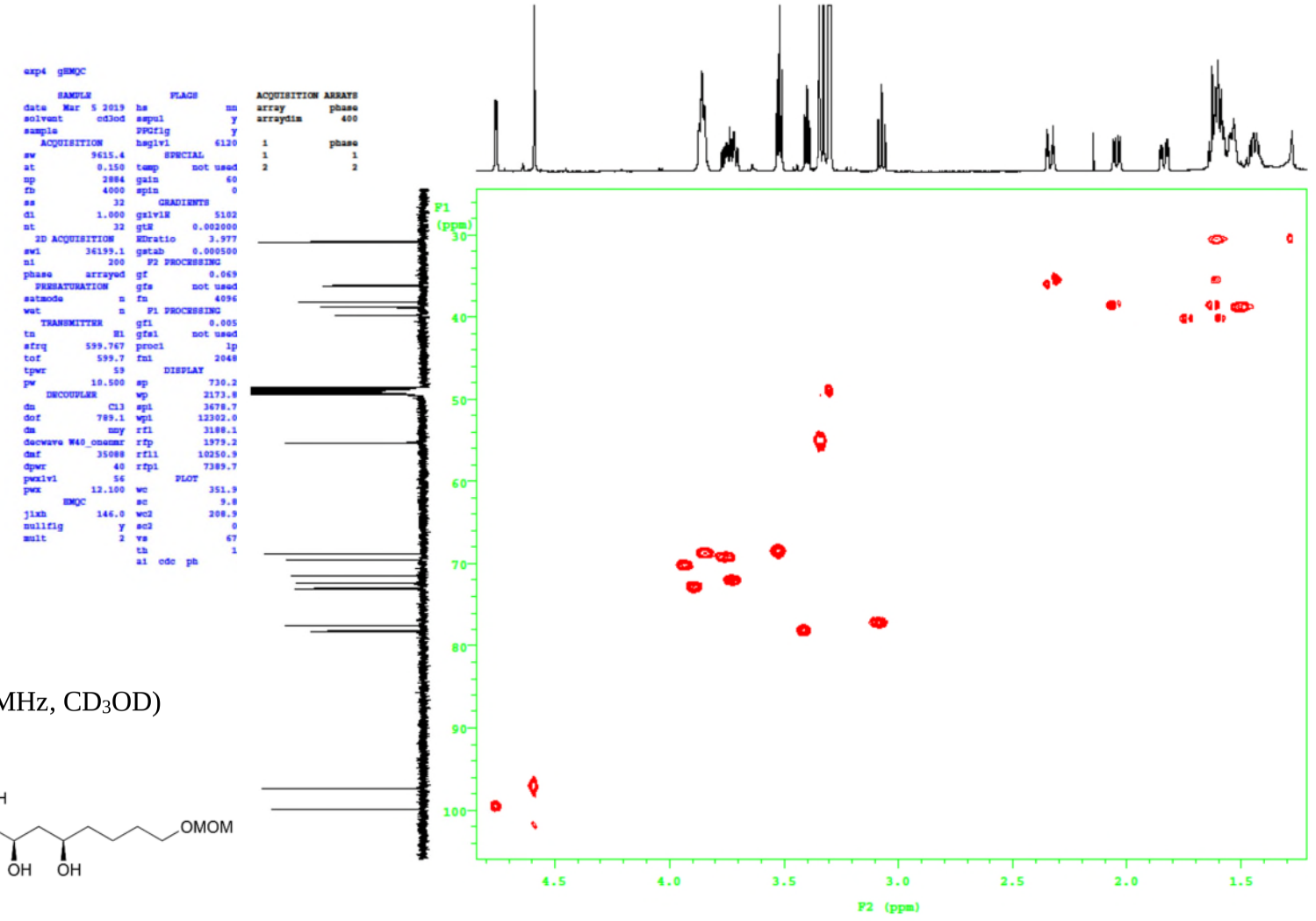
      SAMPLE                FLAGS
date   Mar  8 2019   hs                nn
solvent       cd3od   espul             y
sample                hsglvl          6120
   ACQUISITION          SPECIAL
sw           9615.4   temp        not used
at            0.150   gain              58
np              2884  spin               0
fb              4000    F2 PROCESSING
ss                32   sb             -0.075
d1             1.000   sbe         not used
nt                4   fn               4096
  2D ACQUISITION       F1 PROCESSING
sw1          9615.4   sb1            -0.013
ni              128   sbe1        not used
d2                0   proc1             lp
  PRESATURATION        fn1              4096
satmode           n       DISPLAY
wet               n   sp              -38.9
   TRANSMITTER        wp             3084.6
tn                H1  sp1             -48.1
sfrq         599.767  wp1            3328.8
tof            599.7  rf1            3206.0
tpwr              59  rfp            1979.2
pw             10.500 rfl1           3215.2
    GRADIENTS         rfp1           1979.2
gzlvlE            5102      PLOT
gtE          0.001000  wc              351.9
EDratio         1.000   sc                9.8
gstab        0.000500   wc2             208.9
    DECOUPLER          sc2                 0
dn                C13   vs                169
dm                nnn   th                  5
                        ai  ddc  aw
```

$^{1}H–^{1}H$ COSY (600 MHz, CD_3OD)



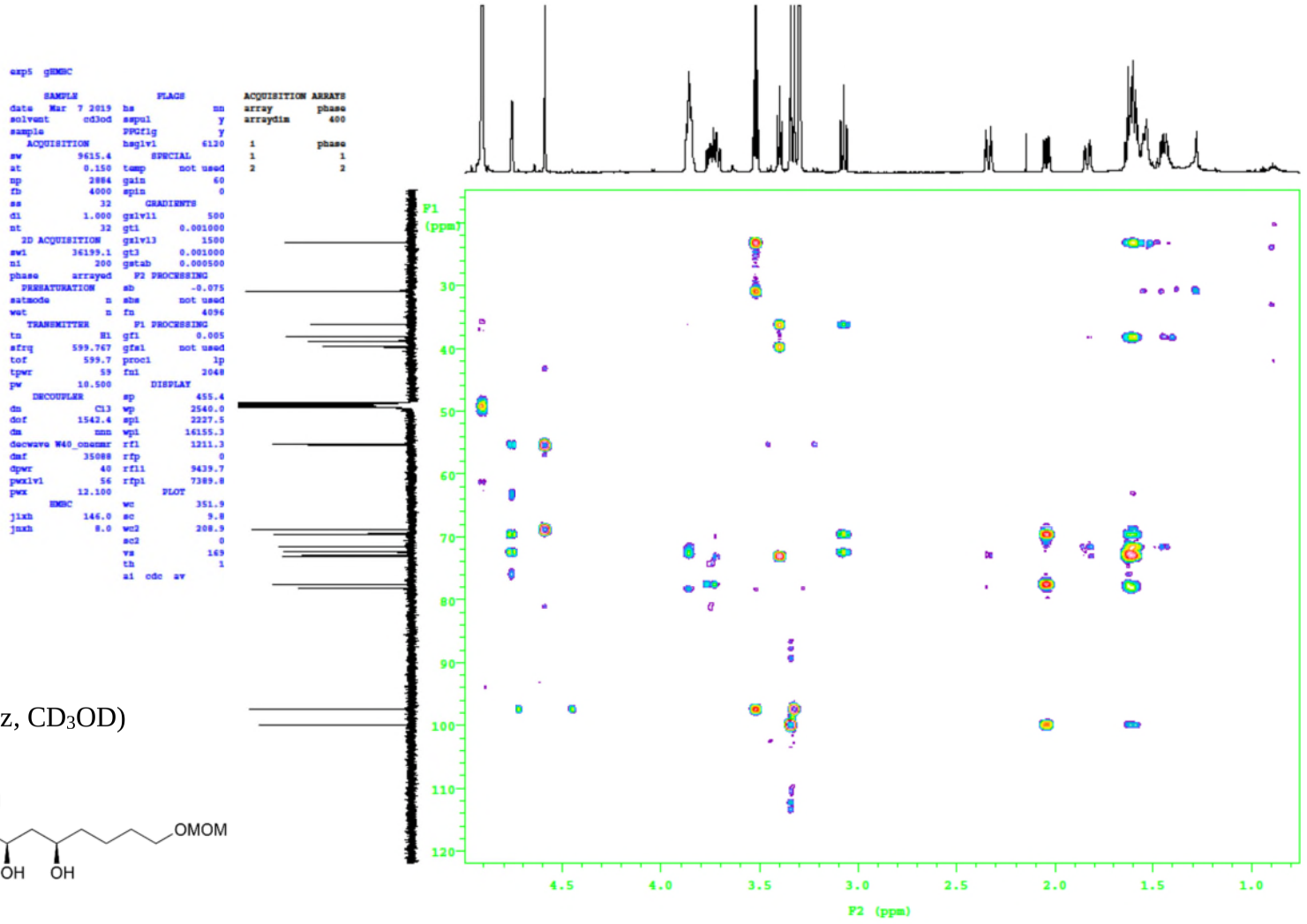
4c





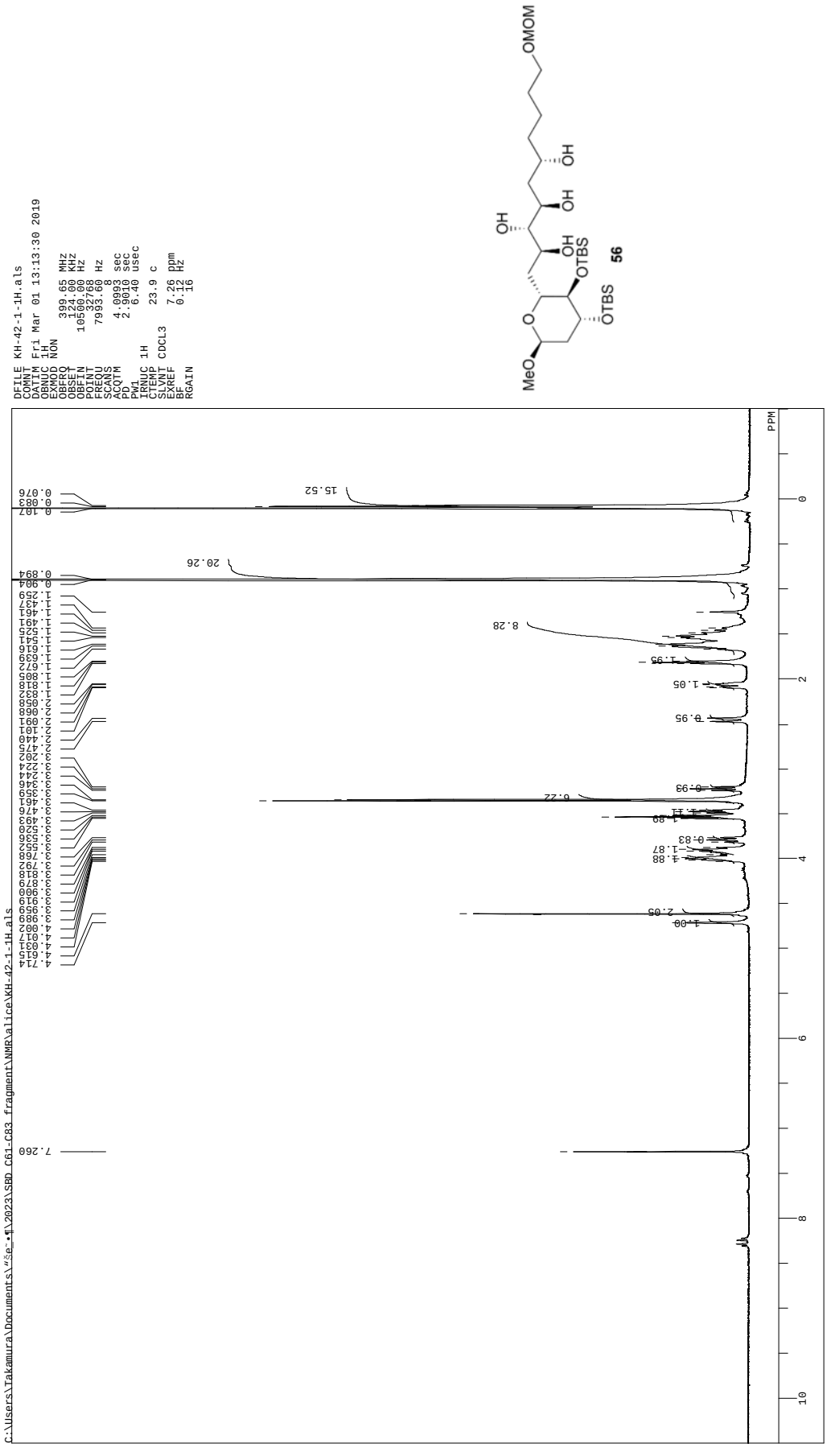
HMQC (600 MHz, CD_3OD)

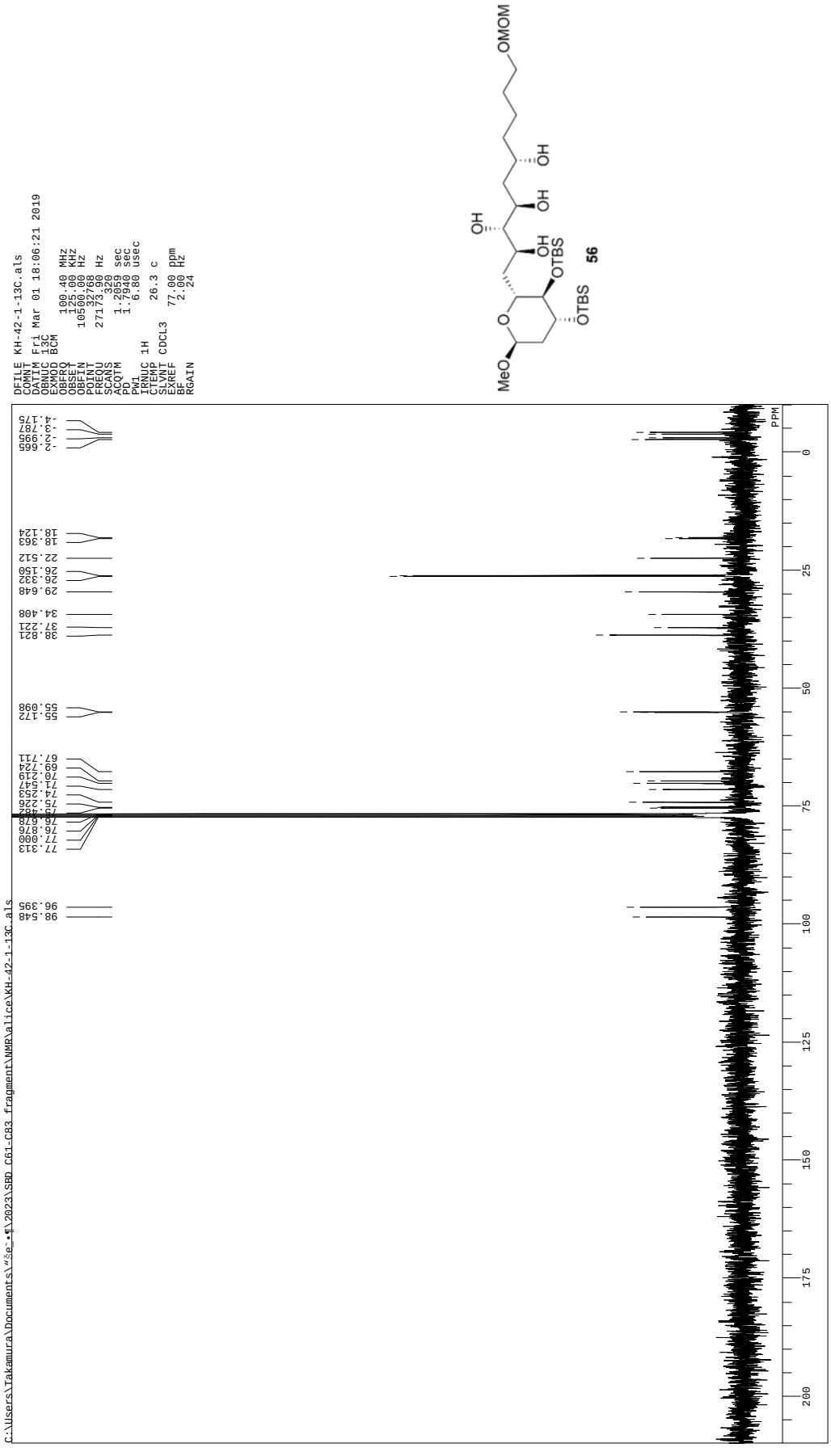
4c

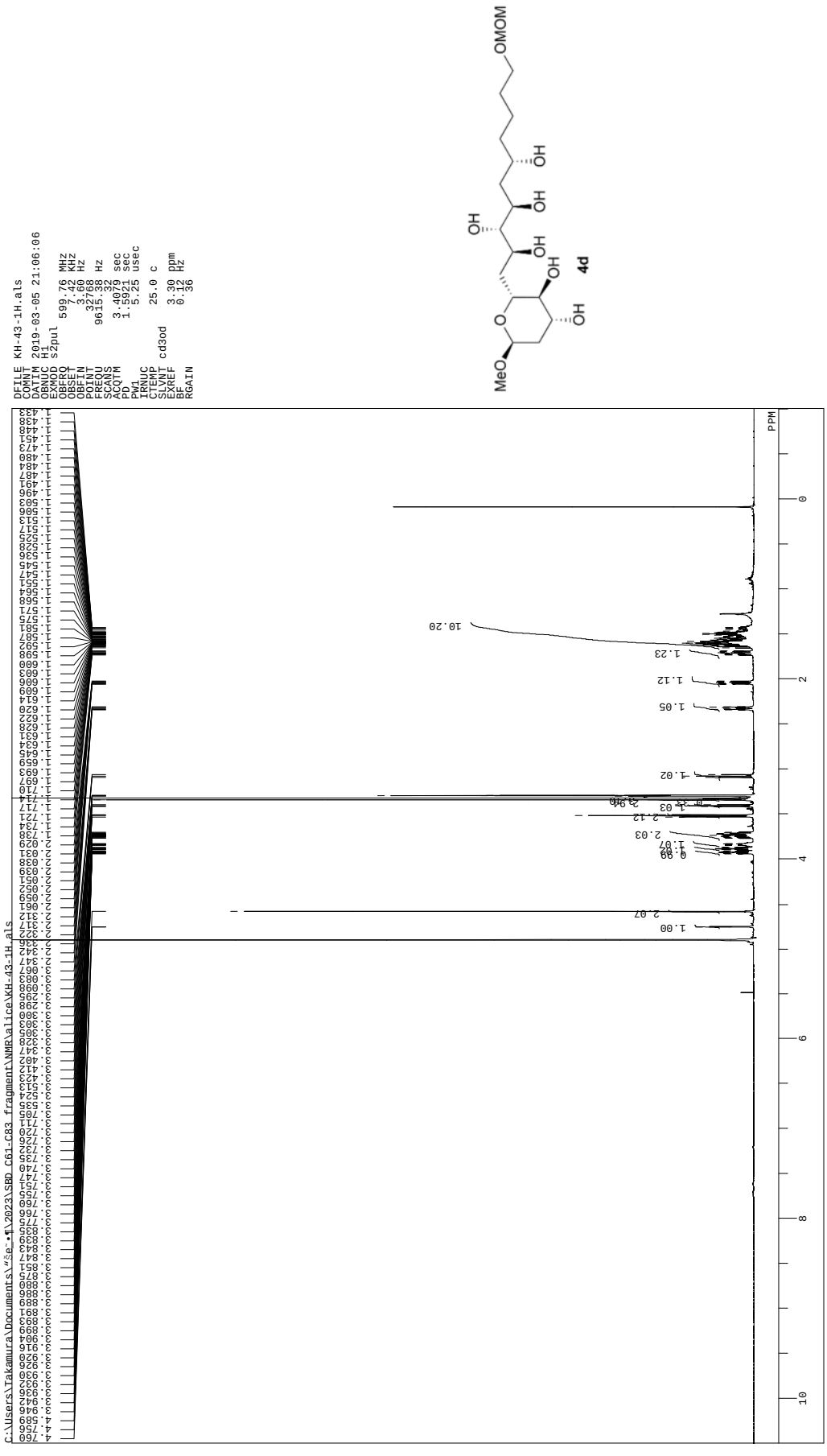


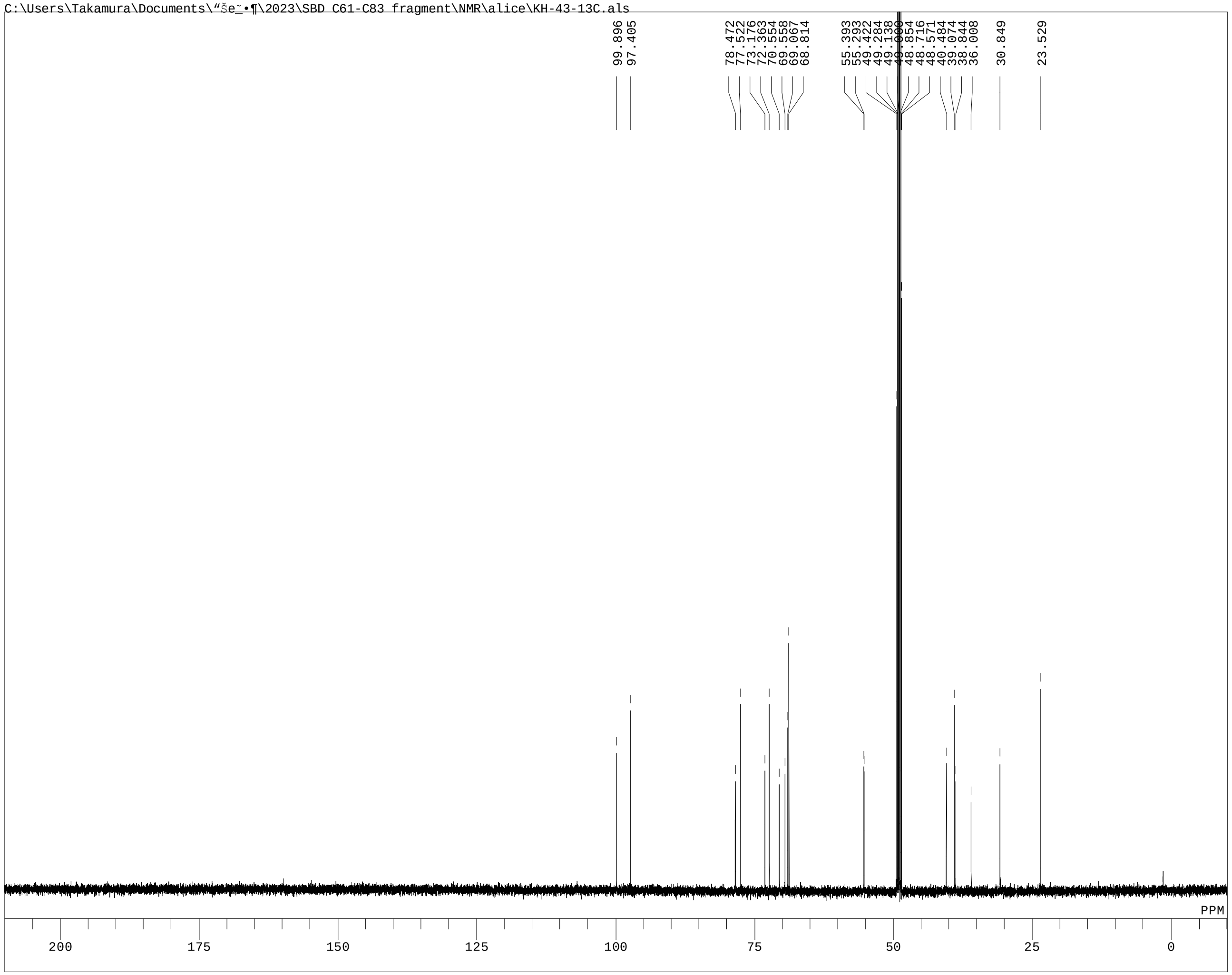
HMBC (600 MHz, CD_3OD)

4c

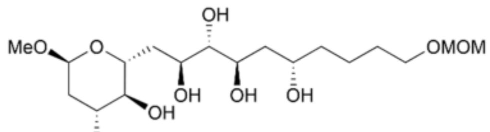

OMOM
OH
OH
OH
OH
OTBS
OTBS
O
MeO
56
DFILE KH-42-1-1H.als
COMNT
DATIM Fri Mar 01 13:13:30 2019
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TEMP 23.9 c
SLVNT CDCl3 7.26 ppm
EXREF 0.12 Hz
BF 16
RGAIN
C:\Users\Takamura\Documents\NMR\2023\SBD_C61-C83_fragment\NMR\alice\KH-42-1-1H.als
PPM


DFILE KH-42-1-13C.als
COMNT
DATIM Fri Mar 01 18:06:21 2019
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 1024
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
TEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
OMOM
OH
OH
OH
OH
OTBS
OTBS
MeO
O
56
C:\Users\Takamura\Documents\ﾏｽﾀｰ•¶\2023\SBD_C61-C83_fragment\NMR\alice\KH-42-1-13C.als
PPM


4d
OMOM
MeO
OH
PPM



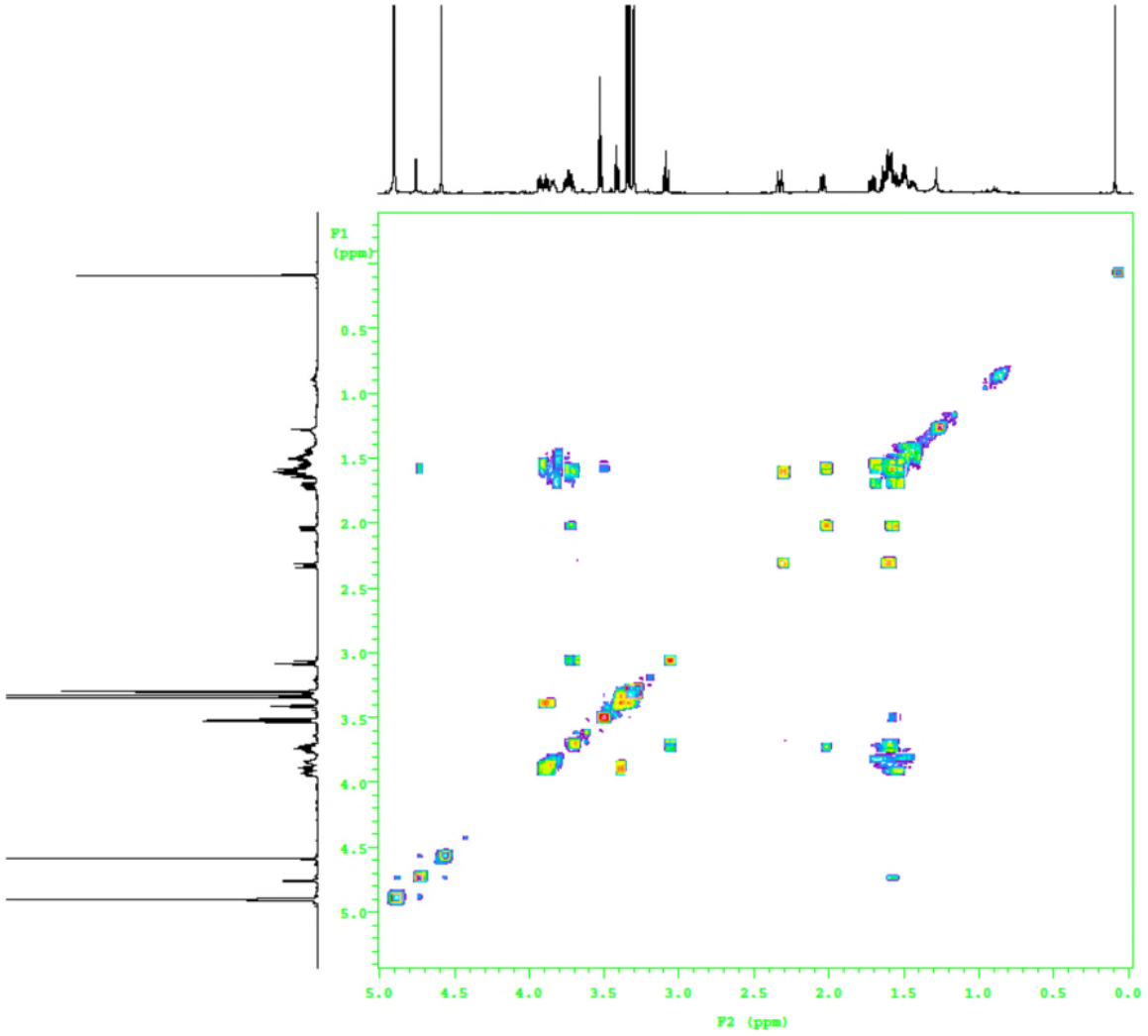
DFILE KH-43-13C.als
COMNT
DATIM 2019-03-05 21:18:38
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.32 KHz
OBFIN 3.00 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60



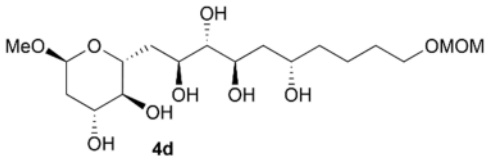
4d

exp3 gCOSY

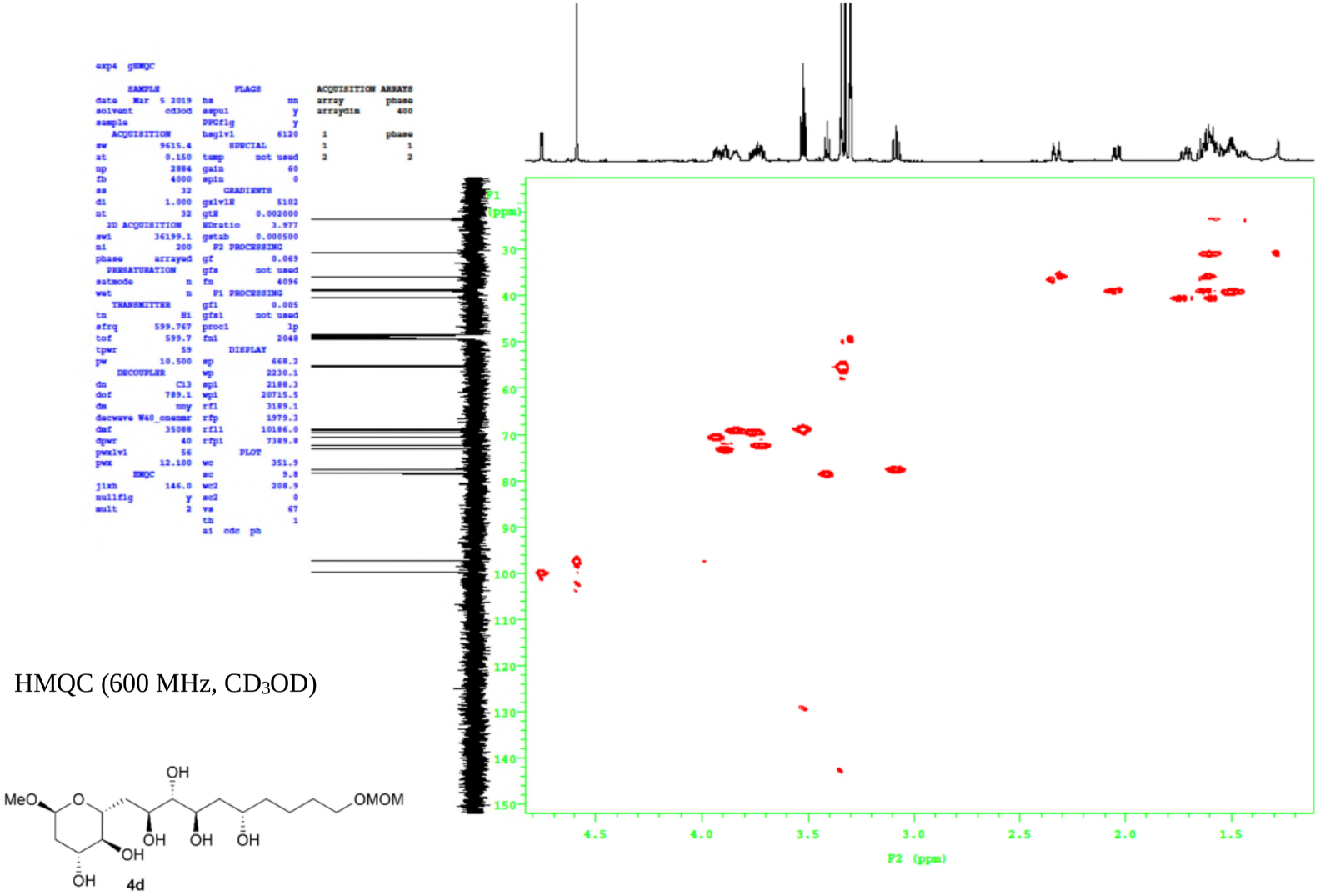
SAMPLE		FLAGS	
date	Mar 6 2019	hs	nn
solvent	cd3od	sspul	y
sample		hsglv1	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	50
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	8	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.013
ni	128	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-15.8
TRANSMITTER		wp	3018.9
tn	H1	sp1	-236.2
sfrq	599.767	wp1	3493.1
tof	599.7	rf1	3206.4
tpwr	59	rfp	1979.2
pw	10.500	rf11	3210.7
GRADIENTS		rfp1	1979.2
gzlvlE	5102	PLOT	
gtE	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	67
dm	nnn	th	4
		ai cdc av	



^{1}H–^{1}H COSY (600 MHz, CD_3OD)

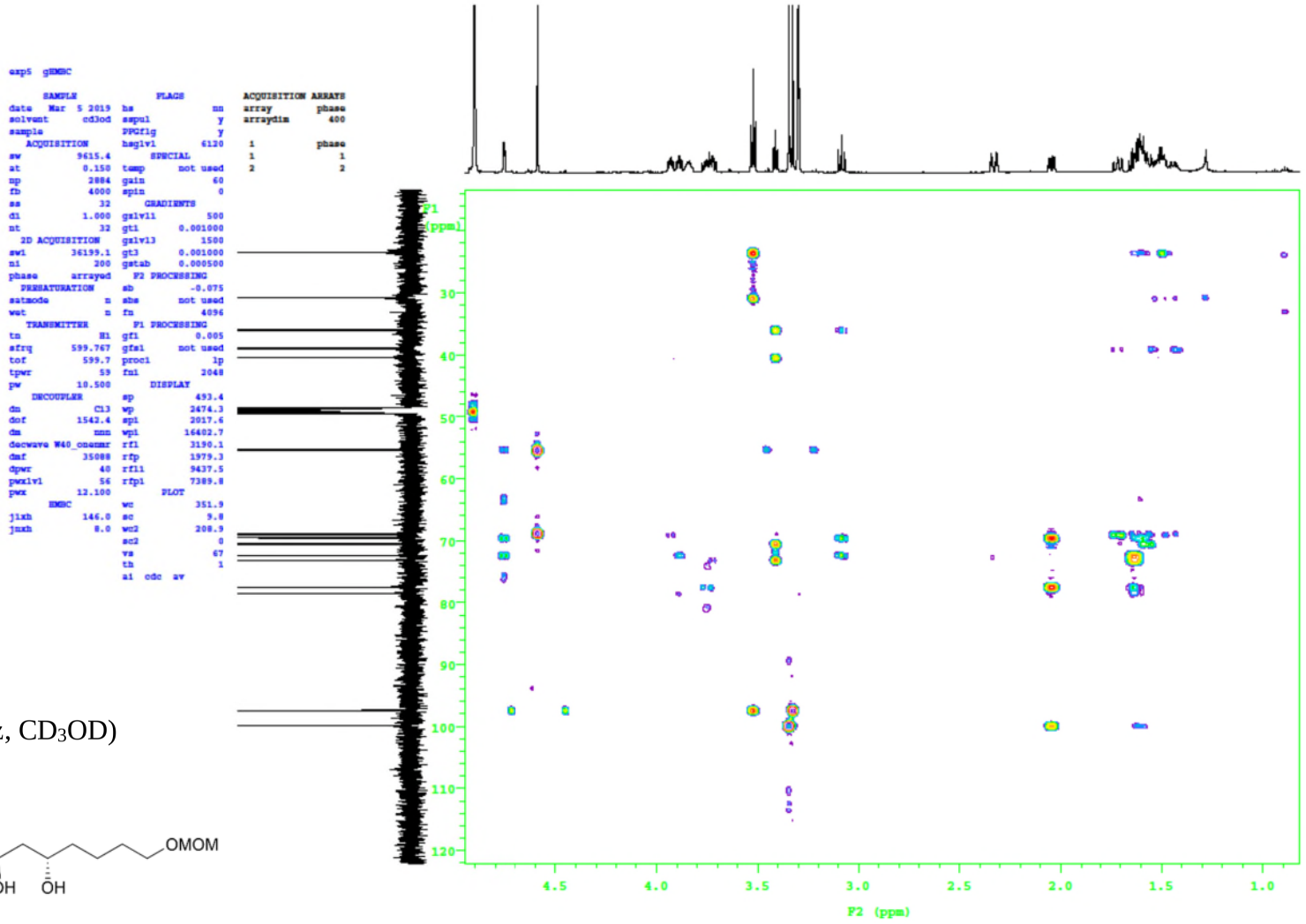


4d

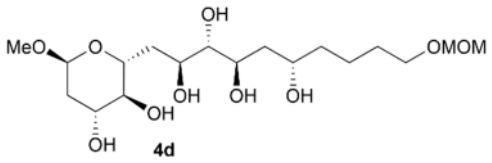


HMQC (600 MHz, CD_3OD)

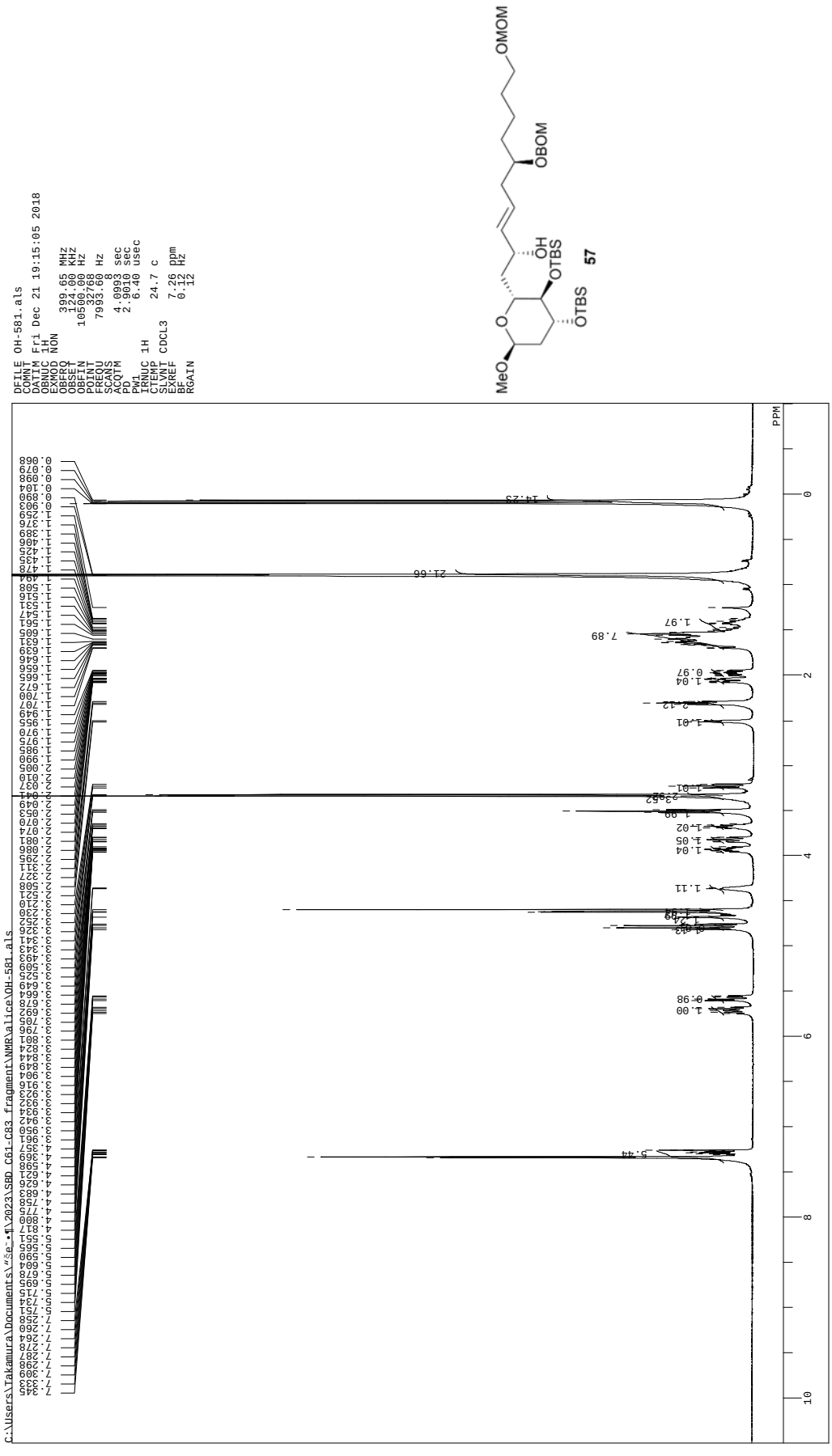
4d



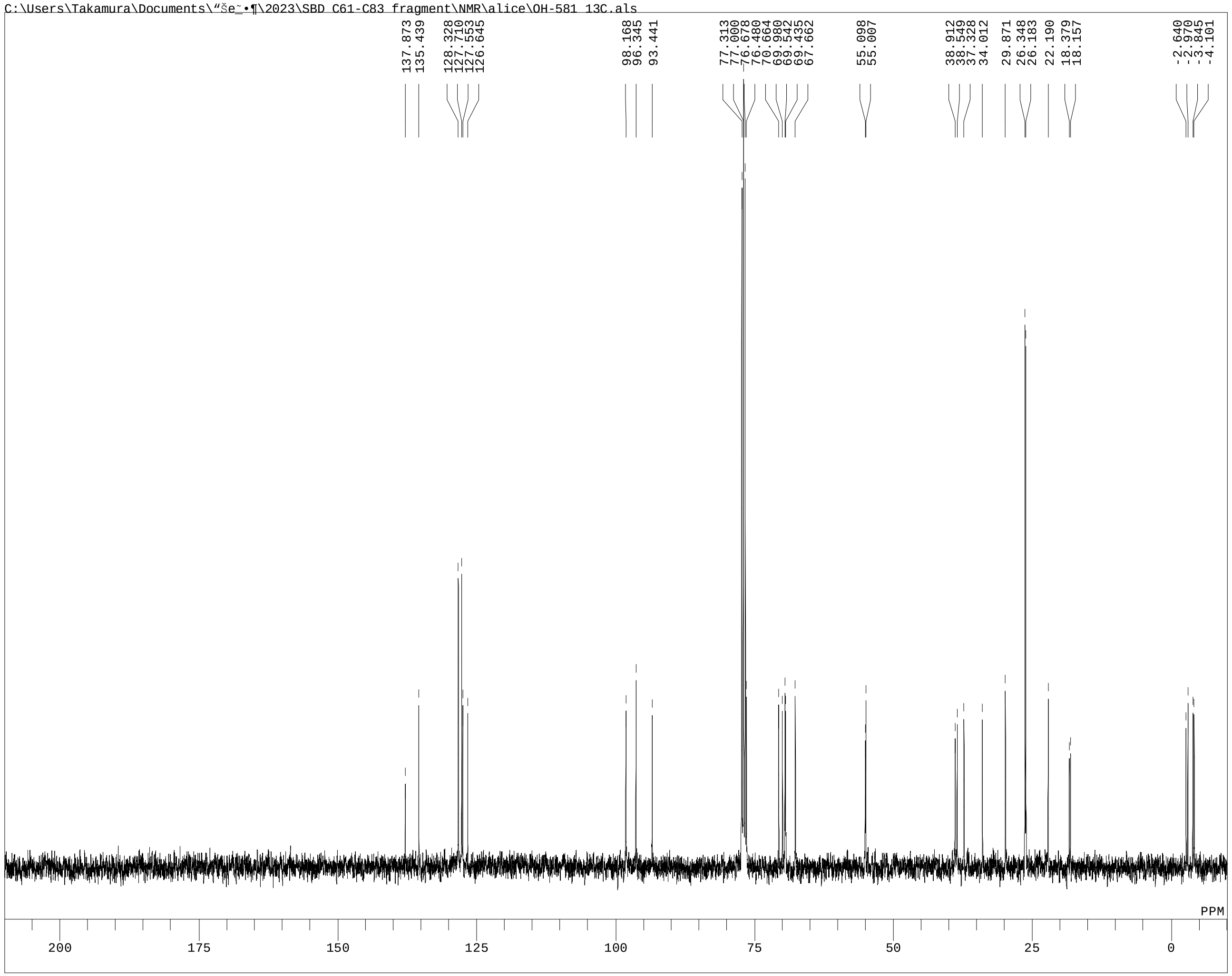
HMBC (600 MHz, CD_3OD)



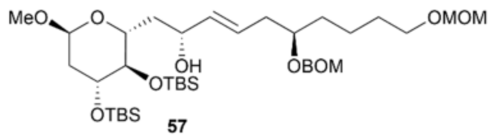
4d


OMOM
OBOM
OH
OTBS
OTBS
MeO
O
57
PPM

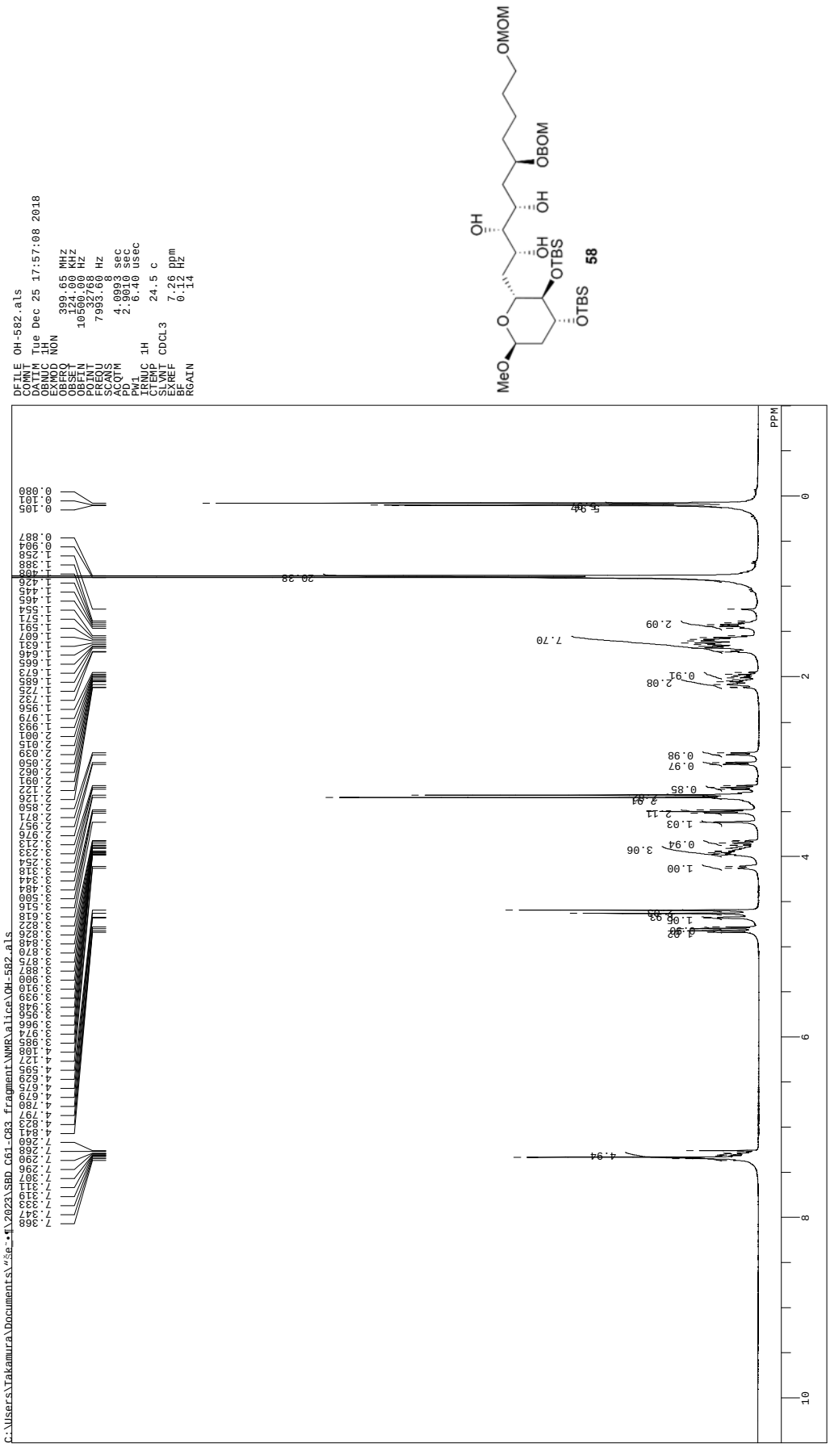
C:\Users\Takamura\Documents\“še‸•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-581 13C.als

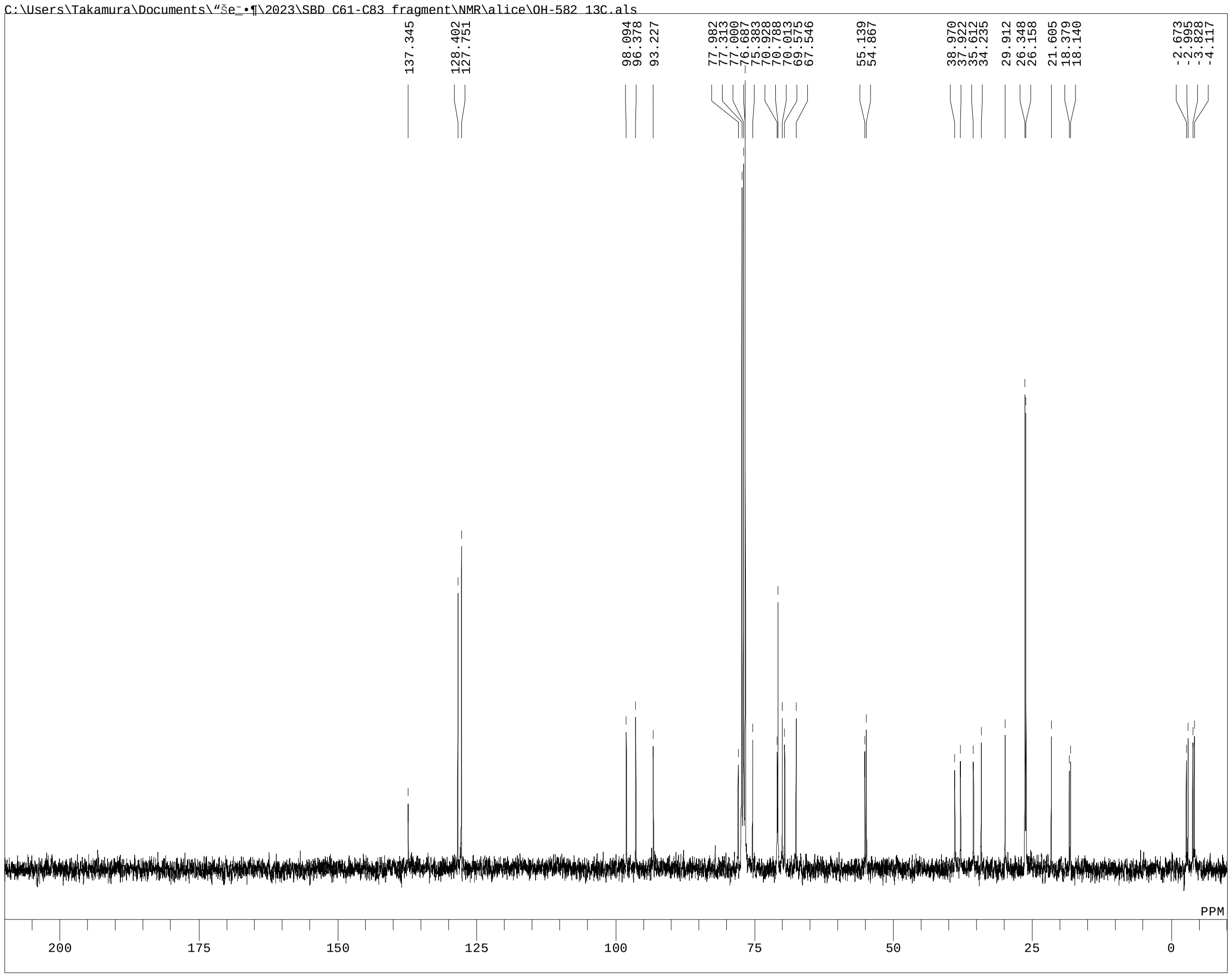


DFILE OH-581 13C.als
COMNT
DATIM Fri Dec 21 19:27:56 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 200
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24

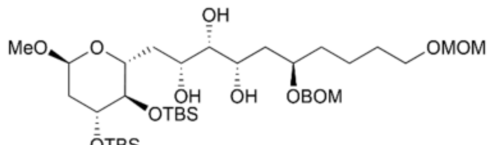


57

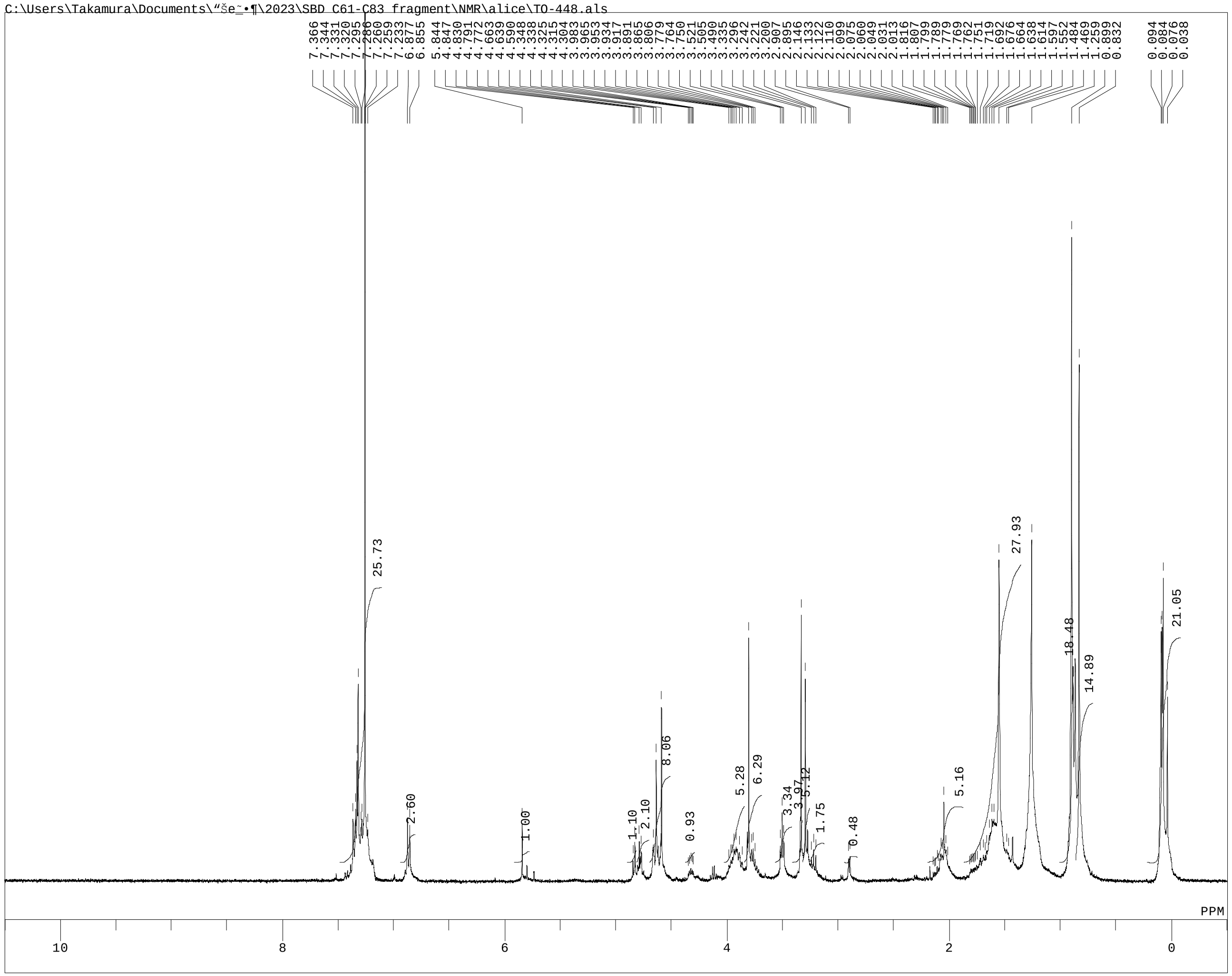

OMOM
OBOM
OH
OH
OH
OTBS
OTBS
58
MeO
O
DFILE OH-582.als
COMNT
DATIM Tue Dec 25 17:57:08 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
TEMP 24.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14
C:\Users\Takamura\Documents\ﾏｽﾀｰ\2023\SBD_C61-C83_fragment\NMR\alice\OH-582.als
PPM



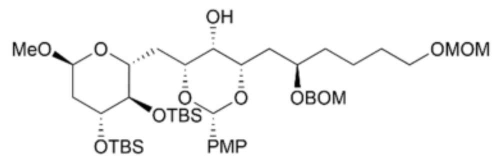

```
DFILE  OH-582 13C.als
COMNT
DATIM  Tue Dec 25 18:13:15 2018
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU     27173.90 Hz
SCANS          300
ACQTM       1.2059 sec
PD          1.7940 sec
PW1           6.80 usec
IRNUC  1H
CTEMP         26.4 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```



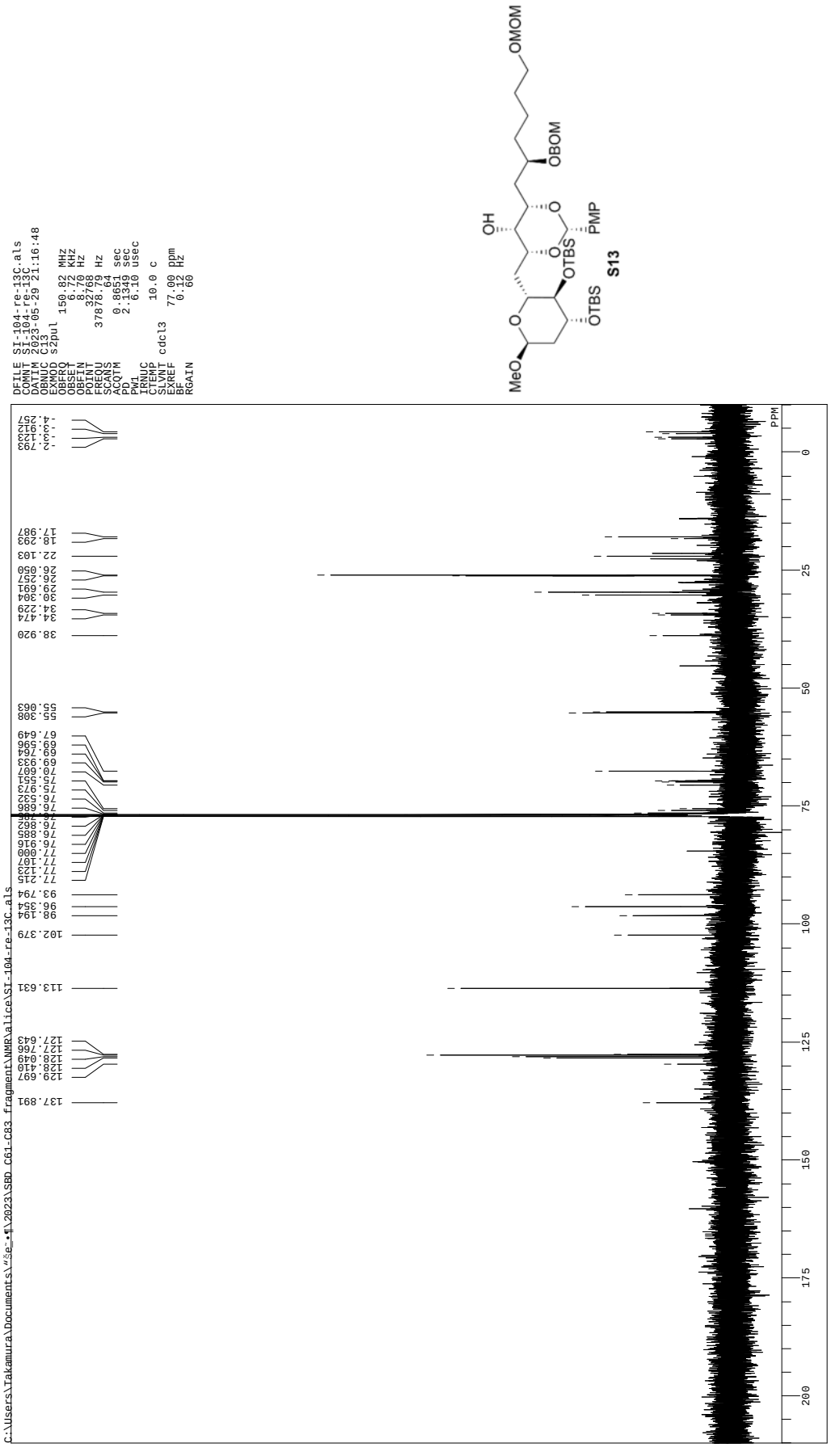
58



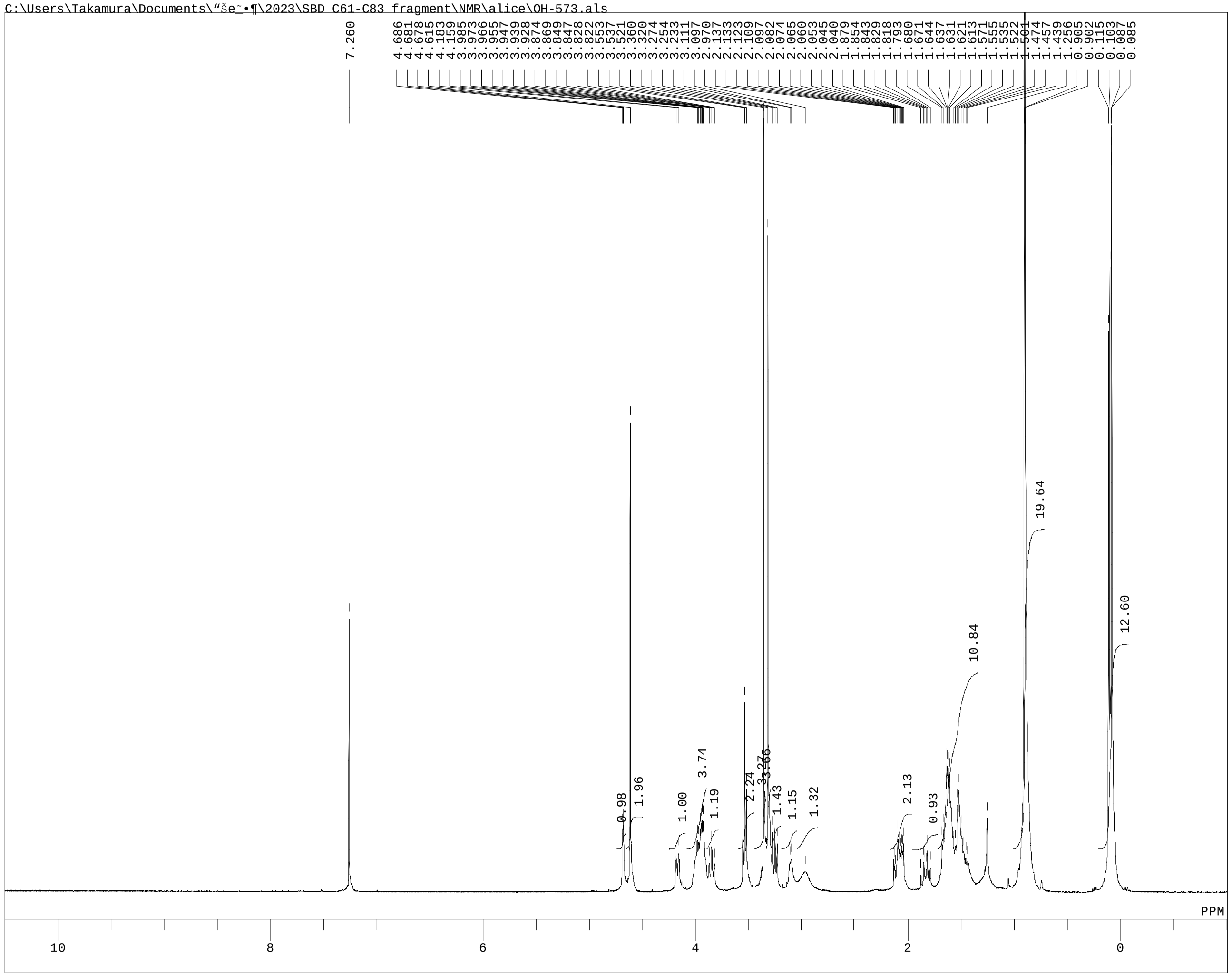
DFILE TO-448.als
COMNT
DATIM Fri Mar 02 21:41:28 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
ACQTM 4.0993 sec
PD 2.9007 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 23



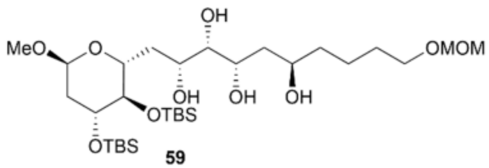
S13


DFILE SI-104-re-13C.als
COMNT SI-104-re-13C
DATIM 23-05-29 21:16:48
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 6.72 KHz
OBFIN 8.70 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1430 sec
PW1 6.10 usec
IRNUC
CTEMP 10.0 c
SLVNT cdcl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
C:\Users\Takamura\Documents\ﾃﾞｰﾀ\2023\SBD_C61-C83_fragment\NMR\alice\SI-104-re-13C.als
137.891
129.697
128.410
128.049
127.766
127.643
113.631
102.379
98.194
96.354
93.794
77.215
77.123
77.107
77.000
76.916
76.885
76.862
76.686
76.532
75.973
75.551
70.607
69.933
69.764
69.596
67.649
55.308
55.063
38.920
34.474
34.229
30.304
29.691
26.257
26.050
22.103
18.293
17.987
4.257
PPM
0
25
50
75
100
125
150
175
200
OMOM
OBOM
OH
O
O
O
OTBS
PMP
MeO
O
OTBS
S13

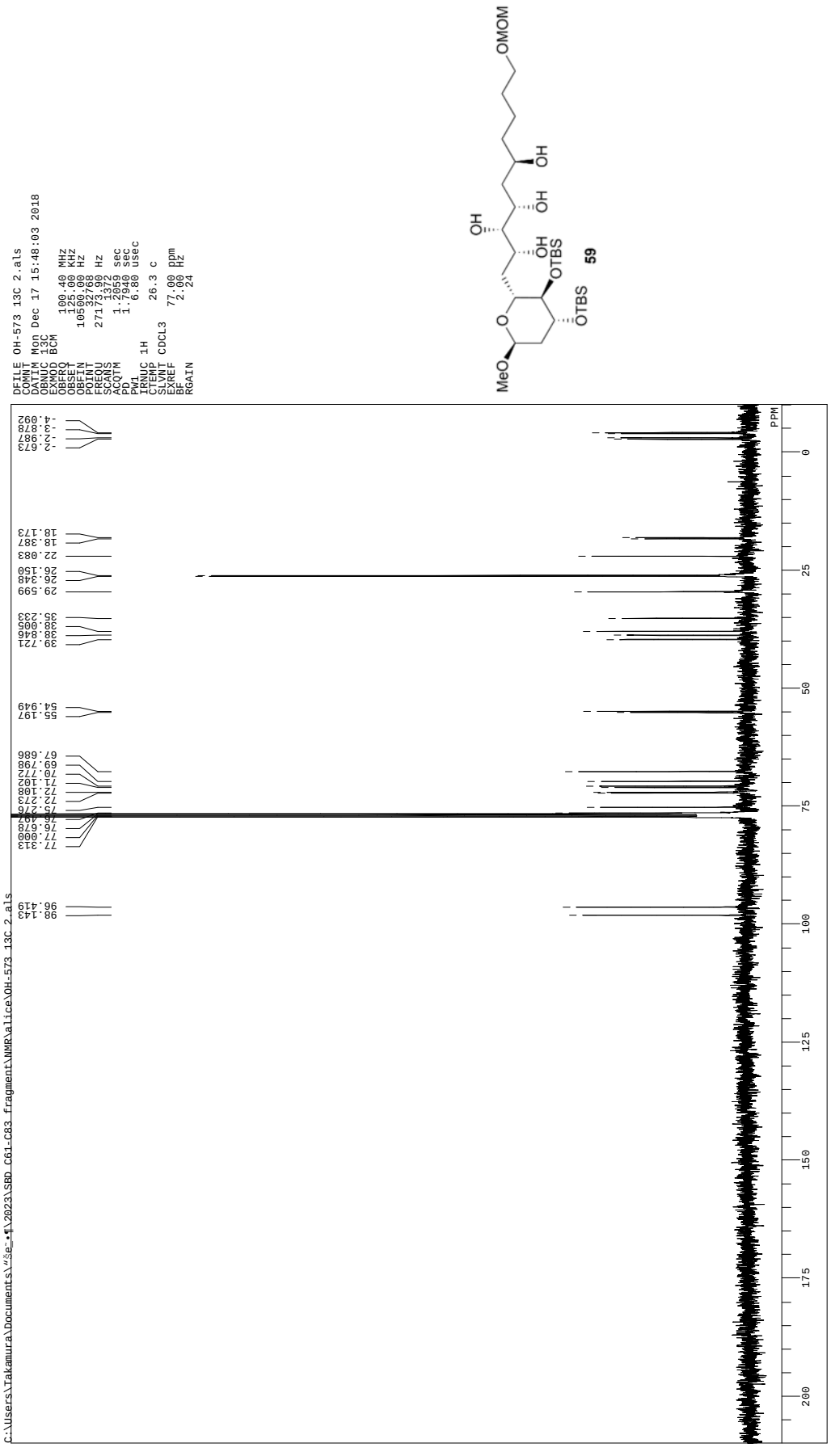
C:\Users\Takamura\Documents\“še_•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-573.als

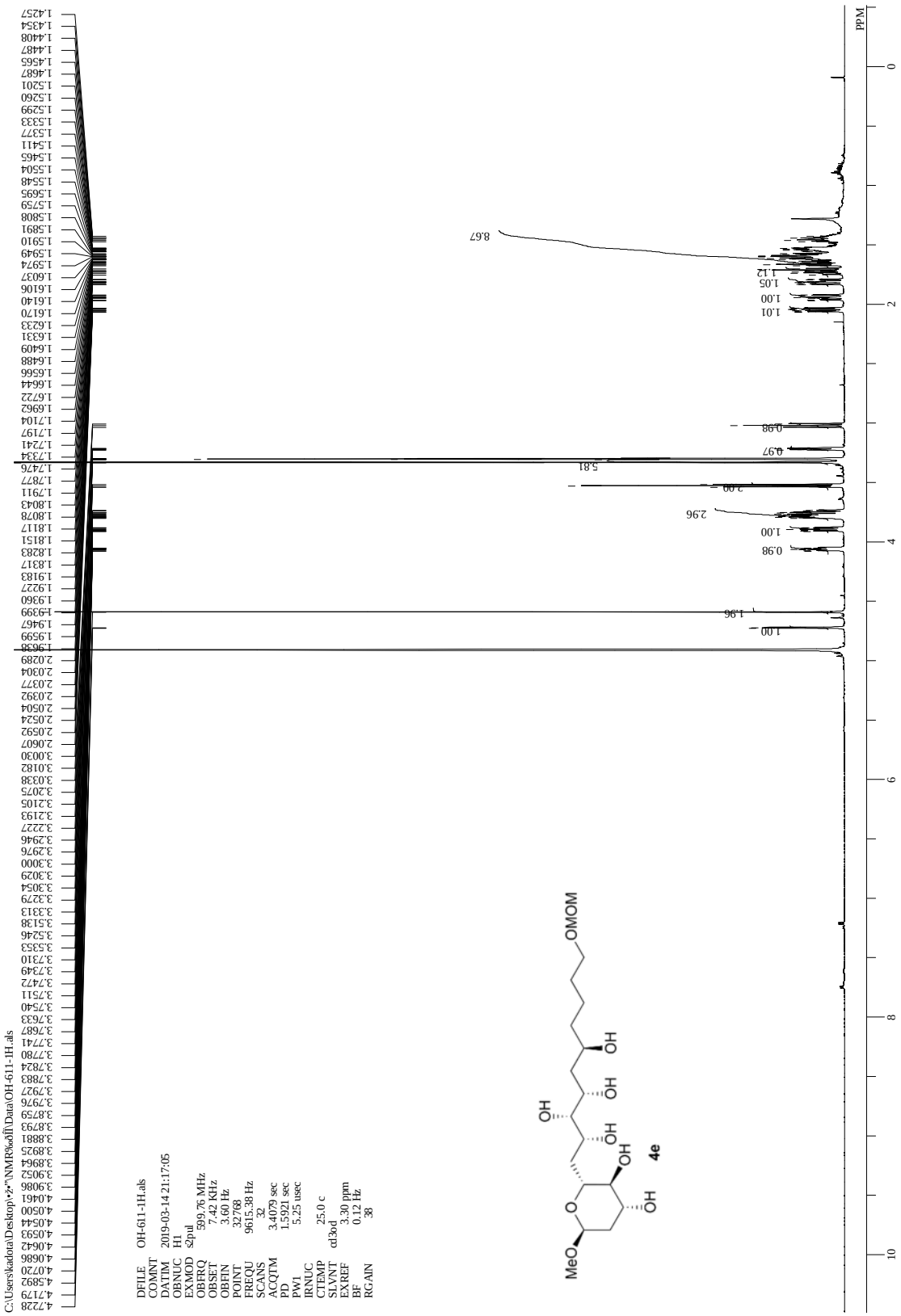


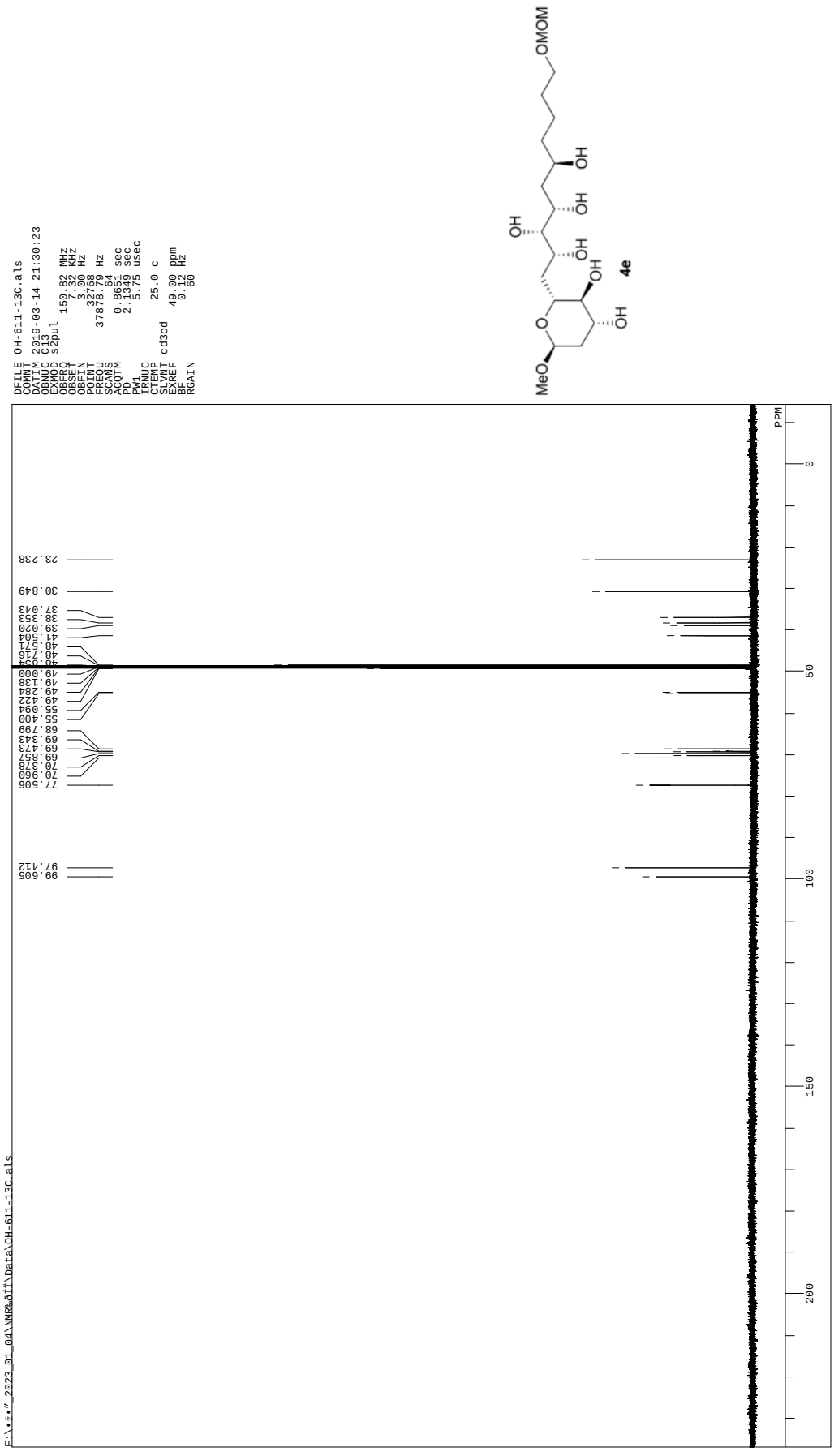
DFILE OH-573.als
COMNT
DATIM Mon Dec 17 14:36:27 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14



59

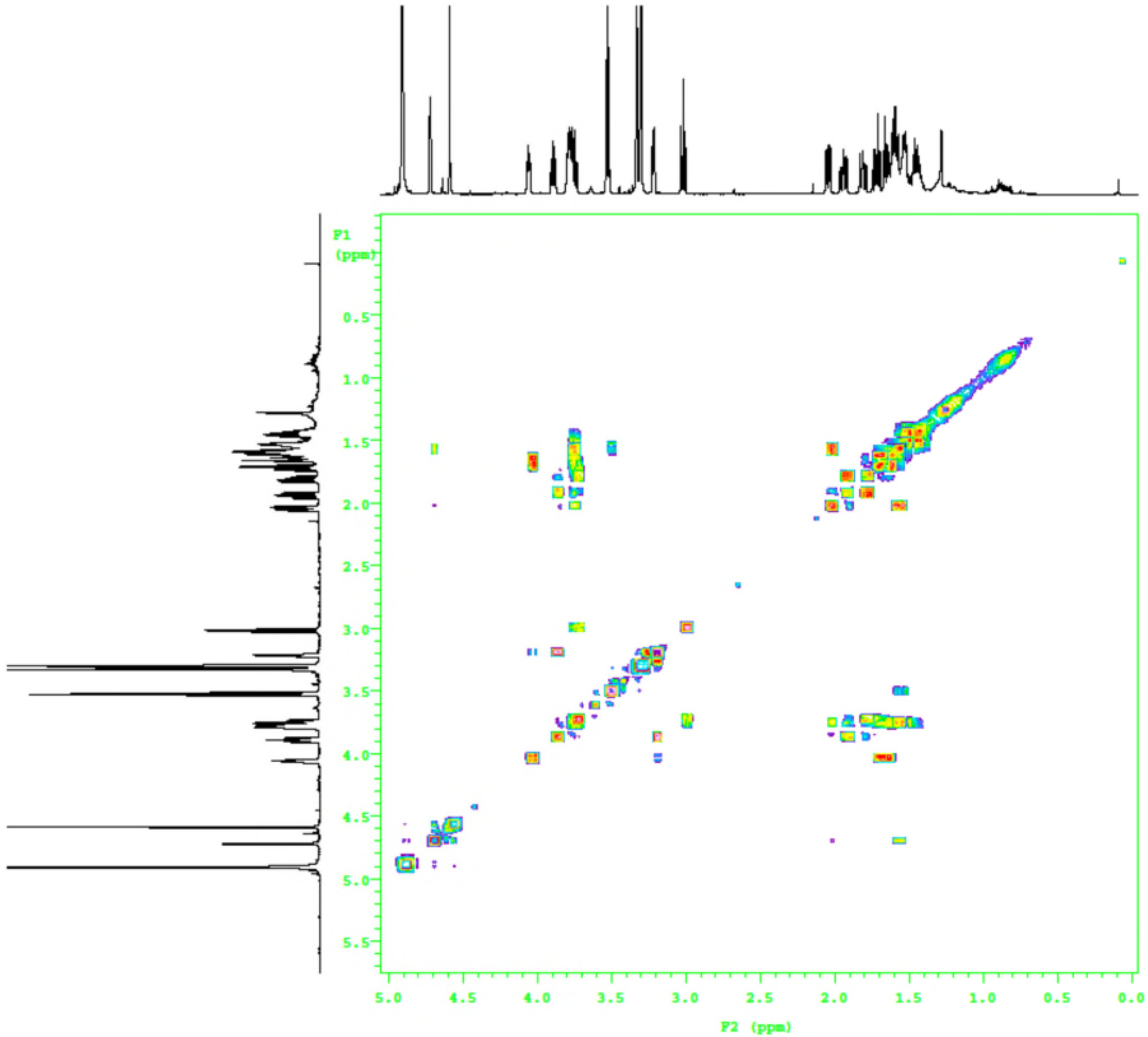

DFILE OH-573 13C 2.als
COMNT
DATIM Mon Dec 17 15:48:03 2018
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.072 Hz
SCANS 1372
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 6.80 usec
INUC 1H
CTEMP 26.3 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
C:\Users\Takamura\Documents\ﾏｽﾀｰﾌｧｲﾙ\2023\SBD_C61-C83_fragment\NMR\alice\OH-573_13C_2.als
PPM
OMOM
OH
OH
OH
OH
OTBS
OTBS
MeO
O
59


C:\Users\kadora\Desktop\データ\NMR%odf\Data\OH-611-1H.als
DFILE OH-611-1H.als
COMNT
DATIM 2019-03-14 21:17:05
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 7.42 KHz
OBFIN 3.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 38
8.67
5.81
3.99
2.96
1.96
1.00
0.98
1.00
1.01
1.00
1.05
1.12
0.98
0.97
OMOM
OH
OH
OH
OH
OH
OH
O
MeO
4e
PPM
0
2
4
6
8
10

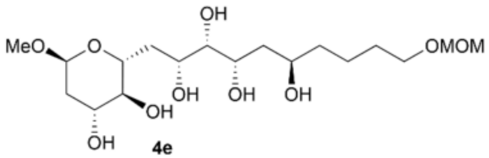

DFILE OH-611-13C.als
COMNT
DATIM 2019-03-14 21:30:23
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 75.42 KHz
OBFIN 3.00 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
23.238
30.849
37.043
38.353
39.020
41.504
48.571
48.716
48.894
49.000
49.138
49.284
49.422
55.094
55.400
68.799
69.343
69.473
69.857
70.337
70.960
77.506
97.412
99.605
PPM
0
50
100
150
200
OMOM
OH
OH
OH
OH
OH
O
MeO
4e

exp3 gCOSY

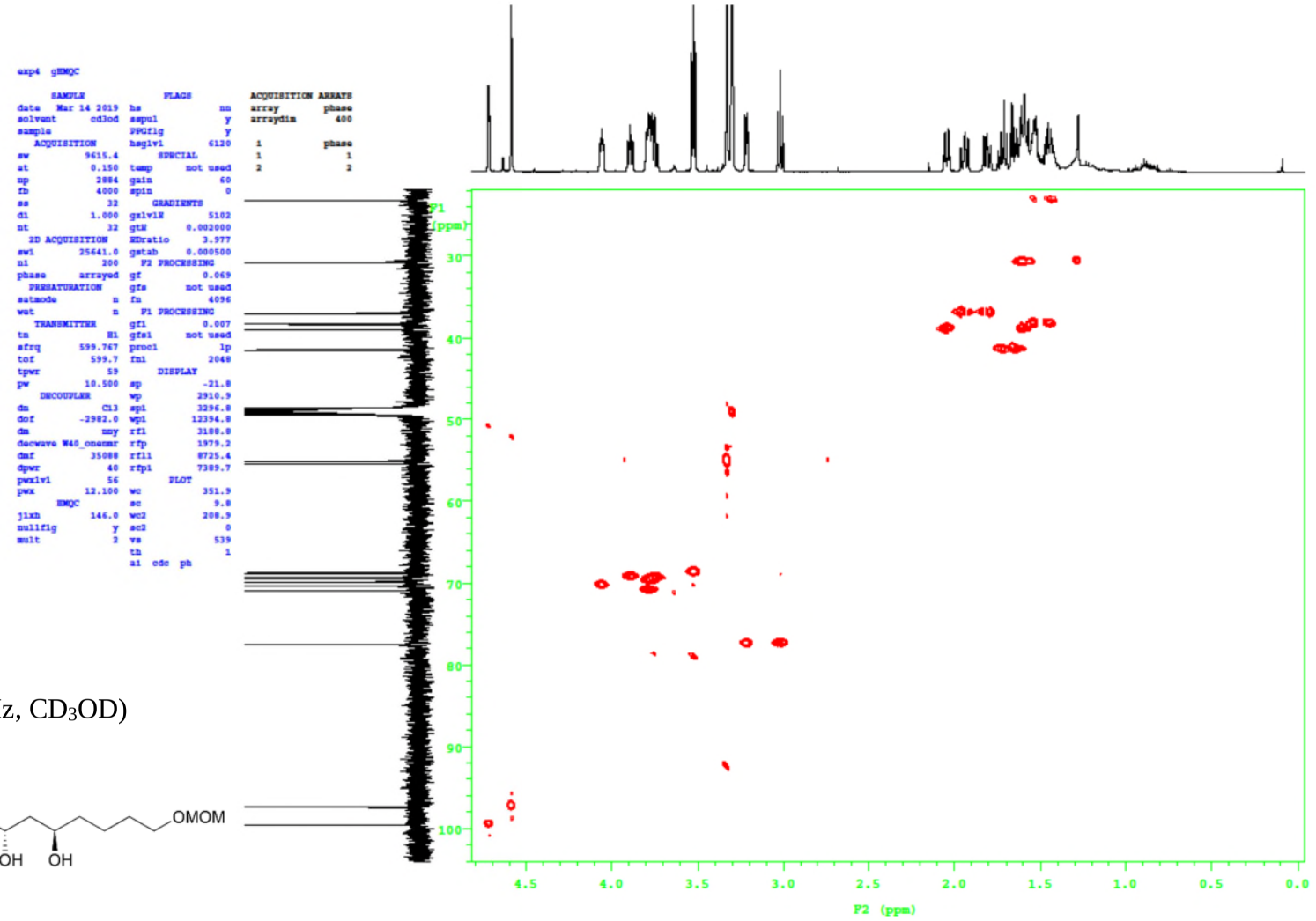
SAMPLE		FLAGS	
date	Mar 15 2019	hs	nn
solvent	cd3od	sspul	y
sample		hsglvl	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	38
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	8	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.013
ni	128	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-22.0
TRANSMITTER		wp	3051.8
tn	H1	sp1	-185.7
sfrq	599.767	wp1	3633.9
tof	599.7	rfl	3207.9
tpwr	59	rfp	1979.2
pw	10.500	rfl1	3211.9
GRADIENTS		rfp1	1979.2
gzlvlE	5102	PLOT	
gtE	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	539
dm	nnn	th	4
		ai cdc av	



^1H–^1H COSY (600 MHz, CD_3OD)

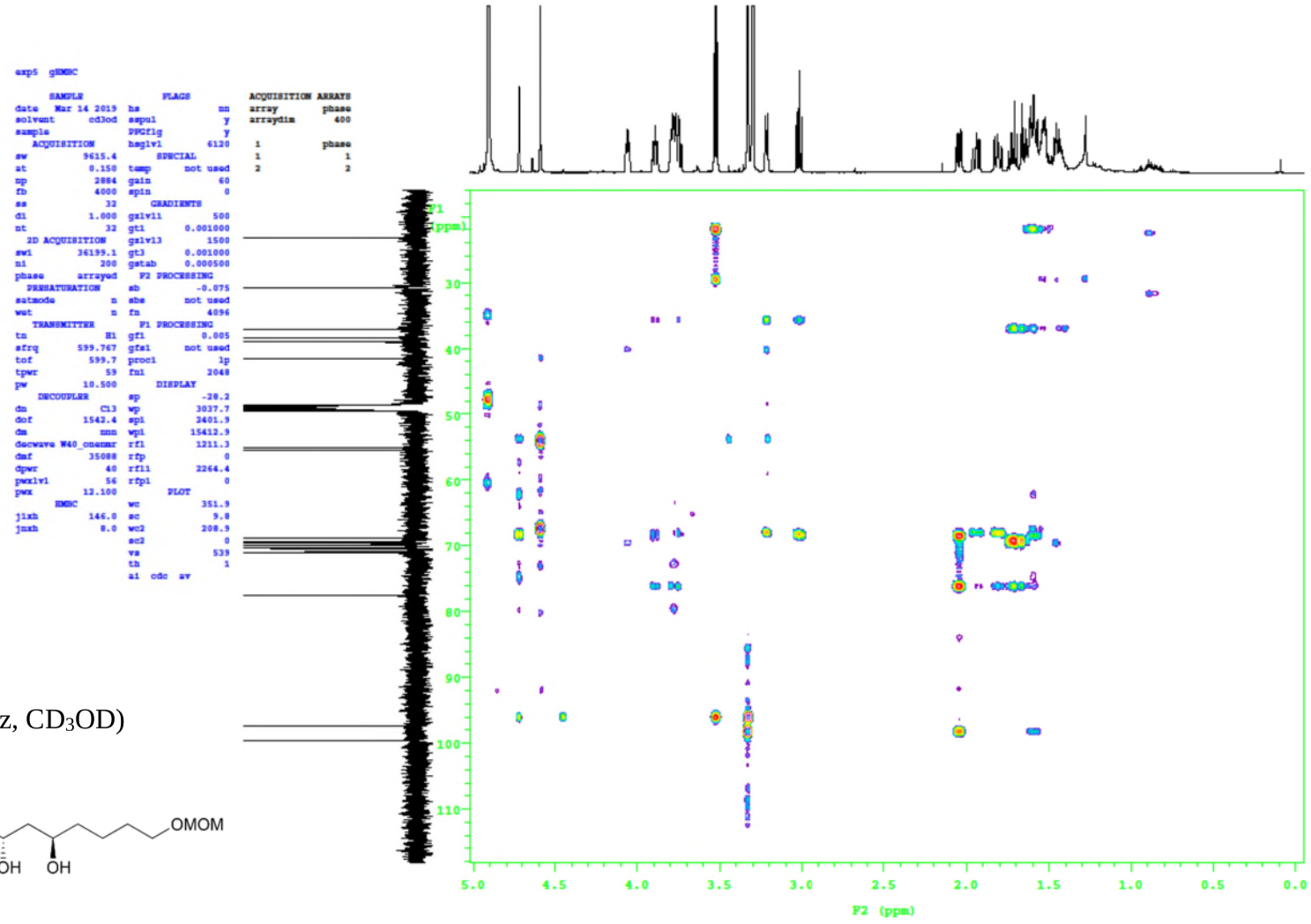


4e



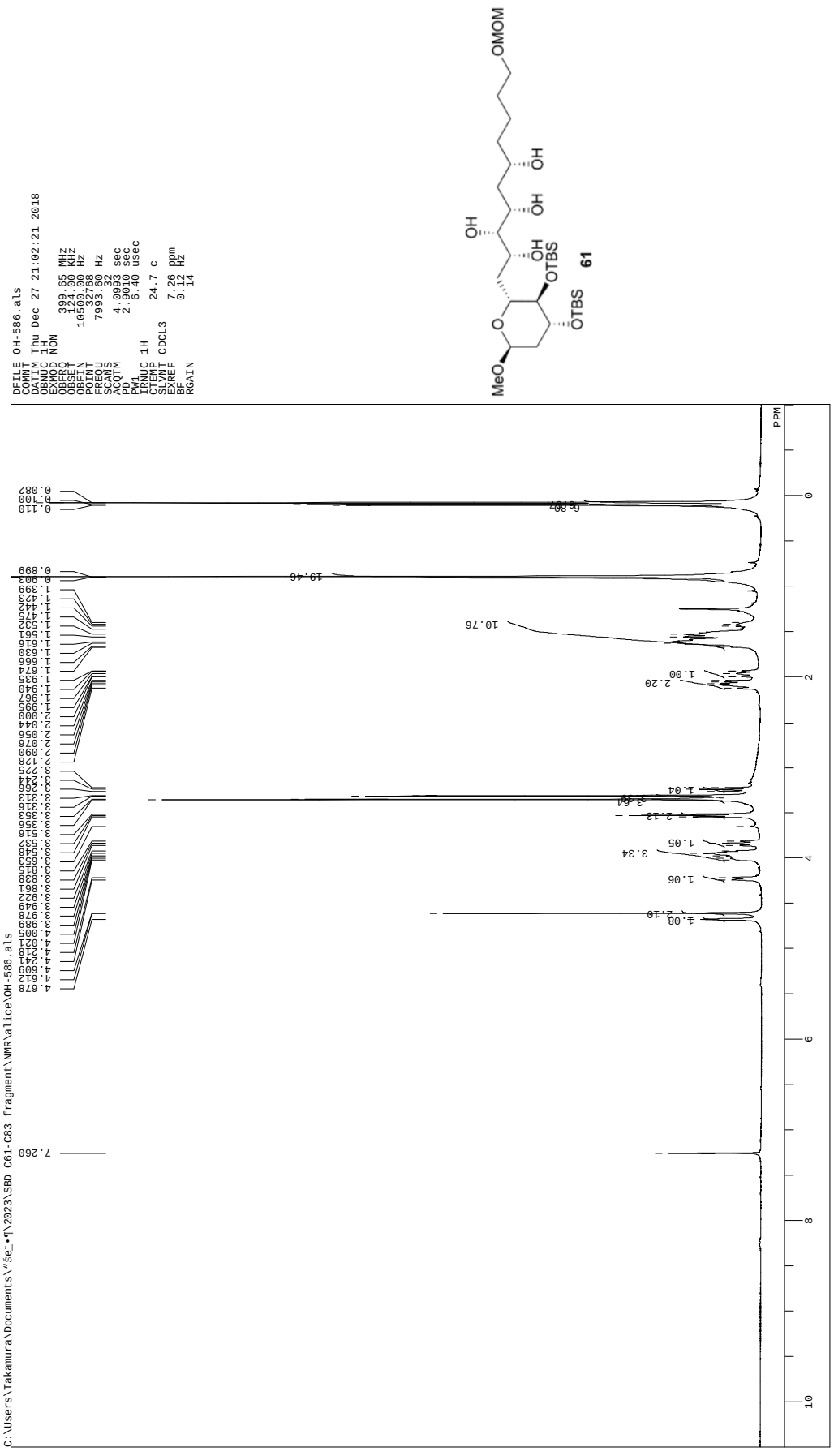
HMQC (600 MHz, CD_3OD)

4e

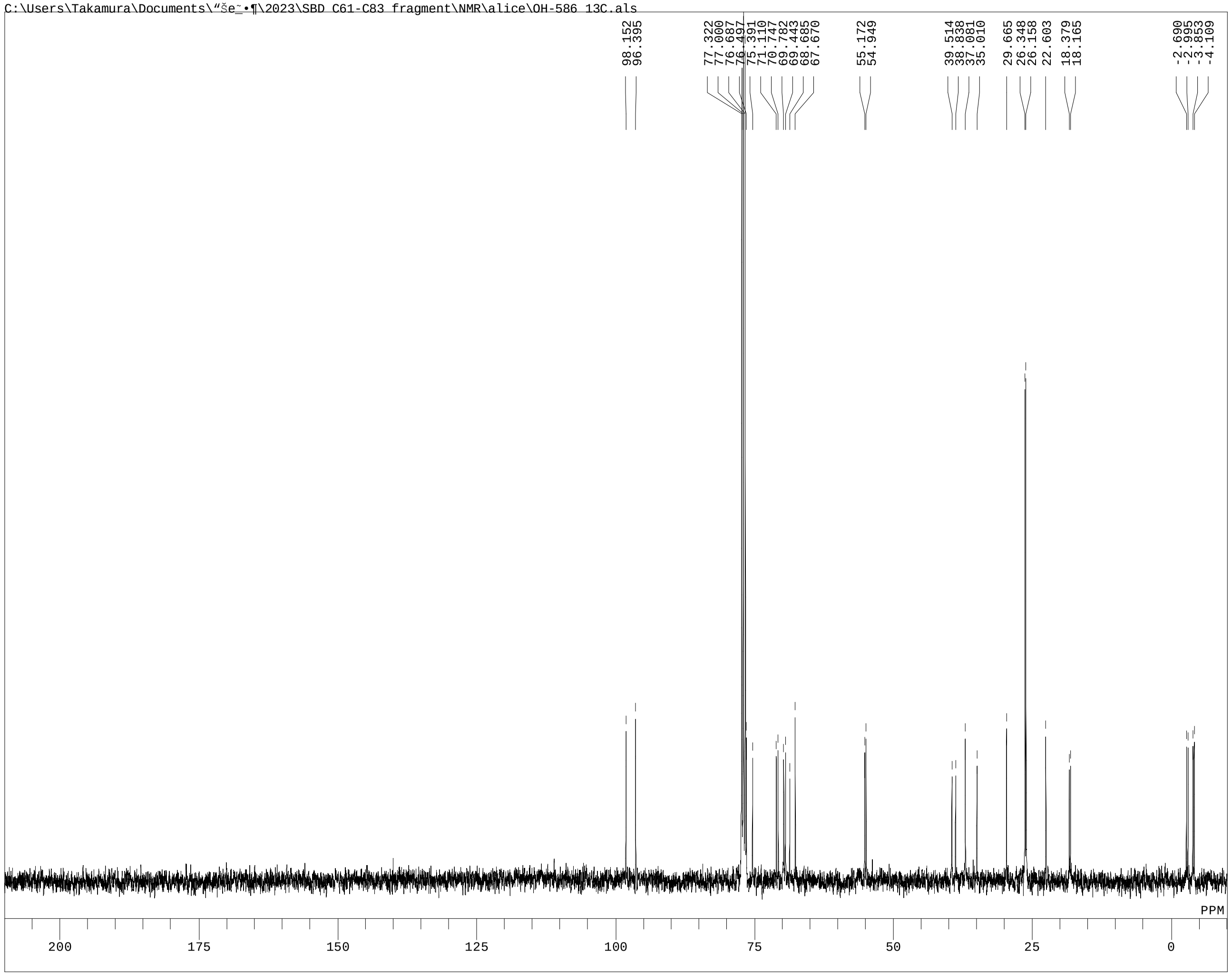


HMBC (600 MHz, CD_3OD)

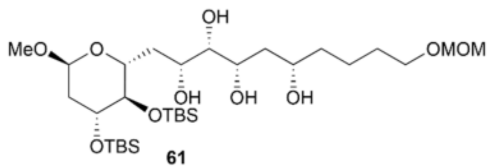
4e


DFILE OH-586.als
COMNT
DATIM Thu Dec 27 21:02:21 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 14.00 KHz
OBFIN 10560.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
ACQTM 4.0903 sec
PD 2.9810 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.7 c
SOLVENT CDCL3
EXREF 7.26 ppm
BF 0.12 HZ
RGAIN 14
OMOM
OH
OH
OH
OH
OTBS
OTBS
MeO
O
61
C:\Users\Takamura\Documents\データ\2023\SBD_C61-C83_fragment\NMR\alice\OH-586.als
PPM

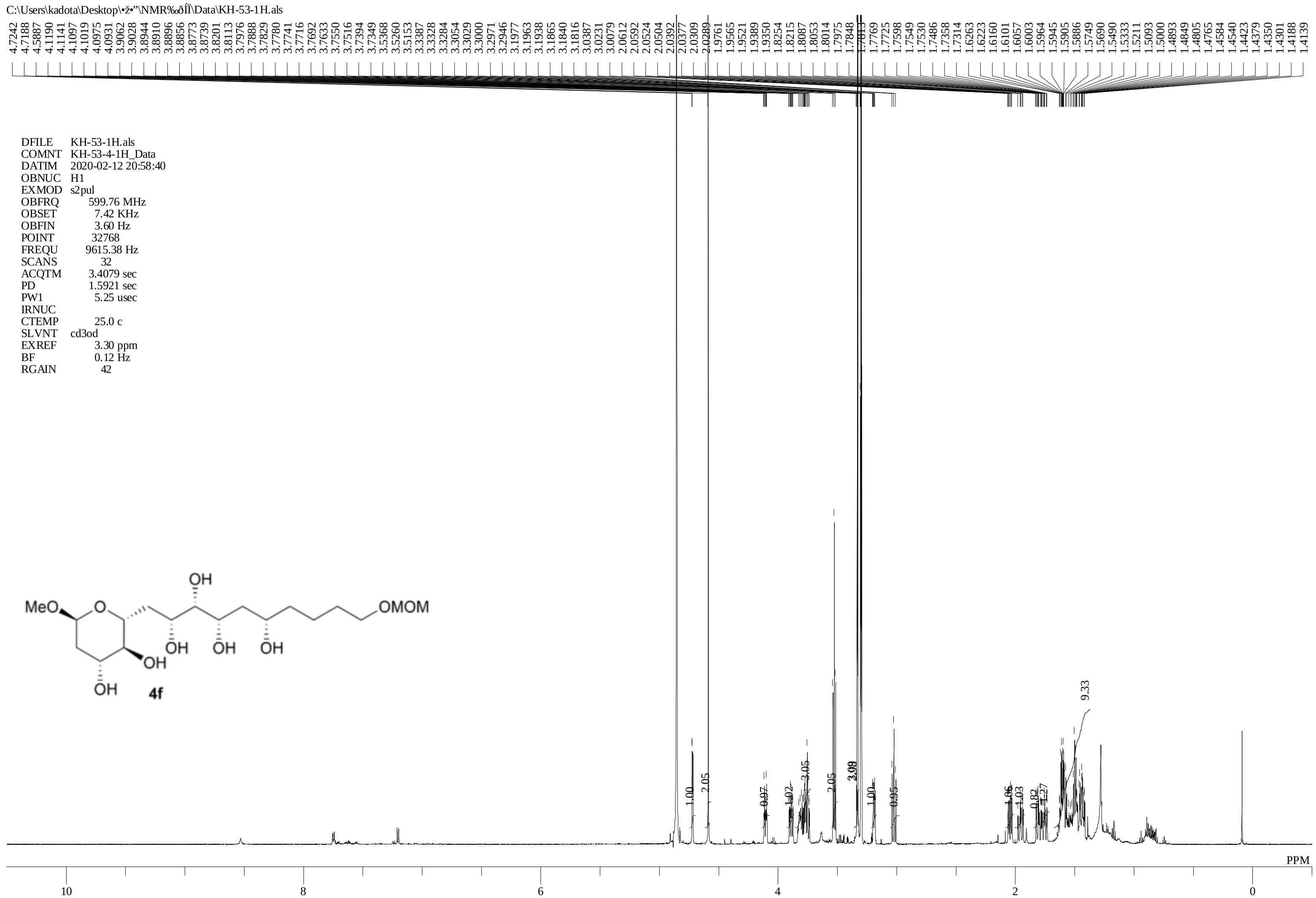
C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-586 13C.als




```
DFILE  OH-586 13C.als
COMNT
DATIM  Thu Dec 27 21:22:39 2018
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU     27173.90 Hz
SCANS          384
ACQTM       1.2059 sec
PD          1.7940 sec
PW1           6.80 usec
IRNUC  1H
CTEMP         26.3 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```



61


C:\Users\kadota\Desktop\•ž•"\NMR‰ðÍÌ\Data\KH-53-1H.als
4.7242 4.7188 4.5887 4.1190 4.1141 4.1097 4.1019 4.0975 4.0931 3.9062 3.9028 3.8944 3.8910 3.8896 3.8856 3.8773 3.8739 3.8201 3.8113 3.7976 3.7888 3.7829 3.7780 3.7741 3.7716 3.7692 3.7633 3.7550 3.7516 3.7394 3.7349 3.5368 3.5260 3.5153 3.3387 3.3328 3.3284 3.3054 3.3029 3.3000 3.2971 3.2946 3.1977 3.1963 3.1938 3.1865 3.1840 3.1816 3.0387 3.0231 3.0079 2.0612 2.0592 2.0524 2.0504 2.0392 2.0377 2.0309 2.0289 1.9761 1.9565 1.9521 1.9389 1.9350 1.8254 1.8215 1.8087 1.8053 1.8014 1.7975 1.7848 1.7813 1.7769 1.7725 1.7598 1.7549 1.7530 1.7486 1.7358 1.7314 1.6263 1.6223 1.6160 1.6101 1.6057 1.6003 1.5964 1.5945 1.5905 1.5886 1.5749 1.5690 1.5490 1.5333 1.5211 1.5093 1.5000 1.4893 1.4849 1.4805 1.4765 1.4584 1.4540 1.4423 1.4379 1.4350 1.4301 1.4188 1.4139
DFILE KH-53-1H.als
COMNT KH-53-4-1H_Data
DATIM 2020-02-12 20:58:40
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 7.42 KHz
OBFIN 3.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 42
MeO
O
OH
OH
OH
OH
OH
OH
OMOM
4f
1.00
2.05
0.97
1.02
3.05
2.05
3.09
1.00
0.95
1.06
1.03
0.82
1.27
9.33
PPM
10
8
6
4
2
0

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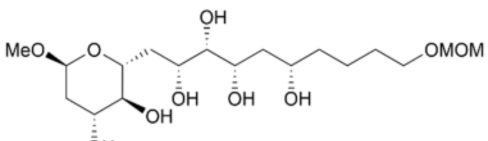
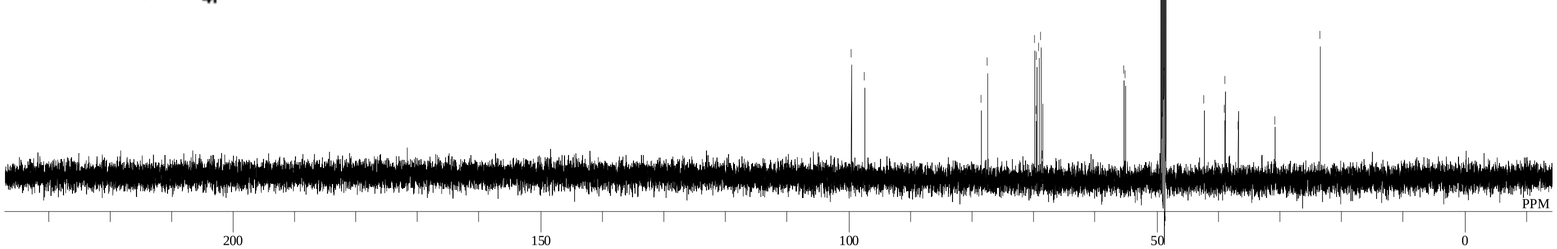
DFILE	KH-53-13C.als
COMNT	KH-53-4-13C_Data
DATIM	2020-02-12 21:03:04
OBNUC	C13
EXMOD	s2pul
OBFRQ	150.82 MHz
OBSET	7.32 KHz
OBFIN	3.00 Hz
POINT	32768
FREQU	37878.79 Hz
SCANS	64
ACQTM	0.8651 sec
PD	2.1349 sec
PW1	5.75 usec
IRNUC	
CTEMP	25.0 c
SLVNT	cd3od
EXREF	49.00 ppm
BF	0.12 Hz
RGAIN	60



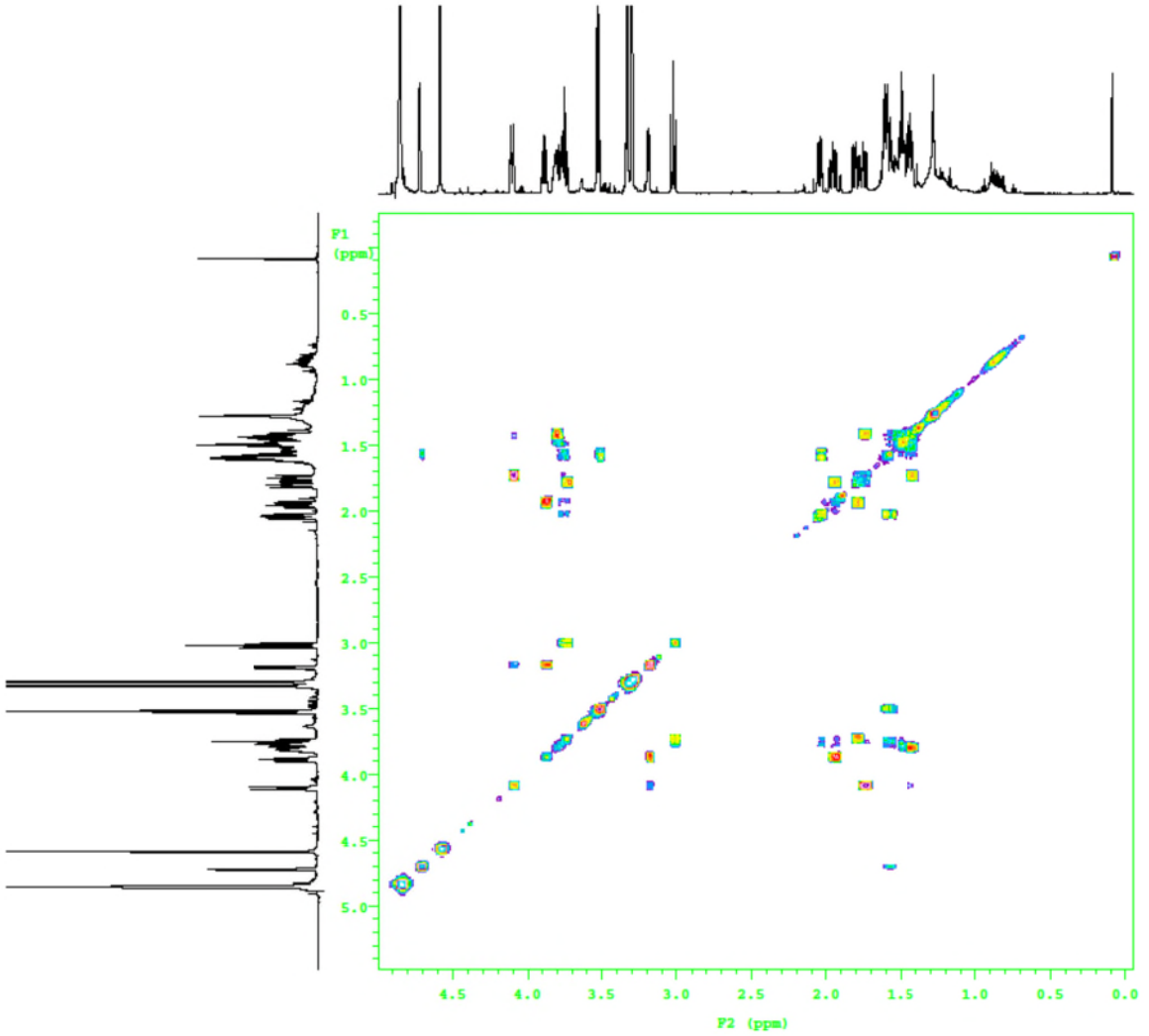
4f



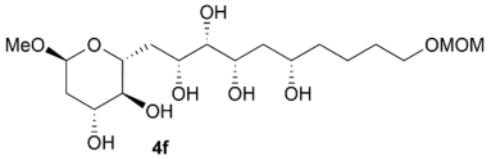
KH-53-4-gCOSY_Data

exp3 gCOSY

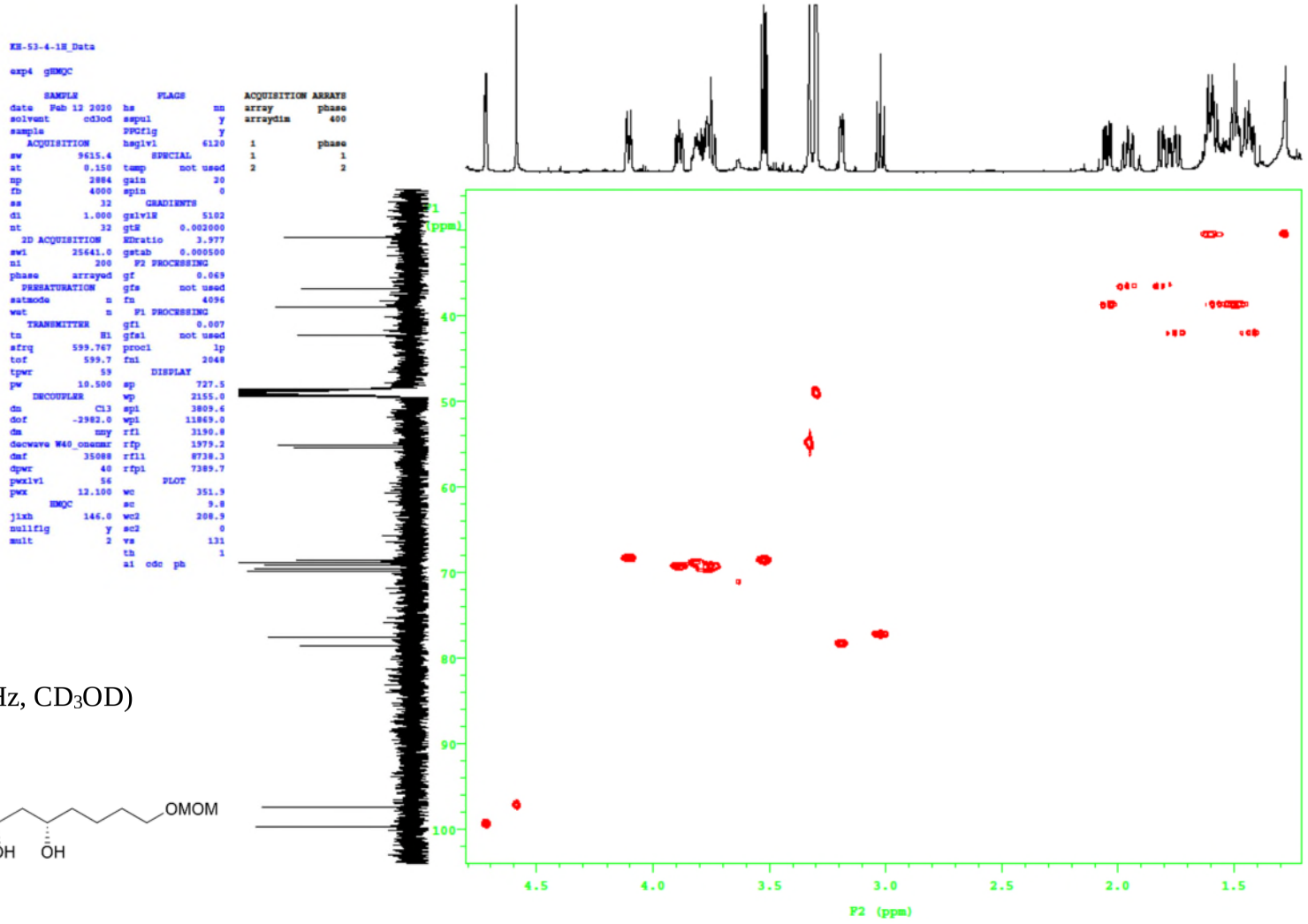
SAMPLE		FLAGS	
date	Feb 13 2020	ha	nn
solvent	cd3od	aspul	y
sample		hsglvl	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	56
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	16	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.027
ni	256	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-28.7
TRANSMITTER		wp	3023.6
tn	H1	spl	-155.3
sfrq	599.767	wp1	3441.4
tof	599.7	rf1	3200.5
tpwr	59	rfp	1979.2
pw	10.500	rf11	3209.6
GRADIENTS		rfp1	1979.2
gs1v1N	5102	PLOT	
gtN	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	131
dm	nnn	th	4
		ai cdc zv	



^{1}H–^{1}H COSY (600 MHz, CD_3OD)

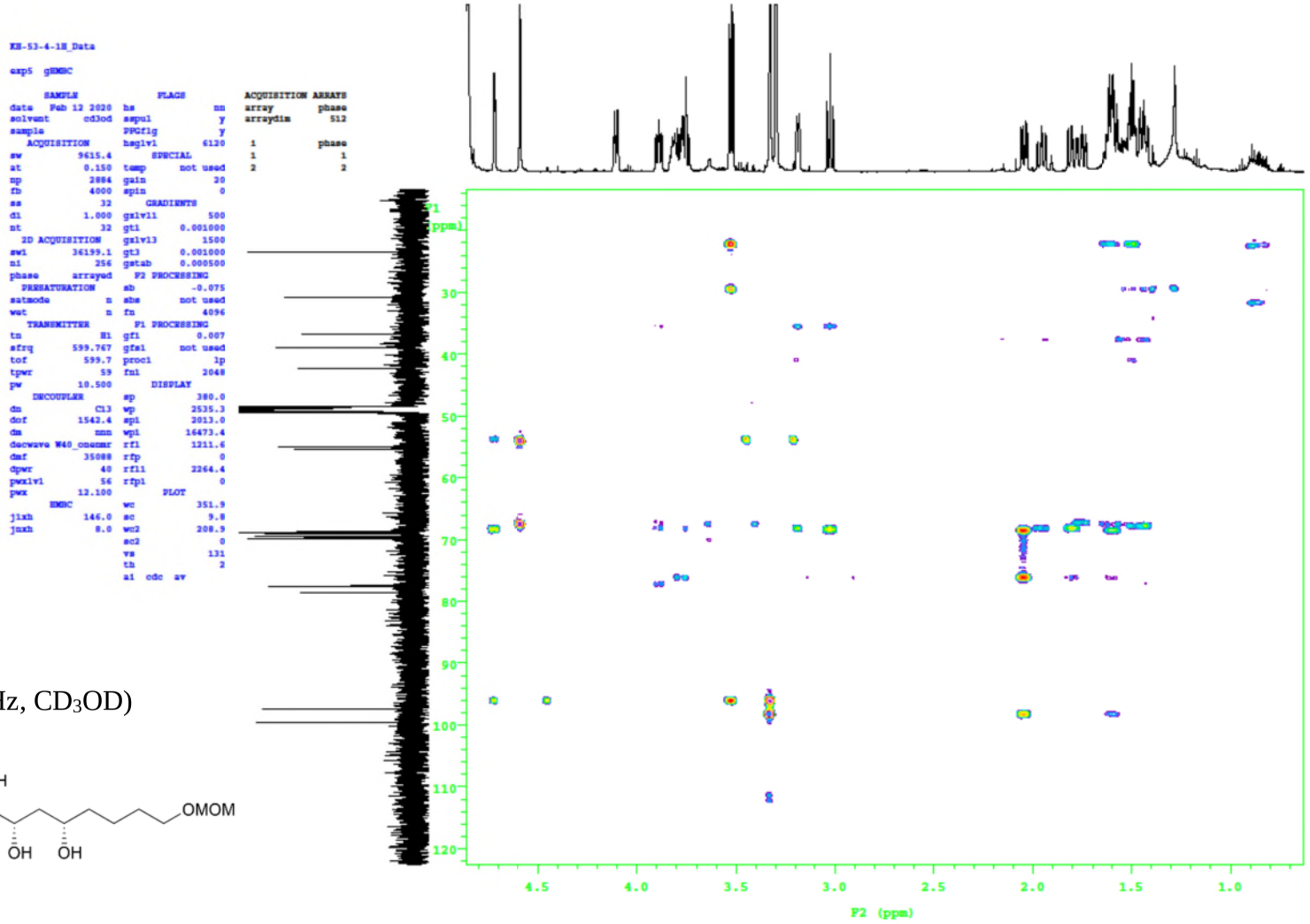


4f



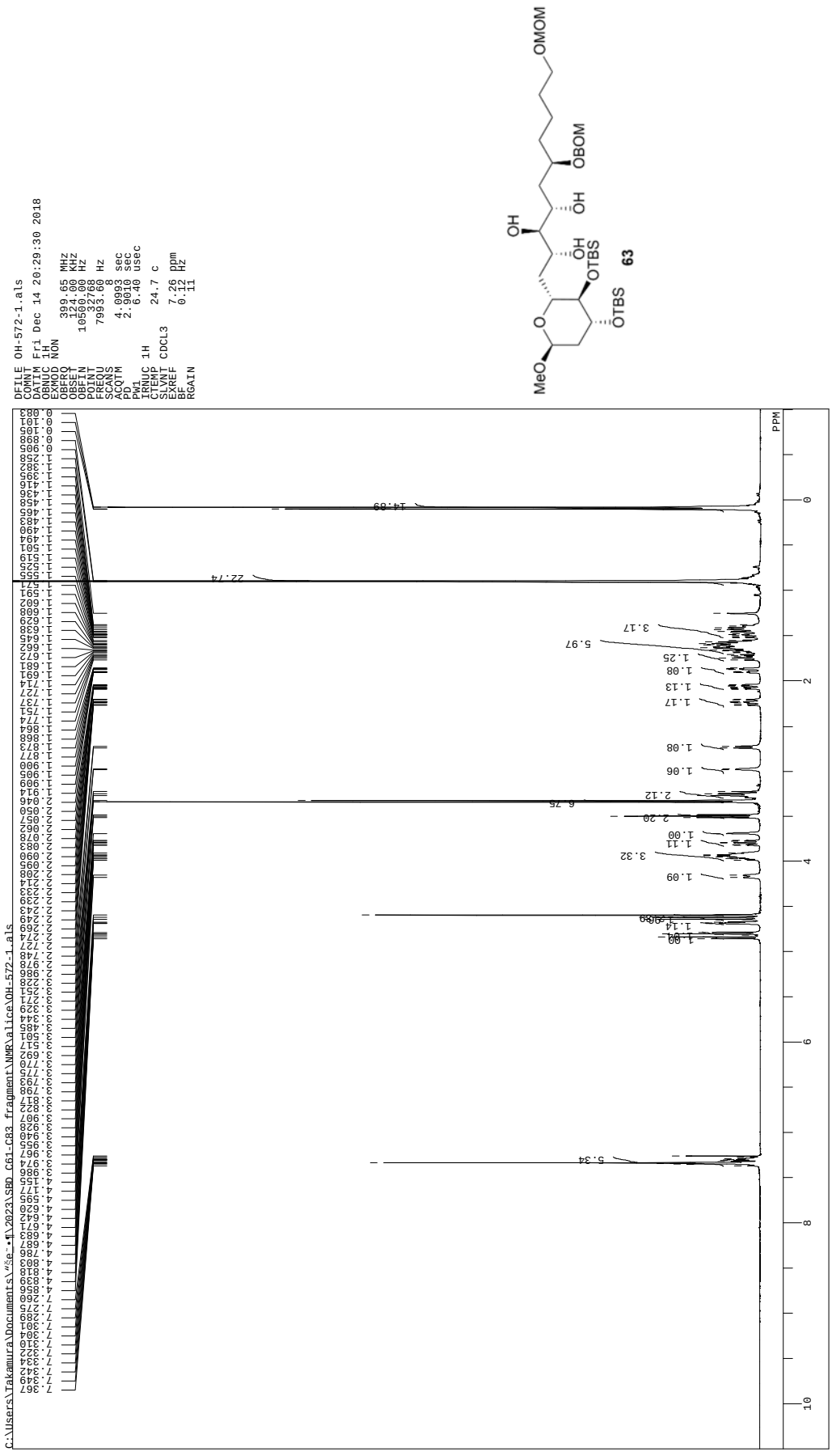
HMQC (600 MHz, CD_3OD)

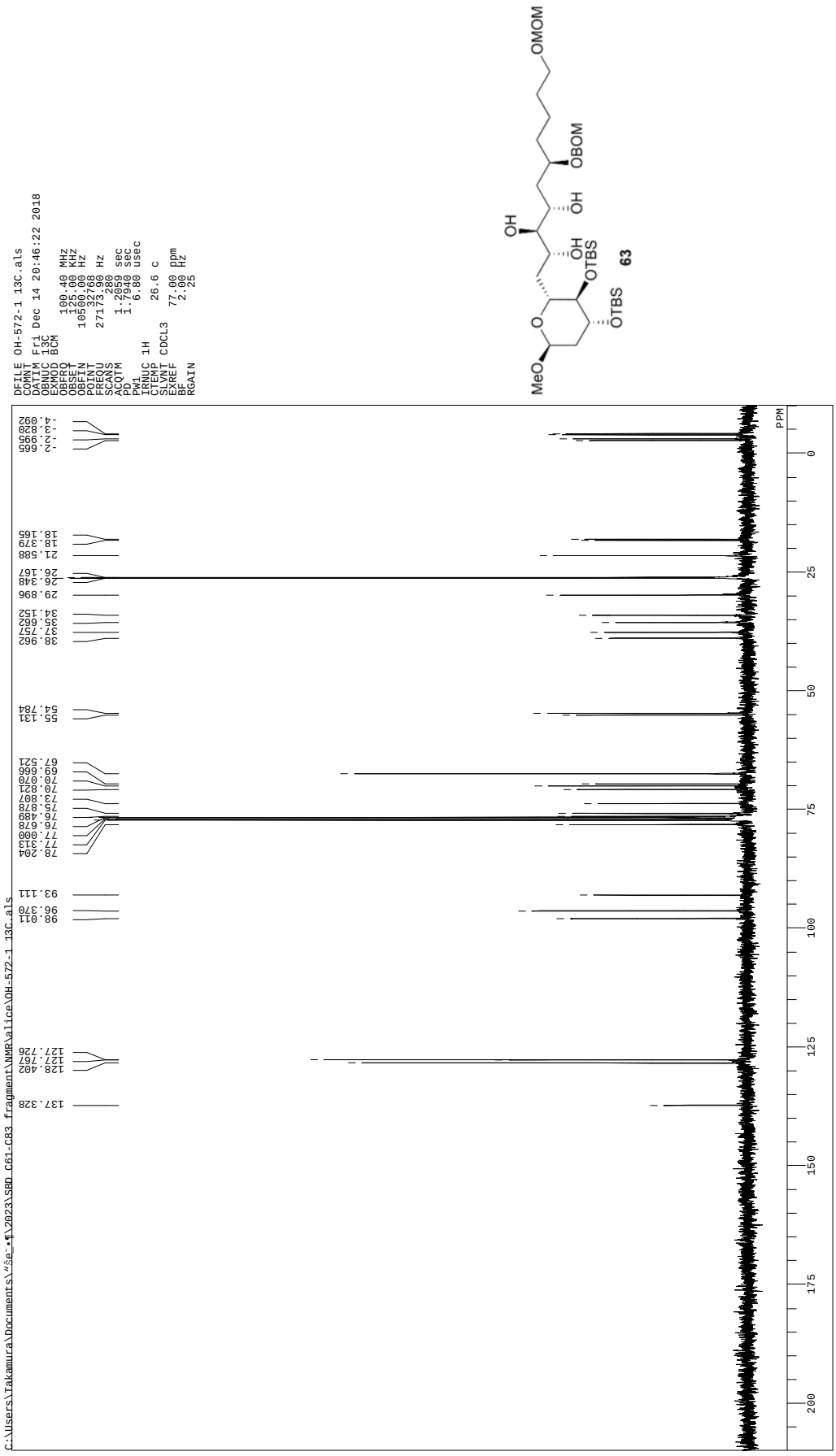
4f

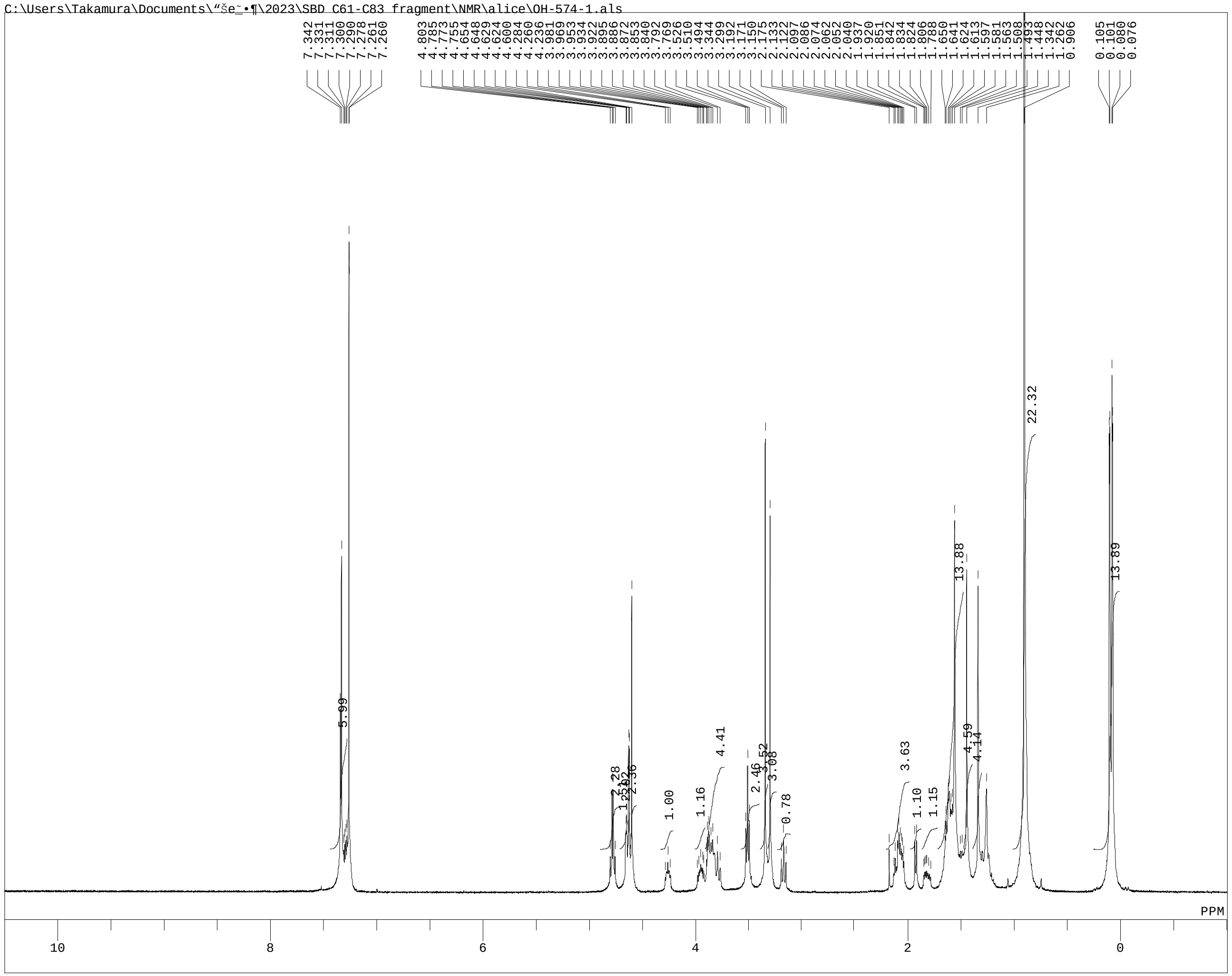


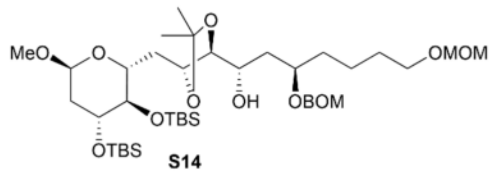
HMBC (600 MHz, CD_3OD)

4f

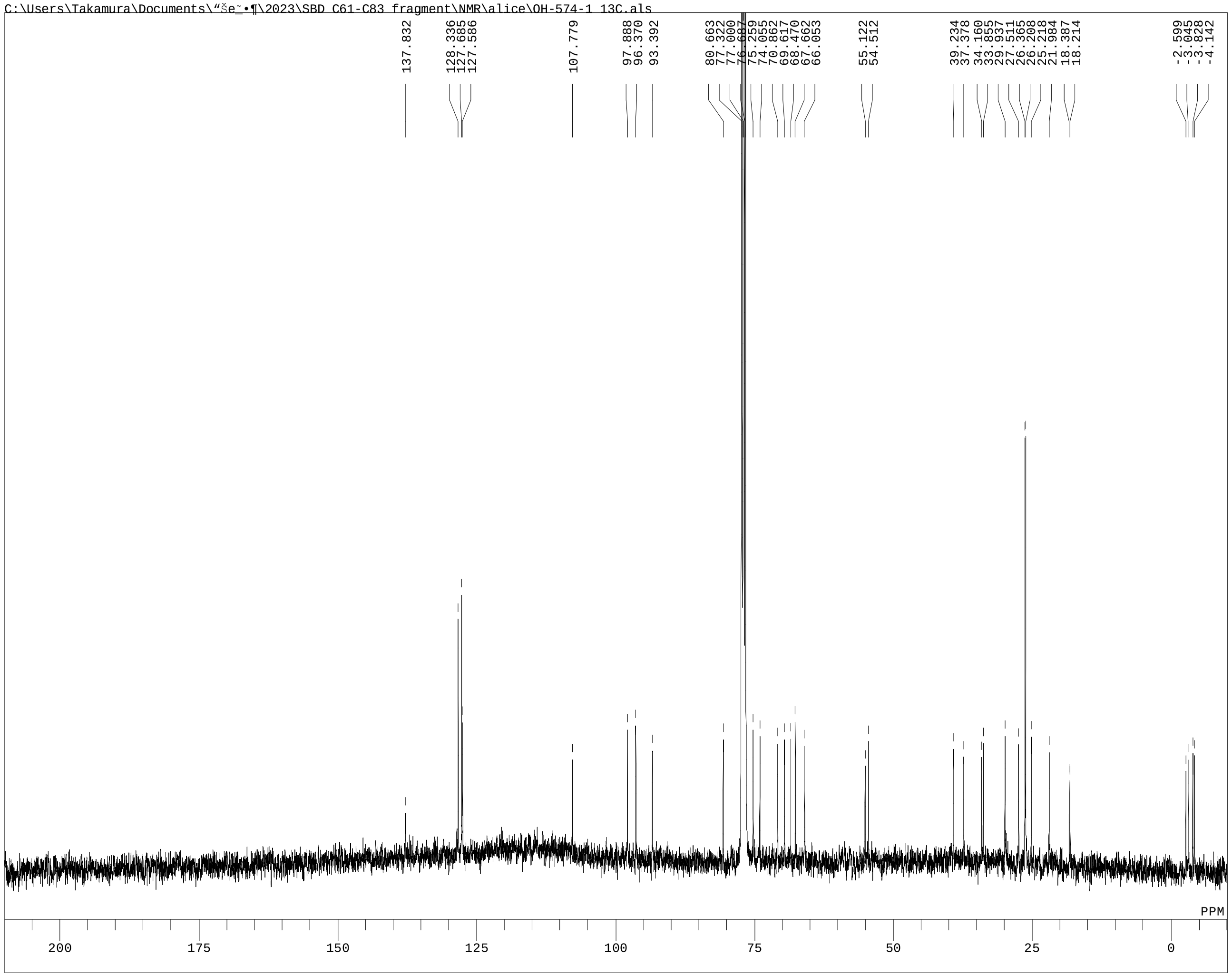

OMOM
OBOM
OH
OH
OH
OTBS
OTBS
MeO
63


OMOM
OBOM
OH
OH
OH
OTBS
OTBS
MeO
O
63
PPM
0
25
50
75
100
125
150
175
200


C:\Users\Takamura\Documents\“še¯•¶\2023\SBD C61-C83 fragment\NMR\alice\OH-574-1.als
7.342 7.331 7.311 7.300 7.290 7.278 7.261 7.260
4.803 4.785 4.773 4.755 4.654 4.648 4.629 4.624 4.600 4.284 4.260 4.236 3.981 3.969 3.953 3.934 3.922 3.895 3.886 3.872 3.853 3.840 3.792 3.769 3.526 3.510 3.494 3.344 3.299 3.192 3.171 3.150 2.175 2.133 2.122 2.097 2.086 2.074 2.062 2.052 2.040 1.937 1.920 1.851 1.842 1.834 1.824 1.806 1.788 1.650 1.641 1.624 1.613 1.597 1.581 1.563 1.508 1.493 1.448 1.342 1.262 0.906
0.105 0.101 0.080 0.076
5.99
2.28 1.25 2.02 2.36 1.00 1.16 4.41 2.46 3.52 3.08 0.78
3.63 1.10 1.15 13.88 4.59 4.14 22.32 13.89
PPM
10 8 6 4 2 0
DFILE OH-574-1.als
COMNT
DATIM Thu Dec 20 00:22:14 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 21


MeO
O
OTBS
OTBS
O
O
OH
OBOM
OMOM

S14

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DFILE  OH-574-1 13C.als
COMNT
DATIM  Thu Dec 20 08:44:21 2018
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU     27173.90 Hz
SCANS        10000
ACQTM       1.2059 sec
PD          1.7940 sec
PW1           6.80 usec
IRNUC  1H
CTEMP         26.1 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```
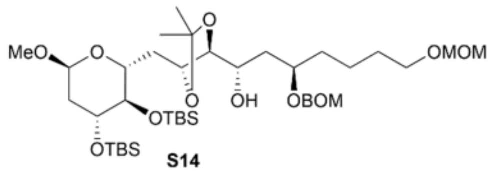
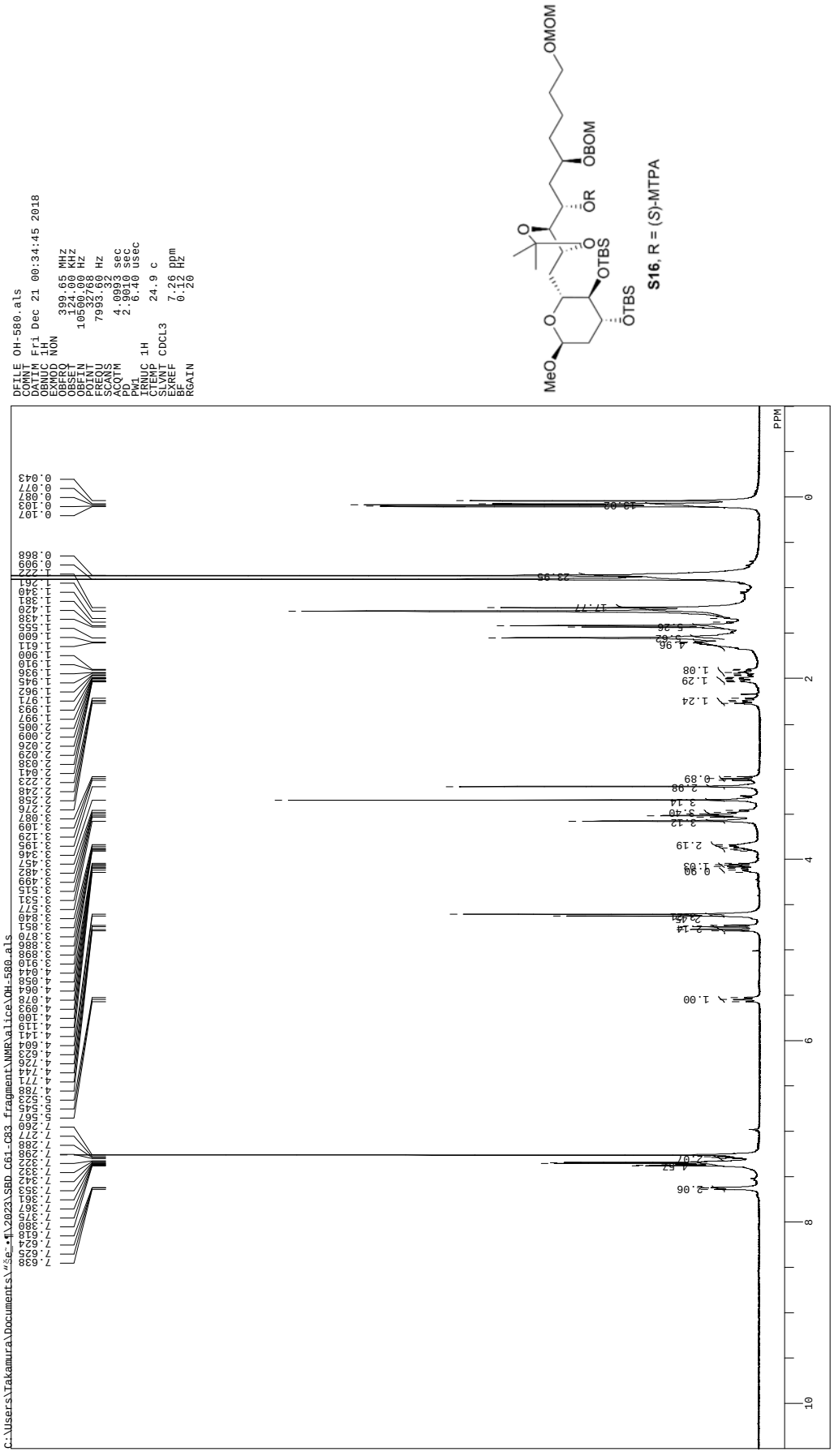
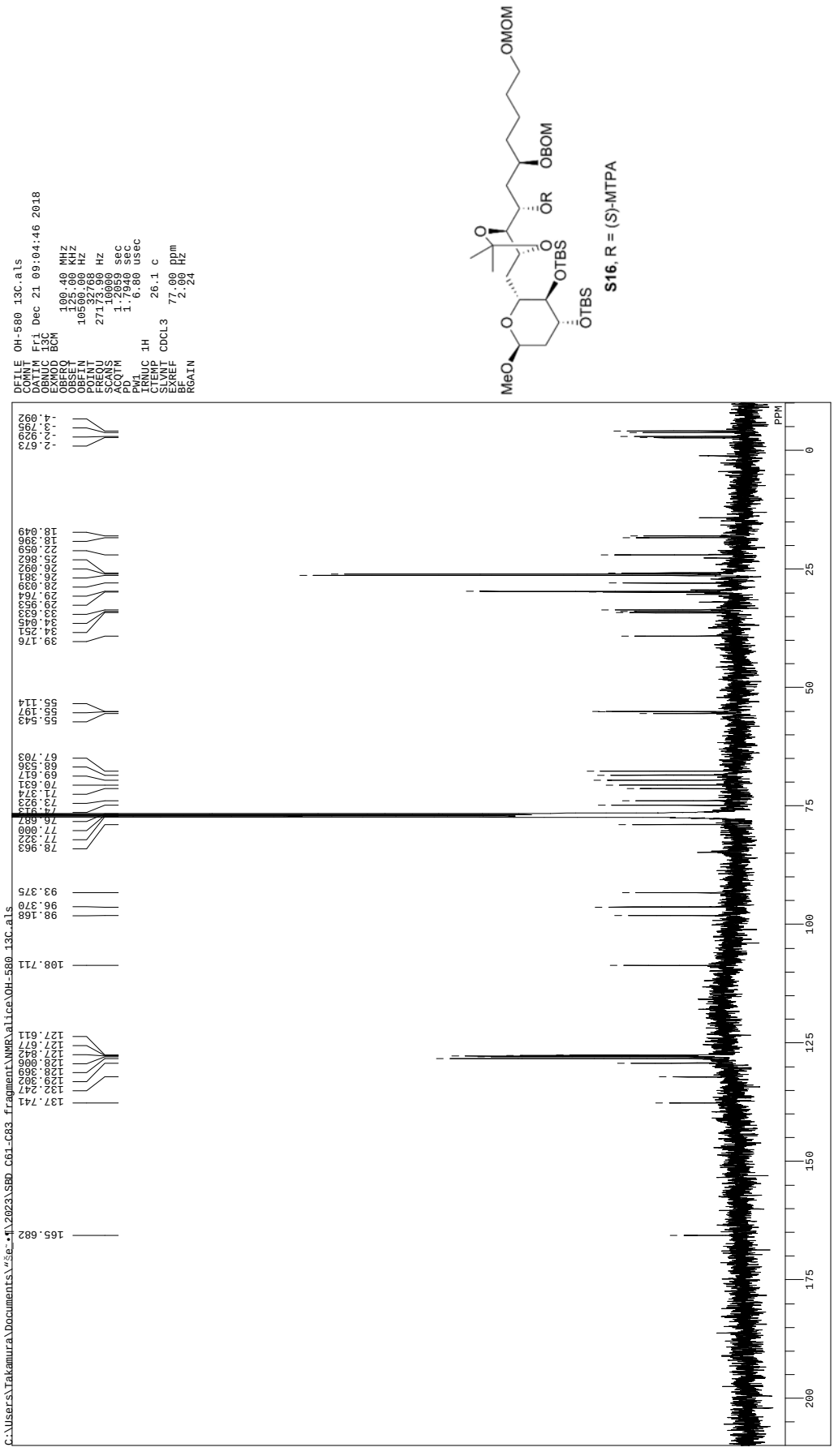
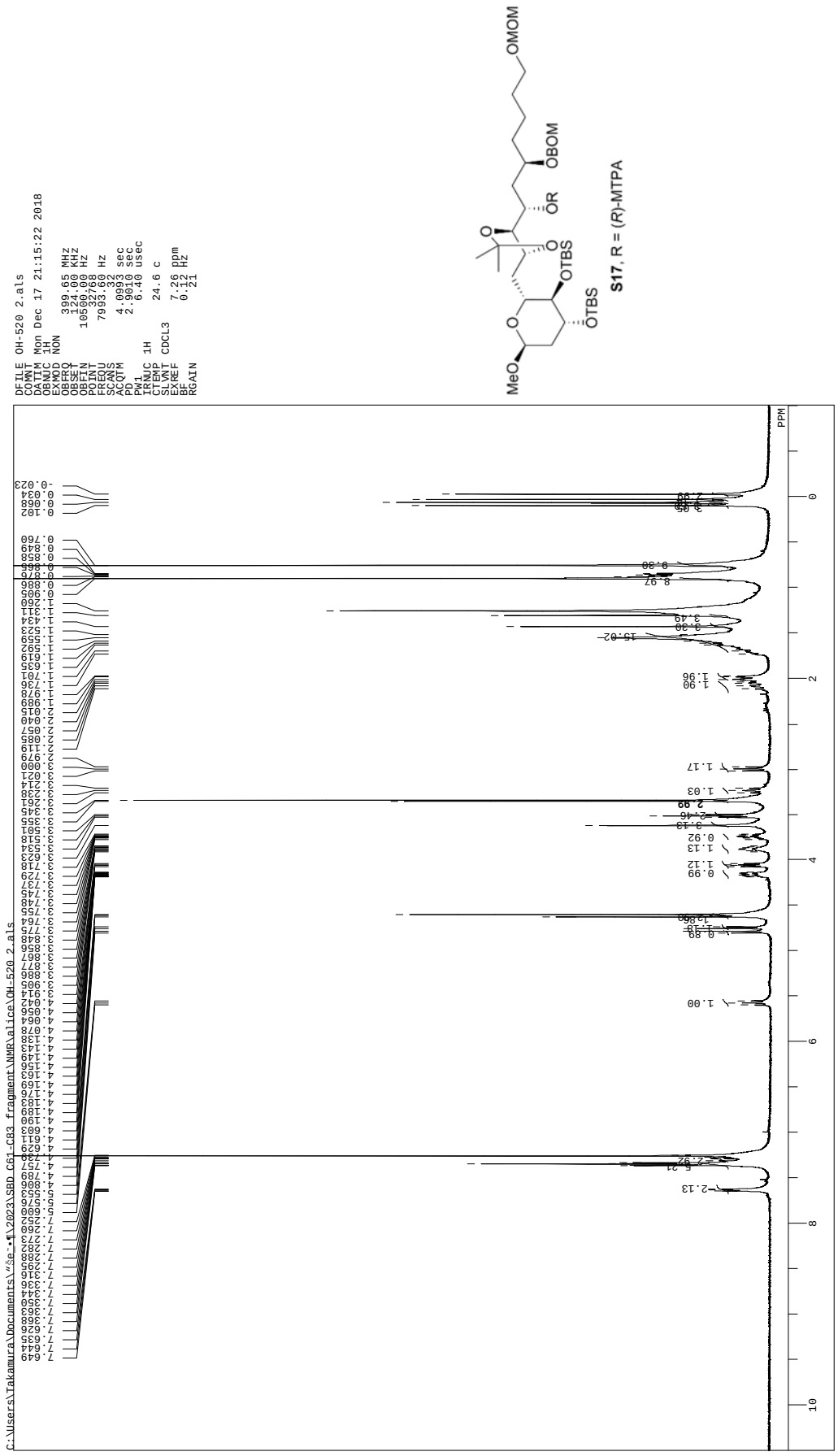
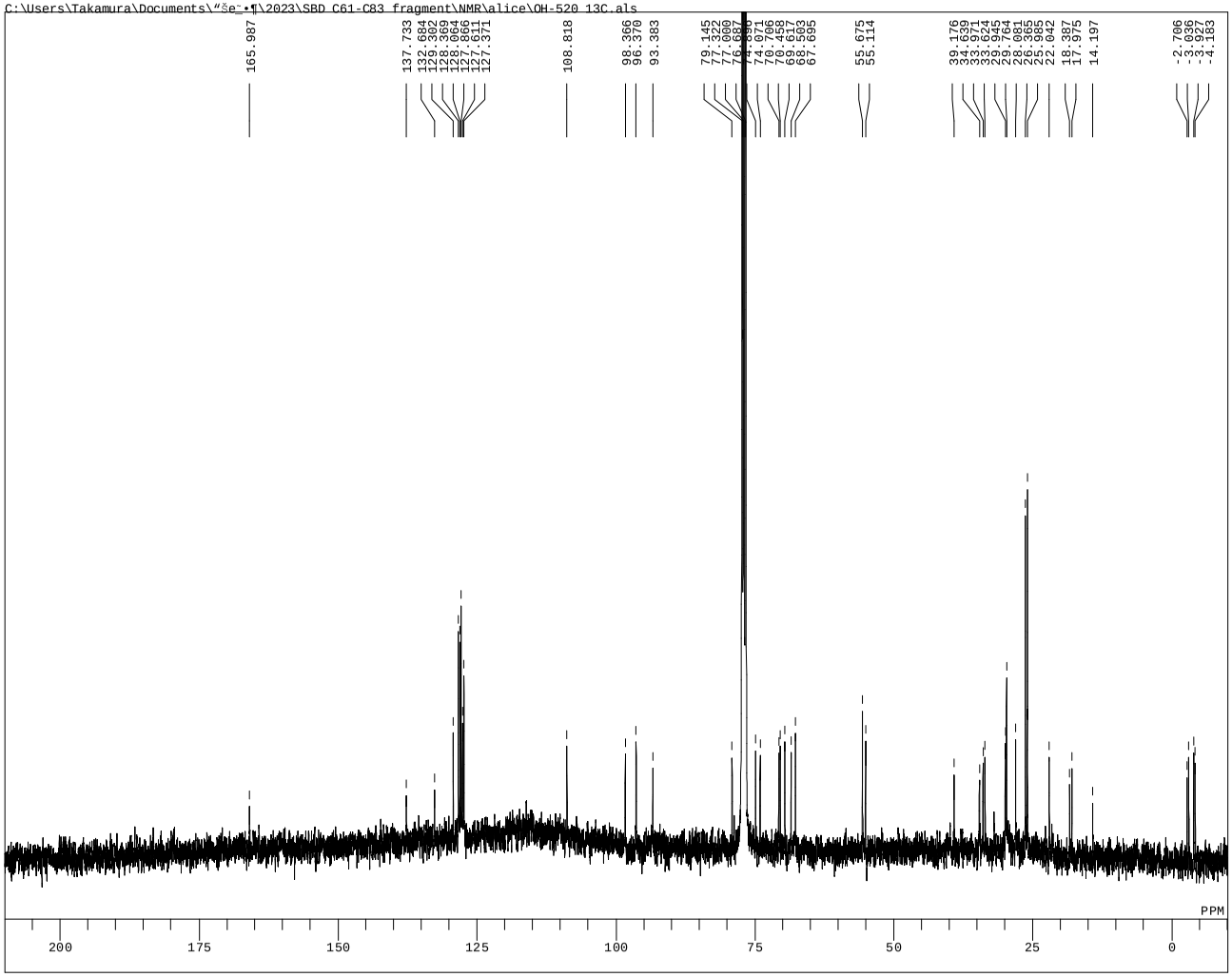



S14

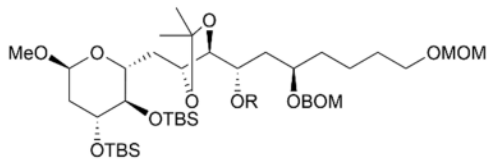

DFILE OH-580.als
COMNT
DATIM Fri Dec 21 00:34:45 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 105927.60 Hz
PTNT 7993.60 Hz
FREQU 32
SCANS 4.0993 sec
ACQTM 2.0000 sec
PD 8.40 usec
PW1
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EFREF 7.26 ppm
BF 0.12 Hz
RGAIN 20
OMOM
OBOM
OR
OTBS
OTBS
MeO
S16, R = (S)-MTPA
PPM
C:\Users\Takamura\Documents\ﾏｽﾀｰ･ﾃﾞｰﾀ\2023\SBD_C61_C83_fragment\NMR\alice\OH-580.als


DFILE OH-580 13C.als
COMNT
DATIM Fri Dec 21 09:04:46 2018
OBNUC 13C
EXMOD BCM
OBSET 100.40 MHz
OBFIN 105500.000 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 1009
ACQTM 1.7940 sec
PD 6.80 usec
PW1
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCl3 77.00 ppm
EXREF 2.000 Hz
BF 2.24
RGAIN
C:\Users\Takamura\Documents\パラメータ\2023\SBD C61-C83 fragment\NMR\alice\OH-580 13C.als
PPM
MeO
OTBS
OTBS
OR
OBOM
OMOM
S16, R = (S)-MTPA

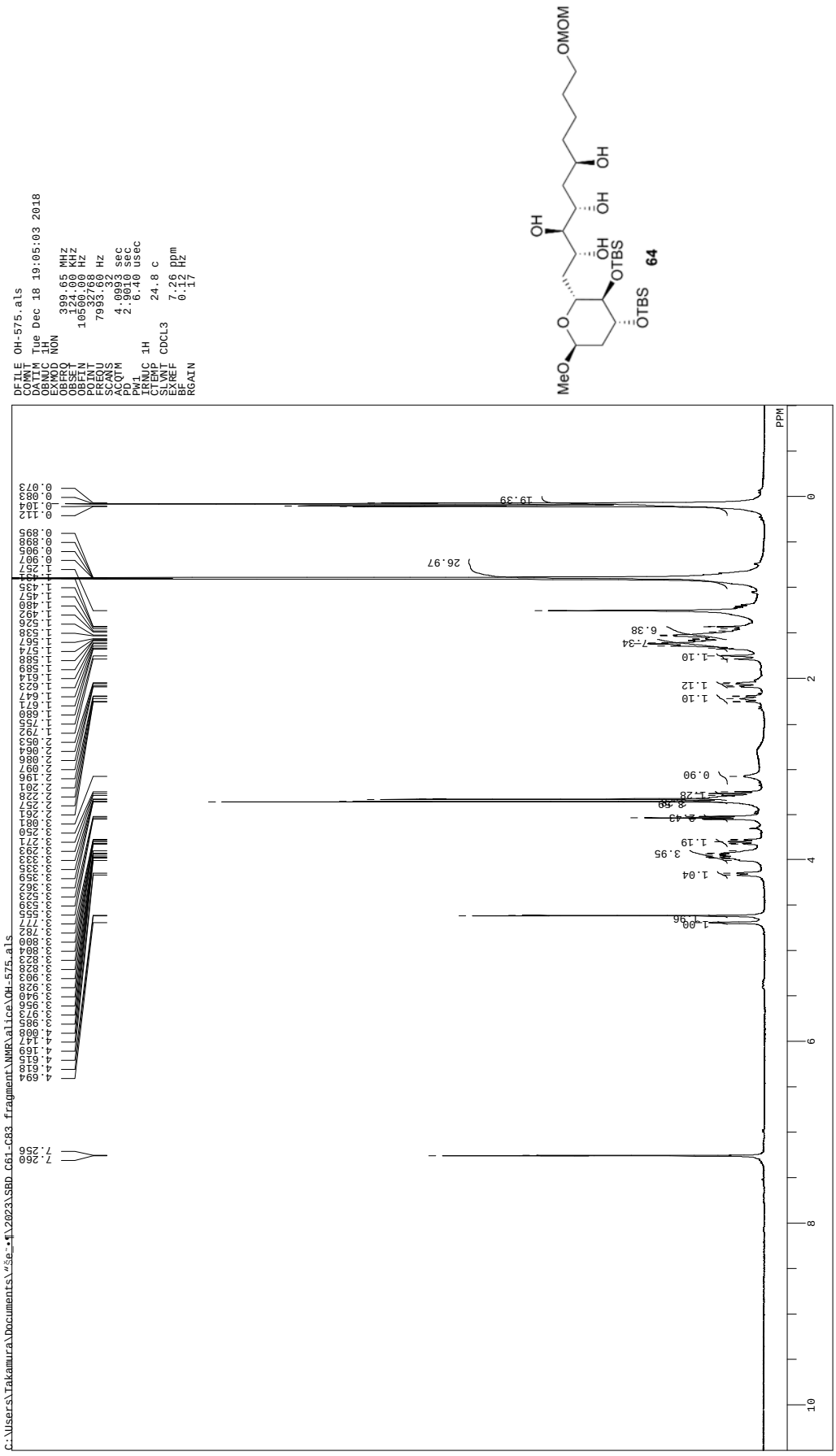

DFILE OH-520 2.als
COMNT
DATIM Mon Dec 17 21:15:22 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 104.00 KHz
OBFIN 1054.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
ACQTM 4.0963 sec
PD 2.0000 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 HZ
RGAIN 21
C:\Users\Takamura\Documents\ﾏｽﾀｰ･1\2023\SBD_C61-C83_fragment\NMR\alice\OH-520_2.als
PPM
OMOM
OBOM
OR
OTBS
OTBS
MeO
S17, R = (R)-MTPA




```
DFILE OH-520 13C.als
COMNT
DATIM Tue Dec 18 06:46:07 2018
OBNUC 13C
EXMOD BCM
OBFRQ        100.40 MHz
OBSET        125.00 KHz
OBFIN      10500.00 Hz
POINT        32768
FREQU      27173.90 Hz
SCANS        10000
ACQTM         1.2059 sec
PD            1.7940 sec
PW1           6.80 usec
IRNUC 1H
CTEMP         26.0 c
SLVNT CDCL3
EXREF        77.00 ppm
BF            2.00 HZ
RGAIN           24
```



S17, R = (*R*)-MTPA


OMOM
OH
OH
OH
OH
OTBS
OTBS
MeO
O
64
DFILE OH-575.als
COMNT
DATIM Tue Dec 18 19:05:03 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 2
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IFNUC 1H
CFDPL
SLVNT CDCl3 24.8 c
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 17
C:\Users\Takamura\Documents\NMR\2023\SBD_CG1_G83_fragment\NMR\alice\OH-575.als
PPM
19.39
26.97
6.38
7.34
1.10
1.12
1.10
0.90
1.28
3.38
2.43
1.19
3.95
1.04
1.00
1.96

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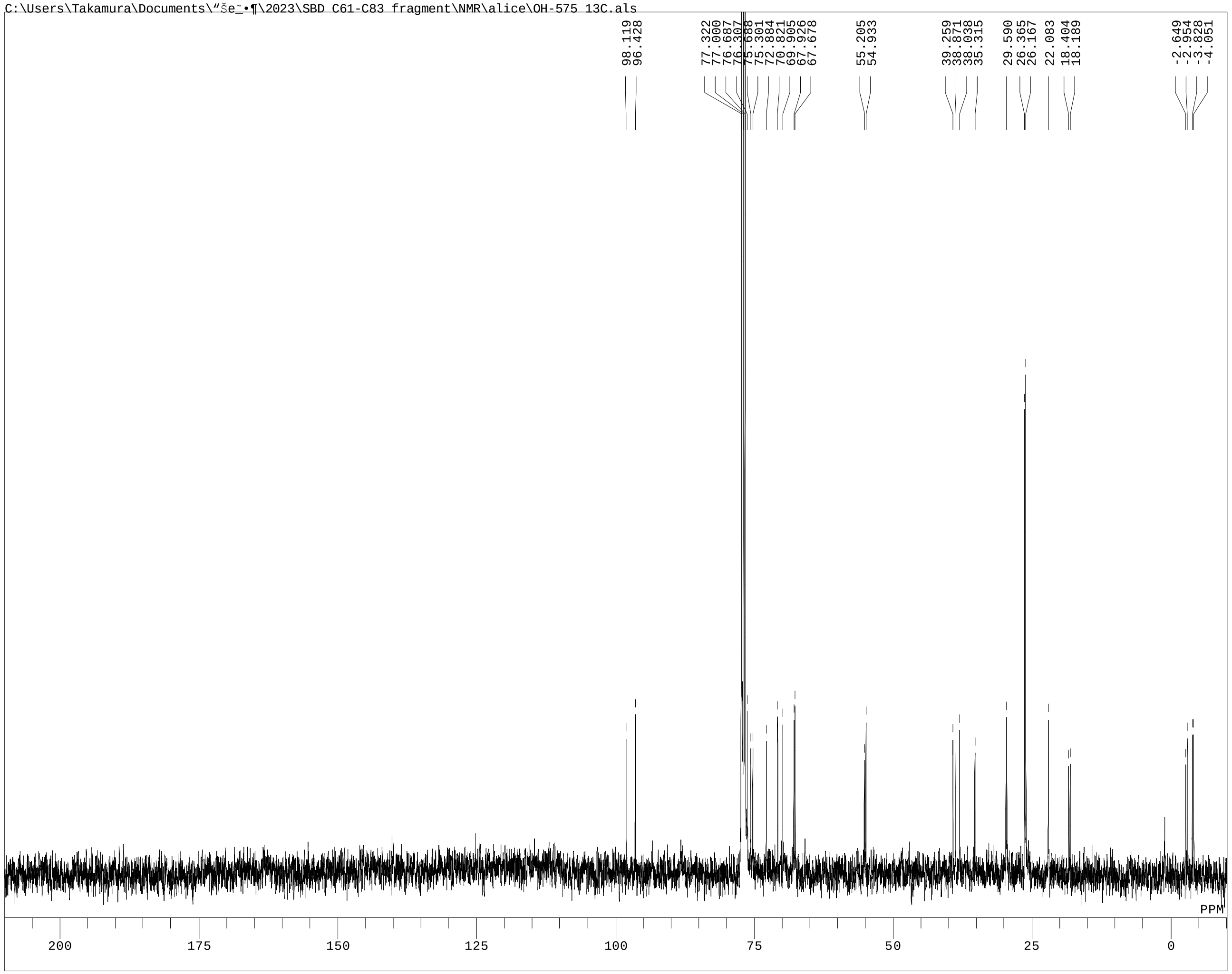
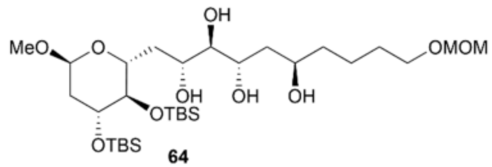



```
DFILE  OH-575 13C.als
COMNT
DATIM  Tue Dec 18 20:12:48 2018
OBNUC  13C
EXMOD  BCM
OBFRQ       100.40 MHz
OBSET       125.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU     27173.90 Hz
SCANS         1184
ACQTM       1.2059 sec
PD          1.7940 sec
PW1           6.80 usec
IRNUC  1H
CTEMP         26.2 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```



64

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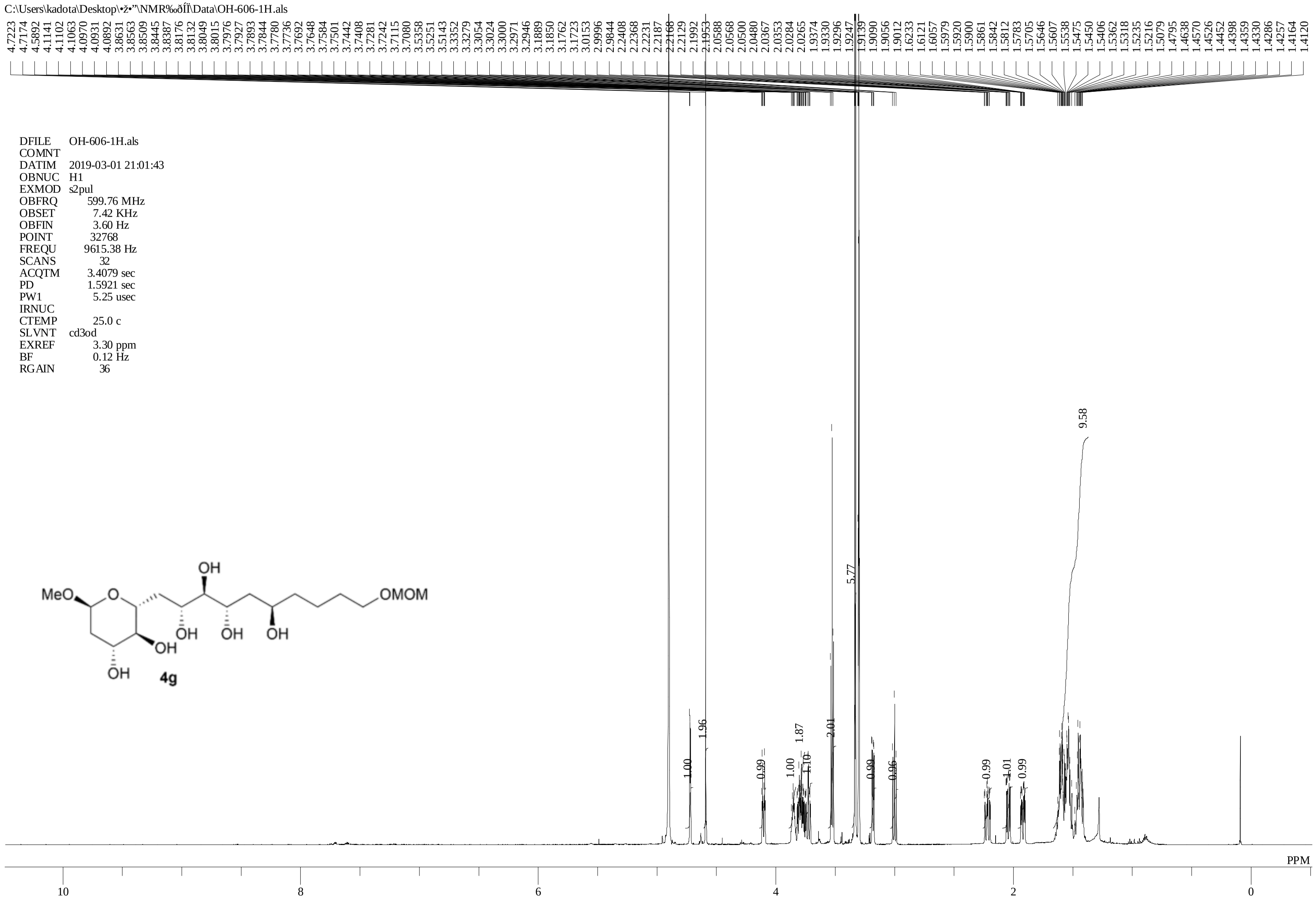
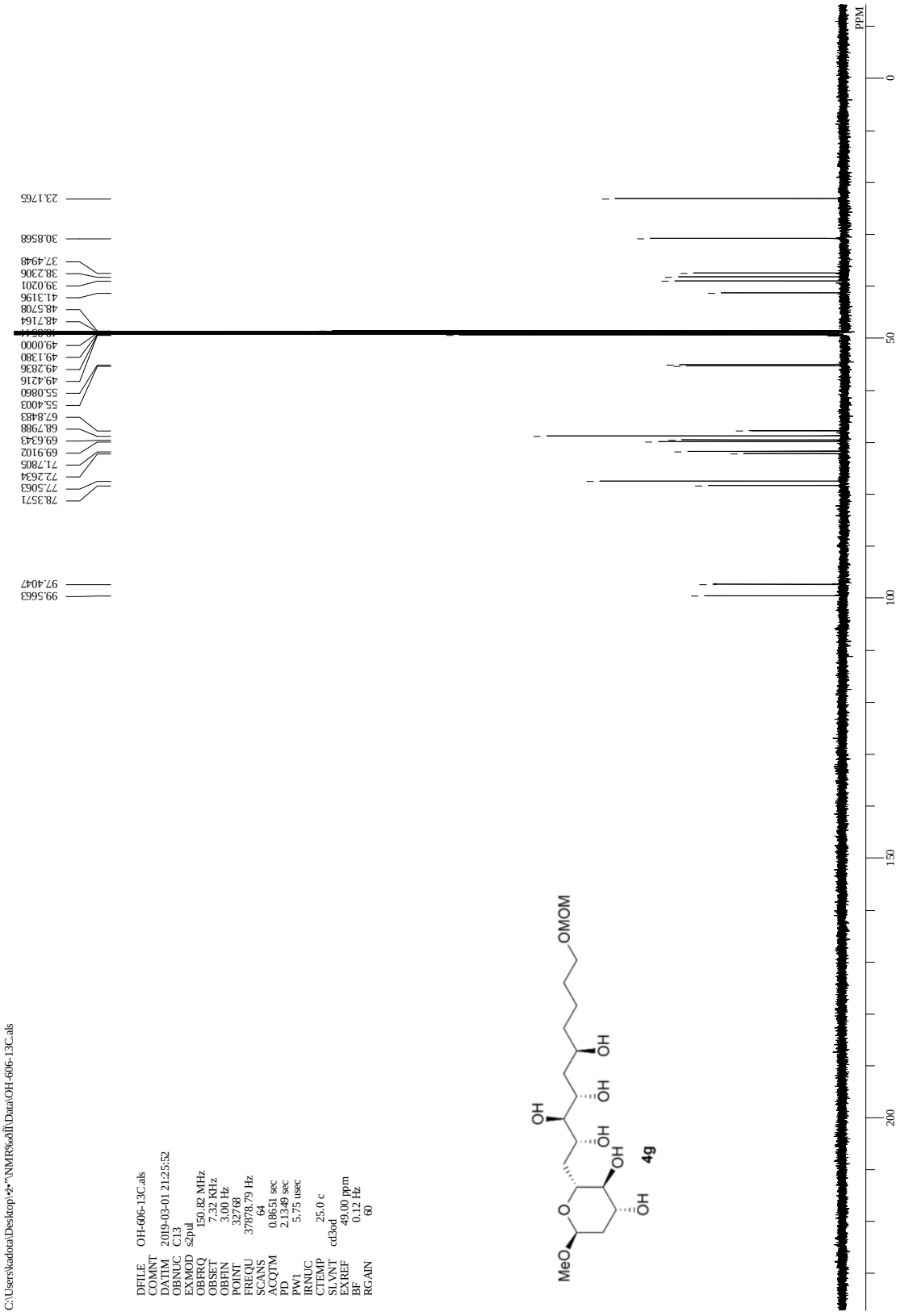
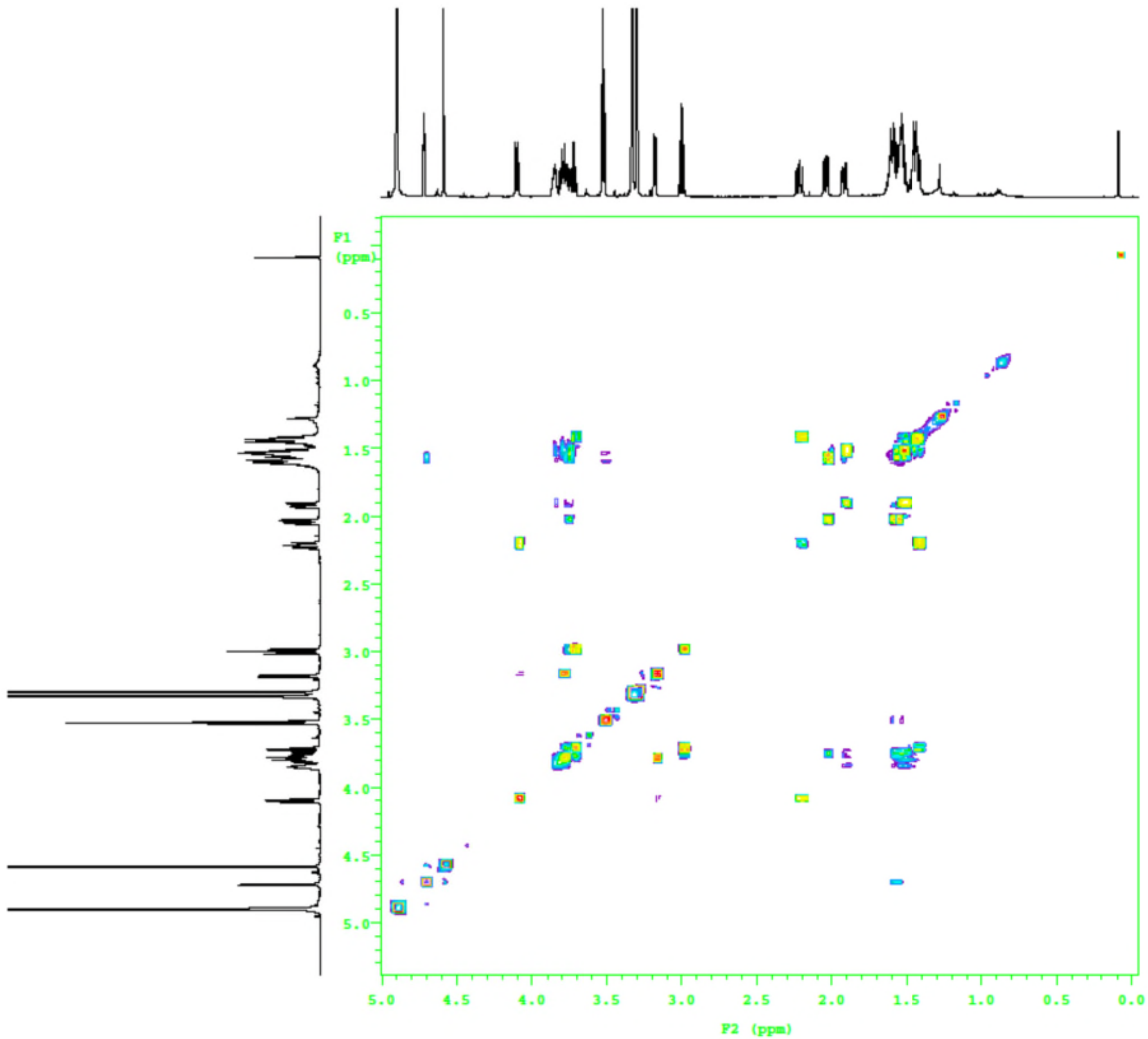


DFILE OH-606-1H.als
COMNT
DATIM 2019-03-01 21:01:43
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 7.42 KHz
OBFIN 3.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 36

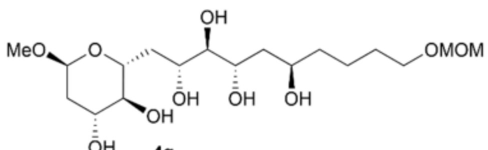
4g


C:\Users\kadota\Desktop\ﾌｧｲﾙ\NMR%odfi\Data\OH-606-13C.als
DFILE OH-606-13C.als
COMNT
DATIM 2019-03-01 21:25:52
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.32 KHz
OBFIN 3.00 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 25.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
23.1765
30.8568
37.4948
38.2306
39.0201
41.3196
48.5708
48.7164
49.0000
49.1380
49.2836
49.4216
55.0860
55.4003
67.8483
68.7988
69.6343
69.9102
71.7805
72.2634
77.5063
78.3571
97.4047
99.5663
OMOM
OH
OH
OH
OH
OH
OH
O
MeO
4g
PPM
0
50
100
150
200

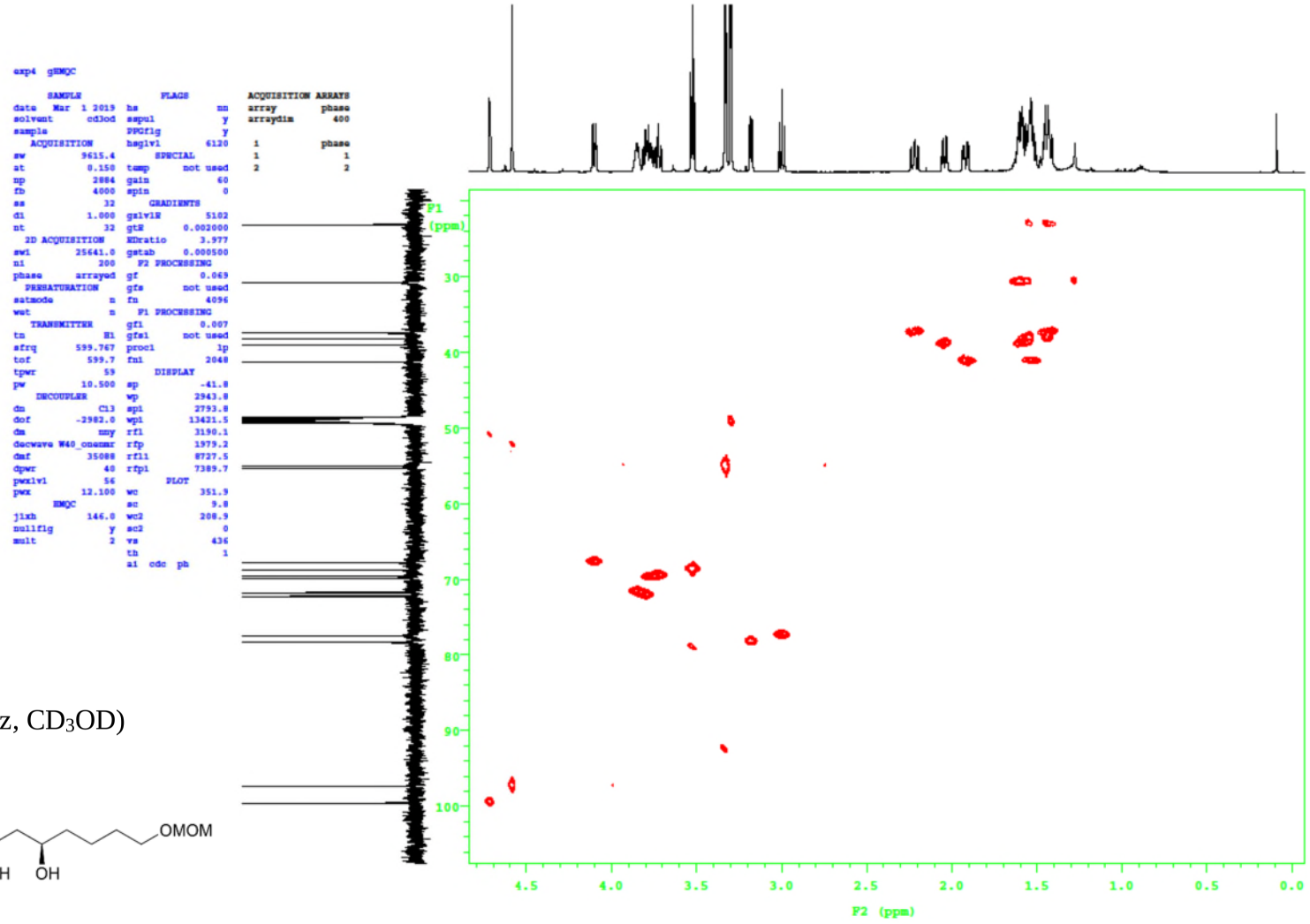
exp3 gCOSY			
SAMPLE		FLAGS	
date	Mar 2 2019	hs	nn
solvent	cd3od	sspul	y
sample		hsglvl	6120
ACQUISITION		SPECIAL	
sw	9615.4	temp	not used
at	0.150	gain	36
np	2884	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	8	fn	4096
2D ACQUISITION		F1 PROCESSING	
sw1	9615.4	sb1	-0.013
ni	128	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	4096
satmode	n	DISPLAY	
wet	n	sp	-23.4
TRANSMITTER		wp	3023.6
tn	H1	sp1	-127.2
sfrq	599.767	wp1	3356.9
tof	599.7	rfl	3204.5
tpwr	59	rfp	1979.2
pw	10.500	rfl1	3209.7
GRADIENTS		rfp1	1979.2
gzlvlE	5102	PLOT	
gtE	0.001000	wc	351.9
EDratio	1.000	sc	9.8
gstab	0.000500	wc2	208.9
DECOUPLER		sc2	0
dn	C13	vs	436
dm	nnn	th	3
		ai cdc av	



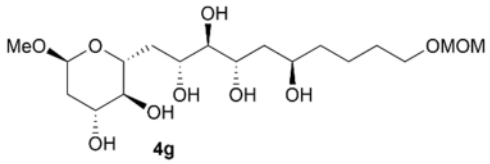
$^1H–^1H$ COSY (600 MHz, CD_3OD)



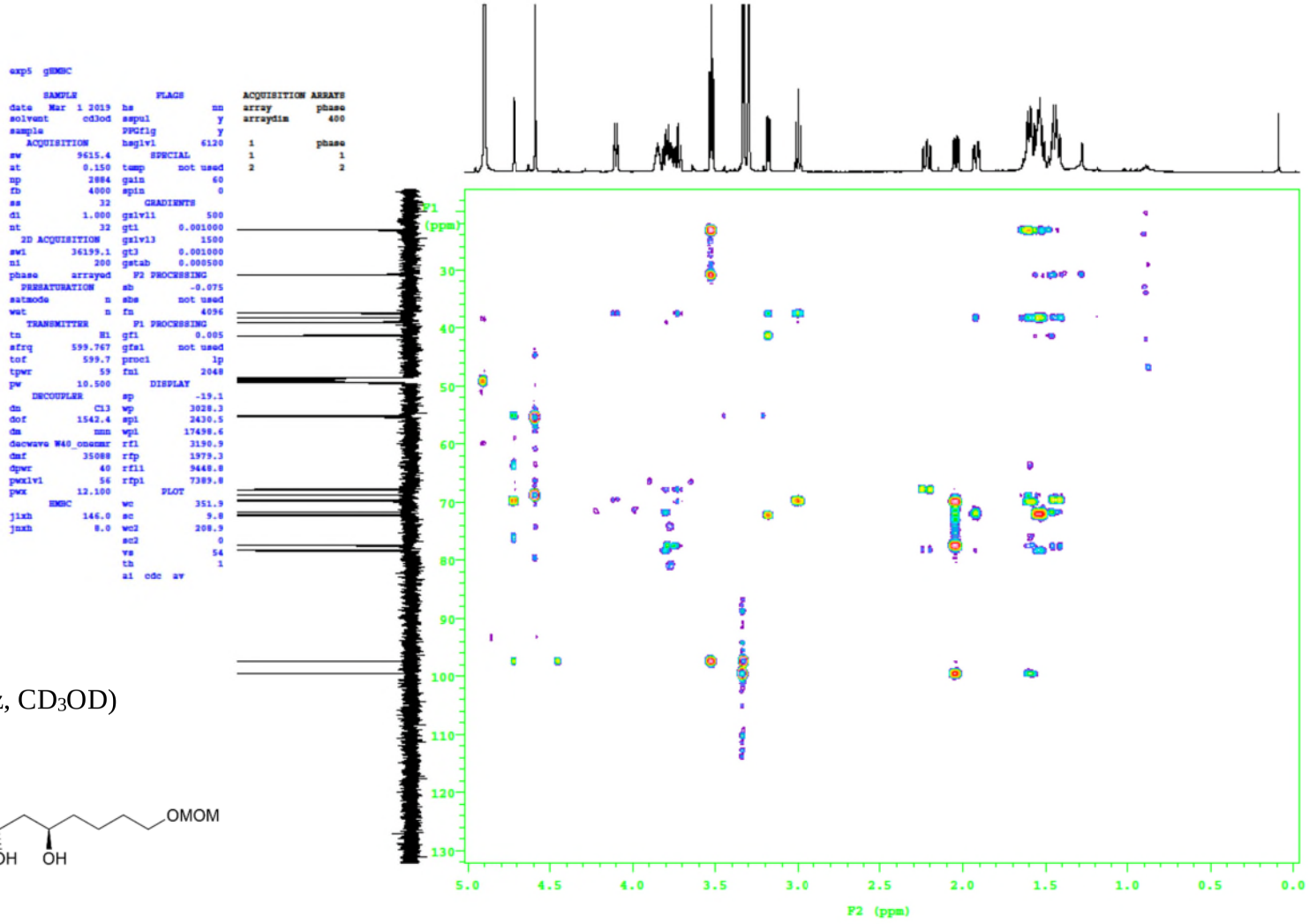
4g



HMQC (600 MHz, CD_3OD)



4g



HMBC (600 MHz, CD_3OD)

4g

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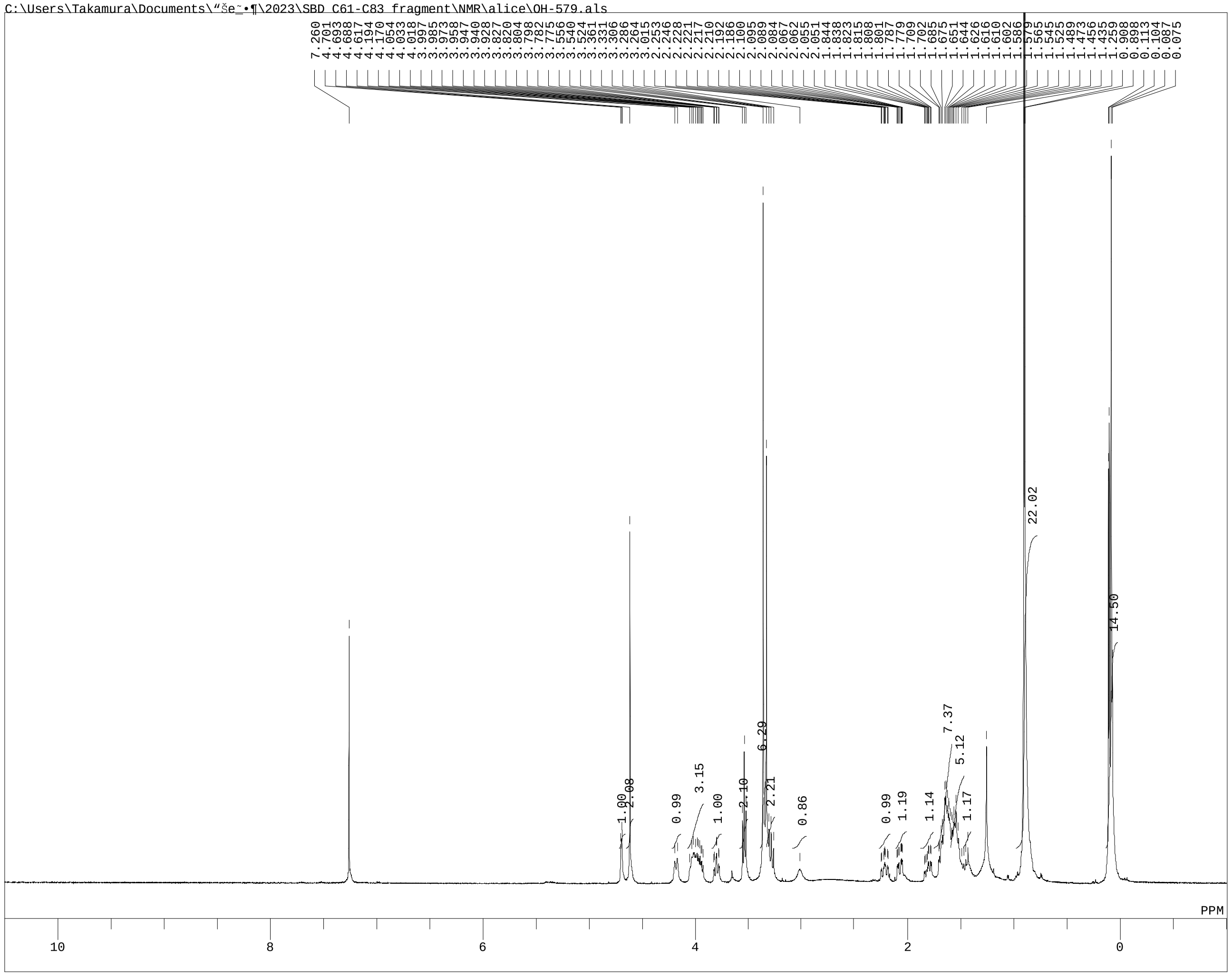
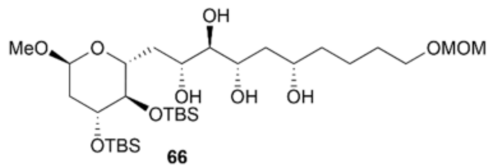


DFILE OH-579.als
COMNT
DATIM Thu Dec 20 17:07:24 2018
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
ACQTM 4.0993 sec
PD 2.9010 sec
PW1 6.40 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 18



66

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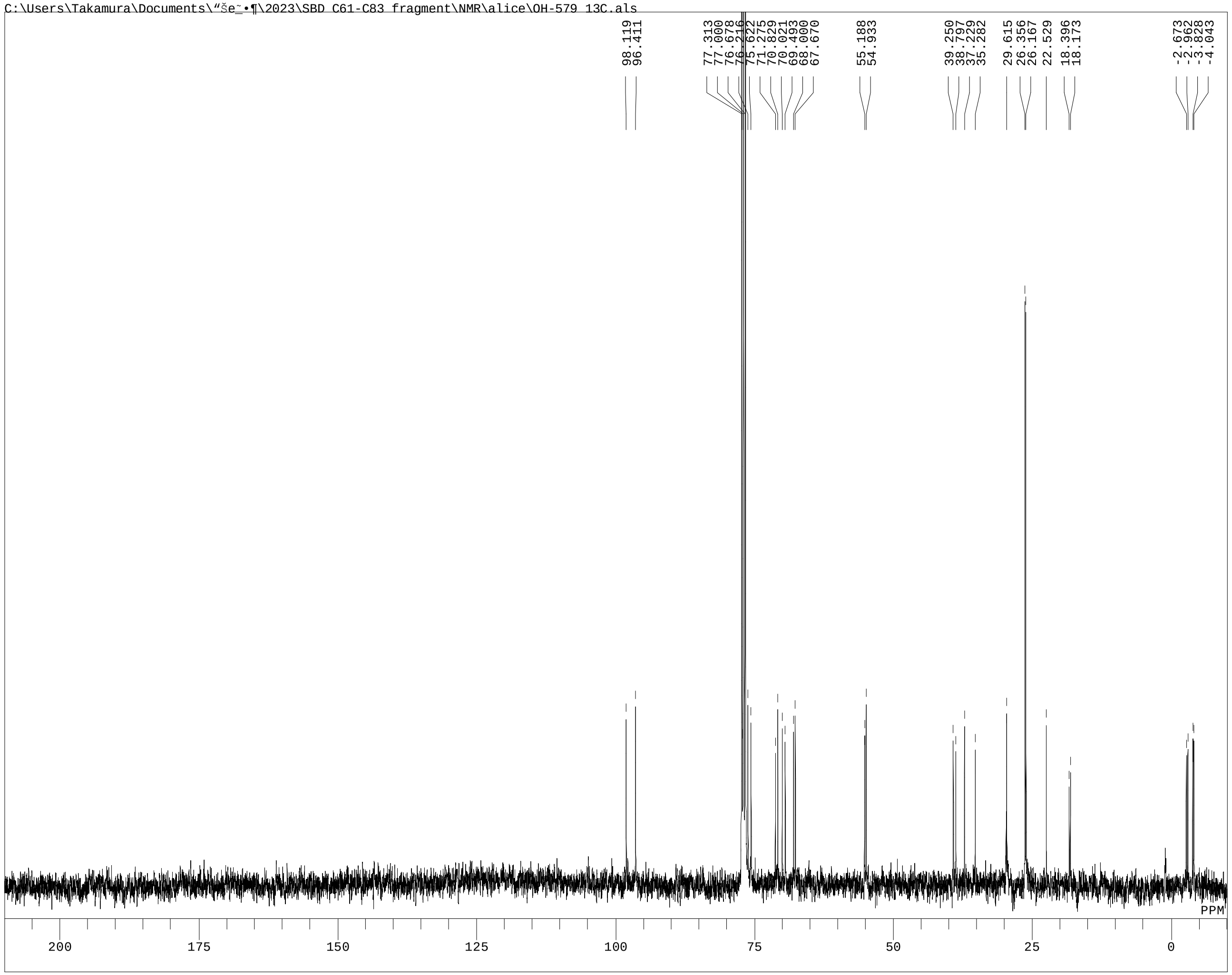
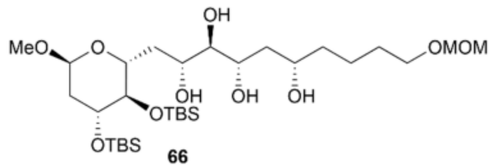
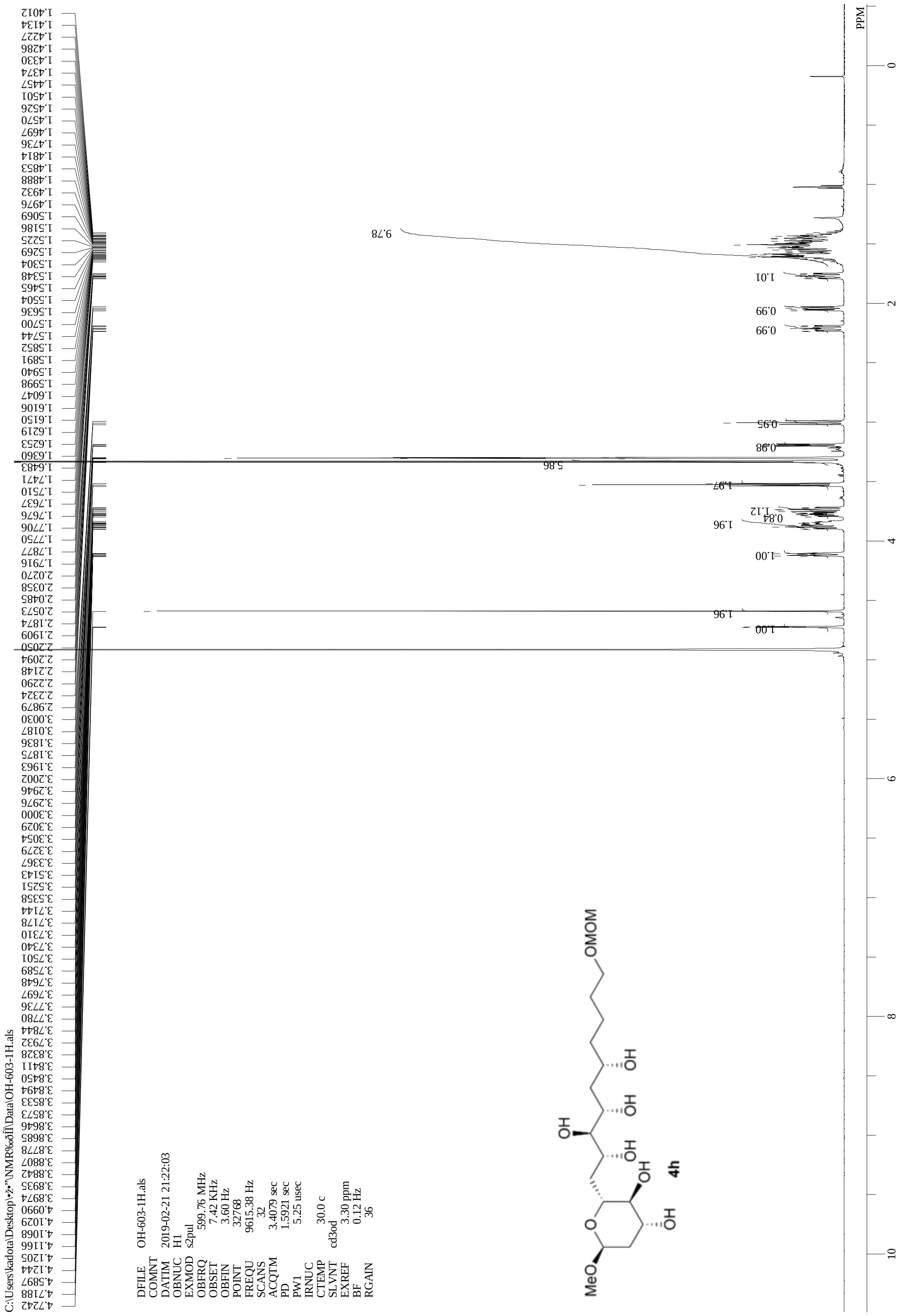


DFILE	OH-579 13C.als
COMNT	
DATIM	Thu Dec 20 17:03:17 2018
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27173.90 Hz
SCANS	1445
ACQTM	1.2059 sec
PD	1.7940 sec
PW1	6.80 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
RGAIN	24



66


C:\Users\kadota\Desktop\•ž•"\NMR‰ðÍ\Data\OH-603-1H.als
1.4012
1.4134
1.4227
1.4286
1.4330
1.4374
1.4457
1.4501
1.4526
1.4570
1.4697
1.4736
1.4814
1.4853
1.4888
1.4932
1.4976
1.5069
1.5186
1.5225
1.5269
1.5304
1.5348
1.5465
1.5504
1.5636
1.5700
1.5744
1.5852
1.5891
1.5940
1.5998
1.6047
1.6106
1.6150
1.6219
1.6253
1.6360
1.6483
1.7471
1.7510
1.7637
1.7676
1.7706
1.7750
1.7787
1.7916
2.0270
2.0358
2.0485
2.0573
2.1874
2.1909
2.2050
2.2094
2.2148
2.2290
2.2324
2.9879
3.0030
3.0187
3.1836
3.1875
3.1963
3.2002
3.2946
3.2976
3.3000
3.3029
3.3054
3.3279
3.3367
3.5143
3.5251
3.5358
3.7144
3.7178
3.7310
3.7340
3.7501
3.7589
3.7648
3.7697
3.7736
3.7780
3.7844
3.7932
3.8328
3.8411
3.8450
3.8494
3.8533
3.8573
3.8646
3.8685
3.8778
3.8807
3.8842
3.8935
3.8974
4.0990
4.1029
4.1068
4.1166
4.1205
4.1244
4.5897
4.7188
4.7242
DFILE OH-603-1H.als
COMNT
DATIM 2019-02-21 21:22:03
OBNUC H1
EXMOD s2pul
OBFRQ 599.76 MHz
OBSET 7.42 KHz
OBFIN 3.60 Hz
POINT 32768
FREQU 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PW1 5.25 usec
IRNUC
CTEMP 30.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 36
9.78
5.86
1.01
0.99
0.99
0.95
0.98
1.97
1.12
0.84
1.96
1.00
1.96
1.00
PPM
0
2
4
6
8
10
OMOM
OH
OH
OH
OH
OH
OH
MeO
O
4h

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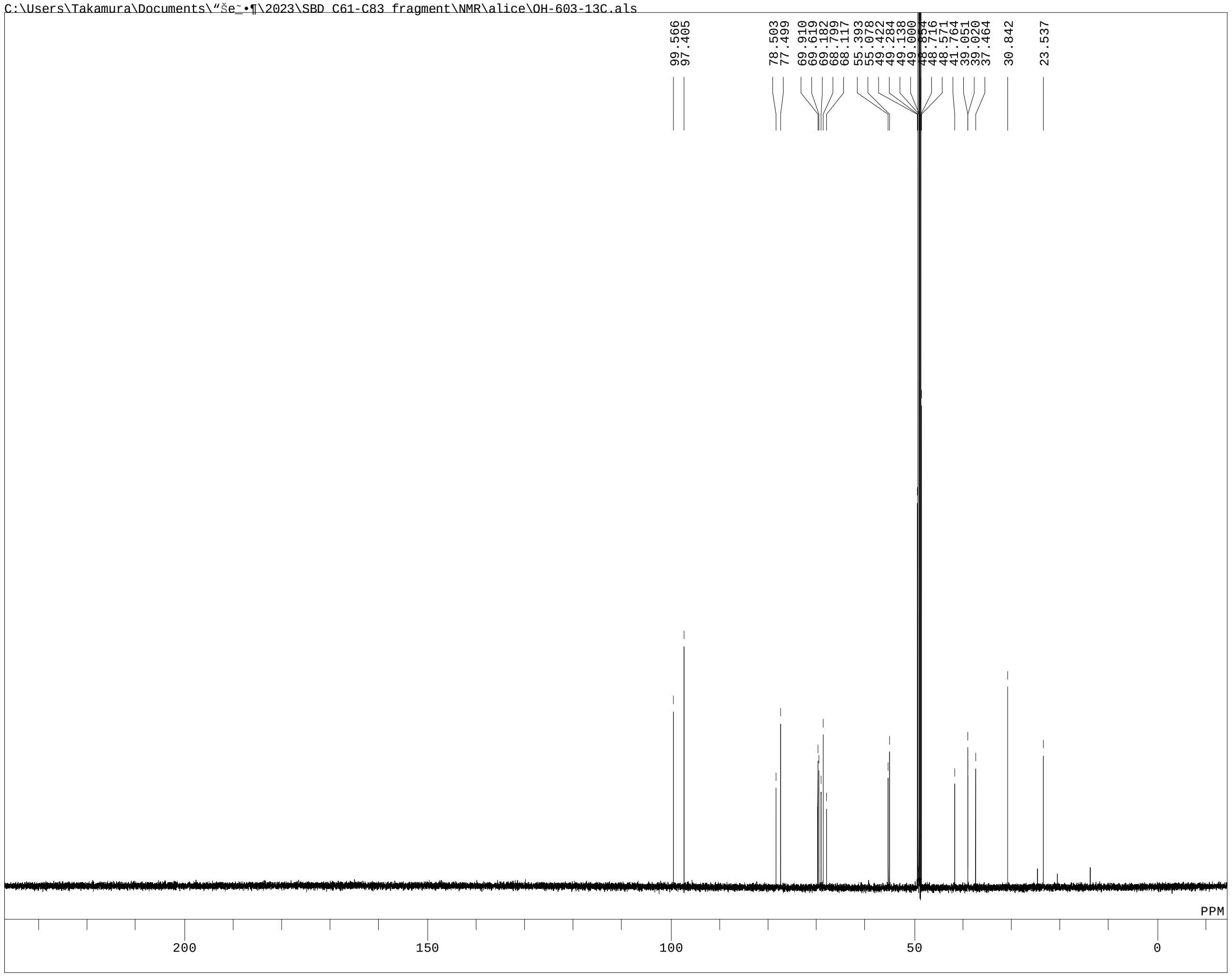
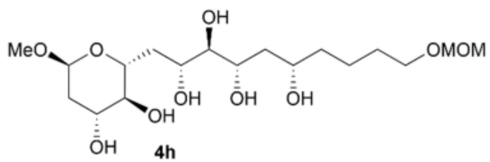
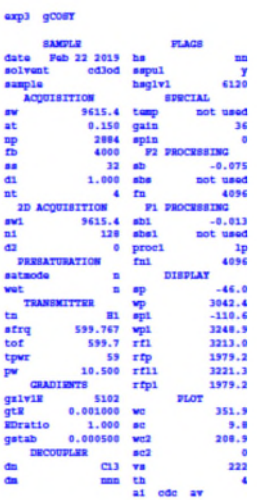


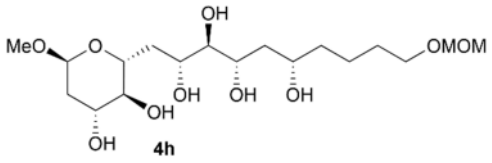
DFILE OH-603-13C.als
COMNT
DATIM 2019-02-21 21:34:39
OBNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.32 KHz
OBFIN 3.00 Hz
POINT 32768
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PW1 5.75 usec
IRNUC
CTEMP 30.0 c
SLVNT cd3od
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60



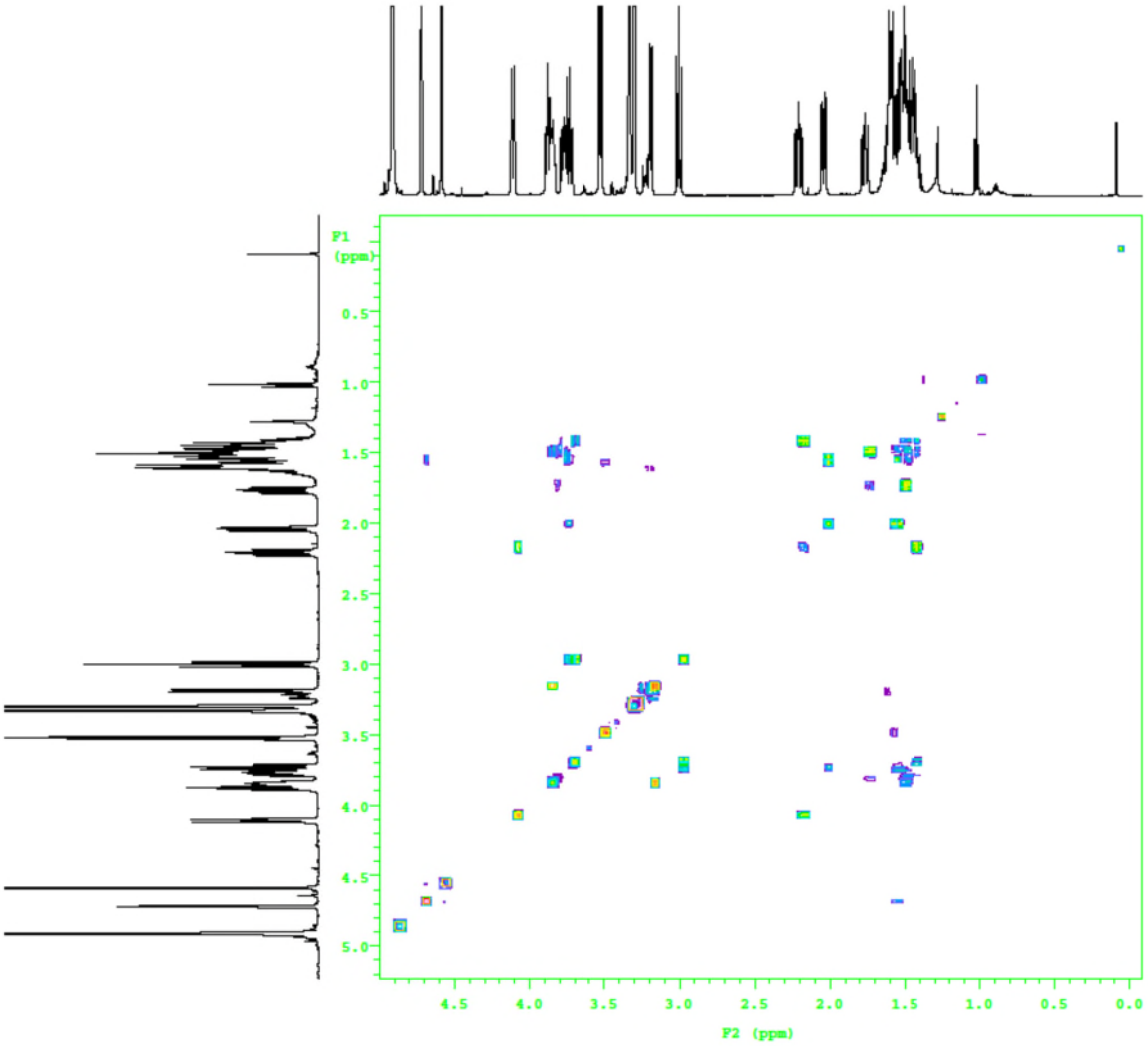
4h

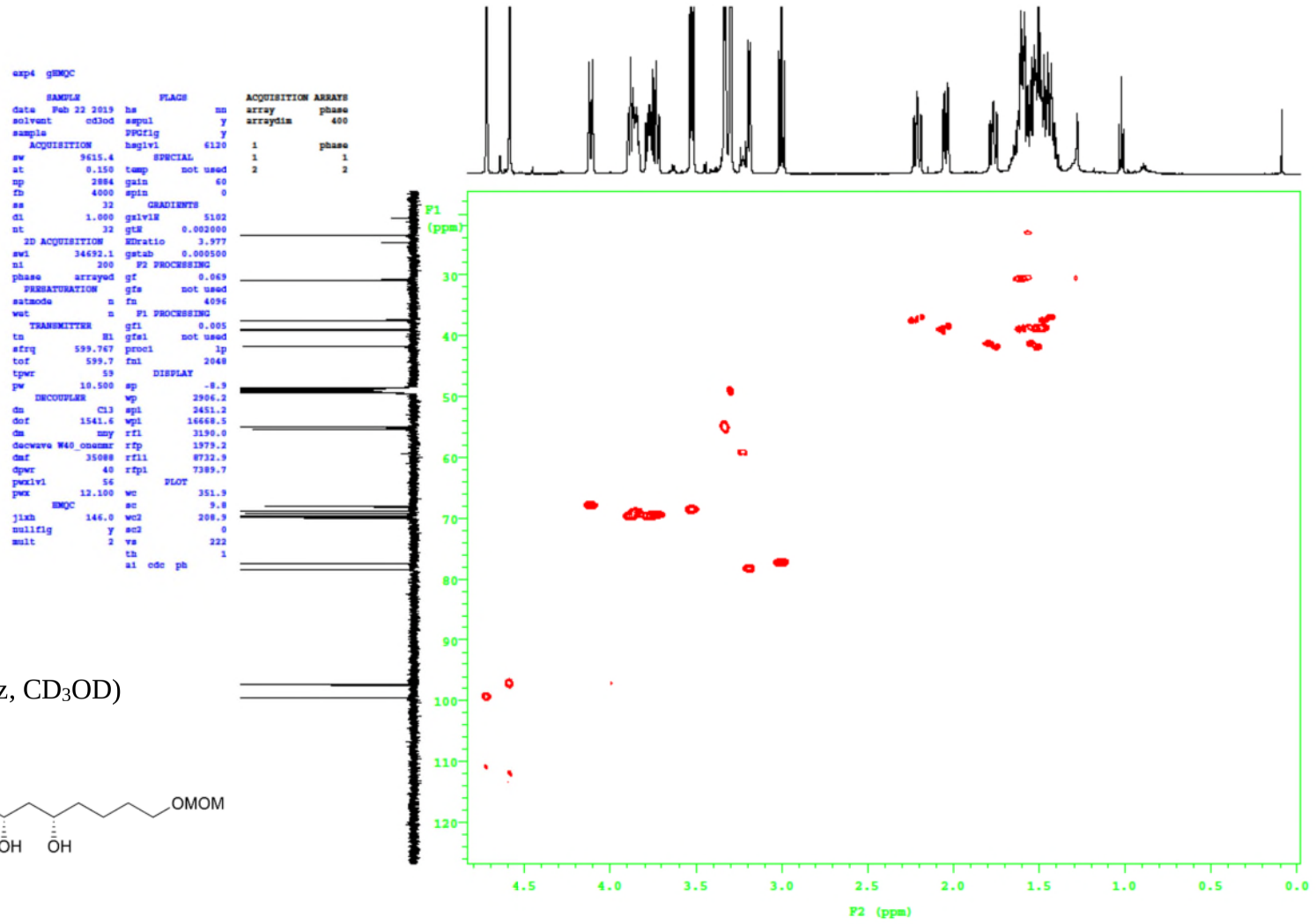


^{1}H–^{1}H COSY (600 MHz, CD_3OD)



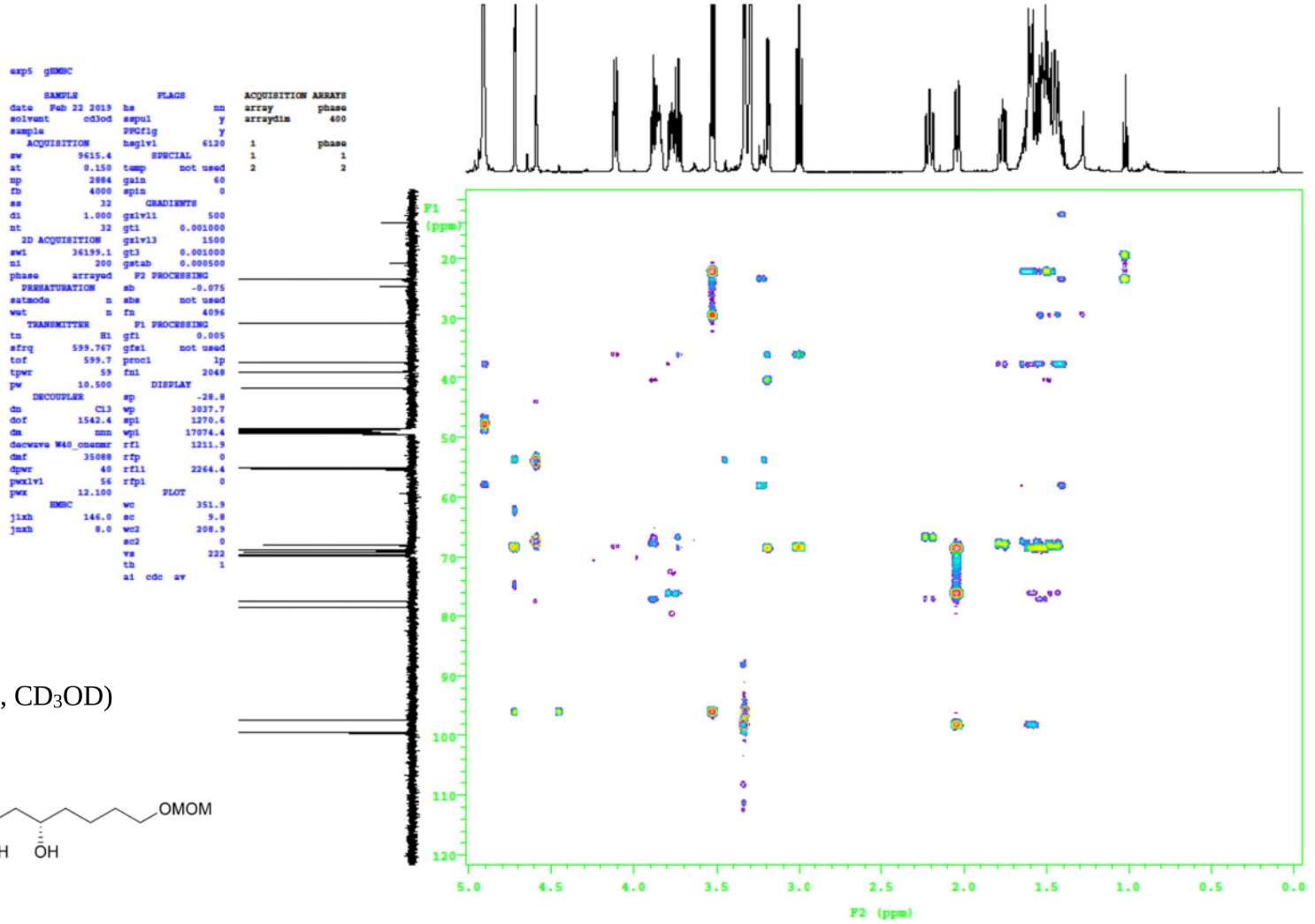
4h



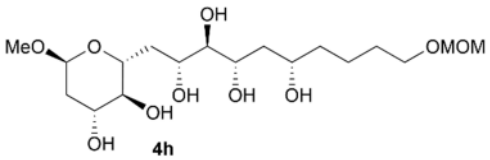


HMQC (600 MHz, CD_3OD)

4h



HMBC (600 MHz, CD_3OD)



4h