

Supplementary Information

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

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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 60F₂₅₄). 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 ¹H NMR, CDCl₃: 7.26 ppm, C₆D₆: 7.16 ppm, CD₃OD: 3.30 ppm; for ¹³C NMR, CDCl₃: 77.0 ppm, C₆D₆: 128.0 ppm, CD₃OD: 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 °C. The mixture was warmed up to 0 °C and stirred at the same temperature for 10 min. The reaction was quenched with Et₃N. The mixture was diluted with EtOAc, washed with saturated aqueous NaHCO₃, H₂O, and brine, and then dried over Na₂SO₄. 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); [α]_D²⁴ +28.9 (*c* 0.96, CHCl₃); IR (neat) 3084, 2956, 2888, 1731, 1653 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₈H₂₆O₉Na [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 °C. The mixture was stirred at room temperature for 1 h. The mixture was neutralized with 1.0 M aqueous HCl at 0 °C. The mixture was diluted with MeOH and dried over Na₂SO₄. 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 °C 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 °C for 2 h. The reaction was quenched with saturated aqueous NH₄Cl at 0 °C. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 2955, 2929, 2886, 2857, 1652 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₄H₇₄O₅Si₄Na [M + Na]⁺ 697.4511, found 697.4508.

Diol S1. To a solution of tetrakis-TBS ether **13** (415 mg, 0.614 mmol) in CH₂Cl₂ (3.1 mL) and MeOH (3.1 mL) was added CSA (42.7 mg, 0.184 mmol) at 0 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with Et₃N. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 3399, 2953, 2929, 2894, 2858, 1649 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₂H₄₆O₅Si₂Na [M + Na]⁺ 469.2782, found 469.2782.

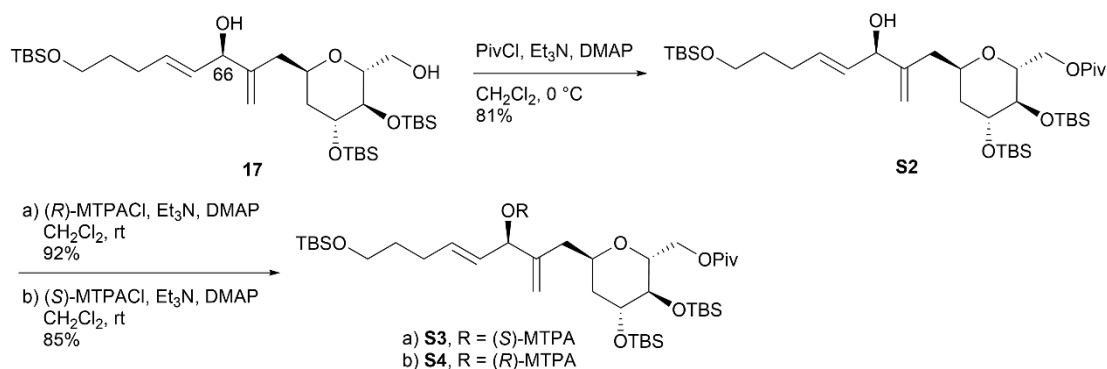
Aldehyde 14. To a solution of diol **S1** (13.3 mg, 29.8 μ mol) in CH₂Cl₂ (1.0 mL) was added MnO₂ (13.0 mg, 0.150 mmol) at room temperature. The mixture was stirred at the same temperature for 5 h. To the mixture was added MnO₂ (13.0 mg, 0.150 mmol) at room temperature. The mixture was stirred at the 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, CHCl₃); IR (neat) 3436, 2954, 2928, 2892, 2857, 1691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{22}\text{H}_{44}\text{O}_5\text{Si}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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 °C. 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); $[\alpha]_{\text{D}}^{22} - 7.3$ (c 1.00, CHCl_3); IR (neat) 3427, 2954, 2929, 2894, 2858 cm^{-1} ; ^1H 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 $\text{C}_{33}\text{H}_{68}\text{O}_6\text{Si}_3\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 667.4221 found 667.4220. Diol **17**: colorless oil; $R_f = 0.51$ (hexane/EtOAc = 2:1); $[\alpha]_{\text{D}}^{21} +15.3$ (c 1.07, CHCl_3); IR (neat) 3409, 2955, 2929, 2894, 2857 cm^{-1} ; ^1H 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 $\text{C}_{33}\text{H}_{68}\text{O}_6\text{Si}_3\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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/Et₃N/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).

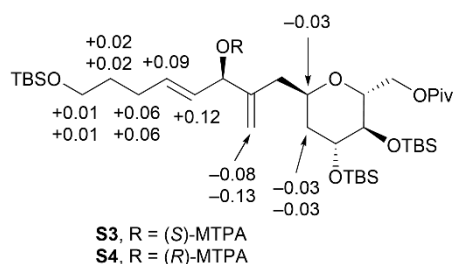


Figure S1. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S3** and **S4**.

Pivalate S2. To a solution of diol **17** (10.0 mg, 15.5 μ mol) in CH₂Cl₂ (1.0 mL) were added DMAP (0.2 mg, 1.55 μ mol), Et₃N (8.7 μ L, 62.0 μ mol), and PivCl (2.3 μ L, 18.6 μ mol) at 0 °C. The mixture was stirred at the same temperature for 30 min. To the mixture were added Et₃N (17 μ L, 0.124 mmol) and PivCl (4.6 μ L, 37.2 μ mol) at 0 °C. The mixture was stirred at the same temperature for 30 min. To the mixture were added Et₃N (26 μ L, 0.186 mmol) and PivCl (6.9 μ L, 55.8 μ mol) at 0 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 3442, 2954, 2929, 2892, 2857, 1733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{38}\text{H}_{76}\text{O}_7\text{Si}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 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); $[\alpha]_{\text{D}}^{22} -11.7$ (c 0.31, CHCl_3); IR (neat) 2952, 2928, 2857, 1748, 1734 cm^{-1} ; ^1H 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 $\text{C}_{48}\text{H}_{83}\text{F}_3\text{O}_9\text{Si}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 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); $[\alpha]_{\text{D}}^{21} +11.7$ (c 0.33, CHCl_3); IR (neat) 2954, 2929, 2857, 1748, 1733 cm^{-1} ; ^1H 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,

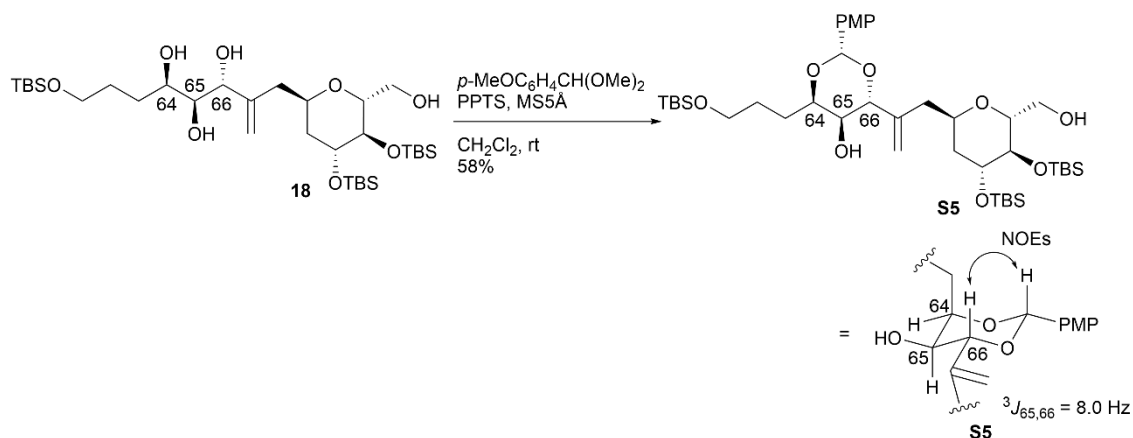
$J = 15.1, 7.3$ Hz, 1 H), 2.11–2.02 (m, 3 H), 1.86 (t, $J = 12.2$ Hz, 1 H), 1.59–1.52 (m, 2 H), 1.39 (d, $J = 14.0$ Hz, 1 H), 1.21 (s, 9 H), 0.90 (s, 9 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.07 (s, 6 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 165.2, 142.5, 136.3, 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 $\text{C}_{48}\text{H}_{83}\text{F}_3\text{O}_9\text{Si}_3\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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 $^\circ\text{C}$. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. 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 $^\circ\text{C}$. 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 $^\circ\text{C}$. 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 $^\circ\text{C}$. 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); $[\alpha]_{\text{D}}^{22} +2.3$ (c 0.81, CHCl_3); IR (neat) 3410, 2956, 2929, 2889, 2858, 1645 cm^{-1} ; ^1H 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 $\text{C}_{39}\text{H}_{84}\text{O}_8\text{Si}_4\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 815.5141, found 815.5140.

Stereochemical Determination of 18. The purified tetraol **18** was treated with p -MeOC₆H₄CH(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 OsO₄-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**.

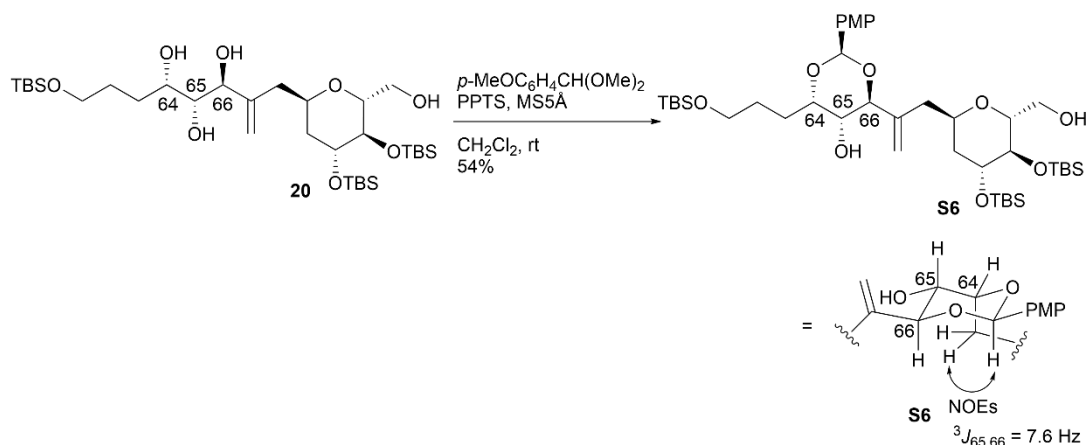
***p*-Methoxybenzylidene Acetal S5.** To a solution of tetraol **18** (14.8 mg, 21.8 μmol) in CH₂Cl₂ (1.0 mL) were added MS5Å (21.8 mg), *p*-MeOC₆H₄CH(OMe)₂ (5.6 μL, 32.7 μmol), and PPTS (0.5 mg, 2.18 μmol) at room temperature. The mixture was stirred at the same temperature for 4 h. The reaction was quenched with Et₃N. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²¹ +3.5 (*c* 0.25, CHCl₃); IR (neat) 3436, 2953, 2928, 2896, 2885, 2857, 1616 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₁H₇₆O₉Si₃Na [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 (CH₂Cl₂/MeOH = 4:1) gave candidate compound **3a** (4.6 mg, quant): colorless oil; $R_f = 0.42$ (CH₂Cl₂/MeOH = 2:1); $[\alpha]_D^{21} +35.2$ (c 0.29, CH₃OH); IR (neat) 3405, 2920, 2850 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₅H₂₈O₈Na [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 H₂O (0.4 mL) were added NMO (27.2 mg, 0.232 mmol) and OsO₄ (0.05 M in 2-propanol, 0.12 mL, 5.80 μ mol) at 0 °C. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous Na₂S₂O₃. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 3398, 2952, 2928, 2889, 2857, 1644 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₃H₇₀O₈Si₃Na [M + Na]⁺ 701.4276, found 701.4273.

Stereochemical Determination of 20. Tetraol **20** was treated with *p*-MeOC₆H₄CH(OMe)₂/PPTS/MS5Å to give *p*-methoxybenzylidene acetal **S6** in 54% yield (Scheme S3). The observed coupling constant (³ $J_{65,66} = 7.6$ 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 OsO₄-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 MS5A (35.1 mg), *p*- $\text{MeOC}_6\text{H}_4\text{CH(OMe)}_2$ (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); $[\alpha]_{\text{D}}^{22} +1.2$ (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 $\text{C}_{41}\text{H}_{76}\text{O}_9\text{Si}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 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 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 4:1) gave candidate compound **3b** (5.4 mg, 99%): colorless oil; R_f = 0.46 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 2:1); $[\alpha]_{\text{D}}^{23}$

+23.4 (*c* 0.36, CH₃OH); ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₅H₂₈O₈Na [M + Na]⁺ 359.1682, found 359.1678.

Alcohol 21. To a solution of diol **16** (85.6 mg, 0.133 mmol) in CH₂Cl₂ (1.3 mL) were added DMAP (3.2 mg, 26.6 μ mol), 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 NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C for 1 h. To the mixture were added 3.0 M aqueous NaOH (1.0 mL, 3.00 mmol) and 30% aqueous H₂O₂ (1.0 mL, 9.75 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²⁸ +2.2 (*c* 0.82, CHCl₃); IR (neat) 3435, 2954, 2929, 2886, 2857, 1642 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₅H₉₈O₇Si₅Na [M + Na]⁺ 913.6057, found 913.6061.

Sulfide 22. To a solution of alcohol **21** (83.1 mg, 93.0 μ mol) in CH₂Cl₂ (0.9 mL) were added Et₃N (26 μ L, 0.186 mmol), DMAP (2.3 mg, 18.8 μ mol), and TsCl (21.4 mg, 0.112 mmol) at 0 °C. The mixture was stirred at room temperature for 4 h. To the mixture were added Et₃N (26 μ L, 0.186 mmol) and TsCl (21.4 mg, 0.112 mmol) at 0 °C. The mixture was stirred at room

temperature for 4 h. To the mixture were added Et₃N (26 μL, 0.186 mmol) and TsCl (21.4 mg, 0.112 mmol) at 0 °C. The mixture was stirred at room temperature for 14 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C for 7 h. To the mixture was added NaI (124 mg, 0.830 mmol) at room temperature. The mixture was stirred at 100 °C for 3 h. The reaction was quenched with saturated aqueous Na₂S₂O₃. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²⁸ -7.6 (*c* 1.32, CHCl₃); IR (neat) 2954, 2929, 2886, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₅₁H₁₀₂O₆SSi₅Na [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 OsO₄ (0.05 M in CH₂Cl₂, 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 NaHSO₃ (272 mg), H₂O (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 H₂O and brine, and then dried over Na₂SO₄. 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 CH₂Cl₂ (0.5 mL) was added *m*CPBA

(69–75%, 11.0 mg, 44.0–47.8 μmol) at $-78\text{ }^\circ\text{C}$. 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); $[\alpha]_{\text{D}}^{28} +3.2$ (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 $\text{C}_{45}\text{H}_{98}\text{O}_8\text{Si}_5\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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 ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 4:1$) 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 °C for 1 h. To the mixture were added 3.0 M aqueous NaOH (0.8 mL, 2.40 mmol) and 30% aqueous H₂O₂ (0.8 mL, 7.80 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²⁸ +4.5 (*c* 1.33, CHCl₃); IR (neat) 3436, 2954, 2929, 2890, 2857, 1638 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₅H₉₈O₇Si₅Na [M + Na]⁺ 913.6057, found 913.6056.

Sulfide 26. To a solution of alcohol **25** (73.6 mg, 82.6 μmol) in CH₂Cl₂ (0.8 mL) were added Et₃N (23 μL, 0.166 mmol), DMAP (2.3 mg, 17.2 μmol), and TsCl (19.1 mg, 0.100 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. To the mixture were added Et₃N (23 μL, 0.166 mmol) and TsCl (19.1 mg, 0.100 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. To the mixture were added Et₃N (46 μL, 0.332 mmol) and TsCl (38.2 mg, 0.200 mmol) at 0 °C. The mixture was stirred at room temperature for 11 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C for 2 h. The reaction was quenched with saturated aqueous Na₂S₂O₃. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. 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 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 $\text{C}_{51}\text{H}_{102}\text{O}_6\text{SSi}_5\text{Na}$ $[\text{M} + \text{Na}]^+$ 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 °C. 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 C₄₅H₉₈O₈Si₅Na [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 (CH₂Cl₂/MeOH = 4:1) gave candidate compound **3b** (2.0 mg, 96%).

Table S1. ¹H 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]	$\Delta\delta = \delta_1 - \delta_{3a}$	$\Delta\delta = \delta_1 - \delta_{3b}$
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 (CD₃OD: 3.30 ppm). ^[b] Data reported in reference 2. Recorded at 800 MHz. ^[c] Recorded at 600 MHz.

Table S2. ¹H 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]	$\Delta\delta = \delta_1 - \delta_{3a}$	$\Delta\delta = \delta_1 - \delta_{3b}$
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 (CD₃OD: 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 CH₂Cl₂ (73 mL) was added K₂CO₃ (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 CH₂Cl₂ (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 Ph₃P=CHCO₂Me (11.4 g, 33.0 mmol) at 0 °C. 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 Na₂S₂O₃, saturated aqueous NaHCO₃, H₂O, and brine, and then dried over Na₂SO₄. 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 H₂ 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 H₂ atmosphere. The catalyst was filtered off and the mixture was washed with Et₂O. 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 °C. The mixture was stirred at the same temperature for 30 min. To the mixture was added BF₃·OEt₂ (1.7 mL, 14.4 mmol) at -78 °C. 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 + 5.0 mL + 5.0 mL) at -78 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with MeOH and saturated aqueous NH₄Cl. The mixture was diluted with EtOAc and washed with H₂O and brine. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over Na₂SO₄. 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 CH₂Cl₂ (21 mL) were added *i*-Pr₂NEt (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*-Pr₂NEt (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 H₂O and brine, and then dried over Na₂SO₄. 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 LiAlH₄ (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 °C. 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 H₂O and brine, and then dried over Na₂SO₄. 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 CH₂Cl₂ (23 mL) were added *i*-Pr₂NEt (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*-Pr₂NEt (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*-Pr₂NEt (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 NH₄Cl. The mixture was diluted with EtOAc, washed with saturated aqueous NH₄Cl, saturated aqueous NaHCO₃, H₂O, and brine, and then dried over Na₂SO₄. 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 K₂CO₃ (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 H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²⁵ +21.4 (*c* 0.99, CHCl₃); IR (neat) 3292, 2928, 2880 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₈H₂₆O₄Na [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 °C. The mixture was stirred at room temperature for 20 min. The reaction was quenched with 3.0 M aqueous HCl at 0 °C. The mixture was diluted MeOH and dried over Na₂SO₄. 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 °C 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 °C 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 °C for 3 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 CH₂Cl₂ (19 mL) and MeOH (19

mL) was added CSA (267 mg, 1.15 mmol) at 0 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with Et₃N. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²³ +63.6 (*c* 1.00, CHCl₃); IR (neat) 3501, 2955, 2930, 2896, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₉H₄₂O₅Si₂Na [M + Na]⁺ 429.2469, found 429.2467.

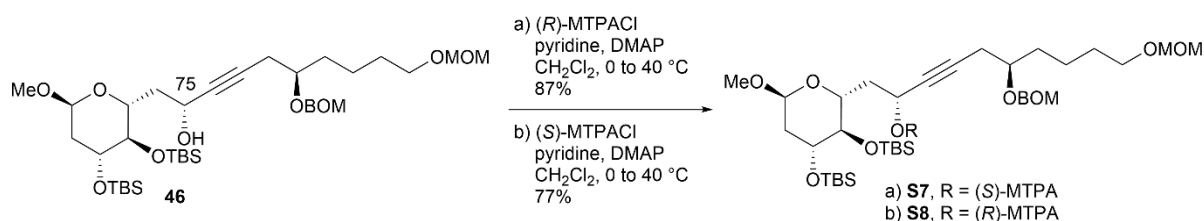
Aldehyde 44. To a solution of alcohol **43** (256 mg, 0.629 mmol) in CH₂Cl₂ (6.3 mL) were added Et₃N (0.17 mL, 1.26 mmol), DMAP (14.6 mg, 0.126 mmol), and TsCl (144 mg, 0.755 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h. To the mixture were added Et₃N (0.51 mL, 3.78 mmol) and TsCl (432 mg, 2.27 mmol) at 0 °C. The mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated aqueous NaHCO₃. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C for 3 h. To the mixture was added NaCN (35.4 mg, 0.722 mmol) at room temperature. The mixture was stirred at 70 °C for 1 h. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 CH₂Cl₂ (4.6 mL) was added DIBAL-H (1.02 M in hexane, 1.0 mL, 1.02 mmol) at -78 °C. 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); [α]_D²³ +59.0 (*c* 0.67, CHCl₃); IR (neat) 2952, 2930, 2896, 2857, 1733 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (100

MHz, CDCl₃) 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 C₂₀H₄₂O₅Si₂Na [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 °C. 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 °C. 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 NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²³ +52.8 (*c* 0.83, CHCl₃); IR (neat) 3435, 2948, 2930, 2894, 2855 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₈H₆₈O₉Si₂Na [M + Na]⁺ 747.4300, found 747.4303. Propargylic alcohol **46**: colorless oil; *R_f* = 0.45 (hexane/EtOAc = 2:1); [α]_D²² +52.3 (*c* 0.95, CHCl₃); IR (neat) 3465, 2952, 2930, 2892, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₈H₆₈O₉Si₂Na [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 method¹ as shown in Scheme S4 and Figure S2.



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

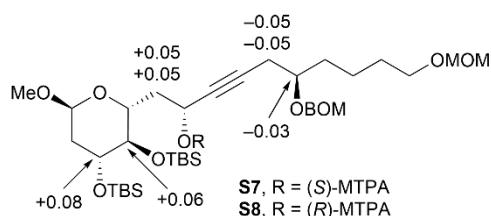


Figure S2. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S7** and **S8**.

(*S*)-MTPA Ester S7. To a solution of alcohol **46** (1.6 mg, 2.21 μmol) in CH₂Cl₂ (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 °C. 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 °C for 20 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 2950, 2928, 2856, 1752 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₈H₇₅F₃O₁₁Si₂Na [M + Na]⁺ 963.4698, found 963.4695.

(*R*)-MTPA Ester S8. To a solution of alcohol **46** (2.8 mg, 3.86 μmol) in CH₂Cl₂ (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 °C. 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 °C for 14 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²² +68.0 (*c* 0.14, CHCl₃); IR (neat) 2953, 2928, 2853, 1753 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₈H₇₅F₃O₁₁Si₂Na [M + Na]⁺ 963.4698, found 963.4701.

Allylic Alcohol 47. To a solution of propargylic alcohol **45** (294 mg, 0.406 mmol) in Et₂O (4.1 mL) was added Red-Al (65% in toluene, 1.2 mL, 4.01 mmol) at 0 °C. The mixture was stirred at reflux for 4 h. The reaction was quenched with saturated aqueous sodium potassium tartrate at 0 °C. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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); [α]_D²⁶ +48.9 (*c* 1.78, CHCl₃); IR (neat) 3465, 3032, 2952, 2930, 2896, 2857 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) 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), 0.07 (s, 3 H), 0.06 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃) 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 C₃₈H₇₀O₉Si₂Na [M + Na]⁺ 749.4456, found 749.4457.

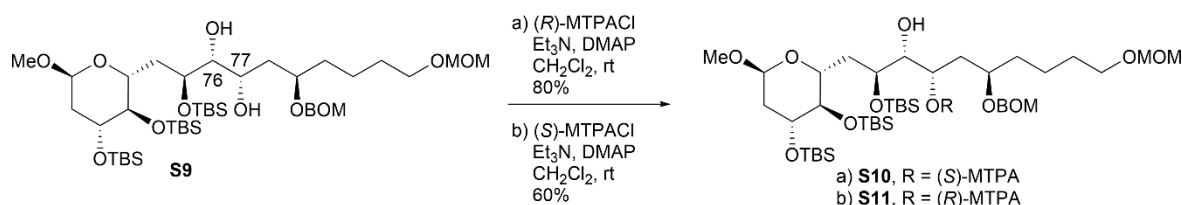
Tris-TBS Ether 48. To a solution of allylic alcohol **47** (113 mg, 0.155 mmol) in CH₂Cl₂ (3.1 mL) were added 2,6-lutidine (54 μ L, 0.465 mmol) and TBSOTf (85 μ L, 0.372 mmol) at 0 °C. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous NaHCO₃. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 2955, 2929, 2896, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (150 MHz, CDCl₃) 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 C₄₄H₈₄O₉Si₃Na [M + Na]⁺ 863.5321, found 863.5323.

Diol 49. To a solution of alkene **48** (64.0 mg, 76.1 μ mol) in pyridine (2.5 mL) was added OsO₄ (0.05 M in CH₂Cl₂, 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 NaHSO₃ (560 mg), H₂O (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 H₂O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na₂SO₄. 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, CHCl₃); IR (neat) 3501, 2954, 2929, 2899, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₄₄H₈₆O₁₁Si₃Na [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, CHCl₃); IR (neat) 3489, 2952, 2930, 2896, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{44}\text{H}_{86}\text{O}_{11}\text{Si}_3\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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 method¹ (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.

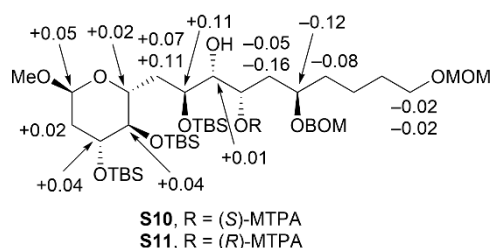


Figure S3. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S10** and **S11**.

(*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); $[\alpha]_{\text{D}}^{22}$ +26.0 (c 0.065, CHCl_3); IR (neat) 3501, 2956, 2928, 2856, 1746 cm^{-1} ; ^1H 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 $\text{C}_{54}\text{H}_{93}\text{F}_3\text{O}_{13}\text{Si}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 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); $[\alpha]_{\text{D}}^{21} +54.3$ (c 0.095, CHCl_3); IR (neat) 3490, 2956, 2928, 2856, 1744 cm^{-1} ; ^1H 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 $\text{C}_{54}\text{H}_{93}\text{F}_3\text{O}_{13}\text{Si}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 1113.5774, found 1113.5775.

Triol 50. A mixture of BOM ether **49** (12.4 mg, 14.2 μmol) and 20% $\text{Pd}(\text{OH})_2/\text{C}$ (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); $[\alpha]_{\text{D}}^{22} +32.0$ (c 0.62, CHCl_3); IR (neat) 3436, 2951, 2929, 2894, 2857 cm^{-1} ; ^1H 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,

CDCl₃) 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 C₃₆H₇₈O₁₀Si₃Na [M + Na]⁺ 777.4800, found 777.4804.

Candidate Compound 4a. To a solution of tris-TBS ether **50** (11.3 mg, 15.0 μ mol) in THF (0.3 mL) was added TBAF (1.0 M in THF, 90 μ L, 90.0 μ mol) 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 μ L, 90.0 μ mol) at room temperature. The mixture was stirred at 40 °C for 3 h. The mixture was filtered through short column chromatography (CH₂Cl₂/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 (CH₂Cl₂/MeOH = 5:1); $[\alpha]_D^{22}$ +57.3 (*c* 0.19, CH₃OH); IR (neat) 3409, 2960, 2925, 2854 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [M + Na]⁺ 435.2206, found 435.2203.

Candidate Compound 4b. To a solution of diol **49** (6.2 mg, 7.08 μ mol) in CH₂Cl₂ (0.2 mL) were added DMAP (1.0 mg, 8.19 μ mol), pyridine (25 μ L, 0.315 mmol), and Ac₂O (22 μ L, 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 μ mol), pyridine (25 μ L, 0.315 mmol), and Ac₂O (22 μ L, 0.236 mmol) at room temperature. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 H₂ 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), Ph₃P (5.6 mg, 21.4 μ mol), and *p*-NO₂PhCO₂H (3.6 mg, 21.4 μ mol) in THF (0.2 mL) was added DEAD (2.2 M in toluene, 9.7 μ L, 21.4 μ mol) at 0 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. 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.

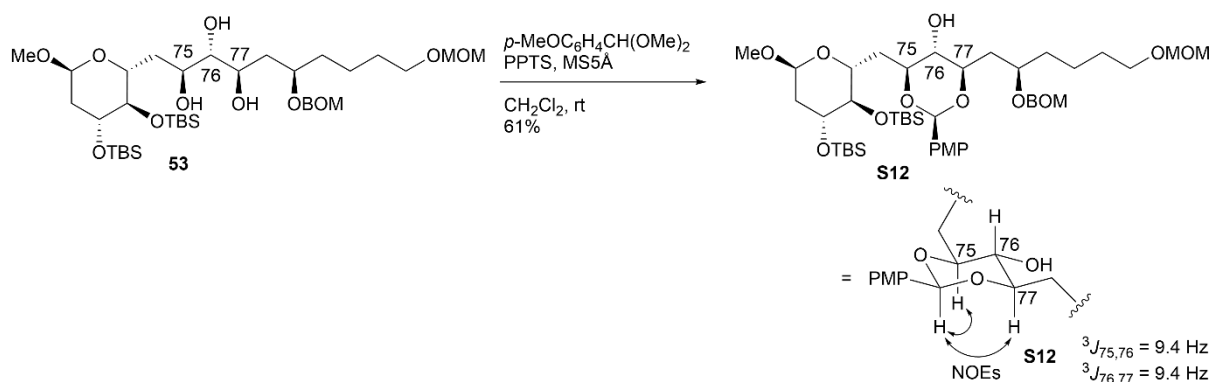
To a solution of the tris-TBS ether obtained above (2.8 mg) in THF (0.2 mL) was added TBAF (1.0 M in THF, 21 μL , 21.0 μmol) at room temperature. The mixture was stirred at the same temperature for 14 h and at 40 °C for 8 h. The mixture was filtered through short column chromatography (EtOAc/MeOH = 5:1). 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 (CH₂Cl₂/MeOH = 5:1); $[\alpha]_D^{22}$ +67.3 (*c* 0.070, CH₃OH); IR (neat) 3398, 2959, 2925, 2851 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [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 H₂ 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 OsO₄ (0.05 M in CH₂Cl₂, 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 NaHSO₃ (136 mg), H₂O (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 H₂O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na₂SO₄. 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 (CH₂Cl₂/MeOH = 20:1); $[\alpha]_D^{22}$ +20.8 (*c* 2.01, CHCl₃); IR (neat) 3486, 2952, 2928, 2900, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{38}\text{H}_{72}\text{O}_{11}\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 783.4511, found 783.4507.

Stereochemical Determination of 53. Triol **53** was treated with *p*-MeOC₆H₄CH(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*-MeOC₆H₄CH(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); $[\alpha]_{\text{D}}^{22} +50.8$ (c 0.021, CHCl_3); IR (neat) 3429, 2956, 2926, 2855 cm^{-1} ; ^1H 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 C₄₆H₇₈O₁₂Si₂Na [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 H₂ atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH₂Cl₂/MeOH = 30:1) gave tetraol **54** (14.0 mg, 76%): colorless oil; *R_f* = 0.58 (CH₂Cl₂/MeOH = 10:1); [α]_D²⁴ +31.8 (*c* 0.70, CHCl₃); IR (neat) 3435, 2952, 2929, 2899, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [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 (CH₂Cl₂/MeOH = 7:1). Concentration and column chromatography (CH₂Cl₂/MeOH = 7:1) gave candidate compound **4c** (7.0 mg, 78%): colorless oil; *R_f* = 0.57 (CH₂Cl₂/MeOH = 4:1); [α]_D²¹ +52.3 (*c* 0.36, CH₃OH); IR (neat) 3304, 2931, 2895, 2871, 2834 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [M + Na]⁺ 435.2206, found 435.2203.

Tetraol 56. To a solution of triol **53** (33.5 mg, 44.0 μmol) in CH₂Cl₂ (0.5 mL) were added pyridine (21 μL, 0.264 mmol), Ac₂O (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 Ac₂O (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 NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 H₂ 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), Ph₃P (43.3 mg, 0.165 mmol), and *p*-NO₂PhCO₂H (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 °C. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. 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 (CH₂Cl₂/MeOH = 30:1) gave tetraol **56** (16.7 mg, 59% in four steps): colorless oil; *R*_f = 0.55 (CH₂Cl₂/MeOH = 10:1); [α]_D²³ +37.7 (*c* 0.44, CHCl₃); IR (neat) 3435, 2952, 2930, 2897, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [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 (CH₂Cl₂/MeOH = 7:1). Concentration and column chromatography (CH₂Cl₂/MeOH = 7:1) gave candidate compound **4d** (7.5 mg, 81%): colorless oil; *R*_f = 0.59 (CH₂Cl₂/MeOH = 4:1); [α]_D²³ +67.9 (*c* 0.38, CH₃OH); IR (neat) 3398, 2928, 2849 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150

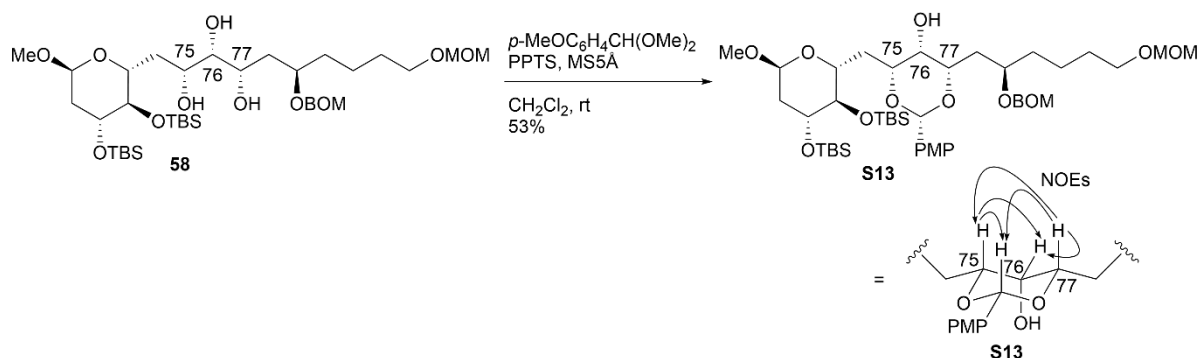
MHz, CD₃OD) δ 99.9, 97.4, 78.5, 77.5, 73.2, 72.4, 70.6, 69.6, 69.1, 68.8, 55.4, 55.3, 40.5, 39.1, 38.8, 36.0, 30.8, 23.5; HRMS (ESI-TOF) calcd for C₁₈H₃₆O₁₀Na [M + Na]⁺ 435.2206, found 435.2211.

Allylic Alcohol 57. To a solution of propargylic alcohol **46** (45.0 mg, 62.1 μ mol) in Et₂O (1.0 mL) was added Red-Al (65% in toluene, 0.19 mL, 0.621 mmol) at 0 °C. The mixture was stirred at reflux for 3 h. The reaction was quenched with saturated aqueous sodium potassium tartrate at 0 °C. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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, CHCl₃); IR (neat) 3478, 2977, 2952, 2931, 2884, 2859 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₈H₇₀O₉Si₂Na [M + Na]⁺ 749.4456, found 749.4460.

Triol 58. To a mixture of allylic alcohol **57** (64.4 mg, 88.6 μ mol) and TMEDA (13 μ L, 0.107 mmol) in CH₂Cl₂ (6.8 mL) was added OsO₄ (0.05 M in CH₂Cl₂, 2.1 mL, 0.105 mmol) at -78 °C. The mixture was stirred at the same temperature for 2 h. To the mixture were added TMEDA (13 μ L, 0.107 mmol) and OsO₄ (0.05 M in CH₂Cl₂, 2.1 mL, 0.105 mmol) at -78 °C. 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 μ L, 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 Na₂SO₄. 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, CHCl₃); IR (neat) 3436, 2953, 2930, 2890, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{38}\text{H}_{72}\text{O}_{11}\text{Si}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 783.4511, found 783.4514.

Stereochemical Determination of 58. Triol **58** was treated with *p*- $\text{MeOC}_6\text{H}_4\text{CH}(\text{OMe})_2$ /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*- $\text{MeOC}_6\text{H}_4\text{CH}(\text{OMe})_2$ (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} ; ^1H 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 $\text{C}_{46}\text{H}_{78}\text{O}_{12}\text{Si}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 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 H₂ atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH₂Cl₂/MeOH = 30:1) gave tetraol **59** (2.2 mg, 97%): colorless oil; R_f = 0.57 (CH₂Cl₂/MeOH = 10:1); $[\alpha]_D^{23}$ +47.9 (c 0.48, CHCl₃); IR (neat) 3418, 2952, 2930, 2897, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [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 (CH₂Cl₂/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 (CH₂Cl₂/MeOH = 3:1); $[\alpha]_D^{22}$ +65.4 (c 0.32, CH₃OH); IR (neat) 3338, 2934 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [M + Na]⁺ 435.2206, found 435.2203.

Tetraol 61. To a solution of triol **58** (37.5 mg, 49.3 μmol) in CH₂Cl₂ (0.5 mL) were added pyridine (24 μL , 0.296 mmol), Ac₂O (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 NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 H₂ 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), Ph₃P (41.4 mg, 0.158 mmol), and *p*-NO₂PhCO₂H (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 °C. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. 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 (CH₂Cl₂/MeOH = 30:1) gave tetraol **61** (18.7 mg, 59% in four steps): colorless oil; *R*_f = 0.51 (CH₂Cl₂/MeOH = 10:1); [α]_D²² +41.1 (*c* 0.94, CHCl₃); IR (neat) 3434, 2978, 2952, 2930, 2897, 2883, 2858 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [M + Na]⁺ 663.3936, found 663.3938.

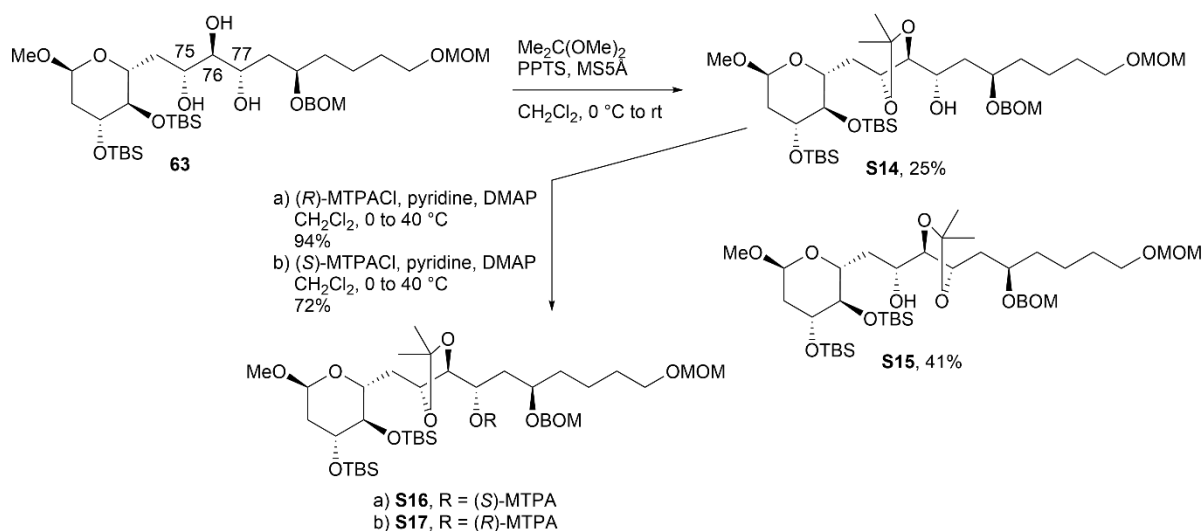
Candidate Compound 4f. To a solution of bis-TBS ether **61** (10.4 mg, 16.2 μmol) in THF (1.0 mL) was added TBAF (1.0 M in THF, 49 μL, 49.0 μmol) at room temperature. The mixture was stirred at the same temperature for 15 h. To the mixture was added TBAF (1.0 M in THF, 60 μL, 60.0 μmol) at room temperature. The mixture was stirred at the same temperature for 8 h. The mixture was filtered through short column chromatography (CH₂Cl₂/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 (CH₂Cl₂/MeOH = 5:1); [α]_D¹⁸ +63.7 (*c* 0.22, CH₃OH); IR (neat) 3366, 2963, 2925, 2854 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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

C₁₈H₃₆O₁₀Na [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 H₂ 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 OsO₄ (0.05 M in CH₂Cl₂, 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 NaHSO₃ (666 mg), H₂O (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 H₂O and brine. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried over Na₂SO₄. 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); [α]_D²¹ +22.7 (*c* 1.83, CHCl₃); IR (neat) 3456, 2972, 2955, 2930, 2899, 2884, 2860 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₈H₇₂O₁₁Si₂Na [M + Na]⁺ 783.4511, found 783.4510.

Stereochemical Determination of 63. Triol **63** was treated with Me₂C(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 method¹ (Figure S4). The absolute configuration at the C76 position of **63** was elucidated based on the *syn*-addition reaction mechanism of OsO₄-catalyzed dihydroxylation.



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

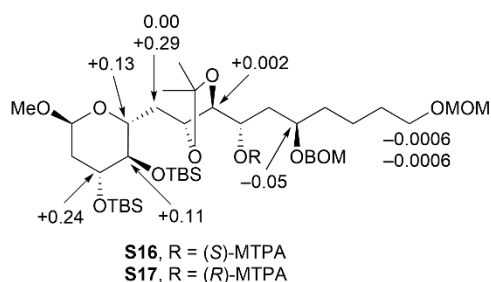


Figure S4. Chemical shift differences ($\Delta\delta_{S-R}$) of MTPA esters **S16** and **S17**.

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), $\text{Me}_2\text{C}(\text{OMe})_2$ (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); $[\alpha]_{\text{D}}^{22} +54.0$ (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 $\text{C}_{41}\text{H}_{76}\text{O}_{11}\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 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); $[\alpha]_{\text{D}}^{24}$ +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 $\text{C}_{51}\text{H}_{83}\text{F}_3\text{O}_{13}\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 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); $[\alpha]_{\text{D}}^{21}$ +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 $\text{C}_{51}\text{H}_{83}\text{F}_3\text{O}_{13}\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 1039.5222, found 1039.5217.

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

MeOH (1.0 mL) was stirred at room temperature for 40 min under H₂ atmosphere. The catalyst was filtered off and the mixture was washed with EtOAc. Concentration and column chromatography (CH₂Cl₂/MeOH = 30:1) gave tetraol **64** (5.7 mg, 95%): colorless oil; *R_f* = 0.54 (CH₂Cl₂/MeOH = 10:1); [α]_D²² +36.5 (*c* 0.29, CHCl₃); IR (neat) 3417, 2952, 2929, 2897, 2857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [M + Na]⁺ 663.3936, found 663.3939.

Candidate Compound 4g. To a solution of bis-TBS ether **64** (18.1 mg, 28.2 μ mol) 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 (CH₂Cl₂/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 (CH₂Cl₂/MeOH = 3:1); [α]_D²² +75.5 (*c* 0.41, CH₃OH); IR (neat) 3366, 2934 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [M + Na]⁺ 435.2206, found 435.2206.

Tetraol 66. To a solution of triol **63** (12.5 mg, 16.4 μ mol) in CH₂Cl₂ (0.2 mL) were added pyridine (7.9 μ L, 98.4 μ mol), Ac₂O (7.0 μ L, 73.8 μ mol), and DMAP (1.0 mg, 8.19 μ mol) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 H₂ 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), Ph₃P (17.2 mg, 65.6 μmol), and *p*-NO₂PhCO₂H (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 °C. The mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous NH₄Cl. The mixture was diluted with EtOAc, washed with H₂O and brine, and then dried over Na₂SO₄. 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 °C. 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 (CH₂Cl₂/MeOH = 30:1) gave tetraol **68** (6.7 mg, 64% in four steps): colorless oil; *R*_f = 0.46 (CH₂Cl₂/MeOH = 10:1); [α]_D²³ +42.8 (*c* 0.34, CHCl₃); IR (neat) 3412, 2952, 2930, 2896, 2860 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₆₄O₁₀Si₂Na [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 (CH₂Cl₂/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 (CH₂Cl₂/MeOH = 3:1); [α]_D²³ +117 (*c* 0.34, CH₃OH); IR (neat) 3399, 2938 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (150 MHz, CD₃OD) 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 C₁₈H₃₆O₁₀Na [M + Na]⁺

435.2206, found 435.2205.

Table S3. ¹H 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 (CD₃OD: 3.30 ppm). ^[b] Data reported in reference 2. Recorded at 800 MHz. ^[c] Recorded at 600 MHz.

Table S4. ¹H 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 (CD₃OD: 3.30 ppm). ^[b] Data reported in reference 2. Recorded at 800 MHz. ^[c] Recorded at 600 MHz.

Table S5. Deviations in the ¹H 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	-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. ¹³C 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 (CD₃OD: 49.0 ppm). ^[b] Data reported in reference 2. Recorded at 150 MHz. ^[c] Recorded at 150 MHz.

Table S7. ¹³C 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 (CD₃OD: 49.0 ppm). ^[b] Data reported in reference 2. Recorded at 150 MHz. ^[c] Recorded at 150 MHz.

Table S8. Deviations in the ¹³C 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

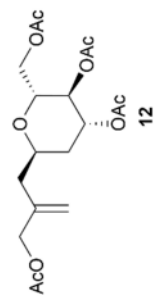
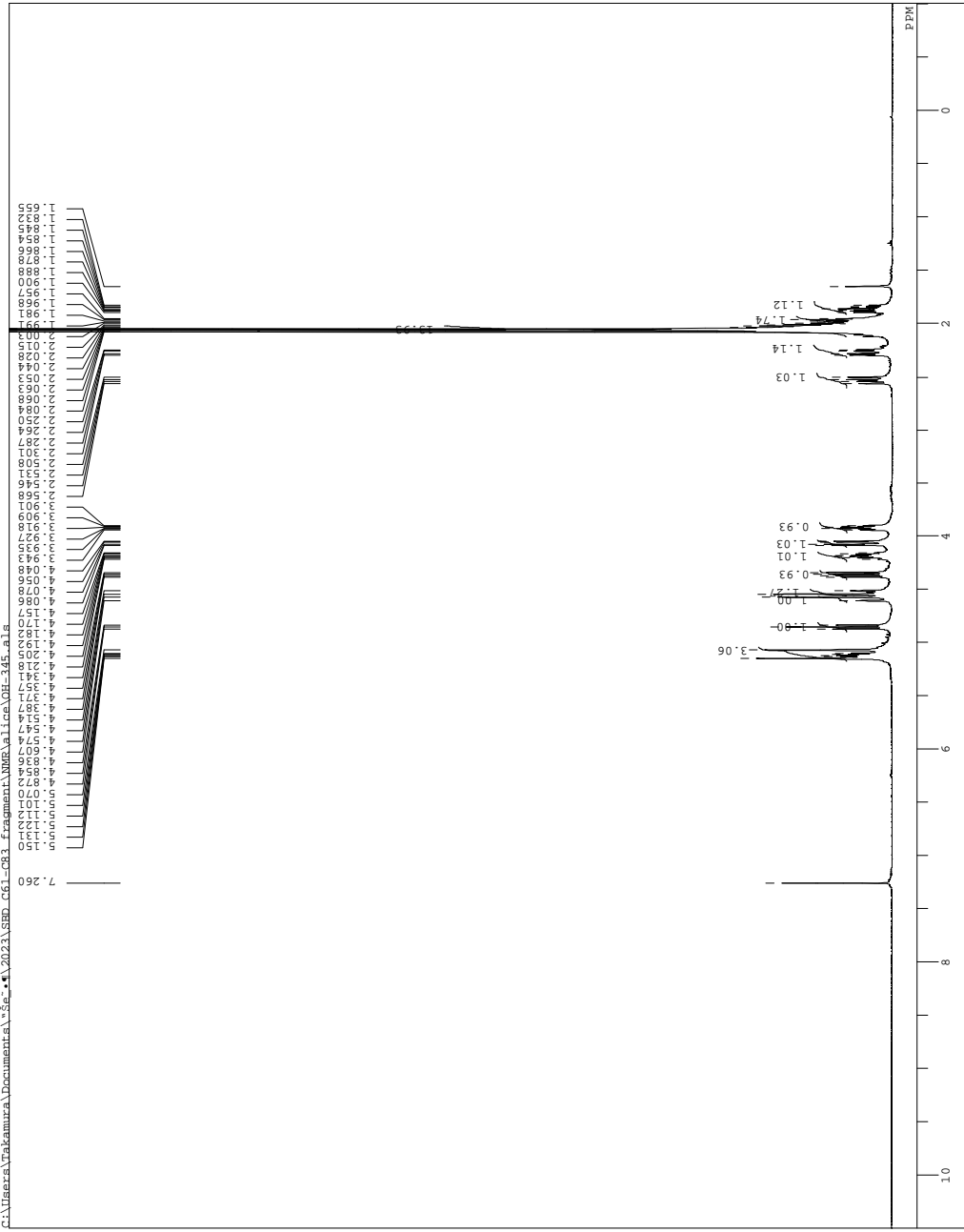
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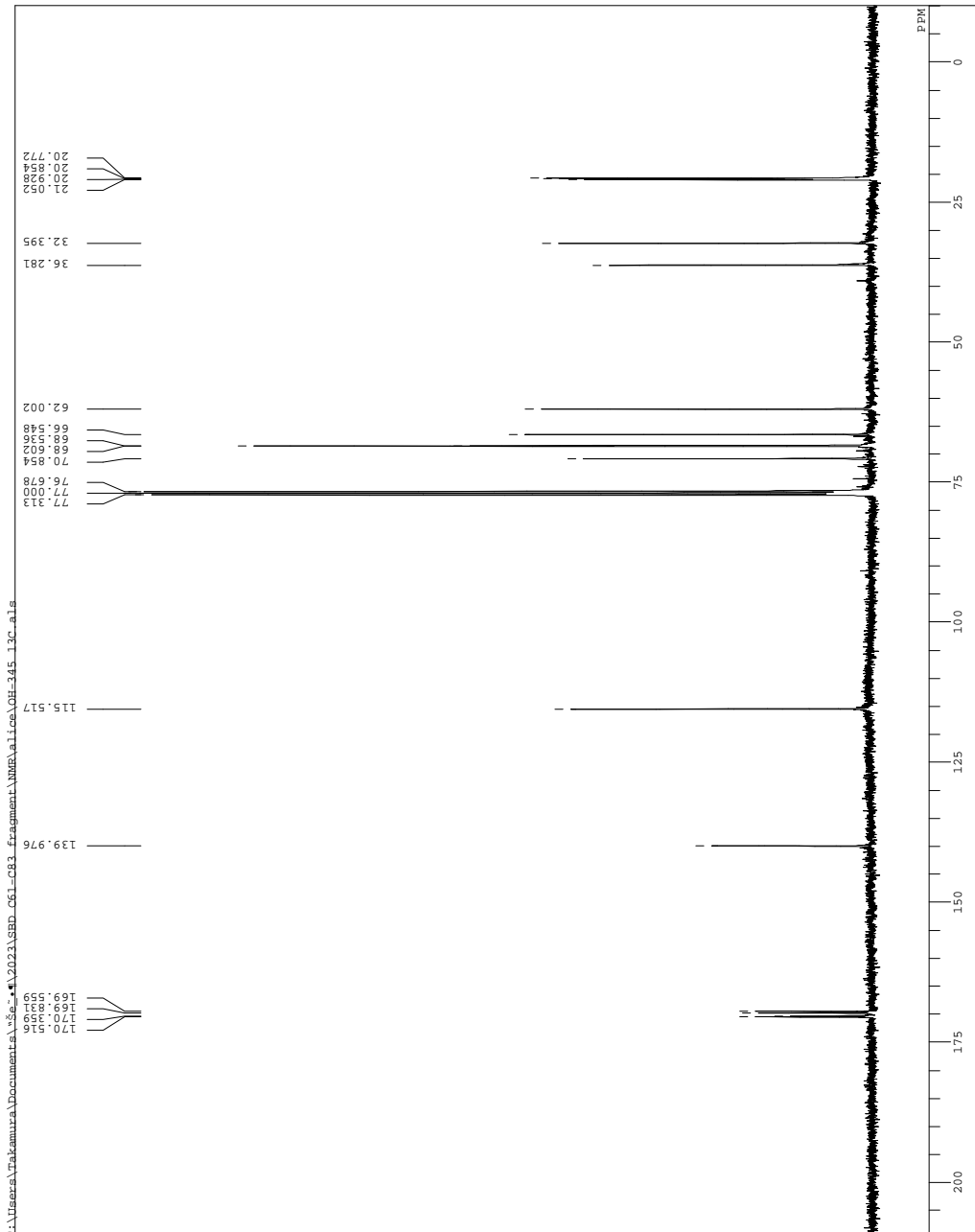
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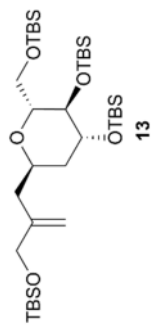
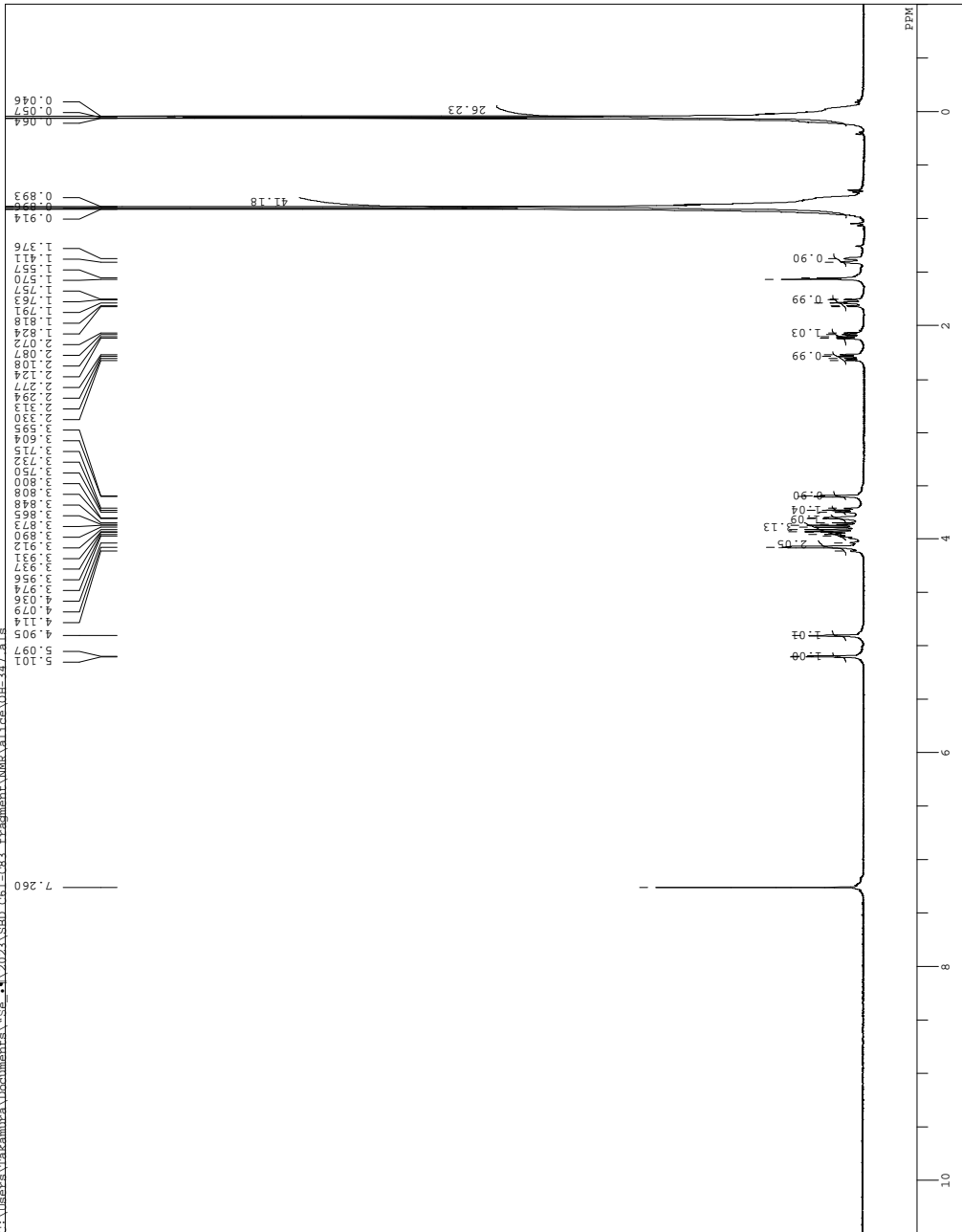


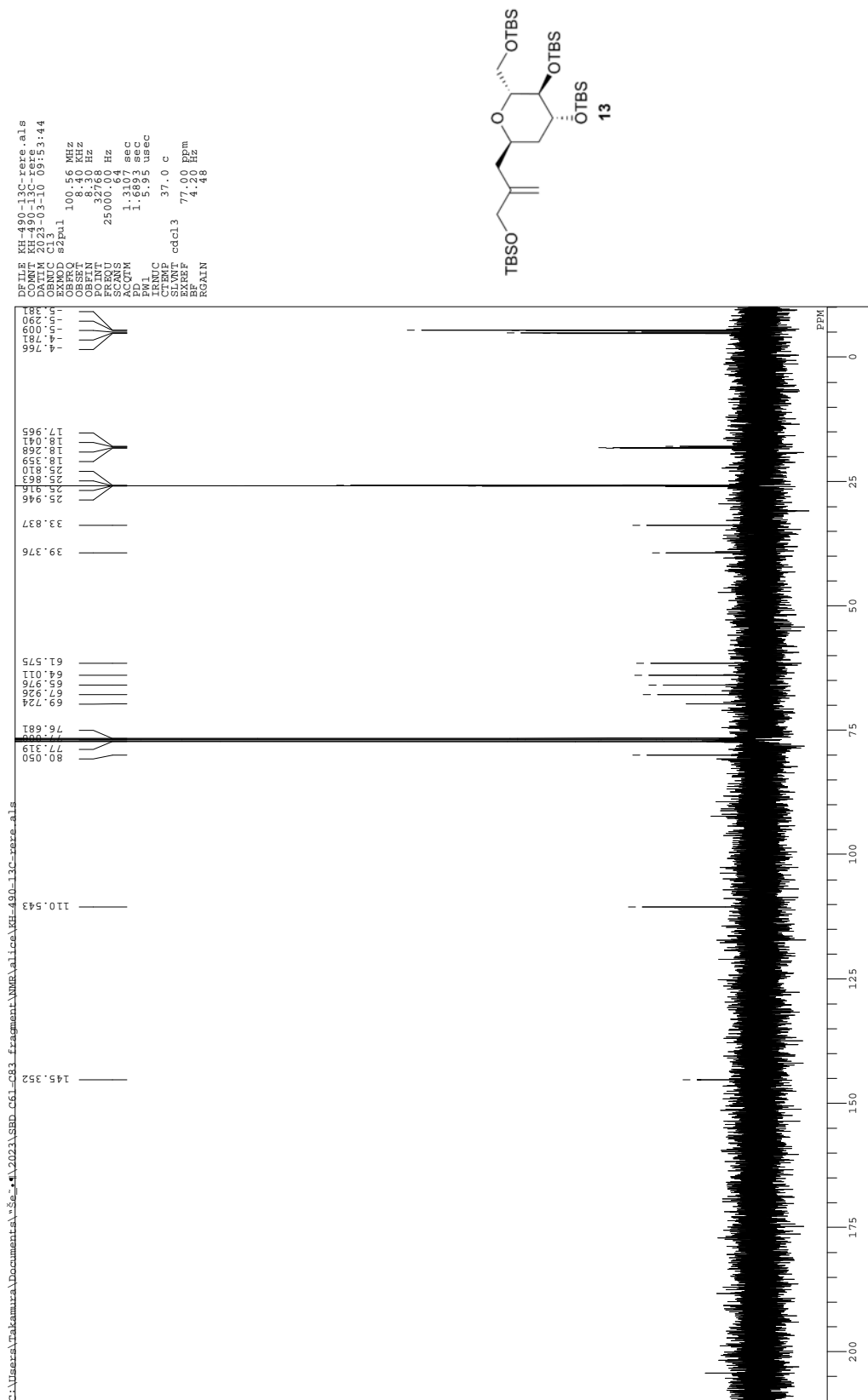
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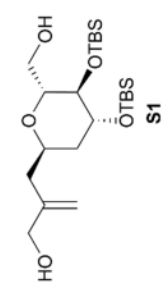
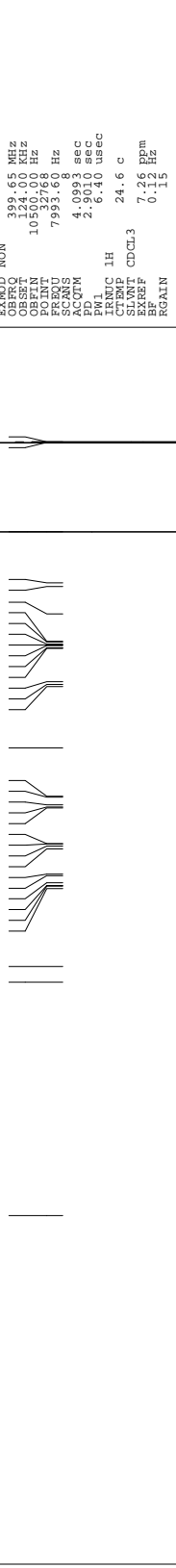
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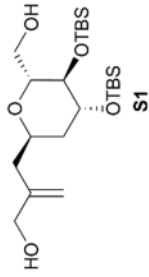
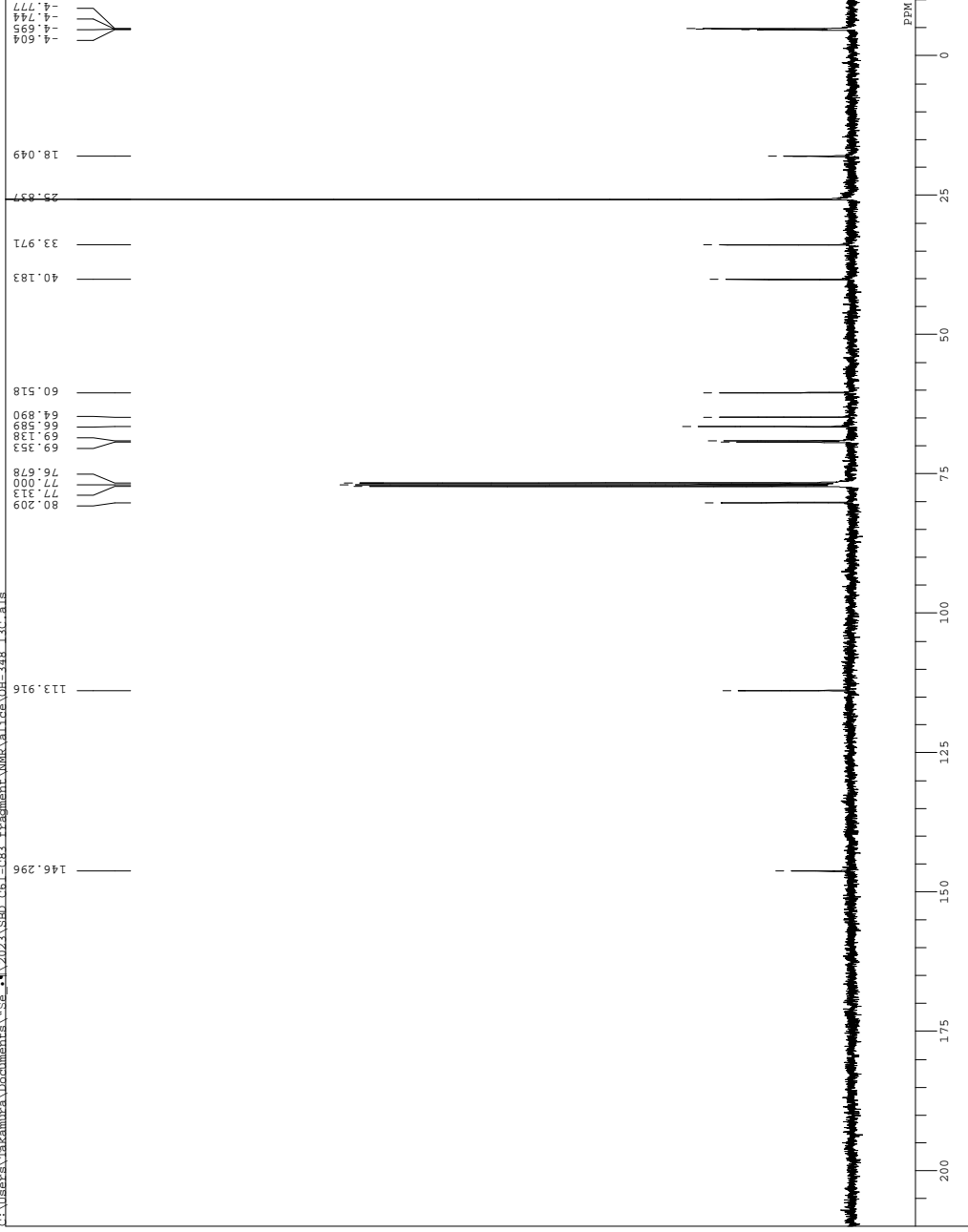


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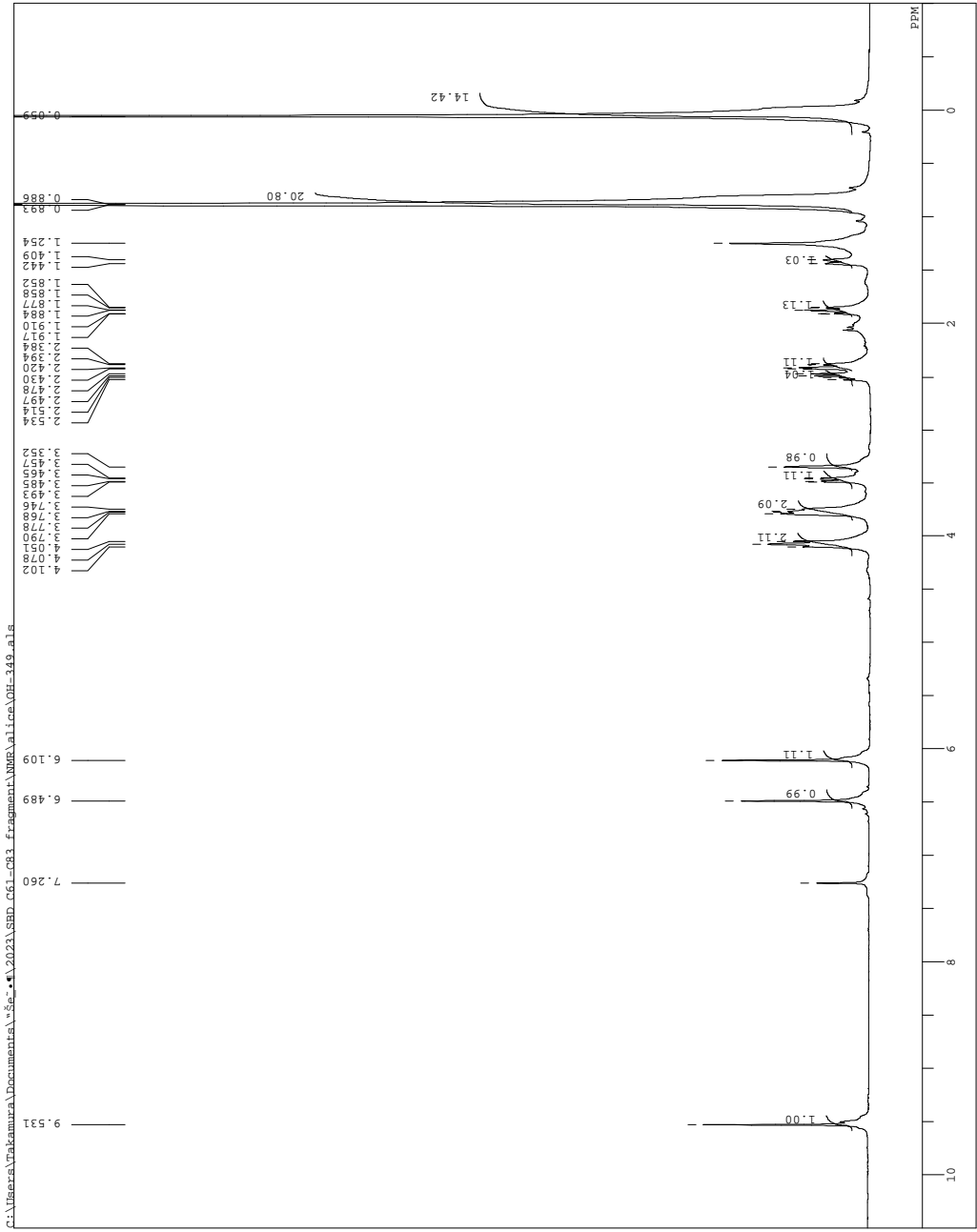
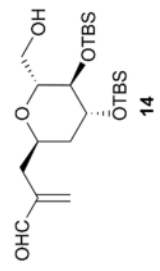
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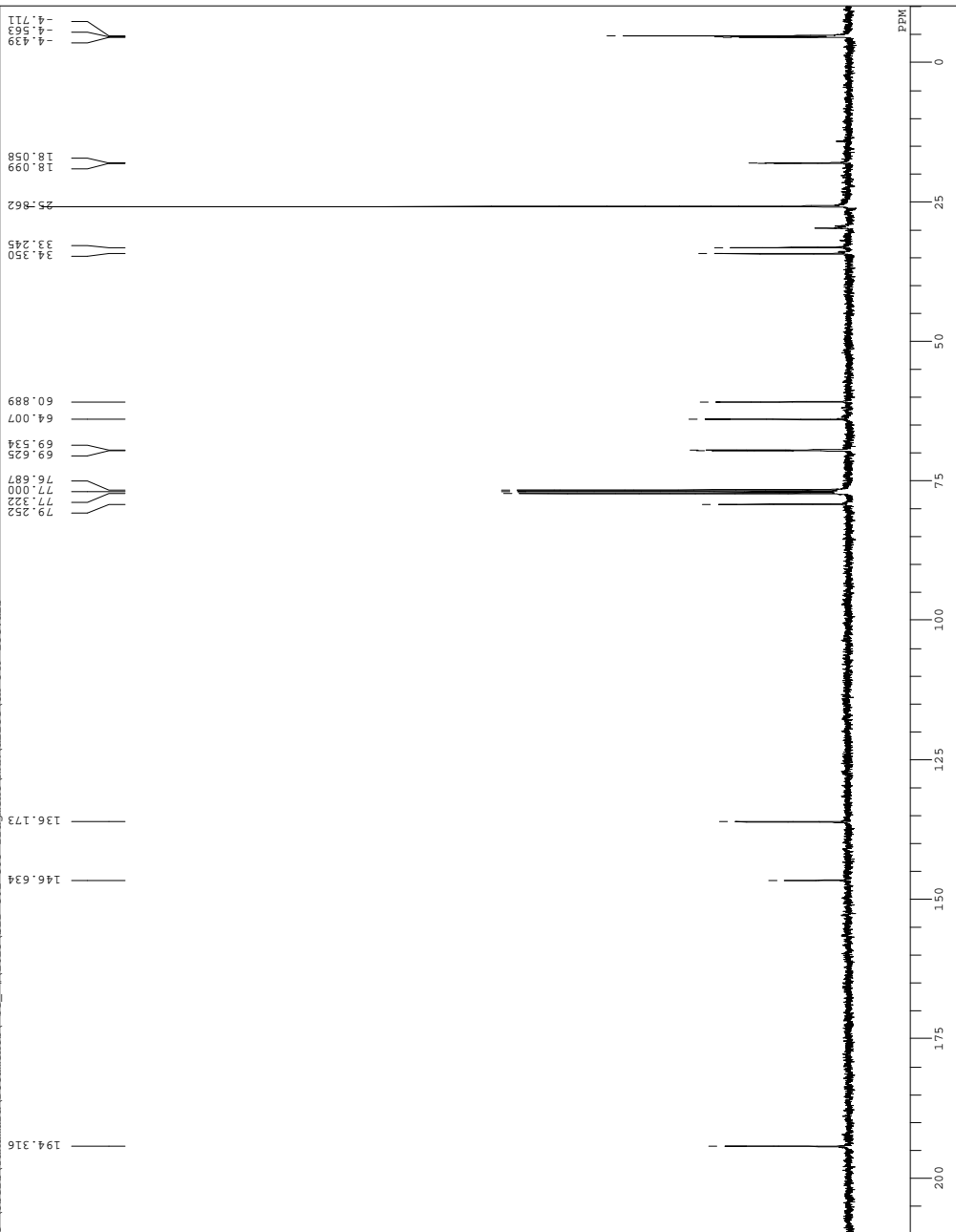
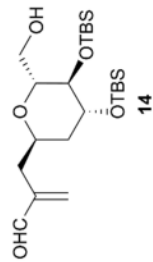
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SFO 125.760 MHz
RG 7993.60 Hz
AQ 4.0993 sec
PD 2.5010 sec
PC 6.40 usec
IRNUC 1H
IRPROG zgpg30
CTEMP 24.5 C
CDCL3
EXREF 7.26 ppm
RGAIN 2.00 Hz
SF 125.760 MHz
RGAIN 1.3

```

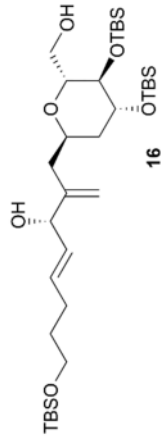
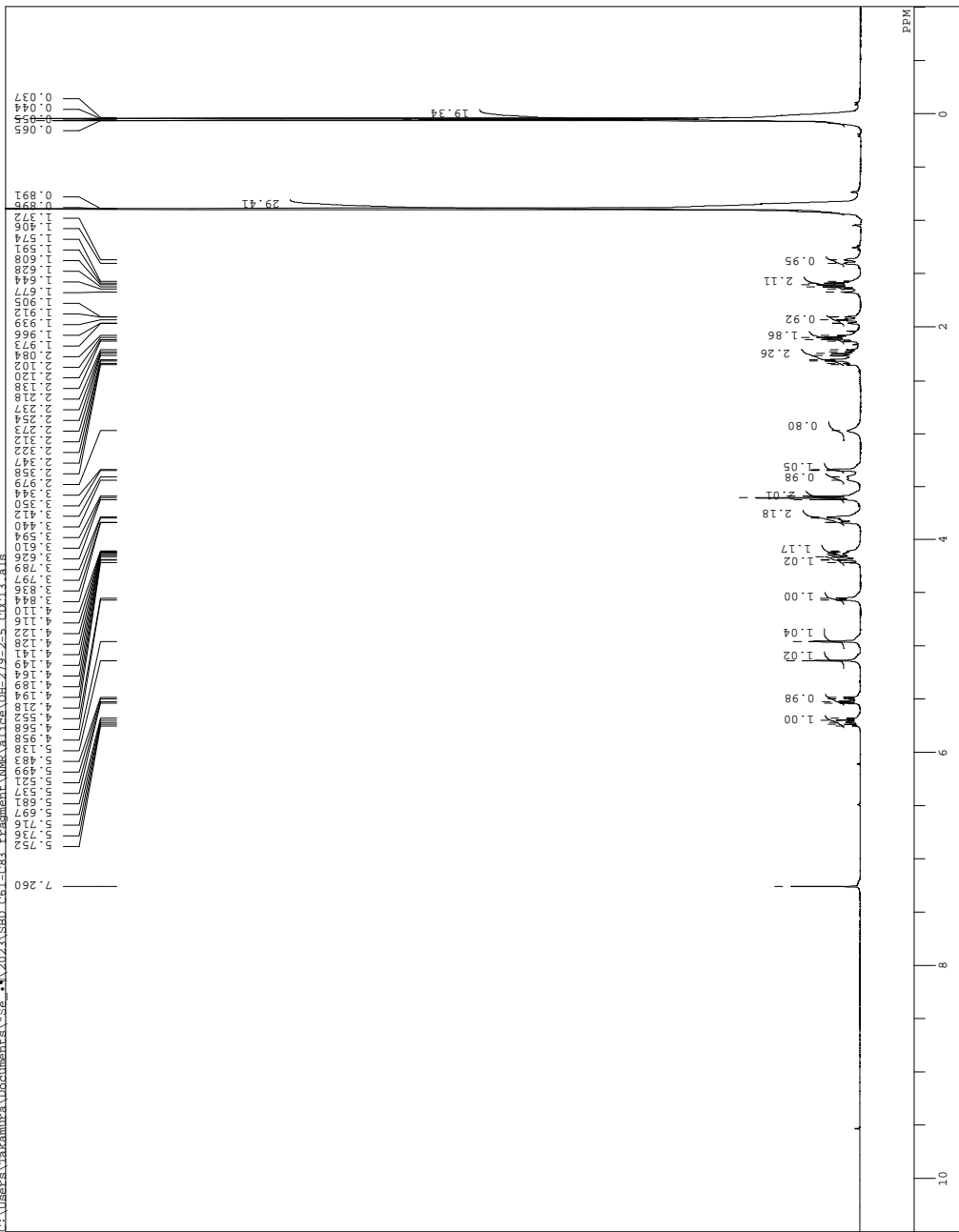


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 FILE OH-349_13C_als
 DATE Thu Jan 11 20:41:14 2018
 INSTR 13C
 ORBIT 13C
 OBSO BCM
 OBSF 100.40 MHz
 OBSF 125.00 KHz
 DRPT 105300.68 Hz
 PRGT 27173.90 Hz
 FREQD 27173.90 Hz
 SCANS 1.656
 PD 1.7940 sec
 PDI 1.7940 sec
 PULP 1H
 PRGM 27.7 c
 SFOV 100.40 MHz
 SOLVT CDCl3
 SIWV 77.00 PPM
 EXPR 2.24
 RGAIN 2.24



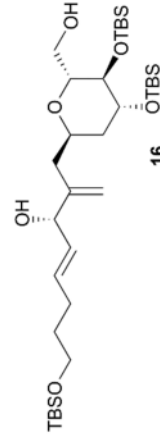
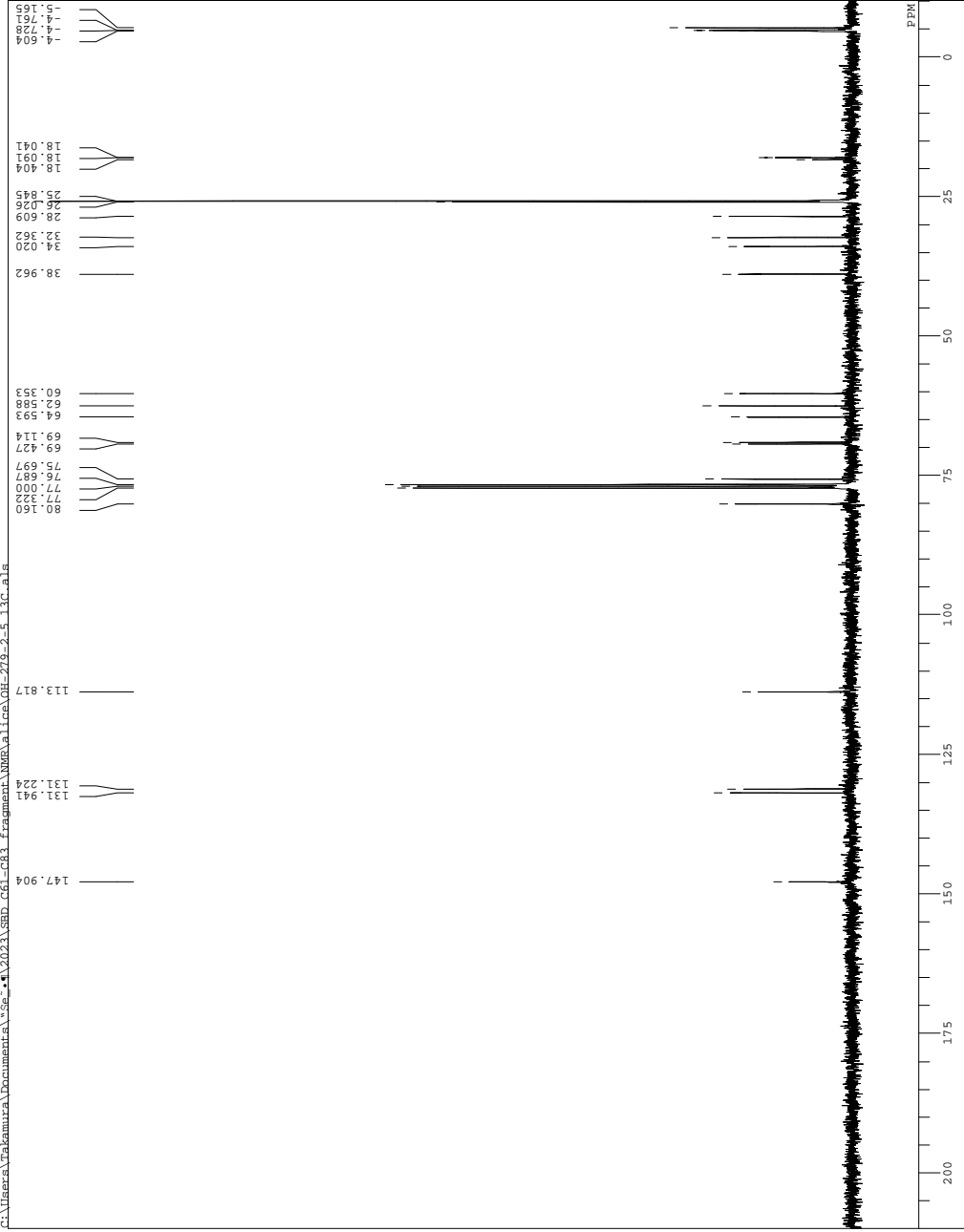
C:\Users\Takatamawa\Documents\5e_4\2023\SRD_061_083_Fragment\NMR\alic\OH-279-2-5_CDCl3_als

OH-279-2-5 CDCl3_als
COM1 Mon Jan 15 18:42:05 2018
DATE
NAME
EXPNO 1
PROCNO 1
PROCPS 1
SFO 399.65 MHz
OBSFQ 399.65 MHz
OBSST 74.00 Hz
PULPROG zgpg30
PROBHD 5mm QNP 1H/13
PULPROG zgpg30
FREQ0 79933.60 Hz
ACQ001 4.0993 sec
PD 2.9010 sec
INSTRUM 1H
TEMP 24.2 c
SOLVENT CDCl3
RF 7.26 MHz
RGAIN 0.12 Hz
RGAIN 1.12

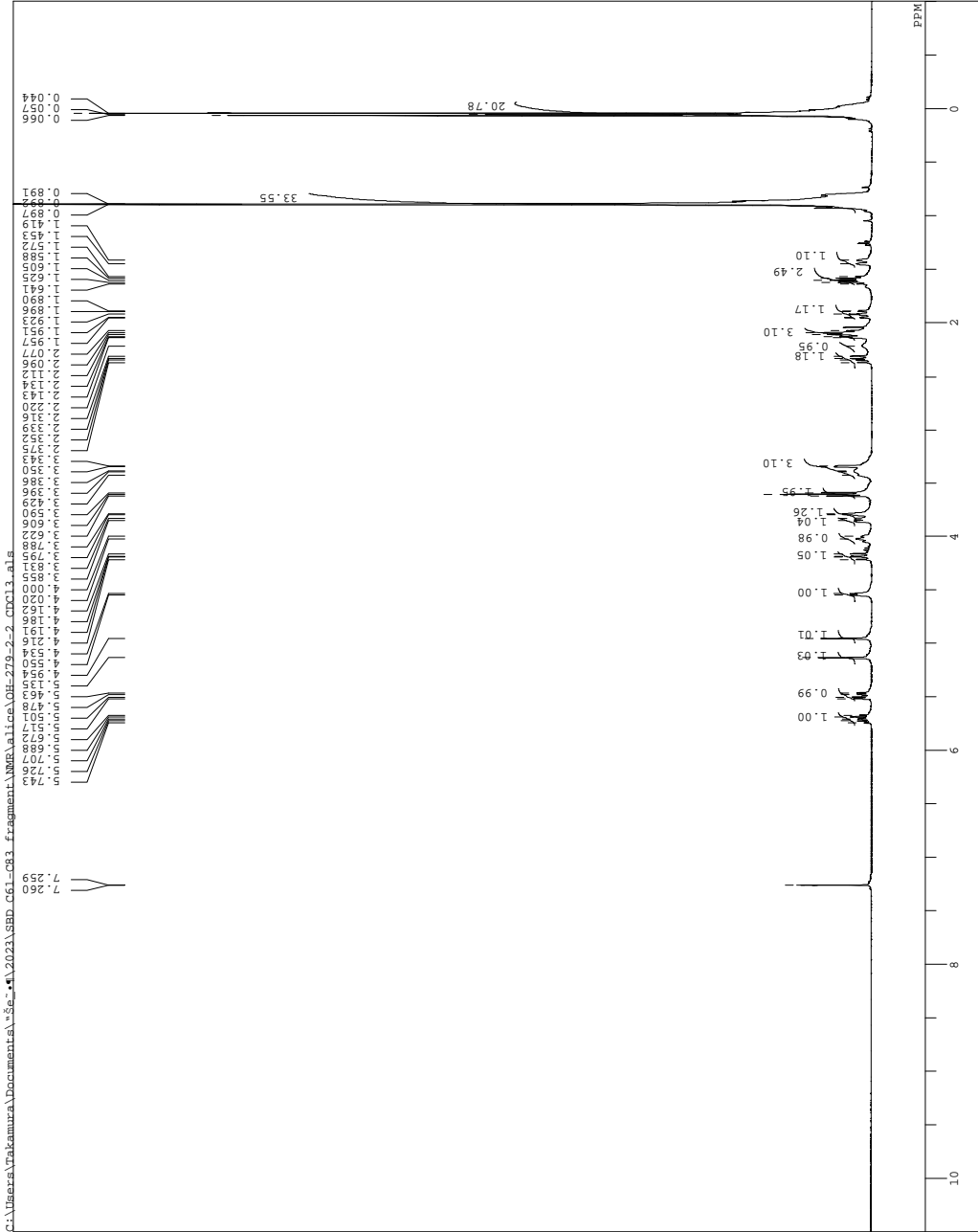


C:\Users\takamura\Documents\data\2021\SED_C61-CB3_fragment\NMR\alices\OH-279-2-5-13C.alc

DFILE OH-279-2-5-13C.alc
CONT
DATE Mon Jan 15 19:07:22 2018
NAME
PROB BBO
PULPROG zgpg30
SFO 100.625 MHz
AQ 1.00000000 sec
RG 32768
FIDRES 0.32768 Hz
AQRES 27173.90 Hz
FREQ 27173.90 Hz
SOLVENT CDCL3
AQC 1.2059 sec
PC 1.7940 sec
PD 6.80 usec
PRNUC 1H
PRNUC2
PRNUC3
P1 27.50 usec
PT 27.50 usec
SOLVENT CDCL3
SLVNT CDCL3
NUC1 13C
RF 2.00 MHz
RGAIN 2.25

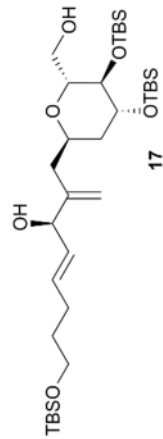
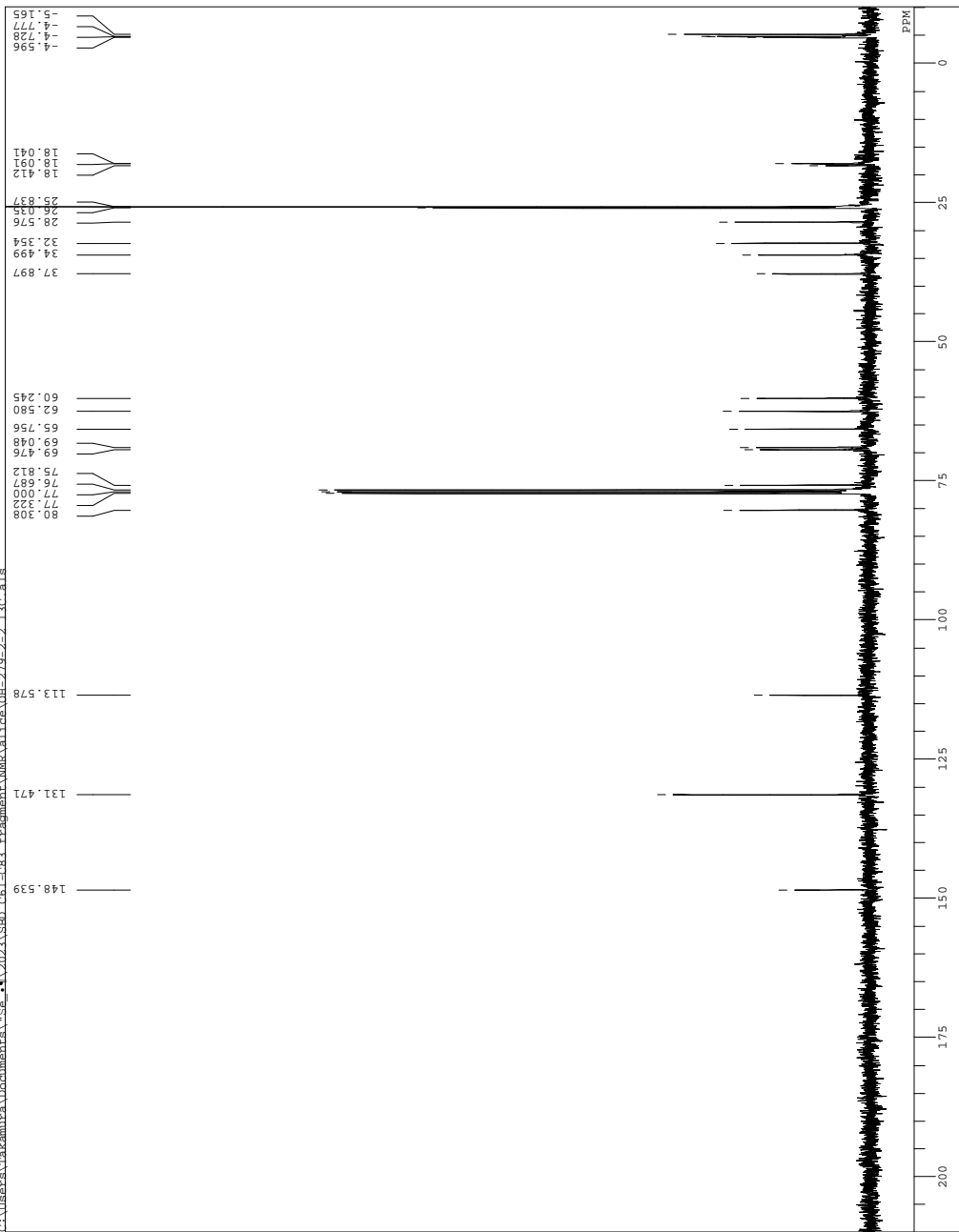


D:\Users\Yrakamura\Documents\Se_4\2023\SRD_cg1-cr3_fragments\NMR\1ca\OH-279-2-2_CDCl3.als
Date_ The Jan 16 11:52:11 2018
COMM OH-279-2-2_CDCl3.als
ORBIT 1H
EXMOD NON
PULPROG zgpg30
399.65 MHz
ORBSF 134.00 KHz
105004.00 Hz
PC 20.00
FREQ0 79373.60 Hz
SCANS 8
ACQTM 4.0973 sec
RG 2.640 usec
PULP1
IRMTC 1H 24.3 c
SI 1000
SOLVENT CDCl3
INSTRUM spect
EXREF 7.26 PPM
RGAIN 0.12 Hz



C:\Users\takamura\Documents\3se*\20231\SED_C61-C83_fragment\NMR\13c\OH-279-2-2_13c_als

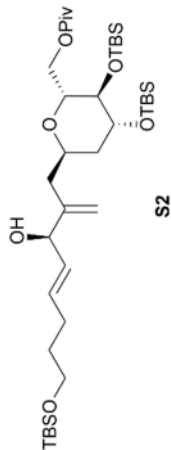
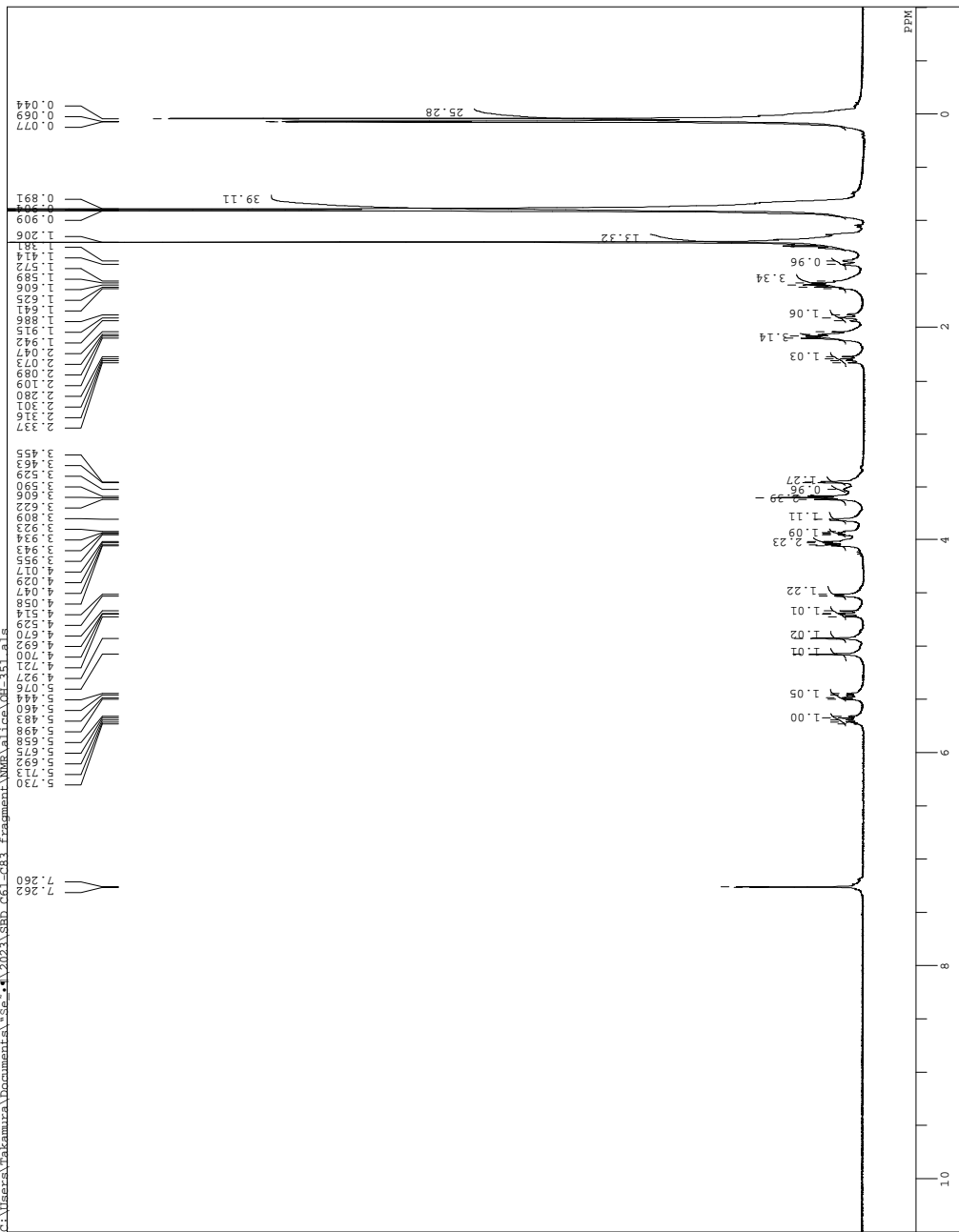
DFILE OH-279-2-2_13c_als
COMPT Tue Jan 16 12:17:53 2018
DALIM 1
EXNO C
EXMOC BCO
OBFREQ 100.40 MHz
OBSF1 100.40 MHz
OBSF2 100.40 MHz
POINT 32768
FREQU 27173.90 Hz
ACQTM 1.2059 sec
PD 1.7940 sec
PRNUC 1H 6.80 usec
PRNUC 13C 27.2 c
SOLVT CDCL3 77.00 ppm
REF BF 2.00 Hz
RGAIN



C:\Users\Takamura\Documents\Se-4\2023\SRD_061-CR3_Fragment\NMR\data\OH-351_als

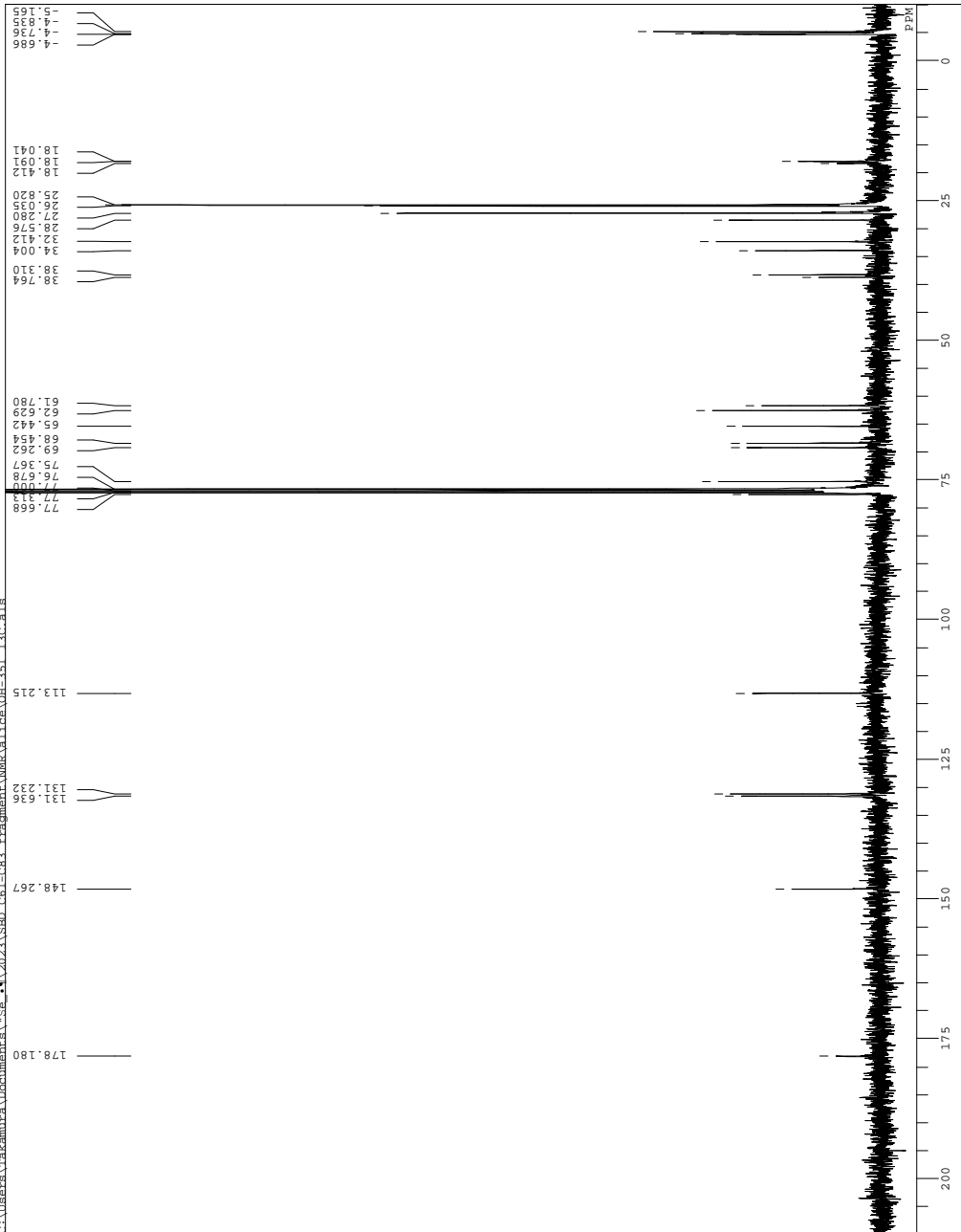
```

PR1 F OH-351_als
COMT Wed Jan 17 20:49:32 2018
C13 100
DMSO d6
PULP 1H
OBFFO NON
399.65 MHz
124.00 KHz
10532768 Hz
7993.60 Hz
FREQU
SCANS 4.0893 sec
PD 2.9010 sec
6.40 usec
PULP 1H 24.4 C
SOLVT CDCl3
SIMP 7.26 PPM
RGAIN 0.12 PPM
0.17
  
```



C:\Users\Takamura\Documents\5c-1\2023\SEB_C61-C81_Fragment\NMR\val\ca\OH-351_13c.a1s

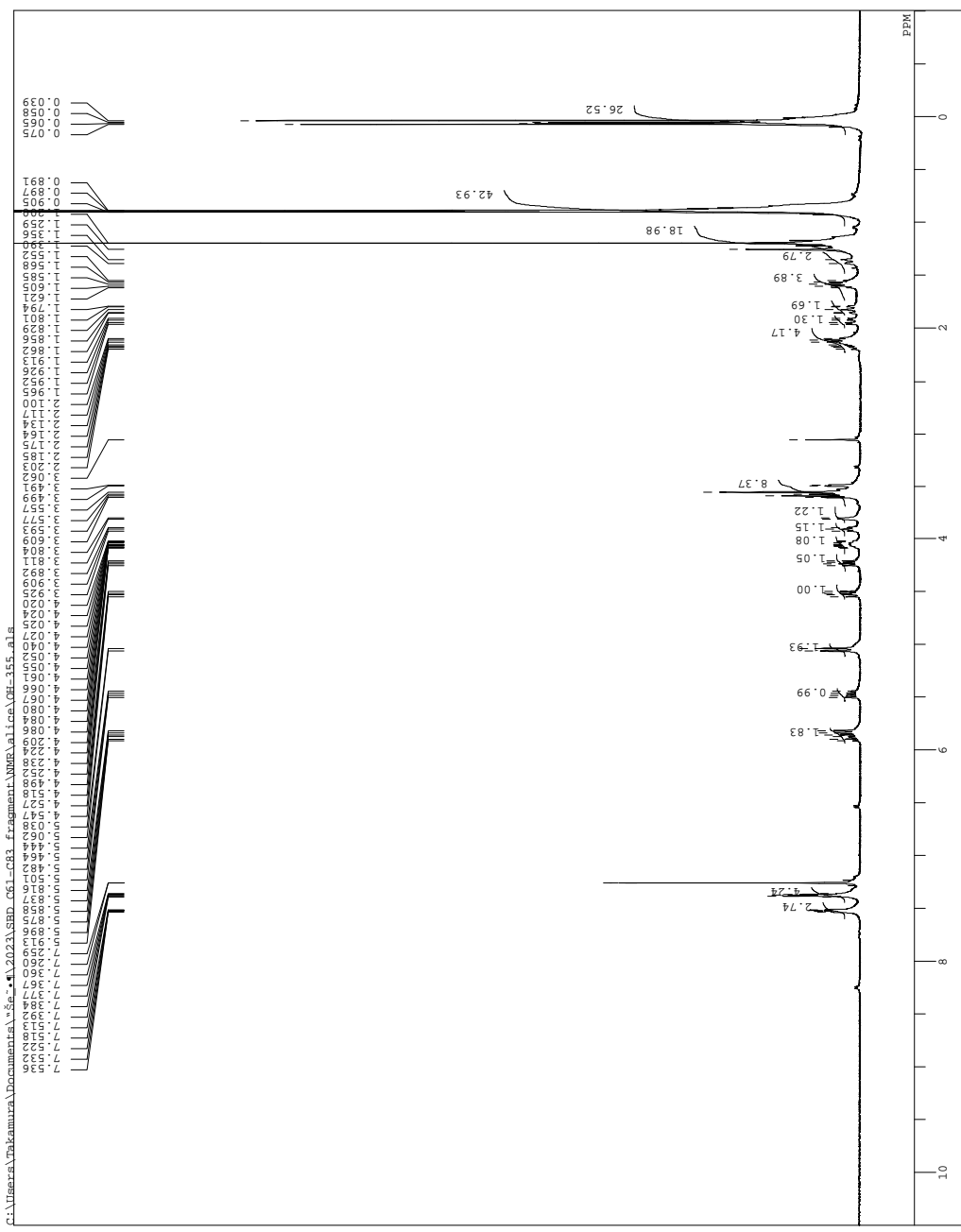
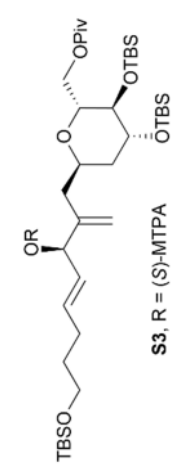
DFILF OH-351_13c.a1s
 COMPT wed Jan 17 21:59:11 2018
 DATEM
 EXMOD B04
 EXMOD B04
 OFREQ 100.40 MHz
 OFREQ 100.40 MHz
 OFSFT 10540.00 Hz
 POINT 32768 Hz
 FREQ0 2717390 Hz
 FREQ1
 ACQTM 1.2059 sec
 PD 1.7940 sec
 INNUC 1H
 CTMP CDCl3 28.1 c
 EXPT 77.00 ppm
 BF 2.00 Hz
 RGAIN 25



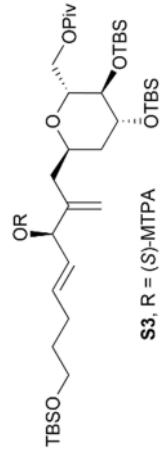
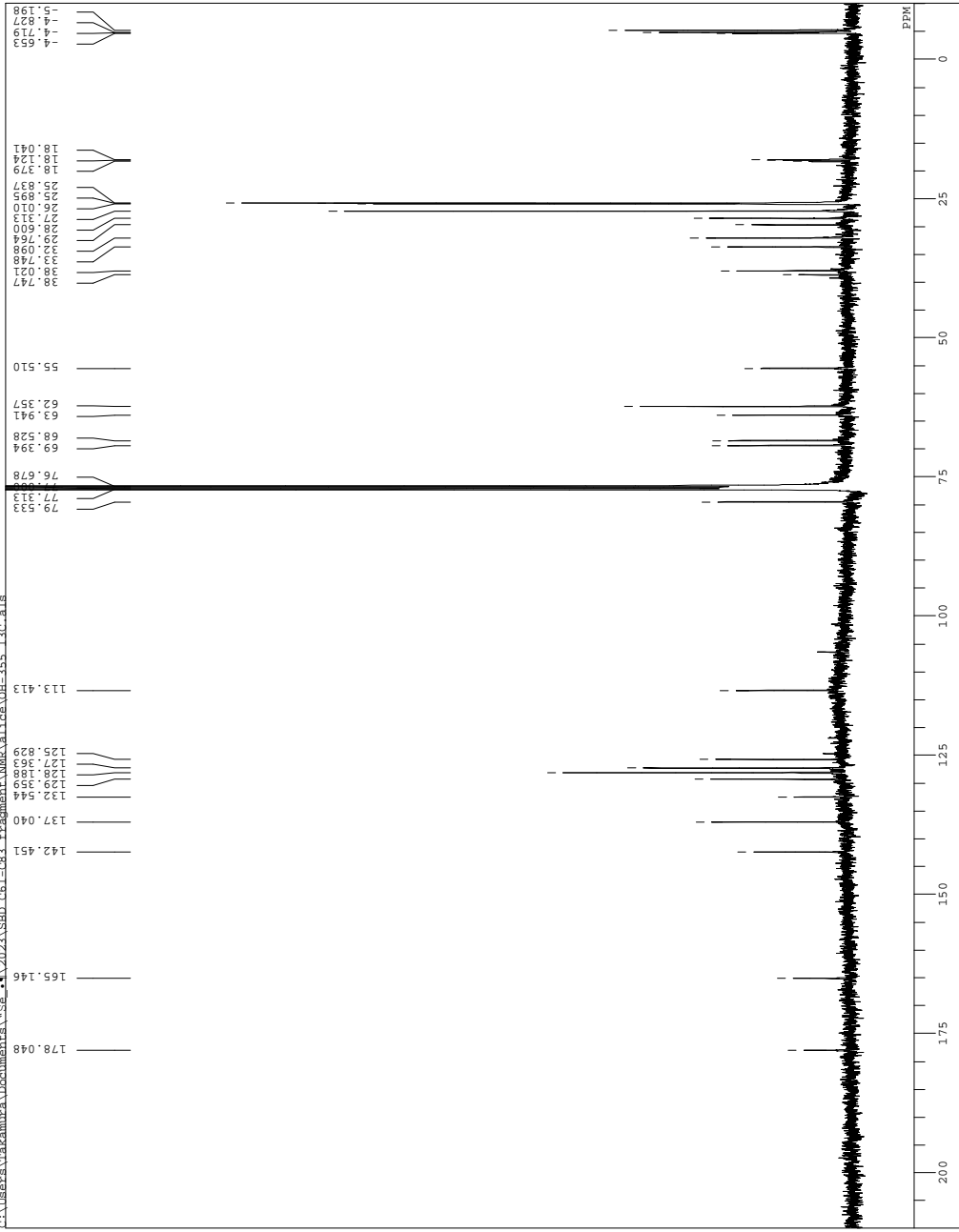
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FILE      OH-355.als
NAME      OH-355
DATE      Tue Jan 23 19:49:46 2018
INSTRUM   spect
PROBHD    5mm
PULPROG   zgpg30
AQ        3.99650000
SFO       399.65 MHz
NUC1      13C
NUC2      13C
OBFTN     124.00 KHz
OBPRG     10590.00 Hz
FREQ      79337.60 Hz
SCANS     4.00000000
SCANS2    2.90100000
SCANS3    6.40000000
PD        2.00000000
PD2       2.00000000
PD3       2.00000000
RG1       24.7 C
RG2       24.7 C
RG3       24.7 C
IRFNC     1.00000000
SOLVENT   CDCL3
EXREF     7.26 PPM
RGAIN     0.11700000

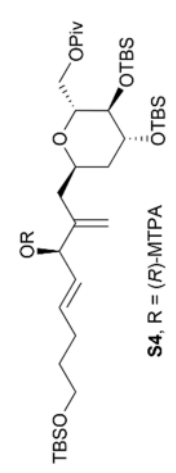
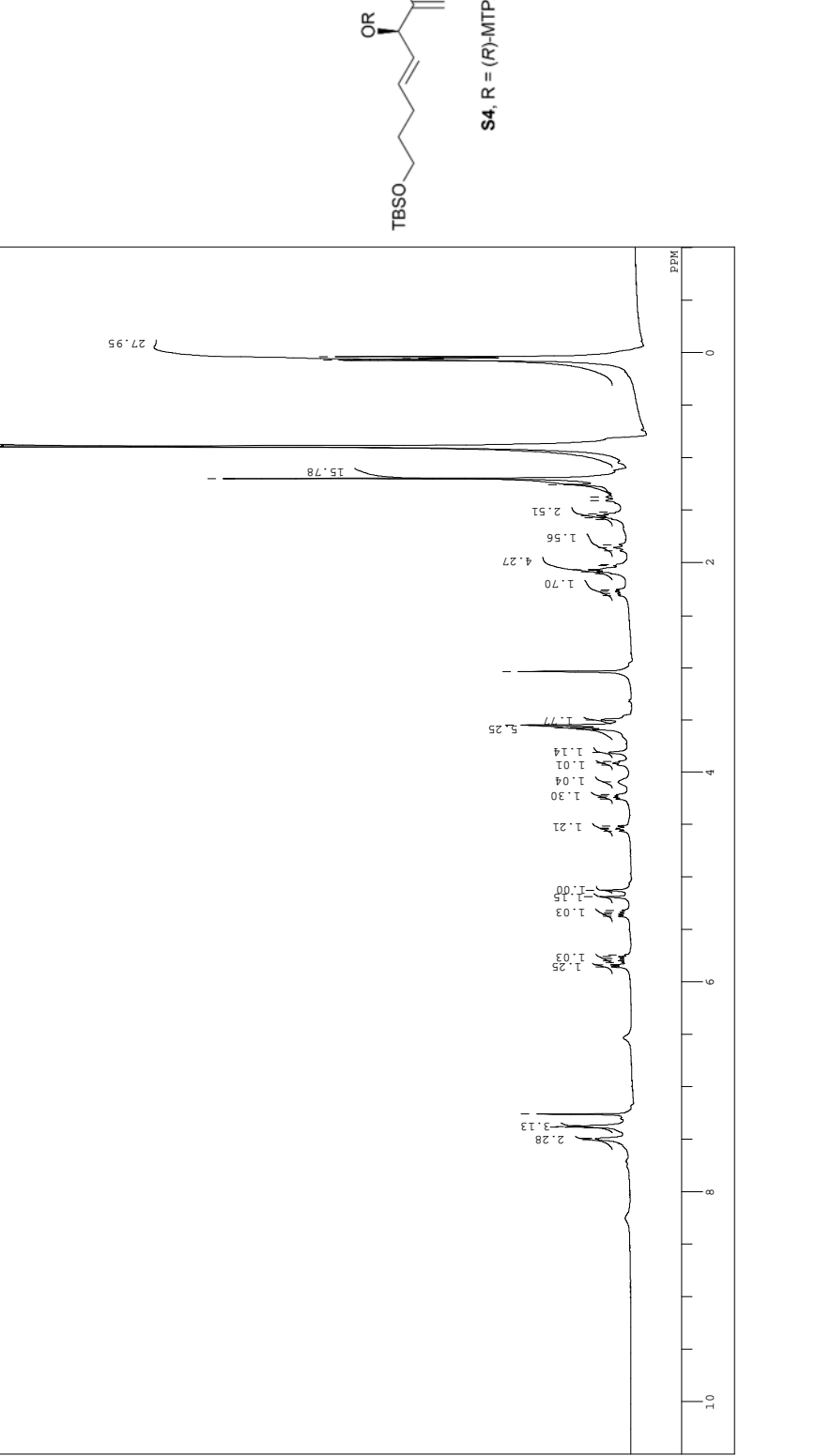
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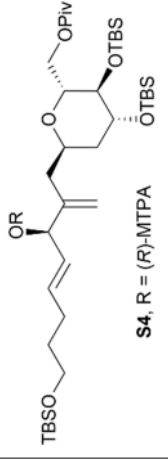
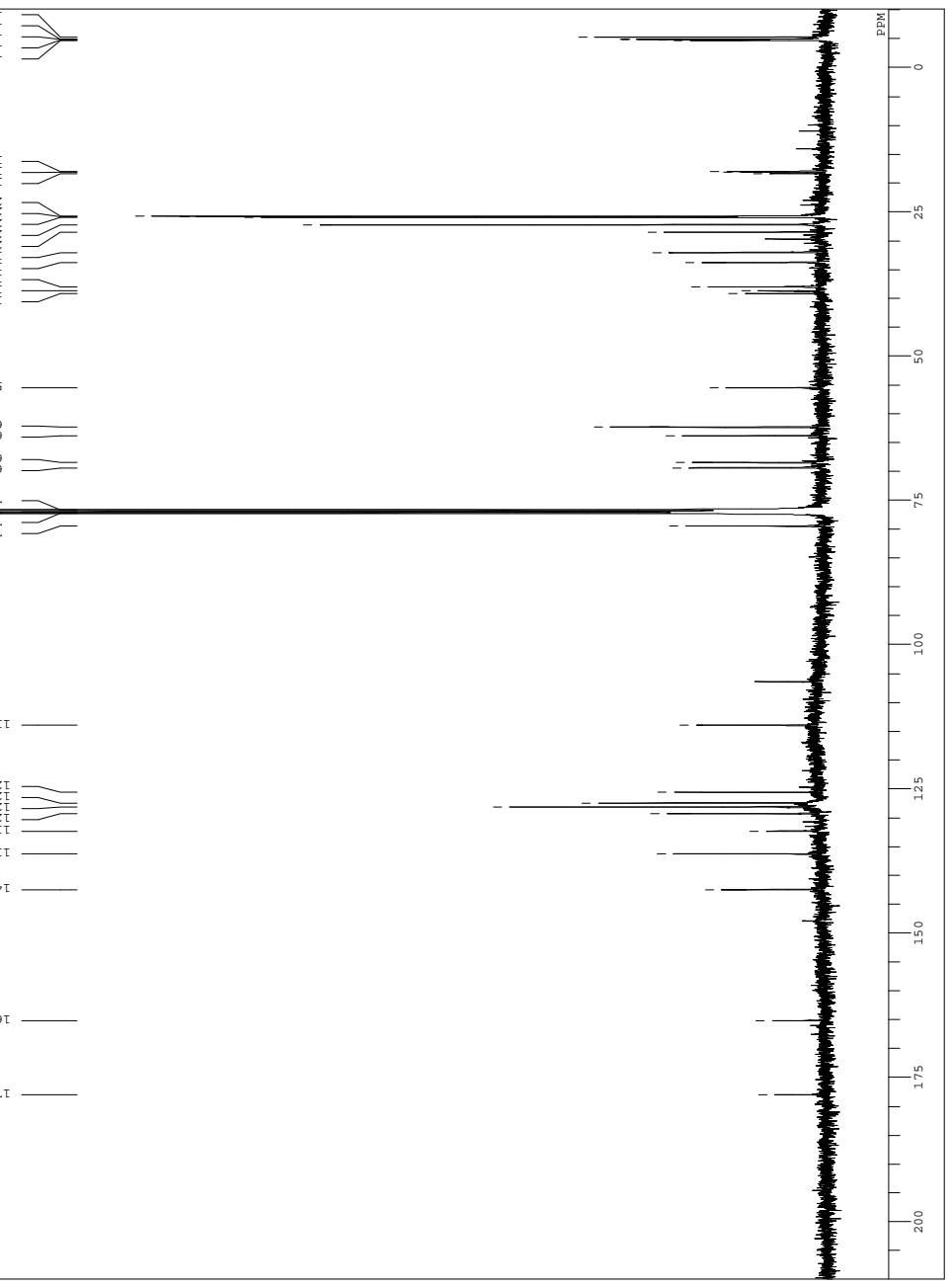
DFILE OH-355_13c.als
OPRTM Wed Jan 24 06:16:47 2018
OBNUC 13C
EXMOD BCM
L 1
F1 100.40 MHz
SFO 125.700 MHz
OBFTN 10500.00 Hz
RESOLV 0.500 Hz
PRQD 2713296 Hz
SCANS 10000
ACQTM 1.2039 sec
PM 1.6780 USEC
PWL
IRNUC 1H
L 1
SOLNT CDCL3
EXREF 77.00 ppm
RGAIN 2.00 Hz



C:\Users\takamura\Documents\Se...2023\BHD_C61-C83_Fragment\MNR\Ice\OH-356.als
 FILE OH-356.als
 COMMT Wed Jan 24 23:04:23 2018
 DATE Wed Jan 24 23:04:23 2018
 DEPT 1H
 PULPROG zgpg30
 PROCNO 1
 AQUIRE 399.65 MHz
 OBSET 124.00 MHz
 FIDRES 0.152768 Hz
 POINT1 7993.60 Hz
 SCANS 4
 ACQTIME 4.0893 sec
 F2 - 2.9010 sec
 PD 6.40 usec
 PULPROG 1H
 CTEMP 24.4 c
 SLOTT CDCL3
 SOLVENT CDCL3
 REF 7.26 ppm
 RGAIN 2.00 ppm
 1.17



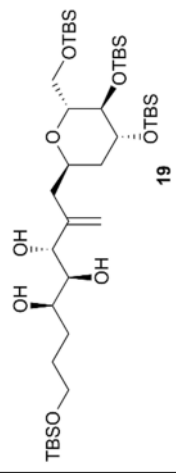
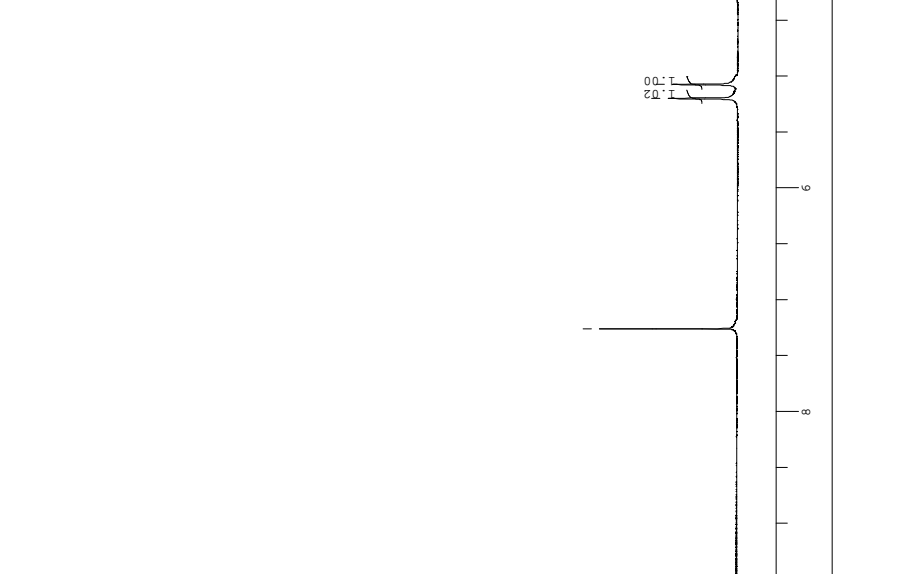
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 OH-356_13C-als
 DATE Thu Jan 25 07:28:54 2018
 TIME 13:55
 INSTR LC
 PULSE PROB 1H
 PROC F2
 AQC 100.40 MHz
 DECOUPL 125.00 MHz
 ORBIT 10532768 Hz
 POINT 27173.90 Hz
 FREQ 100.40 MHz
 SCANN 1.0000 sec
 PD 1.7940 sec
 PULPROG zgpg30
 PWD 6.80 usec
 TEMPC 27.9 C
 SLVNT CDCL3
 SREF 77.00 ppm
 RGAIN 2.25



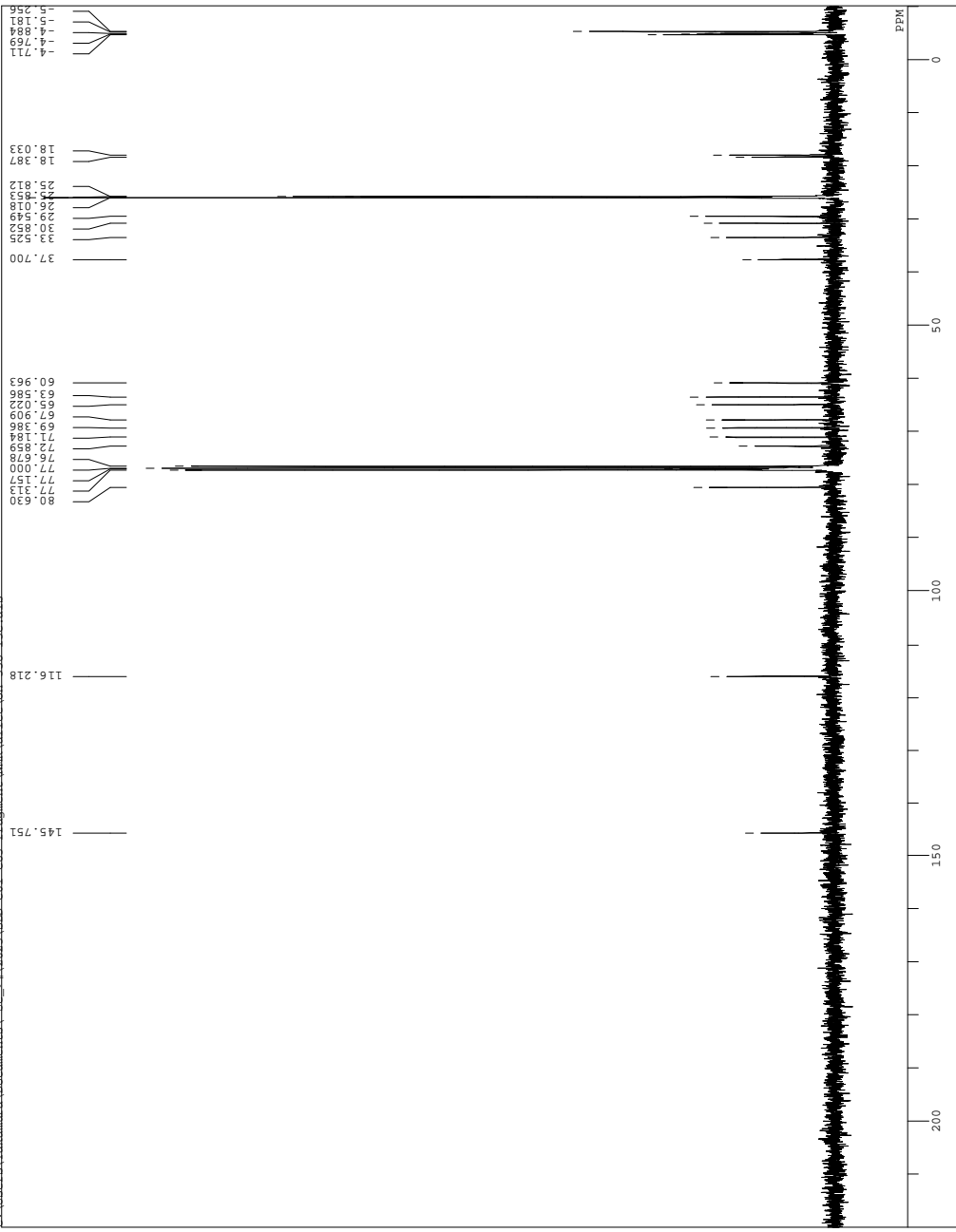
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NAME OH-358.als
DATE_ Mon Jan 29 20:33:41 2018
DIRNAME
PROBHD 5
PULPROG zgpg30
DATTIM Mon Jan 29 20:33:41 2018
OBNUC 1H
DECO 1
AQ 4.00
RG 1.00
SFO 399.65 MHz
OBSEFT 124.00 kHz
RG 1.00
DGT 105307.00 Hz
RG 1.00
FREQ 798337.60 Hz
RG 1.00
SCANS 4
AQ 0.0898 sec
PD 2.9010 sec
DD 6.40 usec
RG 1.00
PWL 24.4 c
RG 1.00
SOLVENT CDCL3
EXREF 7.26 ppm
RGAIN 0.112

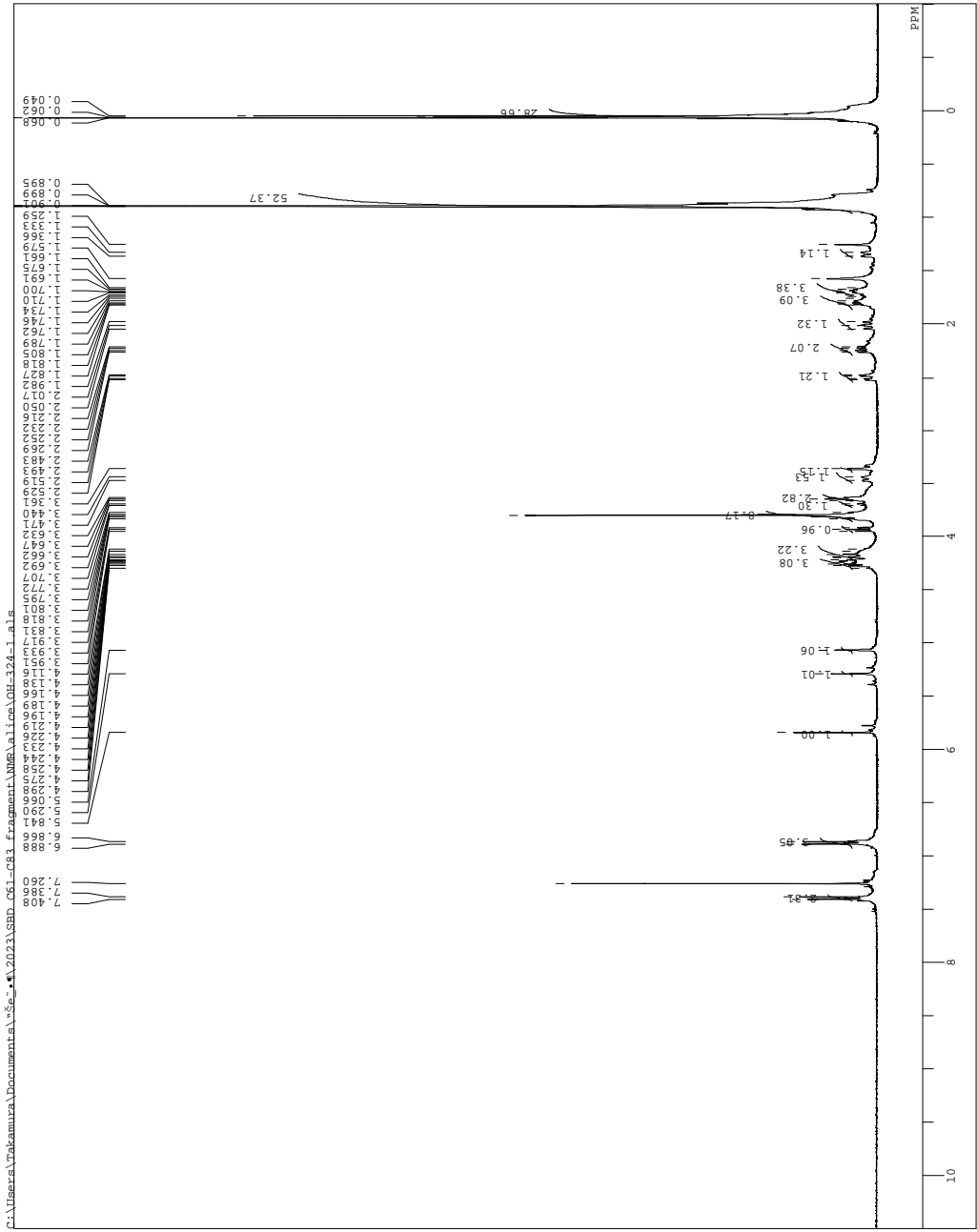
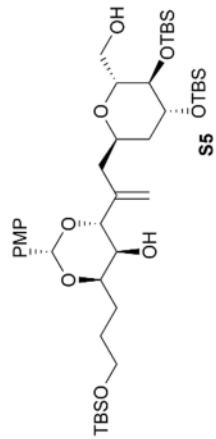
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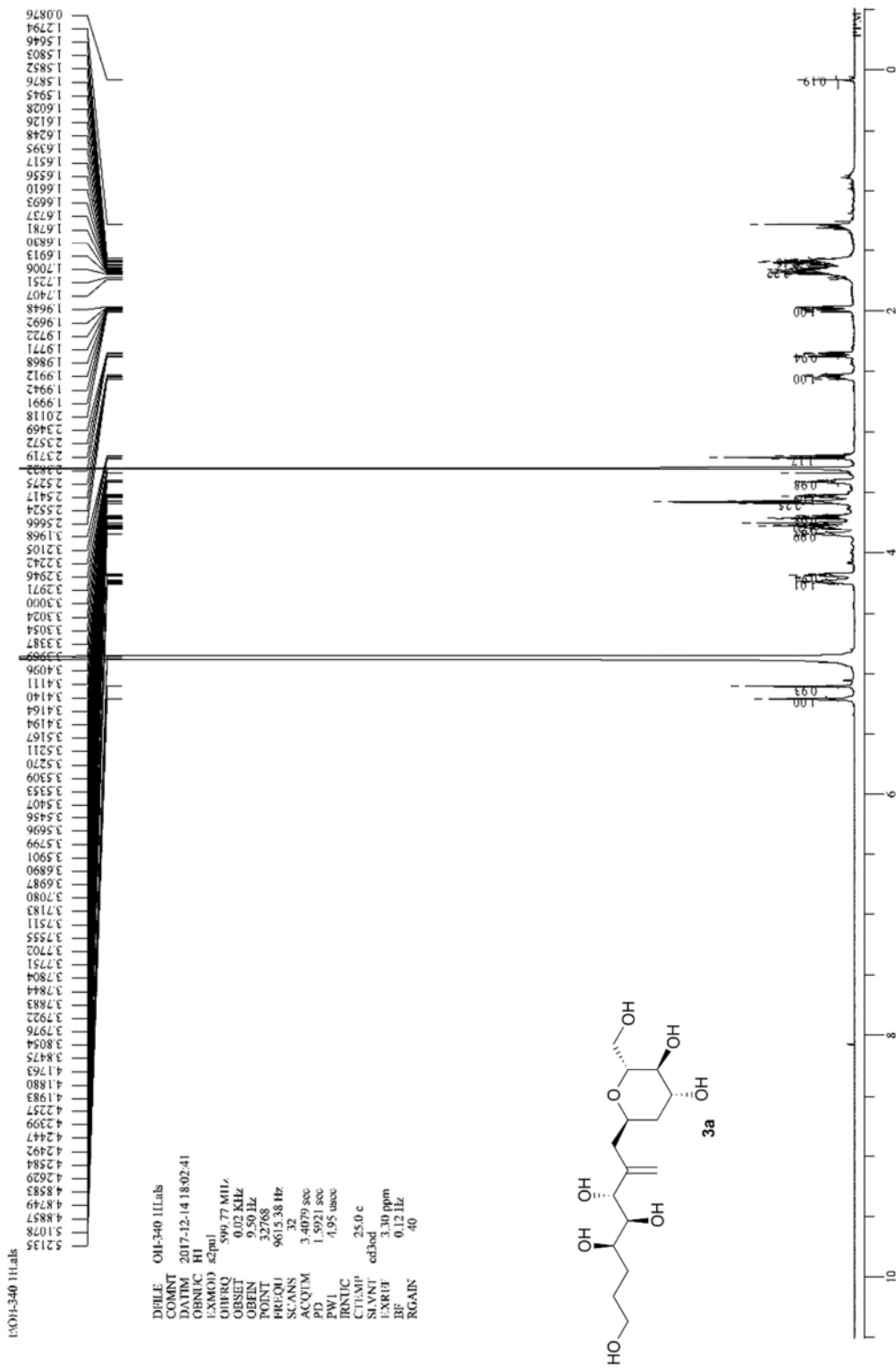


OFID: OH-358_13C_als
 DATE_: Mon Jan 29 21:01:05 2018
 OBNUC: 13C
 OBSRO: ECH
 OBSRT: 100.40 MHz
 OBSF1: 125.00 KHz
 OBSF2: 105.9768 Hz
 FREQ1: 27173.90 Hz
 SCANS: 432
 AQT: 1.432 sec
 PD: 1.7940 sec
 PUL: 6.80 usec
 CTB: 1H
 CTB2: 27.5 c
 SLANT: CDCL3
 EXPT: 77.00 ppm
 EXPE: 2.35 Hz
 RGAIN:



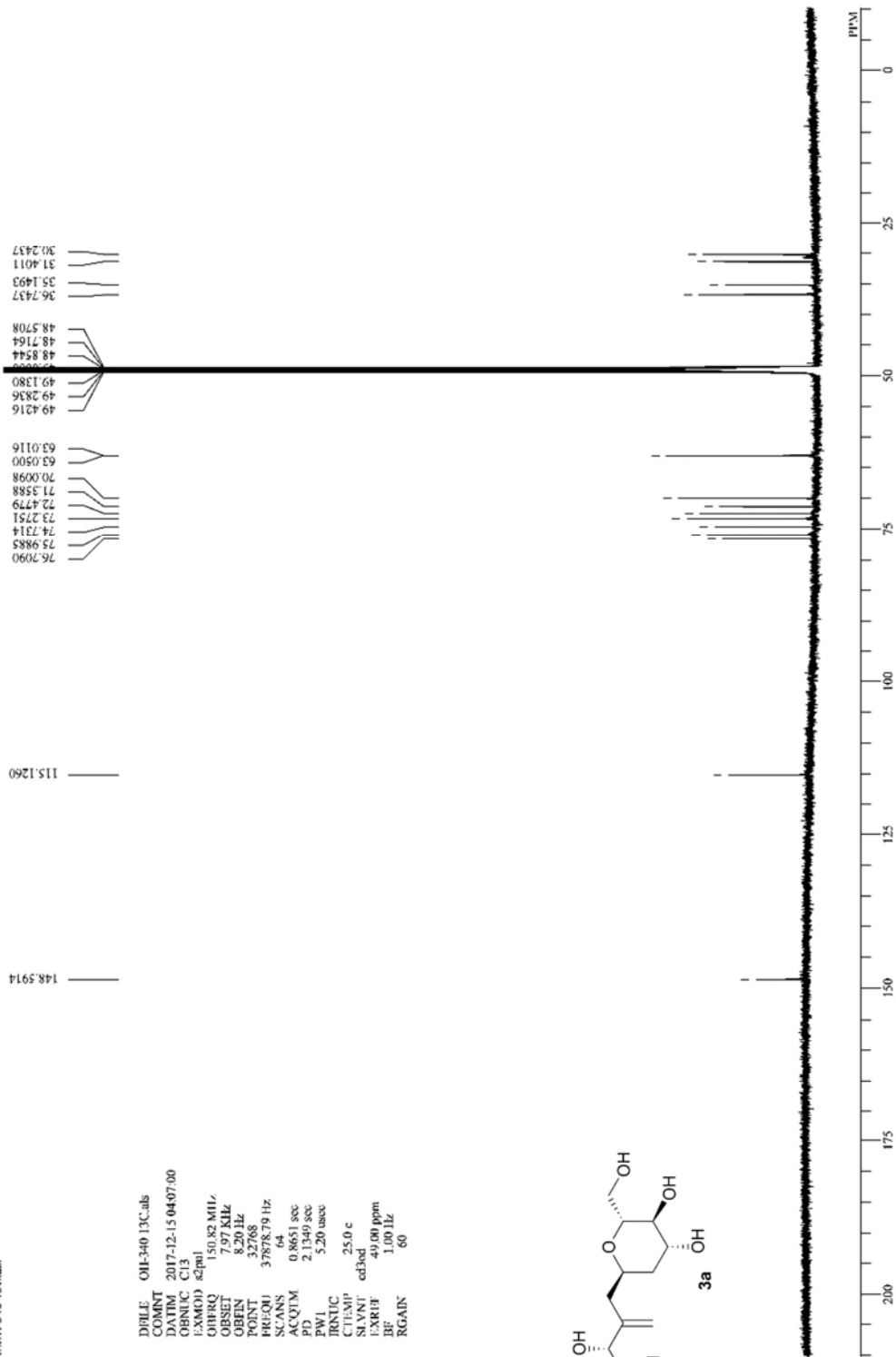
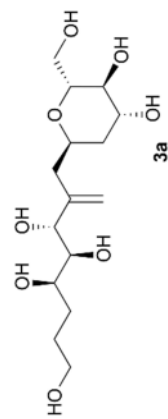
DFIL2 OH-324-1.als
 DATE_ Fri Jan 26 22:00:30 2018
 OBNUC 1H
 OBSOBS 10500.00 Hz
 OBSFREQ 399.65 MHz
 OBSF2 124.00 KHz
 P1 1.00 sec
 P2 2.9016 sec
 P3 6.40 usec
 P4 24.4 c
 IRMUC 1H
 SLVNT CDCL3
 EXREF
 RGAIN 0.17





1:OH1-340 13C.acs

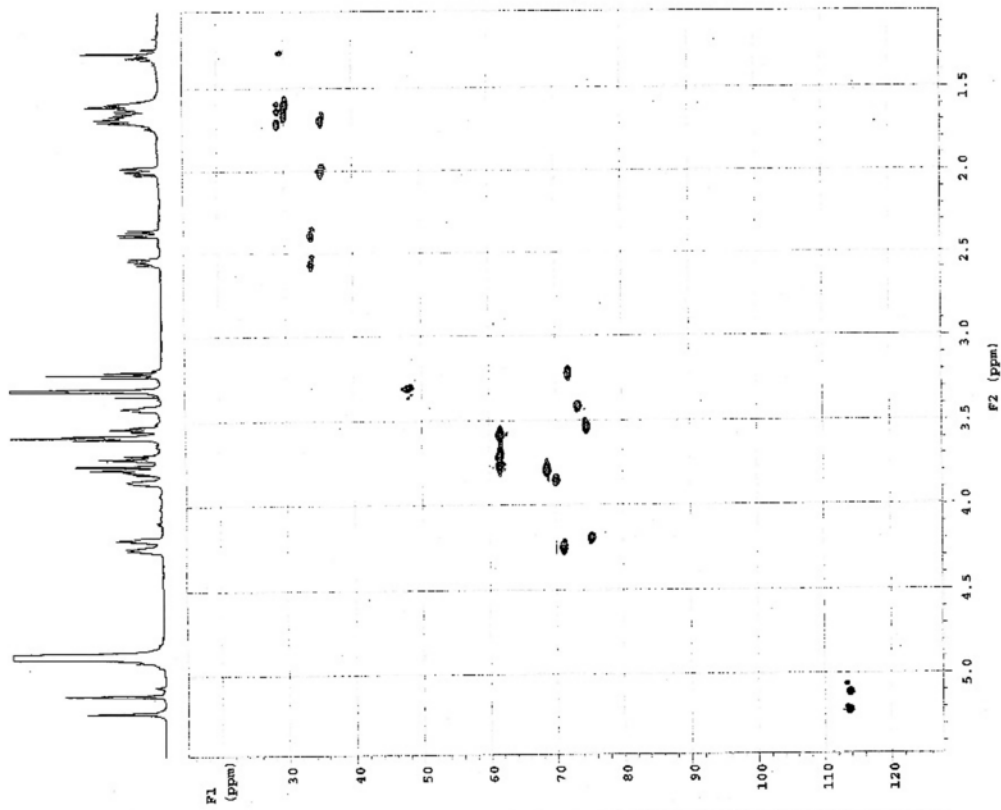
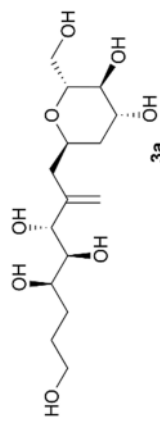
DIRLE OH1-340 13C.acs
COMINT
DATIM 2017-12-15 04:07:00
OBNUIC C13
EXMOD s2(pul)
COPRQ 150.82 MHz
OBSF 7.97 KHz
OBSFEN 8.20 Hz
POINT 32708
PRG00 37878.79 Hz
ACQNY 66.66 Hz
ACQTM 0.8651 sec
PD 2.1349 sec
PWL 5.20 usec
TRNUIC
CTEMP 25.0 c
SIYNT ed3od
EXRFH 49.00 ppm
BF 1.00 Hz
RGAIN 60



copy gmqc

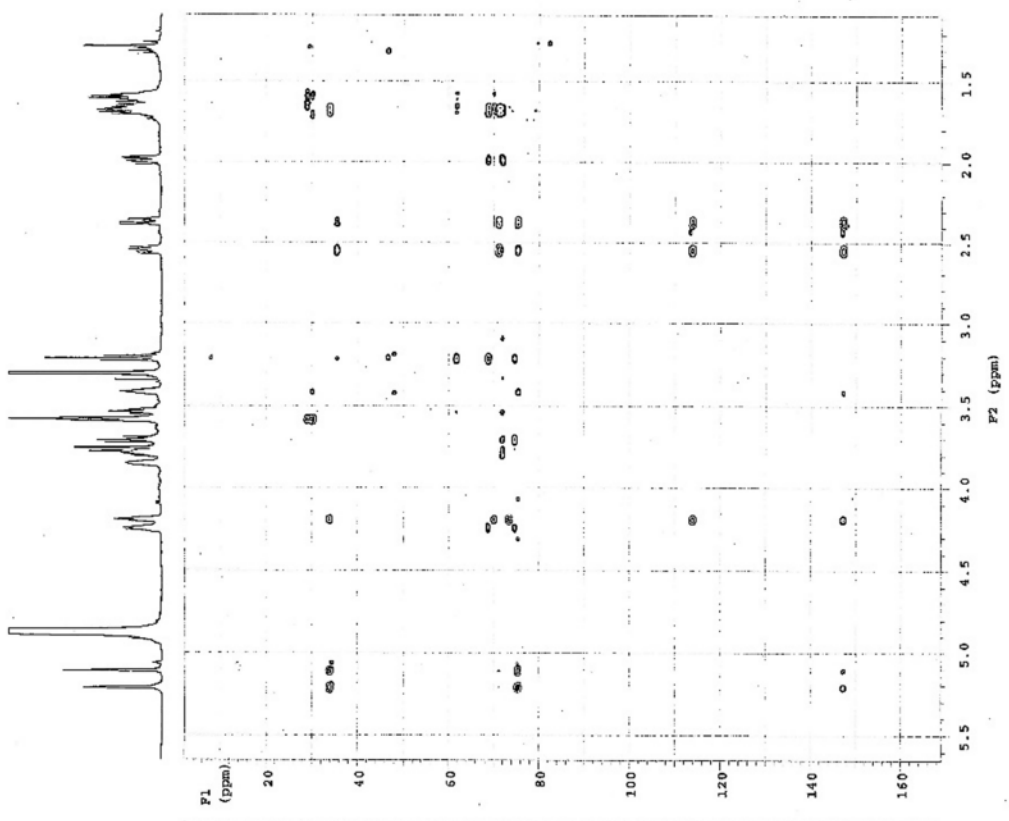
SAMPLE		NAME		ACQUISITION		ABRAYS	
Date	16 Dec 2017	hr	mm	name	name	phase	phase
solvent	CD3OD	name	name	name	name	name	name
nmr	600	freq	mg	mag	mag	1	1
sw	ACQUISITION	mag	6400	mag	6400	1	1
st	9415.4	temp	not used	sf	SPIN	1	1
sp	6.150	not used		sf	SPIN	1	1
sa	2884	gain	40	sf	SPIN	1	1
sb	4000	gain	9	sf	SPIN	1	1
sc	4000	gain	9	sf	SPIN	1	1
sd	1.000	gain	5247	sf	SPIN	1	1
se	32	gain	6.000000	sf	SPIN	1	1
sf	3.977	gain	6.000000	sf	SPIN	1	1
sg	34691.1	gain	6.000000	sf	SPIN	1	1
sh	34691.1	gain	6.000000	sf	SPIN	1	1
si	34691.1	gain	6.000000	sf	SPIN	1	1
sj	34691.1	gain	6.000000	sf	SPIN	1	1
sk	34691.1	gain	6.000000	sf	SPIN	1	1
sl	34691.1	gain	6.000000	sf	SPIN	1	1
sm	34691.1	gain	6.000000	sf	SPIN	1	1
sn	34691.1	gain	6.000000	sf	SPIN	1	1
so	34691.1	gain	6.000000	sf	SPIN	1	1
sp	34691.1	gain	6.000000	sf	SPIN	1	1
sq	34691.1	gain	6.000000	sf	SPIN	1	1
sr	34691.1	gain	6.000000	sf	SPIN	1	1
ss	34691.1	gain	6.000000	sf	SPIN	1	1
st	34691.1	gain	6.000000	sf	SPIN	1	1
su	34691.1	gain	6.000000	sf	SPIN	1	1
sv	34691.1	gain	6.000000	sf	SPIN	1	1
sw	34691.1	gain	6.000000	sf	SPIN	1	1
sx	34691.1	gain	6.000000	sf	SPIN	1	1
sy	34691.1	gain	6.000000	sf	SPIN	1	1
sz	34691.1	gain	6.000000	sf	SPIN	1	1
ta	34691.1	gain	6.000000	sf	SPIN	1	1
tb	34691.1	gain	6.000000	sf	SPIN	1	1
tc	34691.1	gain	6.000000	sf	SPIN	1	1
td	34691.1	gain	6.000000	sf	SPIN	1	1
te	34691.1	gain	6.000000	sf	SPIN	1	1
tf	34691.1	gain	6.000000	sf	SPIN	1	1
tg	34691.1	gain	6.000000	sf	SPIN	1	1
th	34691.1	gain	6.000000	sf	SPIN	1	1
ti	34691.1	gain	6.000000	sf	SPIN	1	1
tj	34691.1	gain	6.000000	sf	SPIN	1	1
tk	34691.1	gain	6.000000	sf	SPIN	1	1
tl	34691.1	gain	6.000000	sf	SPIN	1	1
tm	34691.1	gain	6.000000	sf	SPIN	1	1
tn	34691.1	gain	6.000000	sf	SPIN	1	1
to	34691.1	gain	6.000000	sf	SPIN	1	1
tp	34691.1	gain	6.000000	sf	SPIN	1	1
aq	34691.1	gain	6.000000	sf	SPIN	1	1
ar	34691.1	gain	6.000000	sf	SPIN	1	1
at	34691.1	gain	6.000000	sf	SPIN	1	1
au	34691.1	gain	6.000000	sf	SPIN	1	1
av	34691.1	gain	6.000000	sf	SPIN	1	1
aw	34691.1	gain	6.000000	sf	SPIN	1	1
ax	34691.1	gain	6.000000	sf	SPIN	1	1
ay	34691.1	gain	6.000000	sf	SPIN	1	1
az	34691.1	gain	6.000000	sf	SPIN	1	1
ba	34691.1	gain	6.000000	sf	SPIN	1	1
bb	34691.1	gain	6.000000	sf	SPIN	1	1
bc	34691.1	gain	6.000000	sf	SPIN	1	1
bd	34691.1	gain	6.000000	sf	SPIN	1	1
be	34691.1	gain	6.000000	sf	SPIN	1	1
bf	34691.1	gain	6.000000	sf	SPIN	1	1
bg	34691.1	gain	6.000000	sf	SPIN	1	1
bh	34691.1	gain	6.000000	sf	SPIN	1	1
bi	34691.1	gain	6.000000	sf	SPIN	1	1
bj	34691.1	gain	6.000000	sf	SPIN	1	1
bk	34691.1	gain	6.000000	sf	SPIN	1	1
bl	34691.1	gain	6.000000	sf	SPIN	1	1
bm	34691.1	gain	6.000000	sf	SPIN	1	1
bn	34691.1	gain	6.000000	sf	SPIN	1	1
bo	34691.1	gain	6.000000	sf	SPIN	1	1
bp	34691.1	gain	6.000000	sf	SPIN	1	1
bq	34691.1	gain	6.000000	sf	SPIN	1	1
br	34691.1	gain	6.000000	sf	SPIN	1	1
bs	34691.1	gain	6.000000	sf	SPIN	1	1
bt	34691.1	gain	6.000000	sf	SPIN	1	1
bu	34691.1	gain	6.000000	sf	SPIN	1	1
bv	34691.1	gain	6.000000	sf	SPIN	1	1
bv	34691.1	gain	6.000000	sf	SPIN	1	1
bw	34691.1	gain	6.000000	sf	SPIN	1	1
bx	34691.1	gain	6.000000	sf	SPIN	1	1
by	34691.1	gain	6.000000	sf	SPIN	1	1
bz	34691.1	gain	6.000000	sf	SPIN	1	1
ca	34691.1	gain	6.000000	sf	SPIN	1	1
cb	34691.1	gain	6.000000	sf	SPIN	1	1
cc	34691.1	gain	6.000000	sf	SPIN	1	1
cd	34691.1	gain	6.000000	sf	SPIN	1	1
ce	34691.1	gain	6.000000	sf	SPIN	1	1
cf	34691.1	gain	6.000000	sf	SPIN	1	1
cg	34691.1	gain	6.000000	sf	SPIN	1	1
ch	34691.1	gain	6.000000	sf	SPIN	1	1
ci	34691.1	gain	6.000000	sf	SPIN	1	1
cj	34691.1	gain	6.000000	sf	SPIN	1	1
ck	34691.1	gain	6.000000	sf	SPIN	1	1
cl	34691.1	gain	6.000000	sf	SPIN	1	1
cm	34691.1	gain	6.000000	sf	SPIN	1	1
cn	34691.1	gain	6.000000	sf	SPIN	1	1
co	34691.1	gain	6.000000	sf	SPIN	1	1
cp	34691.1	gain	6.000000	sf	SPIN	1	1
cq	34691.1	gain	6.000000	sf	SPIN	1	1
cr	34691.1	gain	6.000000	sf	SPIN	1	1
cs	34691.1	gain	6.000000	sf	SPIN	1	1
ct	34691.1	gain	6.000000	sf	SPIN	1	1
cu	34691.1	gain	6.000000	sf	SPIN	1	1
cv	34691.1	gain	6.000000	sf	SPIN	1	1
cw	34691.1	gain	6.000000	sf	SPIN	1	1
cx	34691.1	gain	6.000000	sf	SPIN	1	1
cy	34691.1	gain	6.000000	sf	SPIN	1	1
cz	34691.1	gain	6.000000	sf	SPIN	1	1

HMQC (600 MHz, CD₃OD)

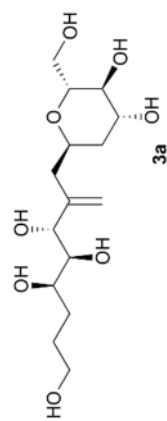


exp3_080604

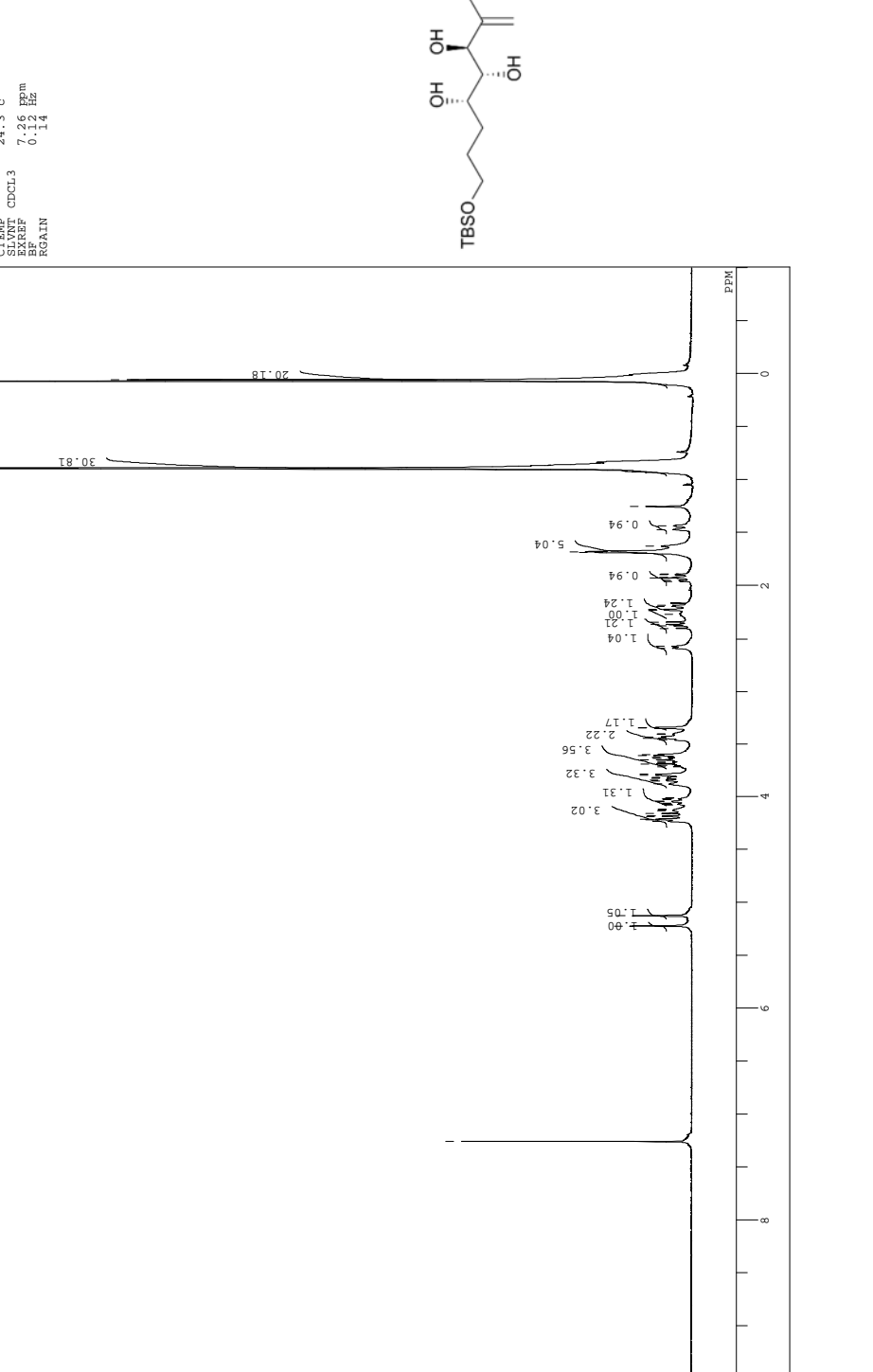
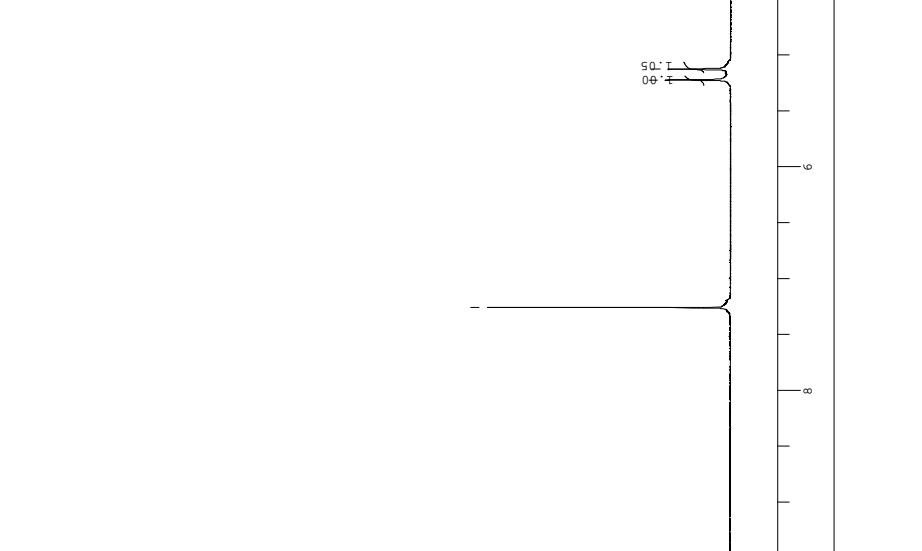
SAMPLES ACQUISITION ARRAY
 date Dec 14 2017 hr in phann
 name 0806 array 400
 sample 0806 7 arrayid
 SW ACQUISITION hsq014 4408 1 phase
 AT 9.150 temp not used . 2
 AP 2866 gain not used 66
 AS 4400 sp1.0 6
 AS 1.000 sp1.01 6
 AS 1.000 sp1.01 6
 AS 32 g1 0.001600
 AS 36199.1 sp3 0.001600
 AS 390 sp4 0.001600
 AS 44000 sp5 0.001600
 Phase arrayed P2 PROCESSING
 PRESENTATION 00 -0.075
 namecode n abs not used
 wct 2 in 4096
 TRANSMITTER P1 PROCESSING
 LA 594.771 sp1 0.0016
 LOF 594.8 sp1 not used
 type 59 501 2048
 PW 9.900 DISPLAY
 DECOUPLER 659.2
 ON C13 WP 2777.2
 OFF 1544.0 WP 2777.2
 SW 1544.0 WP 2777.2
 decouple W4 channel W11 25134.3
 Amf 15688 rfp 1293.0
 spwr 40 rfp1 2564.3
 pwr1 85 rfp1 2564.3
 pwr 8.000 WC 2607 1584.0
 f1sh 144.0 ac 0
 f1wh 8.0 WC2 148.0
 ADIABATIC ac2 0
 purification comm: sub- vs 218
 3000000 2500000
 p001v1180 54 at cdc av 4
 p001v180 490.0



HMBC (600 MHz, CD₃OD)

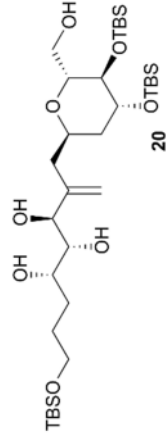
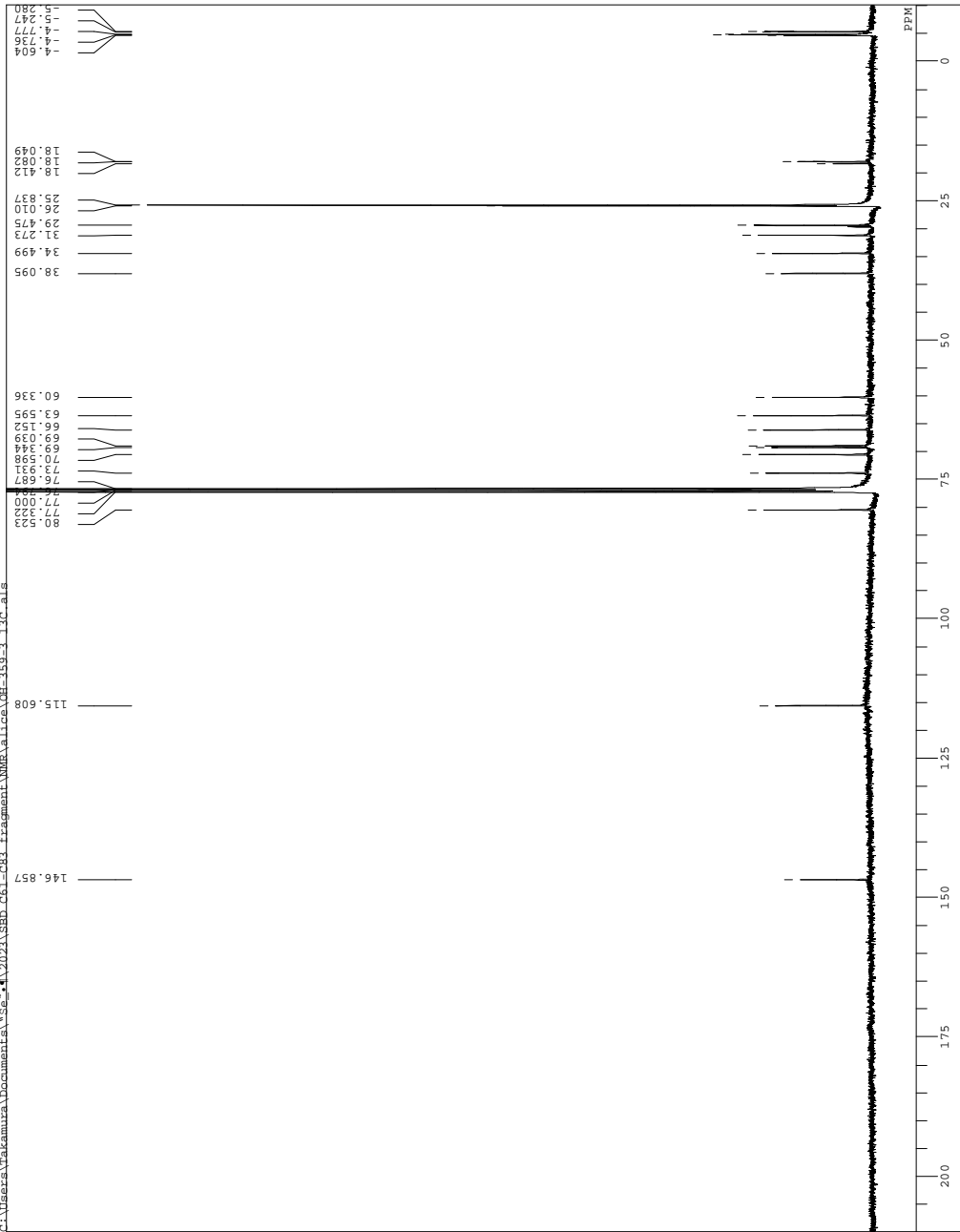


C:\Users\takamura\Documents\Se*\4\2023\SRD_C61-CB3_Fragment\MRE\alica\OH-359-3_als
 FILE OH-359-3_als
 DATE Tue Jan 30 22:11:20 2018
 DATIM
 OBNUC 1H
 EXPRD NON
 EXPRF
 OBSST 399.65 MHz
 OBSST 124.00 MHz
 OBSST 10500.00 Hz
 FREQ0 7953760 Hz
 SCANS 4.0000
 PD QTM 2.9010 sec
 PD QTM 6.40 usec
 FW1
 LRNUC 1H
 SLVNT CDCL3 24.3 C
 EXREF 7.26 ppm
 RGAIN 0.14



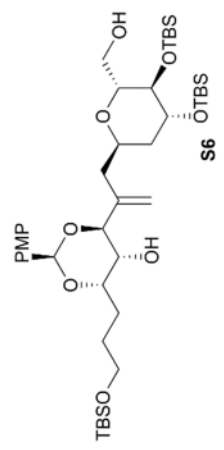
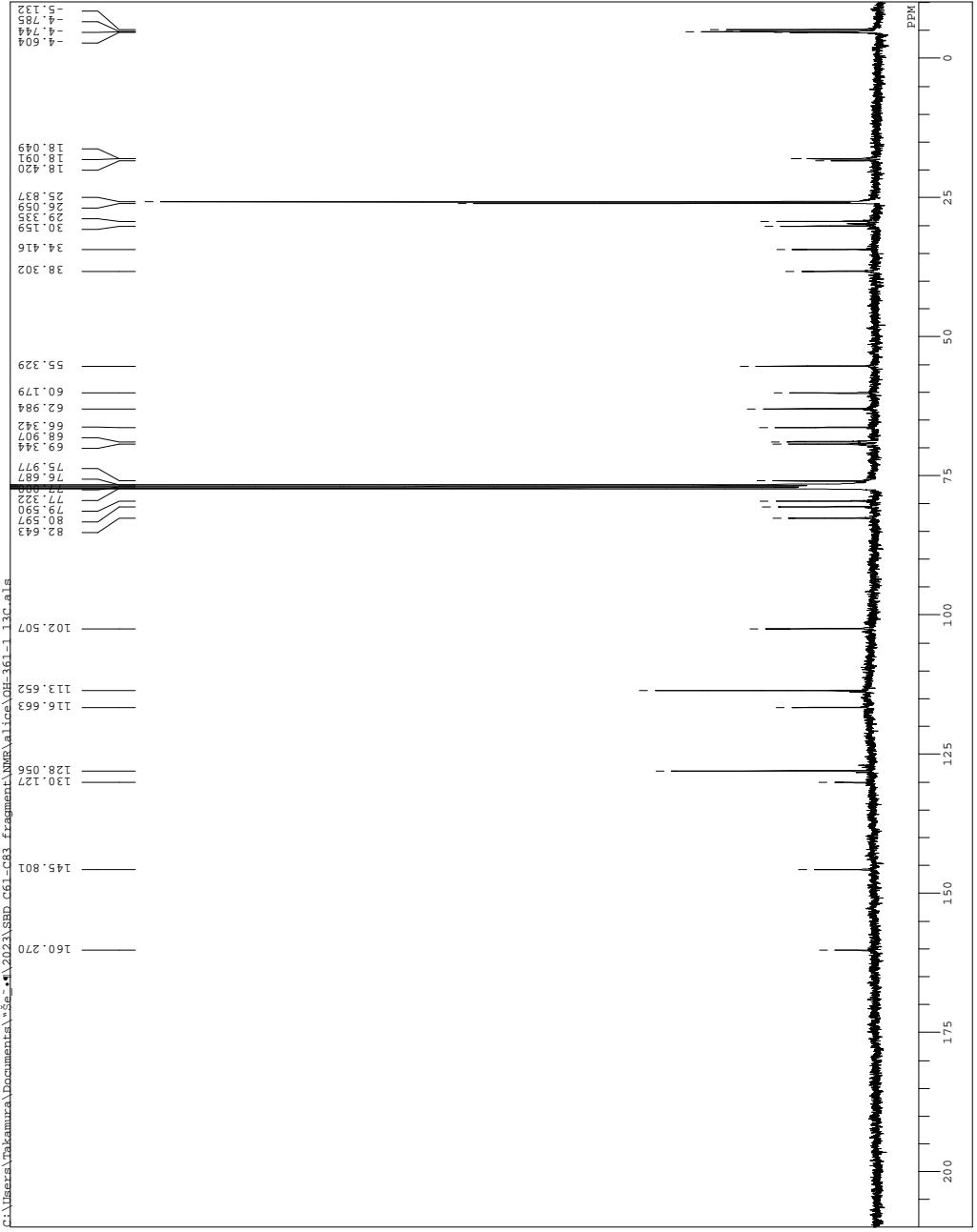
C:\Users\Takamura\Documents\se*\2021\SRD_c61_c83_fragment\MMR\alic\OH-359-3_13c_als

OH-359-3_13c.als
COMPT Mg Jan 31 06:39:51 2018
ORBIT 13C
EXMOD BCM
OBSFQ 100.40 MHz
OBSF2 10500.00 Hz
PCINT 32768
SCANS 2711000 Hz
ACQTM 1.2859 sec
PULP 1.7940 sec
PRG1 6.60 usec
IRNUC 1H 27.9 c
CTEMP CDCL3 77.00 PPM
EXREF BF 2.00 Hz
RGAIN 25

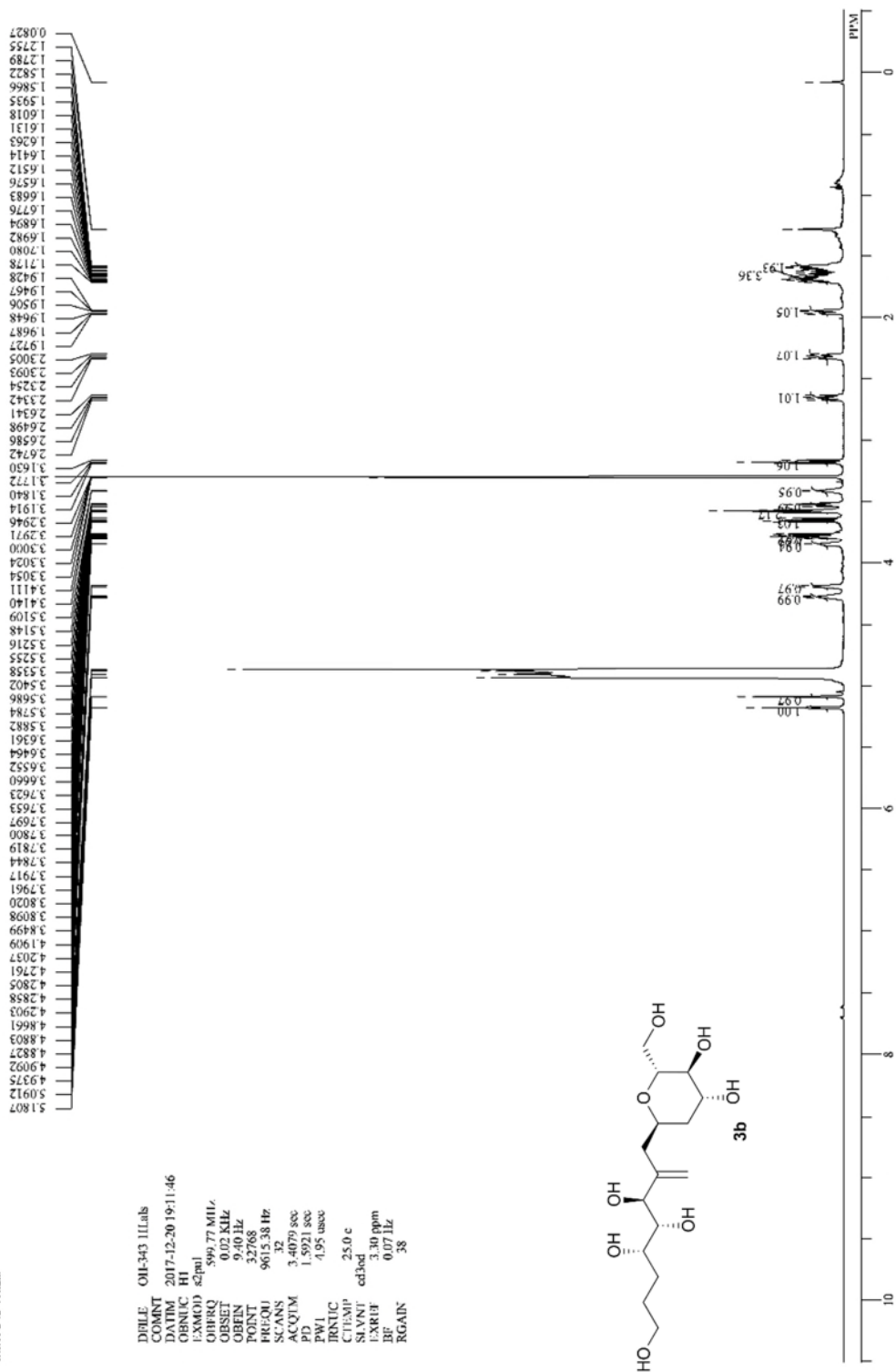


C:\Users\takamura\Documents\Se_#\2023\SDP_C61-CB3_fragment\NMR\data\OH-361-1_13C.nls

OFSI OH-361-1_13C.nls
 COMMT Sat Feb 03 06:52:00 2018
 DATIM Sat Feb 03 06:52:00 2018
 OBANOC 13C
 OBPRO BCR
 OBPRO 100.40 MHz
 OBSEI 125.00 MHz
 OBSEI 10532768 Hz
 POINT 27173.90 Hz
 FREQU 10000 sec
 SCANS 1.7940 sec
 PDQTN 6.80 usec
 P1 27.9 c
 CTEMP CDCL3 77.00 Ppm
 SLVNT CDCL3 77.00 Ppm
 SREF 2.25
 RGAIN

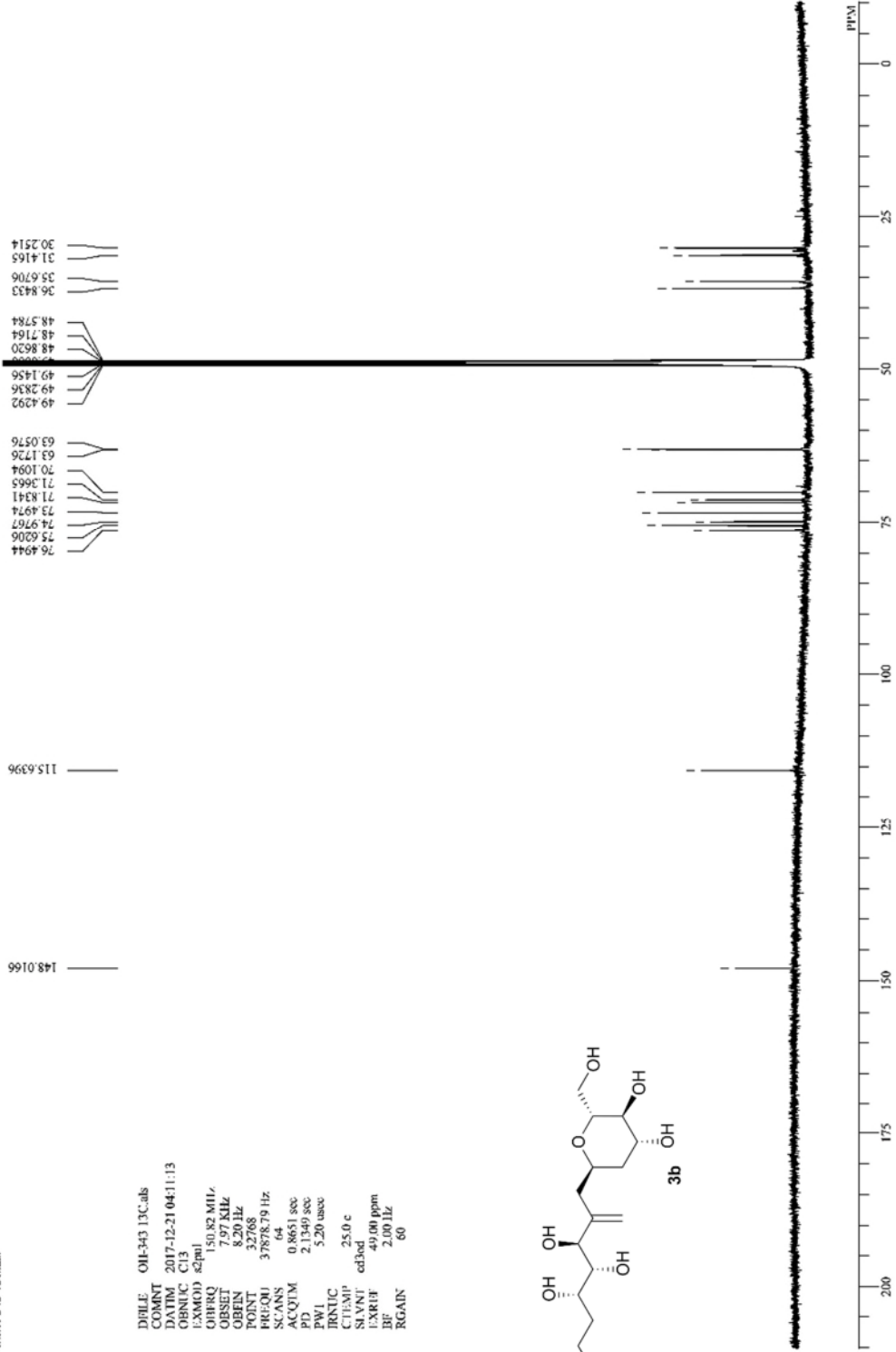
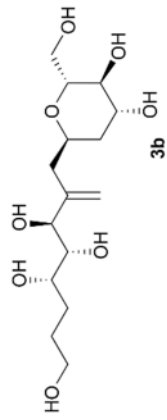


13OH-343 1H.nk

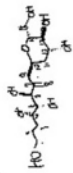


13001-343 13C.als

DIRILE OII-343 13C.als
COMNT
DATIM 2017-12-21 04:11:13
OBJNIC C13
EXMOD s2(m)
OFRQ 150.82 MHz
OBSF 7.97 kHz
OBEN 8.20 Hz
POINT 32768
PREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PWL 5.20 usoc
RNUC
CNAME 25.0 c
SINUT ed3ad
EXRTF 49.00 ppm
RF 2.00 Hz
RGAIN 60



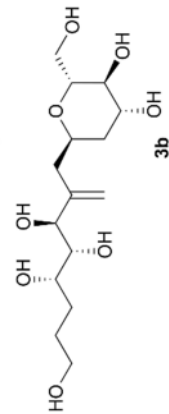
COSY



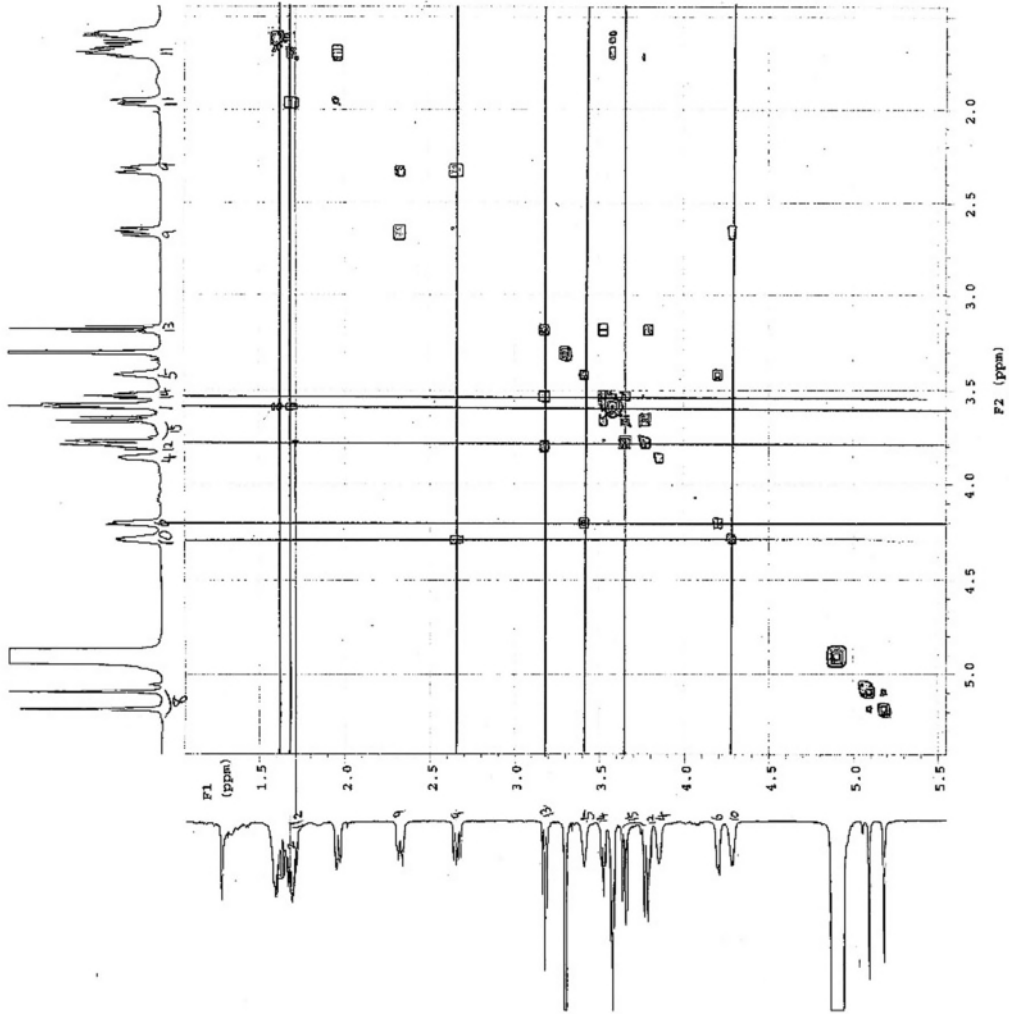
```

exp3 8057
=====
date_ 2017 11 28 11:14:58
solvent_ cd3od
sample_ 4094
=====
ACQUISITION
pr 5615.4 temp not used
at 6.136 gain 16
sp 4480 sfls 0
ss 32 sb -0.075
dl 1.000 sbw not used
nt 16 fn 4094
=====
2D ACQUISITION
ac 5615.4 sbw -0.075
sd 190 sbw not used
sz 0 proc1
=====
PRESENTATION
satmode n fcn1 DEPTAN
wt 864.1 n sp 2188.1
sc TRANSMITTE NI sp 2596.2
kErn 599.770 wfl 2596.2
totf 599.7 rfl 3190.4
tprc 59 rfp 3190.3
pr 9.909 fill 3186.2
=====
PARAMETERS
S1A18 0.001000 WC PLOT 198.0
EVALUO 1.000 RC
SPRSH 0.000500 WC2 198.0
dn DRUMFLAR C13 VS 282
cm non ch. cdc 4r 2
  
```

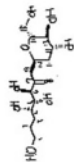
¹H-¹H COSY (600 MHz, CD₃OD)



3b

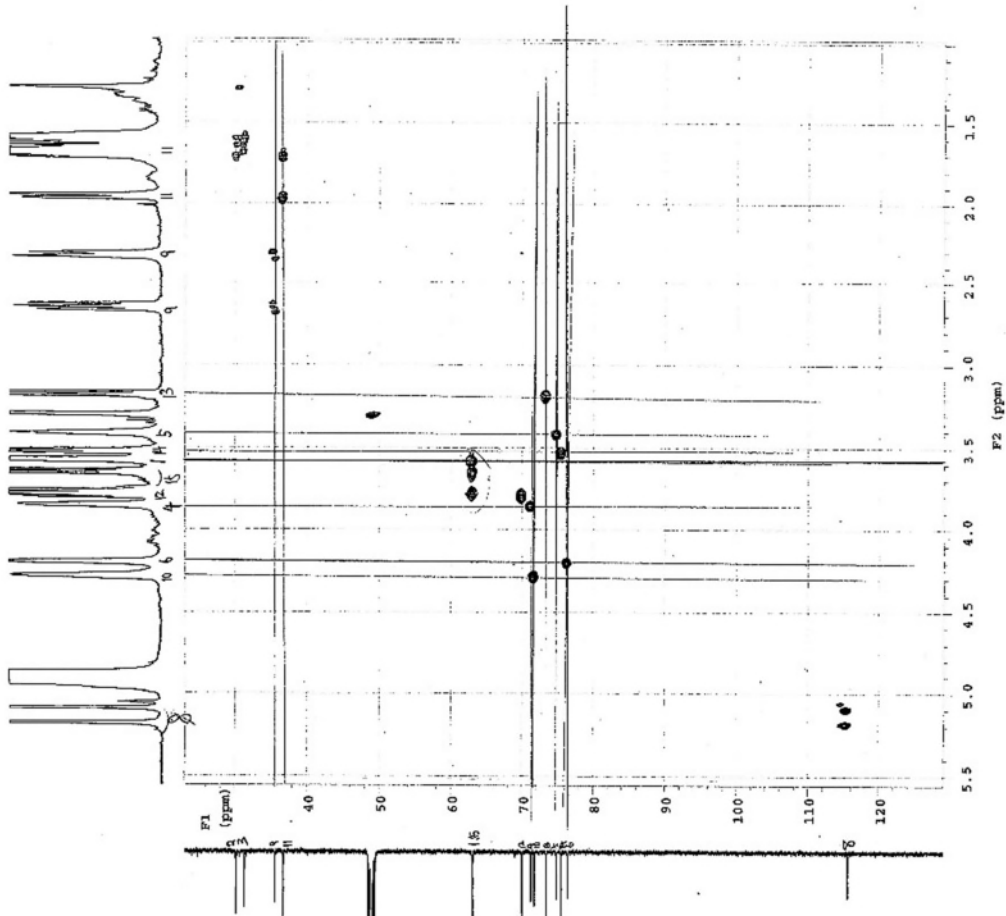


HMQC

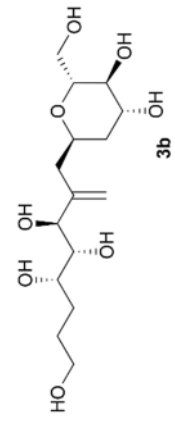


```

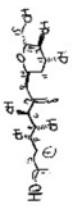
exp3 gsmqc
Date: Tue 20 2017 08:51:47 AM
Sample: 400
Acquisition: 9611.4
P1: 0.150
P2: 2.000
P3: 0.000
P4: 1.000
P5: 1.000
P6: 1.000
P7: 1.000
P8: 1.000
P9: 1.000
P10: 1.000
P11: 1.000
P12: 1.000
P13: 1.000
P14: 1.000
P15: 1.000
P16: 1.000
P17: 1.000
P18: 1.000
P19: 1.000
P20: 1.000
P21: 1.000
P22: 1.000
P23: 1.000
P24: 1.000
P25: 1.000
P26: 1.000
P27: 1.000
P28: 1.000
P29: 1.000
P30: 1.000
P31: 1.000
P32: 1.000
P33: 1.000
P34: 1.000
P35: 1.000
P36: 1.000
P37: 1.000
P38: 1.000
P39: 1.000
P40: 1.000
P41: 1.000
P42: 1.000
P43: 1.000
P44: 1.000
P45: 1.000
P46: 1.000
P47: 1.000
P48: 1.000
P49: 1.000
P50: 1.000
P51: 1.000
P52: 1.000
P53: 1.000
P54: 1.000
P55: 1.000
P56: 1.000
P57: 1.000
P58: 1.000
P59: 1.000
P60: 1.000
P61: 1.000
P62: 1.000
P63: 1.000
P64: 1.000
P65: 1.000
P66: 1.000
P67: 1.000
P68: 1.000
P69: 1.000
P70: 1.000
P71: 1.000
P72: 1.000
P73: 1.000
P74: 1.000
P75: 1.000
P76: 1.000
P77: 1.000
P78: 1.000
P79: 1.000
P80: 1.000
P81: 1.000
P82: 1.000
P83: 1.000
P84: 1.000
P85: 1.000
P86: 1.000
P87: 1.000
P88: 1.000
P89: 1.000
P90: 1.000
P91: 1.000
P92: 1.000
P93: 1.000
P94: 1.000
P95: 1.000
P96: 1.000
P97: 1.000
P98: 1.000
P99: 1.000
P100: 1.000
  
```



HMQC (600 MHz, CD₃OD)

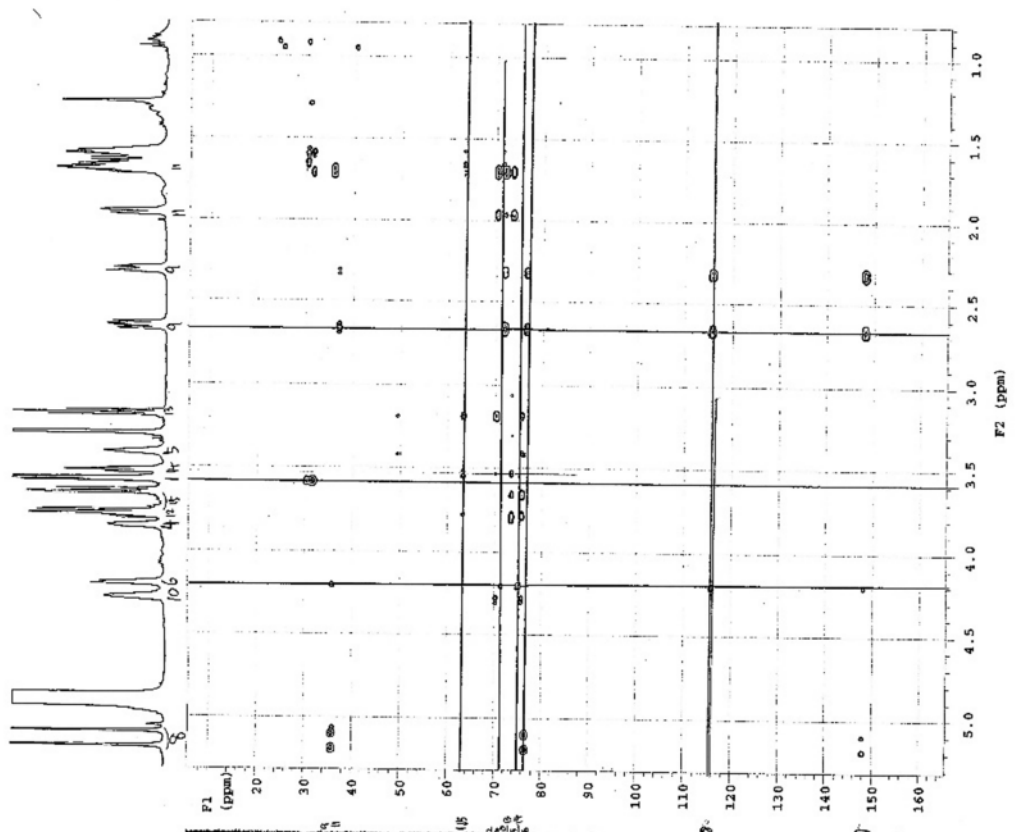


HMBC

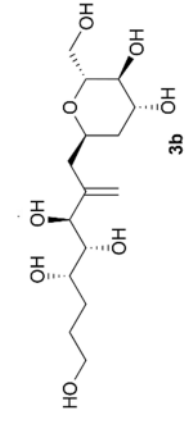


EXP3 080620

DATE	20 2017	TIME	08:15
SOLVENT	CDCl3	CONC	100.0
ACQUISITION	9615.4	SCANS	4608
NUC1	13C	CPD	1
NUC2	1H	PCPD	1
PPM1	0.150	TEMP	300.2
CPD	2884	GCN	60
AC	4000	ORIGIN	0
DC	1.00	CHARGE	0
RE	32	FILE	0.001000
2D ACQUISITION	9615.4	SCANS	1500
NUC1	13C	CPD	1
NUC2	1H	PCPD	1
PPM1	0.150	TEMP	300.2
CPD	2884	GCN	60
AC	4000	ORIGIN	0
DC	1.00	CHARGE	0
RE	32	FILE	0.001000
TRANSMITTER	H1	RECEIVER	H1
PROBHD	5mm QNP 1H/13		
PROBHT	5mm QNP 1H/13		
PROBHD2	5mm QNP 1H/13		
PROBHT2	5mm QNP 1H/13		
PROBHD3	5mm QNP 1H/13		
PROBHT3	5mm QNP 1H/13		

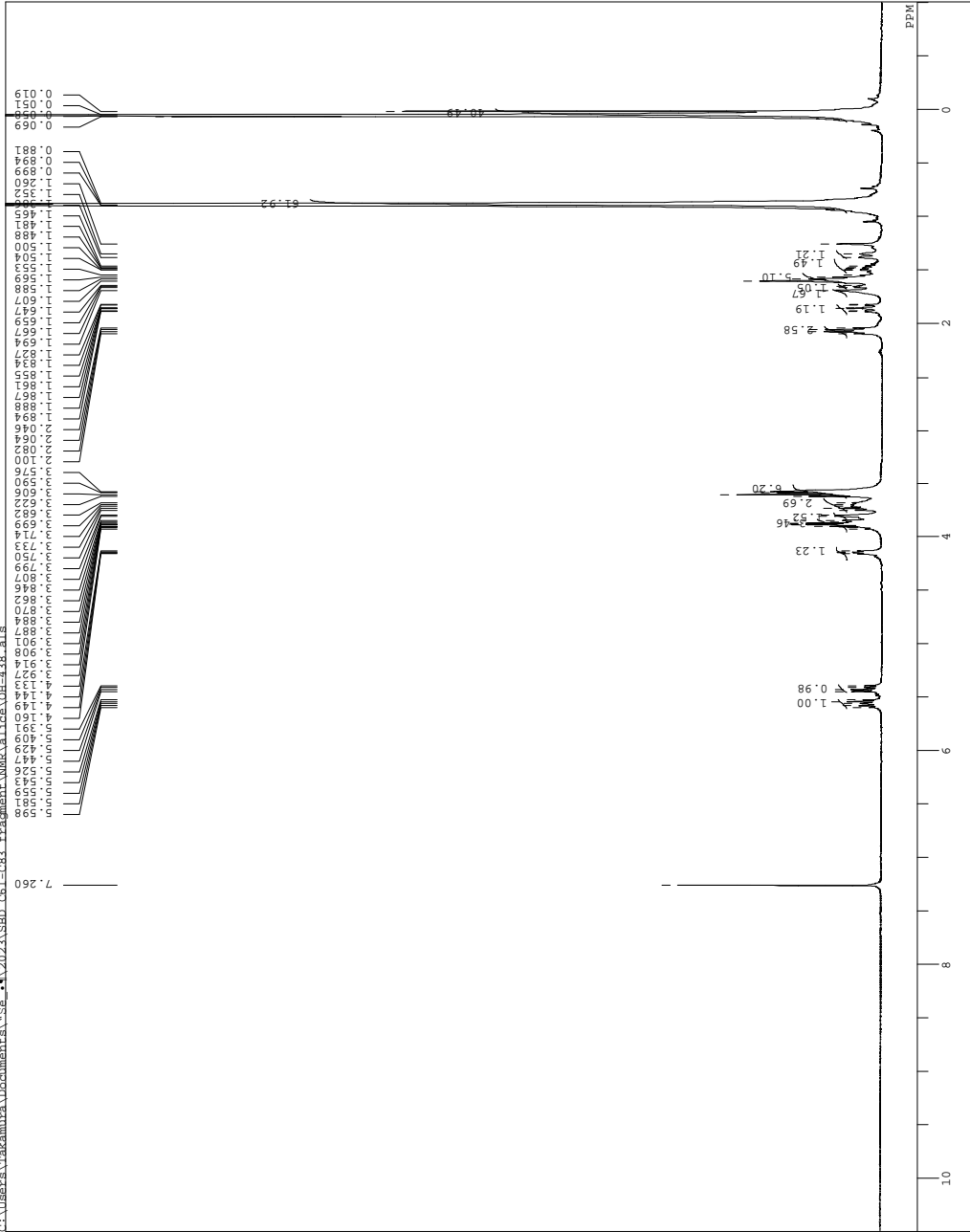


HMBC (600 MHz, CD₃OD)

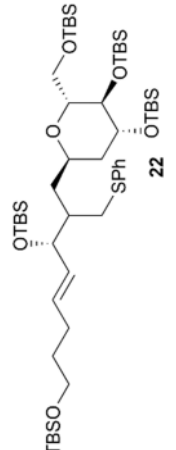
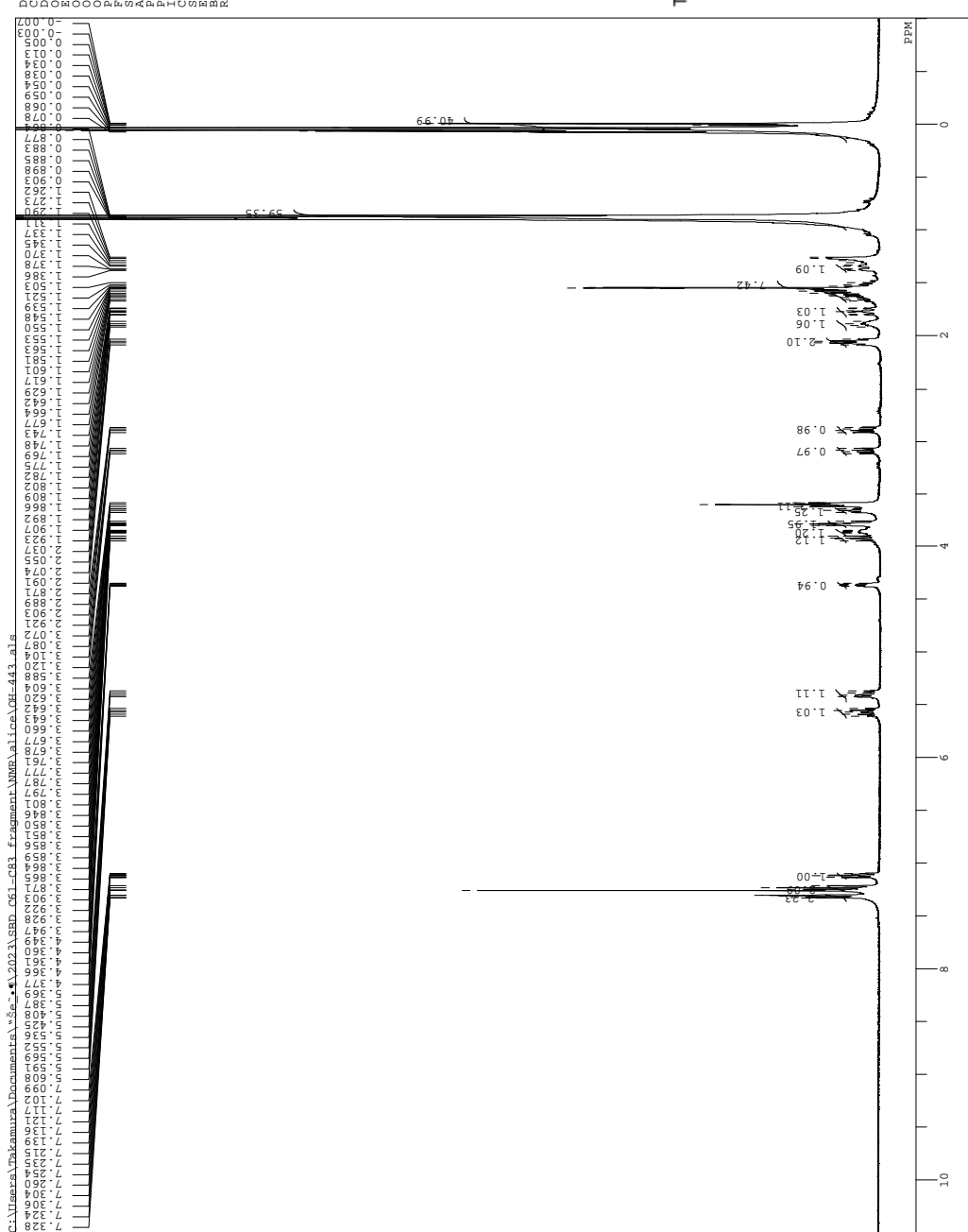


```

PFILE OH-438.als
CONV Mri Jul 23 20:20:44 2018
CIRCUIT 1
EXMOD NON
IRNUC 1H 399.65 MHz
PROBHD 5
PULPROG zgpg30
AQ 124.00 MHz
RG 10500.00 Hz
DELTA 7.26
PC 1.00
SFO 300.13 MHz
F2 300.13 MHz
NUC1 1H
NUC2 13C
SCANS 8
ACQTM 4.093 sec
RG 2.640 MHz
PWL 6.40 uSec
IRNUC 1H 27.6 c
CIRCUIT 1
SLANT CDCL3
EXREF 7.26 ppm
RGAIN 0.12 Hz
RGAIN
  
```

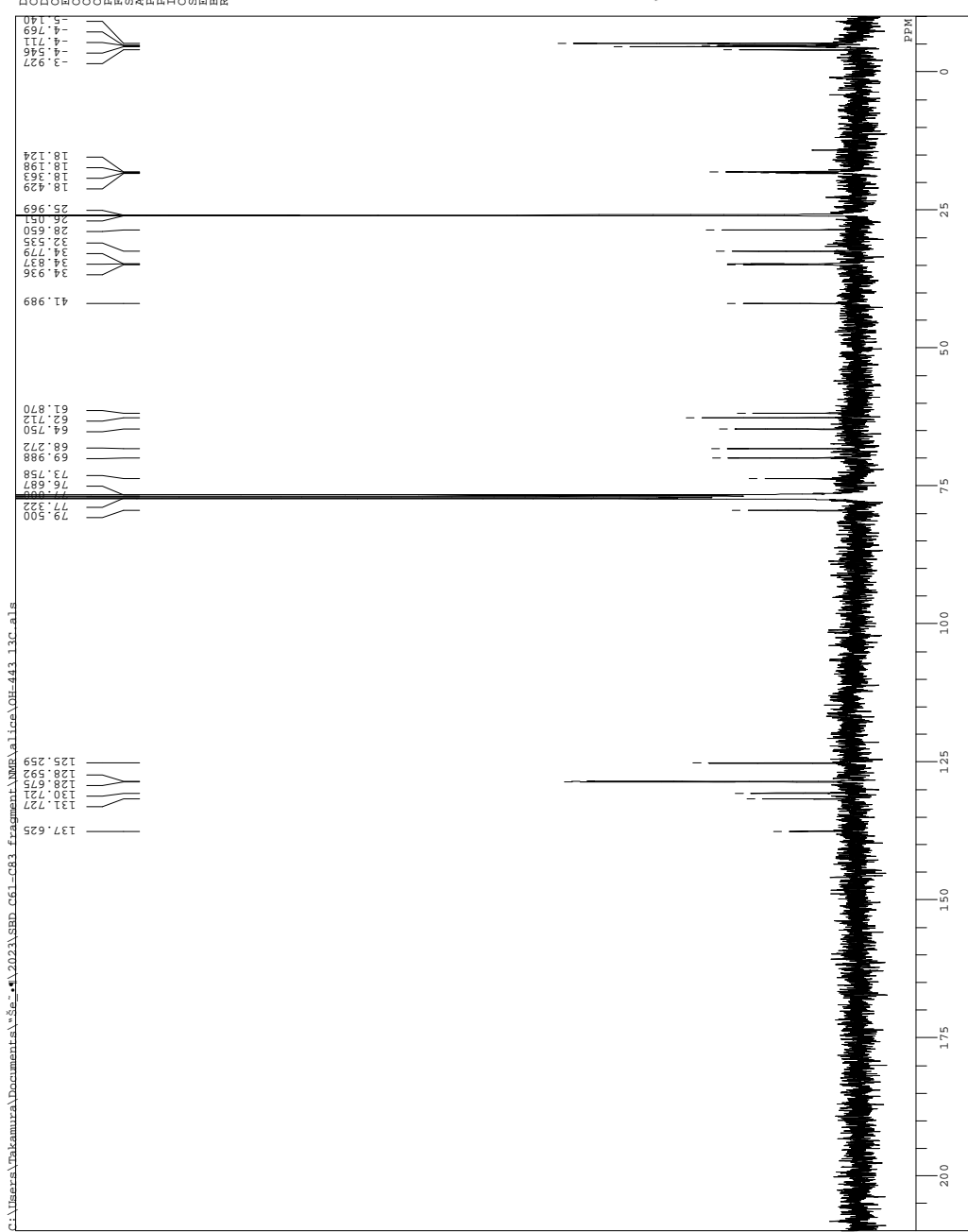


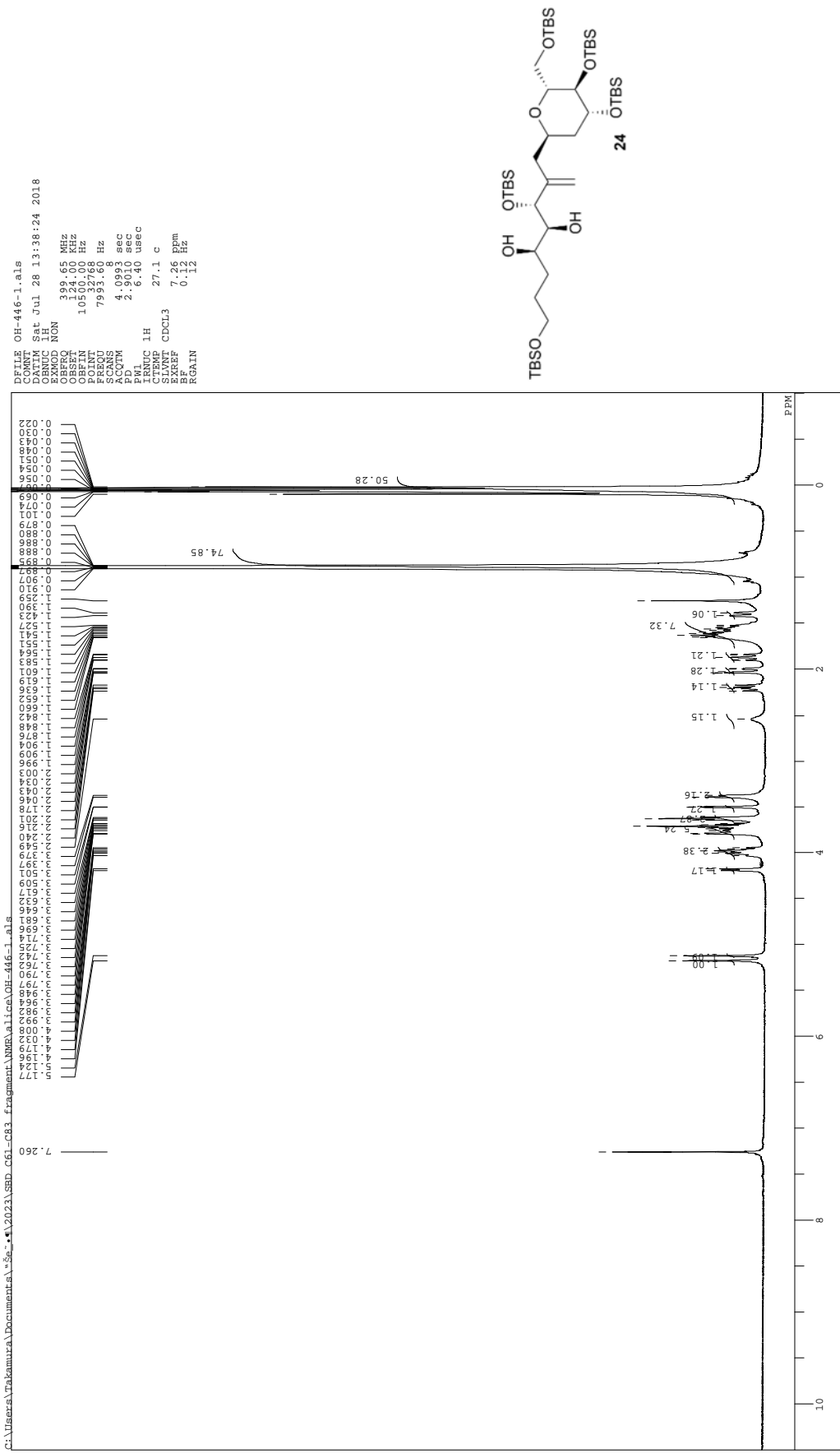
C:\Users\Takamura\Documents\4-5c-4\2023\SED_C61-C63_fragment\NMR\data\CH-443.a1s
 DF L1: 0H-443.a1s
 Date_ Time: Thu Jul 26 16:12:27 2018
 Operator: CH
 EXMDC: NON
 OBSF1: 399.55 MHz
 OBSF2: 124.00 KHz
 OBF1N: 10500.00 Hz
 FREQ1: 79927.60 Hz
 F2: 0.000000
 ACQTM: 4.0993 sec
 PULPROG: zgpg30
 PULP1: 2.640 usec
 PULPROG2: none
 IRNUC1: 1H
 IRNUC2: 13C
 SLOWT: CDCL3
 EXREF: 7.26 ppm
 REF1: 0.12 Hz
 REF2: none
 REF3: none



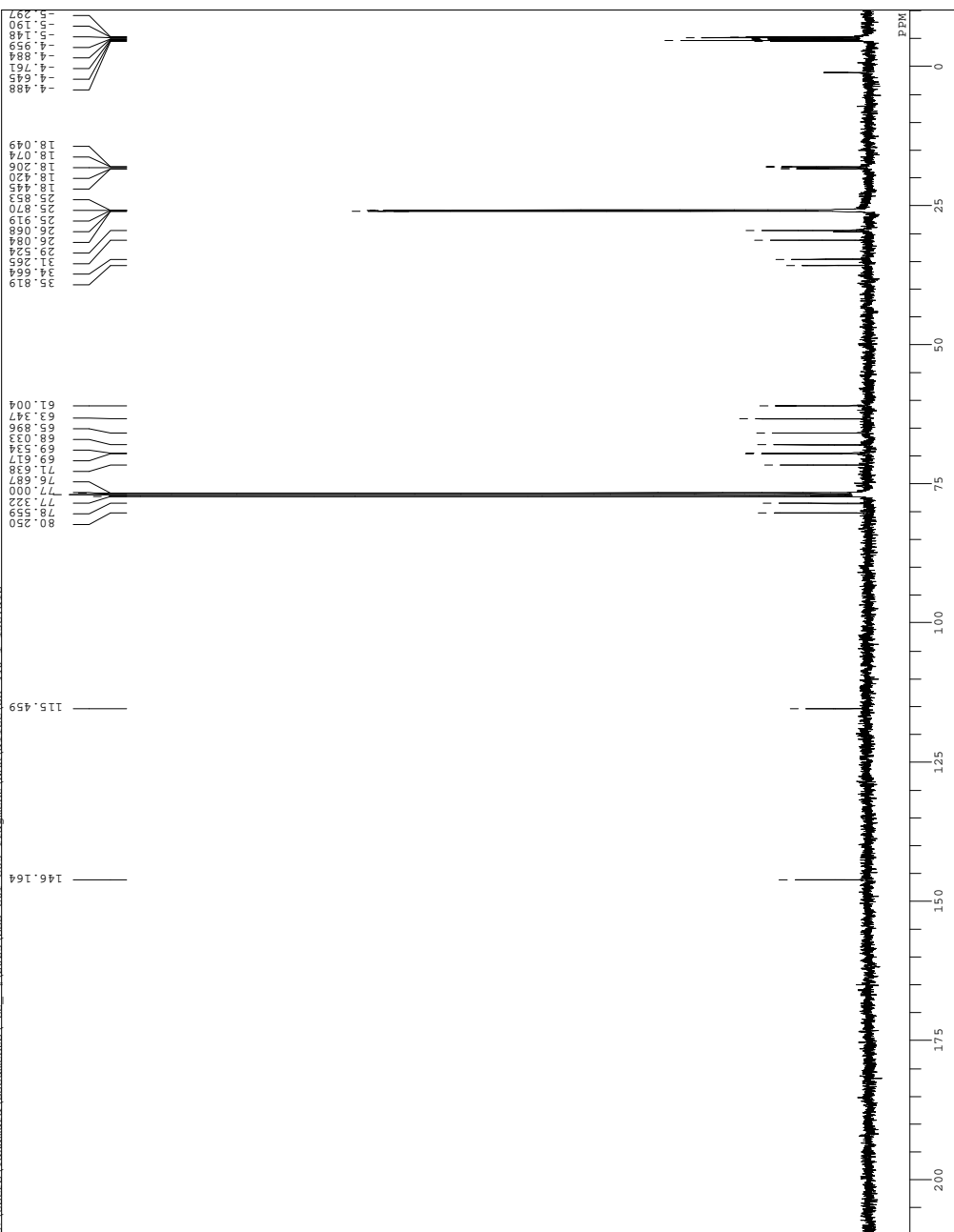
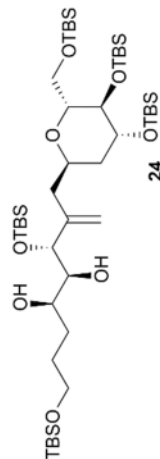
C:\Users\Takamura\Documents\3e-4\2023\SED_C61-CB3_fragment_NMR\alice\OH-443_13C_als

DFILE OH-443_13C_als
 DATE_ TIME Thu Jul 26 17:36:03 2018
 CONV 13C
 EXMOD BCM
 IRNUC 100.40 MHz
 OBSFQ 125.00 KHz
 OBSF1 10500.00 Hz
 PRPT 27173.90 Hz
 SCANS 1560
 ACQTM 1.20000 sec
 PULP 1.60000 usec
 PW1
 IRNUC 1H 29.3 c
 CH1P CDCL3
 SLWT EXREF 77.00 PPM
 EXREF 2.00 Hz
 RGAIN



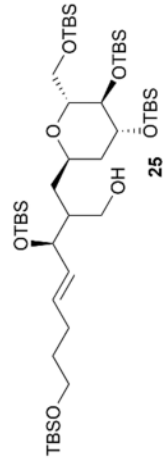
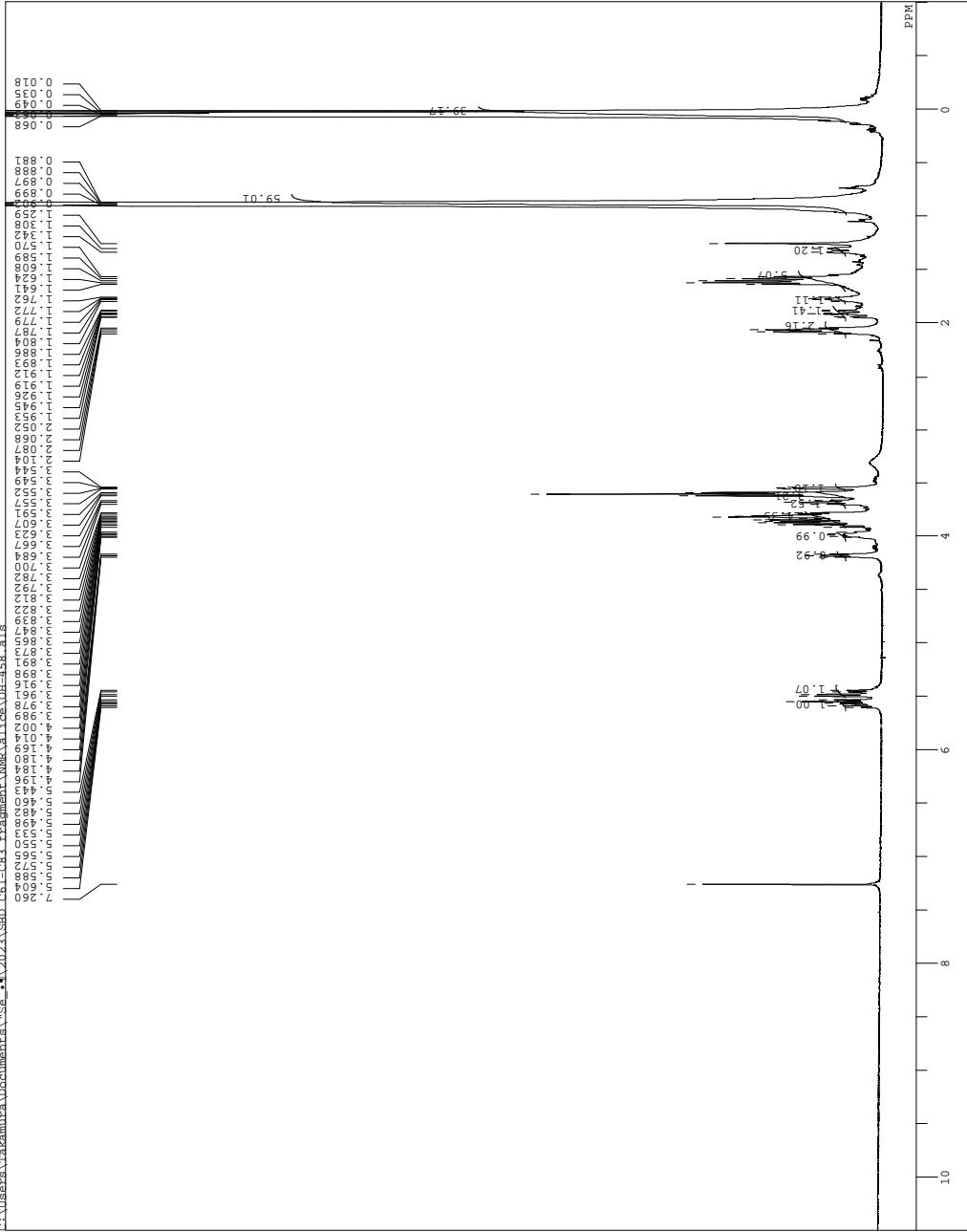


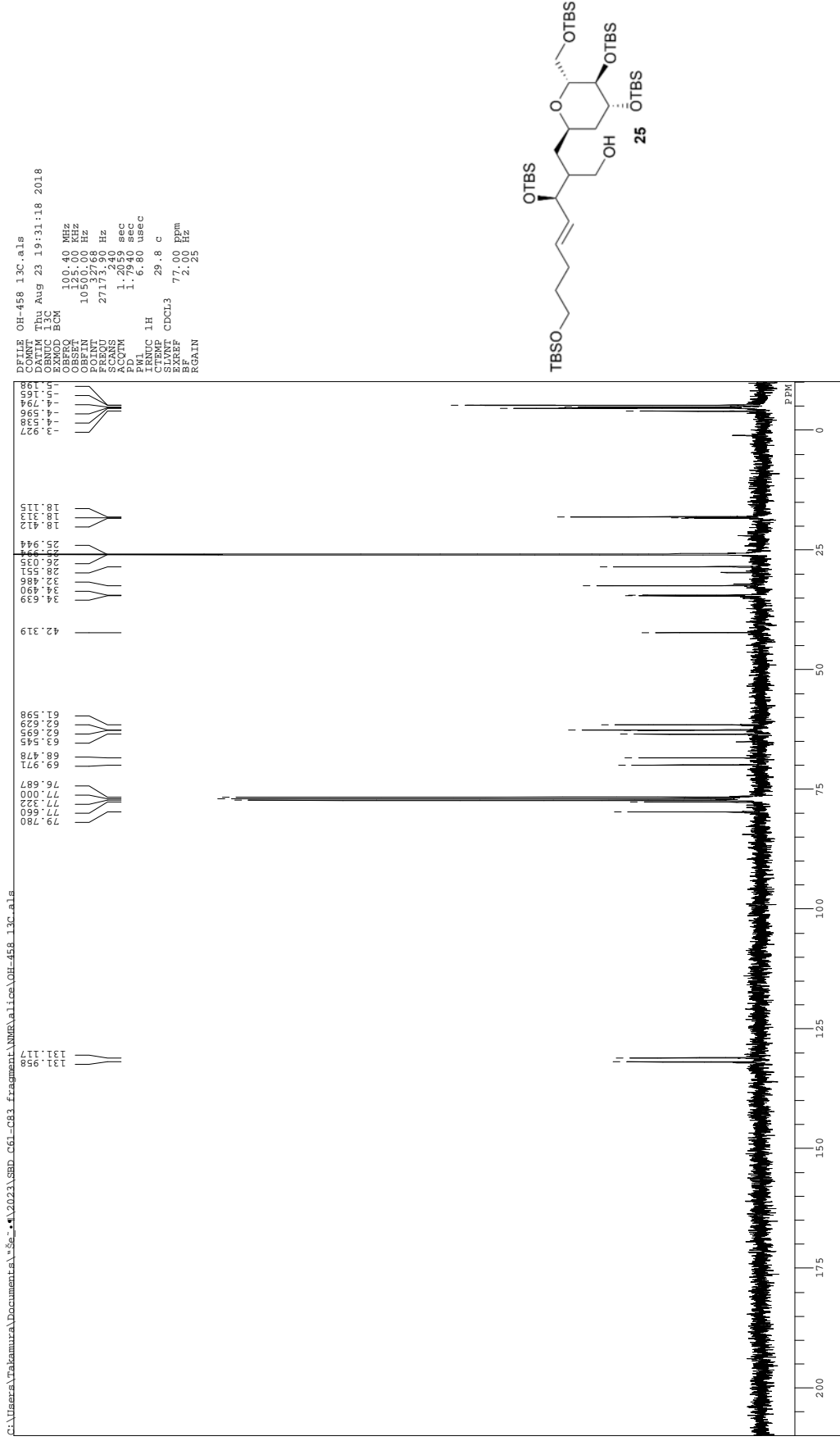
DP46 OH-446-1 13C-als
 DATE_ Sat Jul 28 14:35:39 2018
 DATA 13C
 INSTRUM NUC1
 PROCNO 1
 F2 F4
 CMPTED 1
 OBSERV 100.40 MHz
 OBSF2 125.00 KHz
 OBSF1 10650.00 Hz
 FREQ 27173.99 Hz
 PROC 744
 SCANS 1
 P1 1.790 sec
 PD 1.680 usec
 PWD 29.1 C
 CRUC 1H
 CRUC 1H
 ACQ 1H
 SLSVNT CDCL3 77.00 PPM
 EXREF 2.24 Hz
 RGAIN



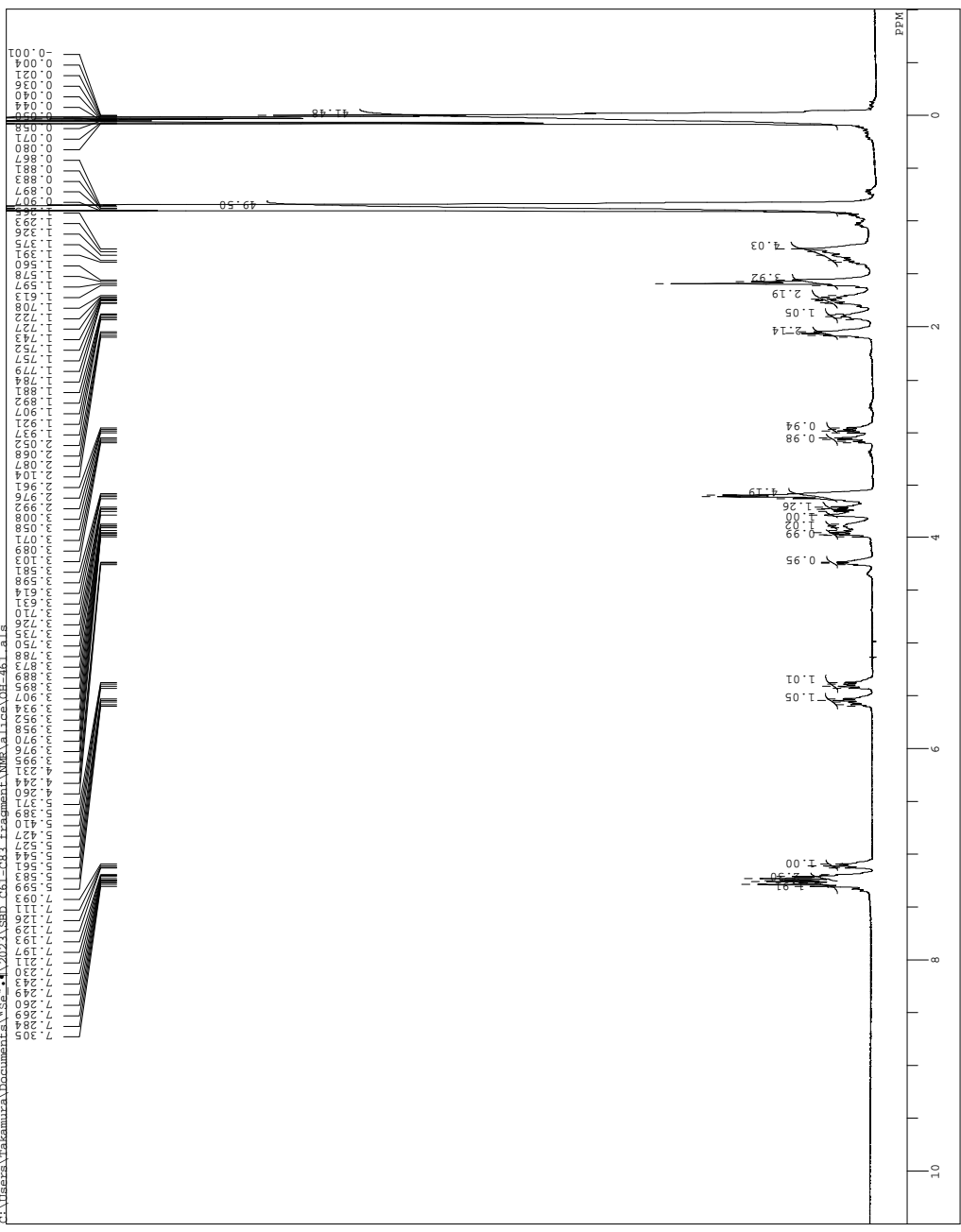
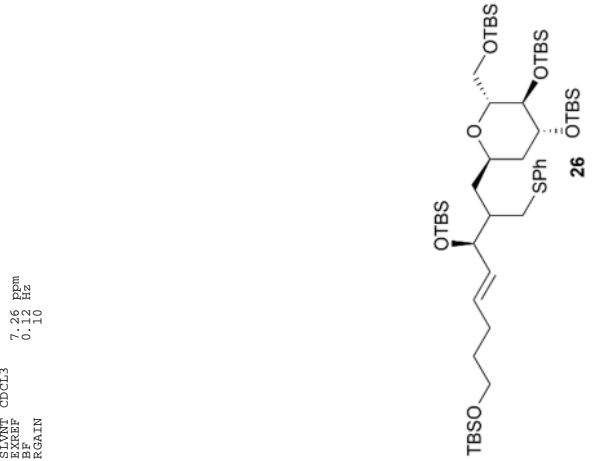
C:\Users\takamura\Documents\Se...*\2023\SD_C61-C83_Fragment\NMR\Alice\OH-458.a1s

DTF: OH-458.a1s
COMT:
DATE: Thu Aug 23 19:15:52 2018
NAME:
PROC:
PULSE:
PROG:
RETO:
SOLV:
NAME:
DATE:
TIME:
FREQ: 399.65 MHz
PULP: 124.00 kHz
PULW: 10.000000 Hz
PULPR: 37.68 Hz
FREQ: 7993.60 Hz
SOLV:
ACQ: 4.0983 sec
PROC: 2.9010 sec
PULP: 6.40 usec
PULW: 1H
PULPR: 27.7 c
SOLV: CDCL3
SOLV: 7.56 ppm
REF: 0.12 Hz
RGAIN: 0.19



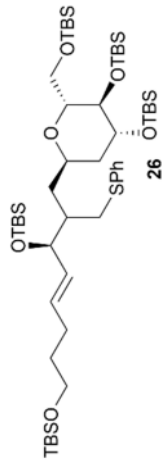
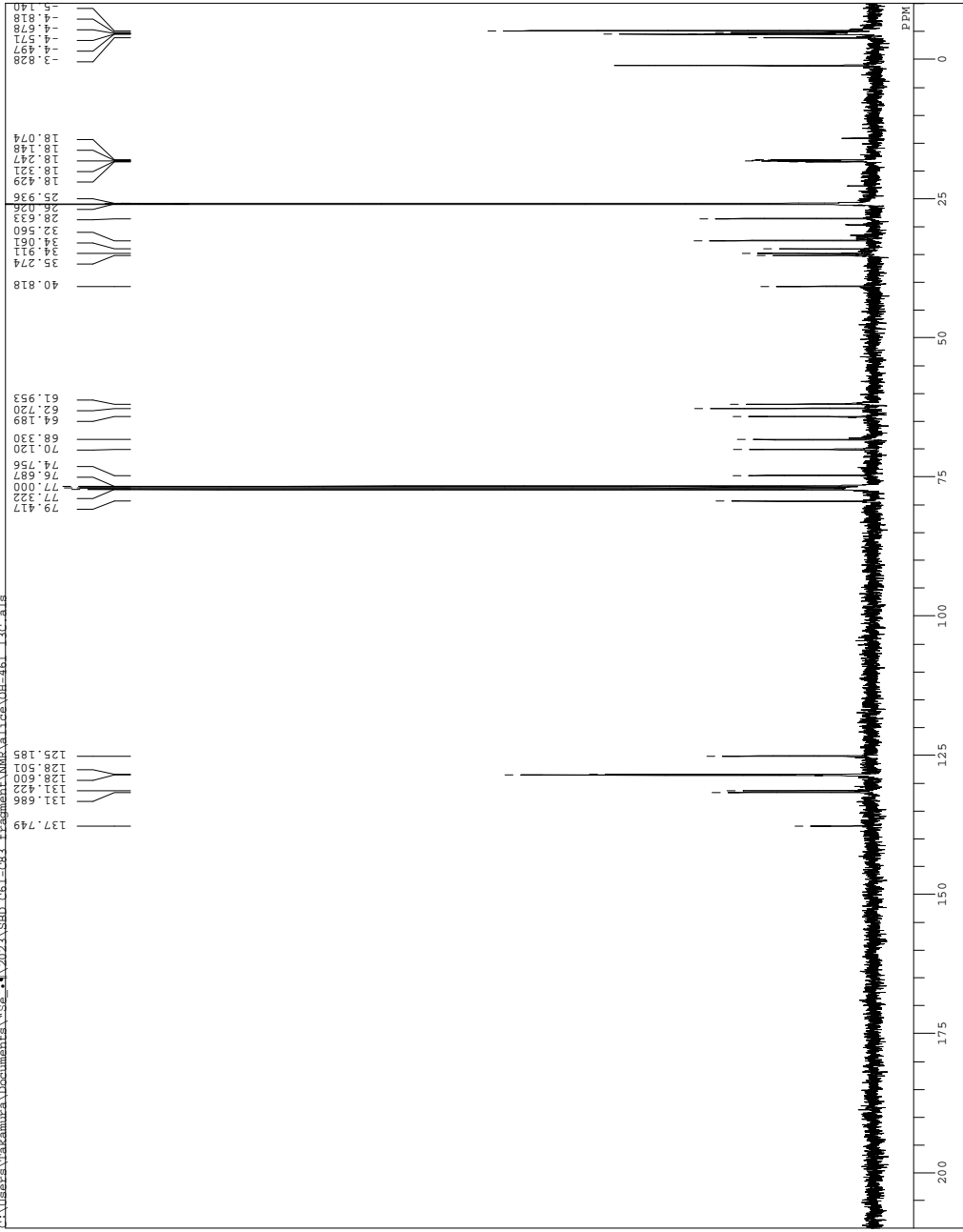


C:\Users\Takamura\Documents\Se...1\2021\SHD_061-C81-Fragment\NMR\alica\OH-461_als
 FILE OH-461_als
 DATE Mon Aug 27 16:22:39 2018
 INSTR LH
 ORBITON
 PULPROG zgpg30
 PROCNO 1
 F2 399.65 MHz
 F1 124.00 KHz
 OFFSET 10500.00 Hz
 AQC 1.00000000
 FREQ0 79931.00 Hz
 FREQ1 79931.00 Hz
 F2OFF 0.00000000
 SCANS 8
 DS 4.00000000
 P1 2.00000000 sec
 P2 6.40000000 usec
 P3 0.00000000
 P4 0.00000000
 P5 0.00000000
 P6 0.00000000
 P7 0.00000000
 P8 0.00000000
 P9 0.00000000
 P10 0.00000000
 P11 0.00000000
 IRNUC LH 27.9 C
 SFO 124.00000000 MHz
 SLVNT CDCL3
 EXREF 7.26 ppm
 RGAIN 0.10 Hz



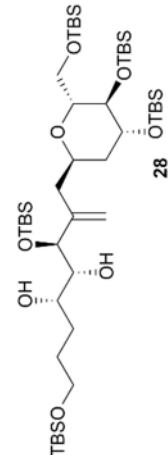
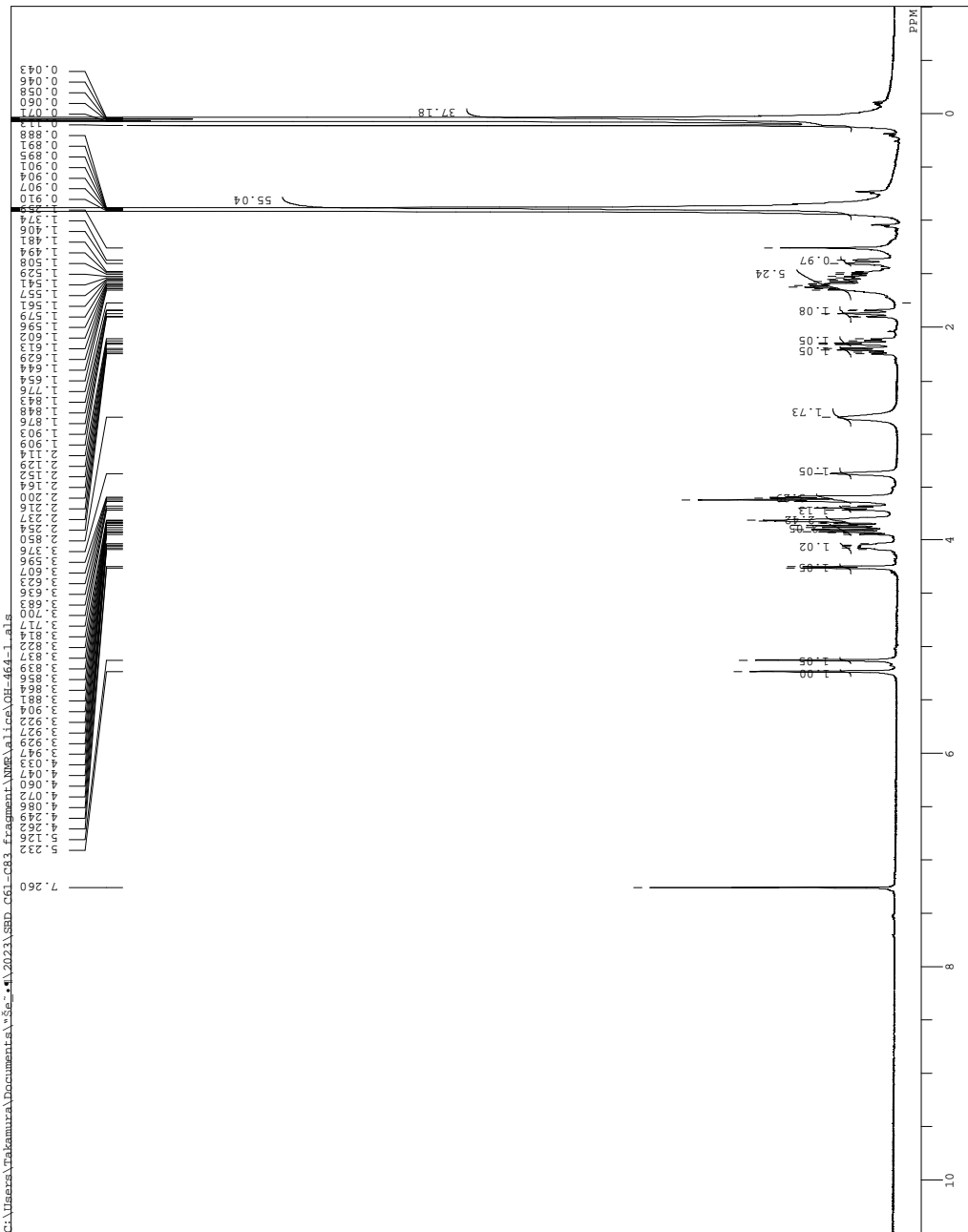
C:\Users\takamura\Documents\Seq_4\2023\SD_C61-CH3_fragment\NMR\alice\OH-461_13C_als

F1 F2 OH-461_13C_als
 COM1
 DATE_ Mon Aug 27 17:06:11 2018
 GENUC 13C
 ECH
 OBSFRO 100.40 MHz
 OBSF2 125.00 KHz
 PULPROG zgpg30
 FREQ1 27173.30 Hz
 SCANS 1.7060 sec
 PD 1.7940 sec
 P1 6.80 usec
 P2 29.4 c
 CTEMS 1H
 SLVNT CDCL3
 SLSF 77.00 ppm
 HXREF
 RGAIN 2.25



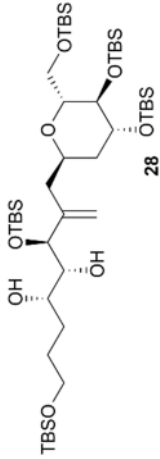
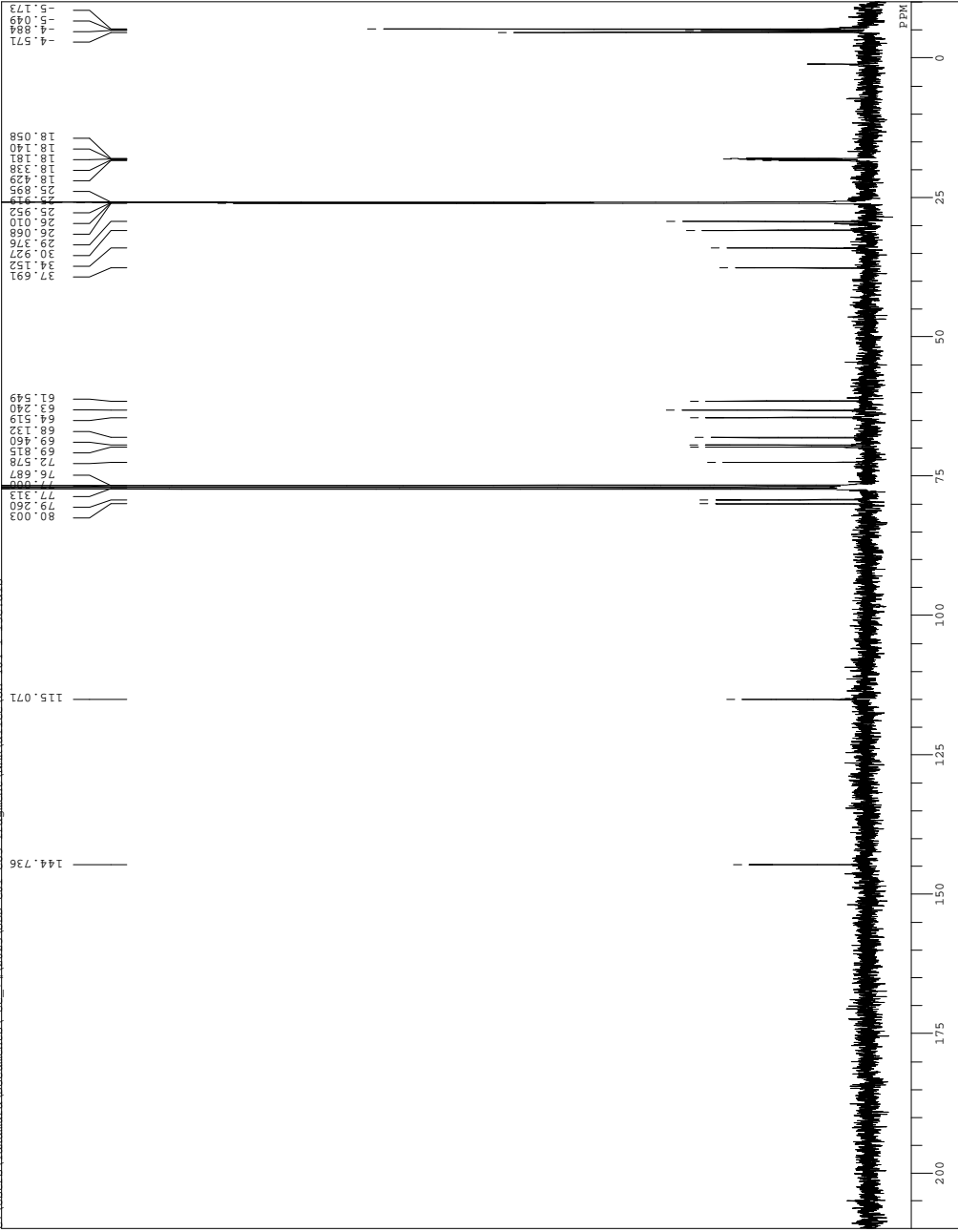
```

NAME      OH-464-1.als
PRFILE   OH-464-1.als
DATE      Wed Aug 29 13:45:28 2018
INSTRUM  spect
PROBHD   5mm
PULPROG  zgpg30
SFO      399.65 MHz
AQ       124.00 kHz
RG       10500.00 Hz
WDW      EM
SSB      0
GB       0
EC       0
PRF      79931.60 Hz
SCANS    4
DS       8
AQTM     2.9013 sec
RGTM     6.40 usec
FWD      1
IRFREQ   27.9 C
SOLVENT  CDCL3
SOLVENT  7.26 ppm
EXREF    0.11 Hz
RGAIN    0.11
  
```

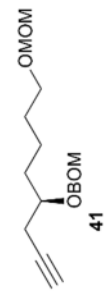
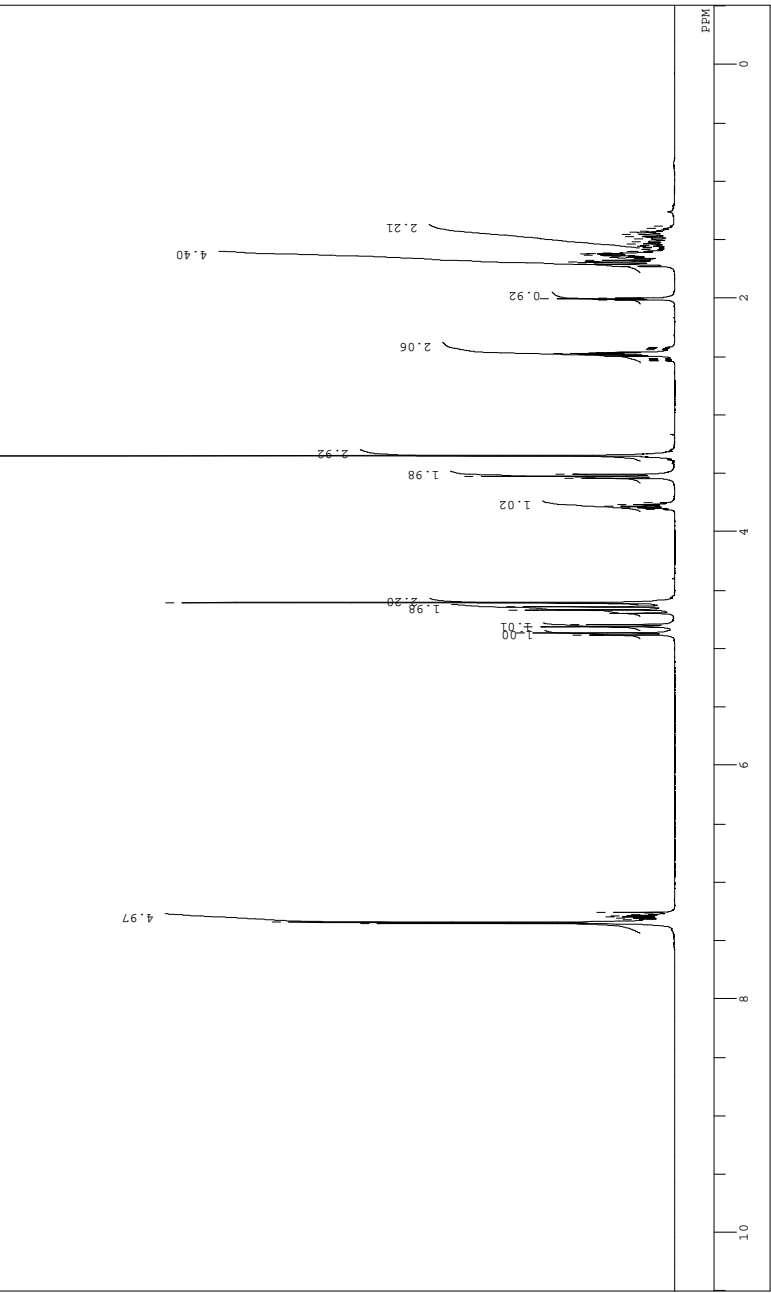


C:\Users\takamura\Documents\5e_4\2021\5BD_C61-C83_fragment\NMR\alice\OH-464-1_13C_alis

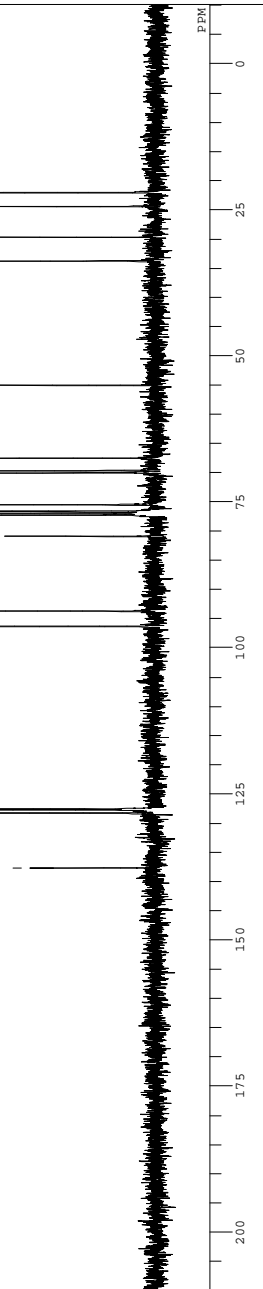
DP11E OH-464-1_13C_alis
 DATE_ Wed Aug 29 14:09:02 2018
 DATIM 13C
 P1 13C
 PROCN ECM
 OBSO 100.40 MHz
 OBSF1 125.00 KHz
 OBSF2 10500.00 Hz
 FREQ0 27173.96 Hz
 SCANS 380
 ACQ01 1.7940 sec
 PD01M 1.6780 usec
 PUL 1H
 PRNUC 1H 29.7 C
 SLVNT CDCL3
 EXREF 77.00 FPM
 RGAIN 2.24



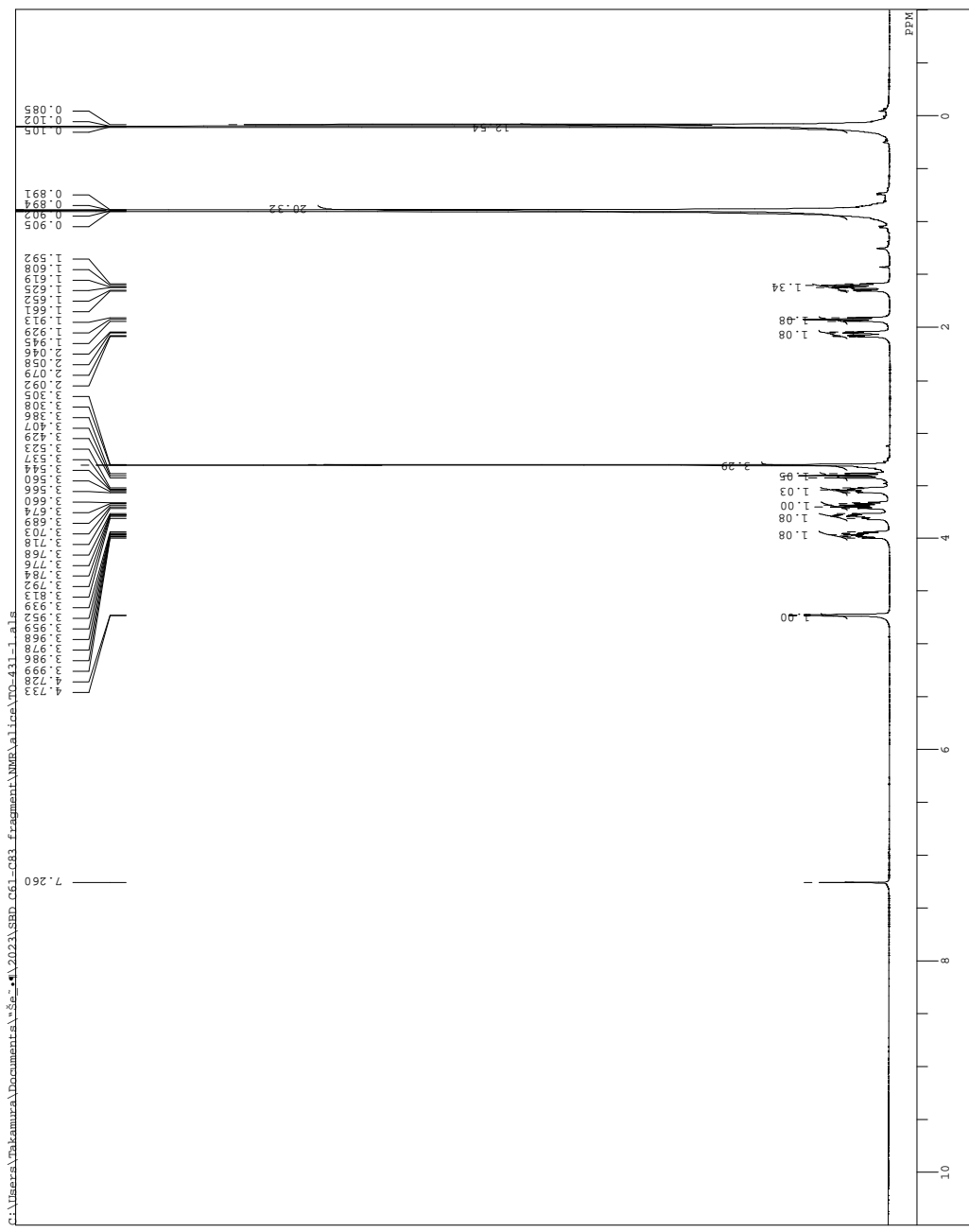
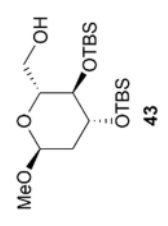
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 Date Thu Nov 22 16:45:30 2018
 DTIME 1.19
 ORBIT 1H
 PULPROG zgpg30
 PROCNO 1
 F2 399.65 MHz
 F1 124.00 KHz
 OBF1 10500.00 Hz
 OBF2 7953.60 Hz
 FREQ 4.0888
 SCANS 8
 PC 2.9030 sec
 PD 6.40 usec
 PM 1.1H
 IPRMC 25.2 C
 SOLVENT CDCL3
 EXREF 7.26 PPM
 EXRES 0.13 Hz
 RGAIN



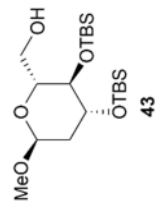
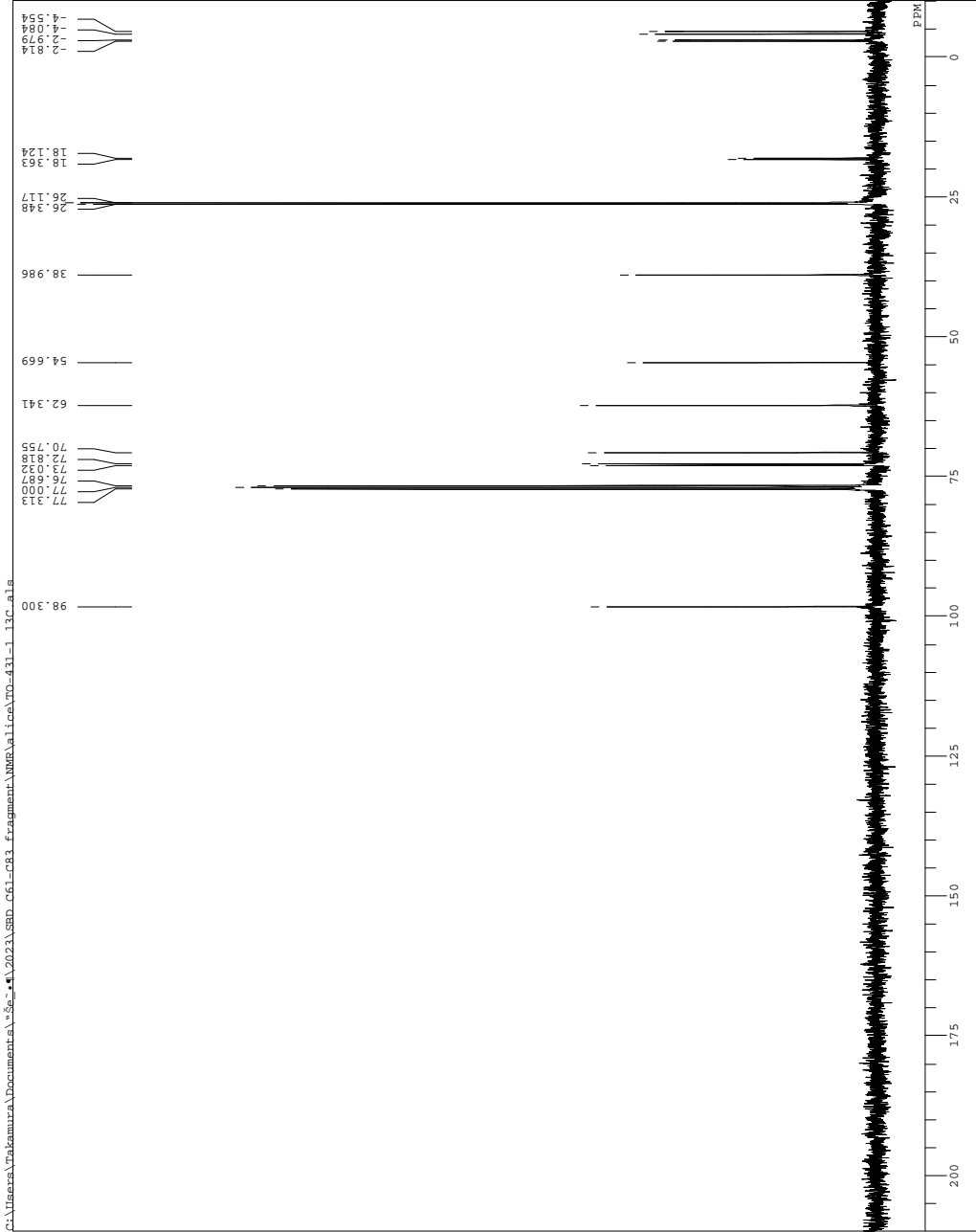
C:\Users\Takanawa\Documents\Se_4\2021\SSB_G61-G83_Fragment\NMR\alicat\TO-441_13C_als
 DFIL: TO-441_13C_als
 COMPT Thu Nov 22 17:03:04 2018
 CONV 13
 ORNTC BCM
 EXMOD BCM
 ORSC 130.40 MHz
 OBSOL 135.00 MHz
 OFIN 10500.00 Hz
 POINT 27173268
 SCANS 840 Hz
 ACQTM 1.2059 sec
 PUL 1.6800 usec
 P1 27.30 usec
 IRNUC 1H
 STNUC 13C
 STINT CDCL3 27.3 c
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 24



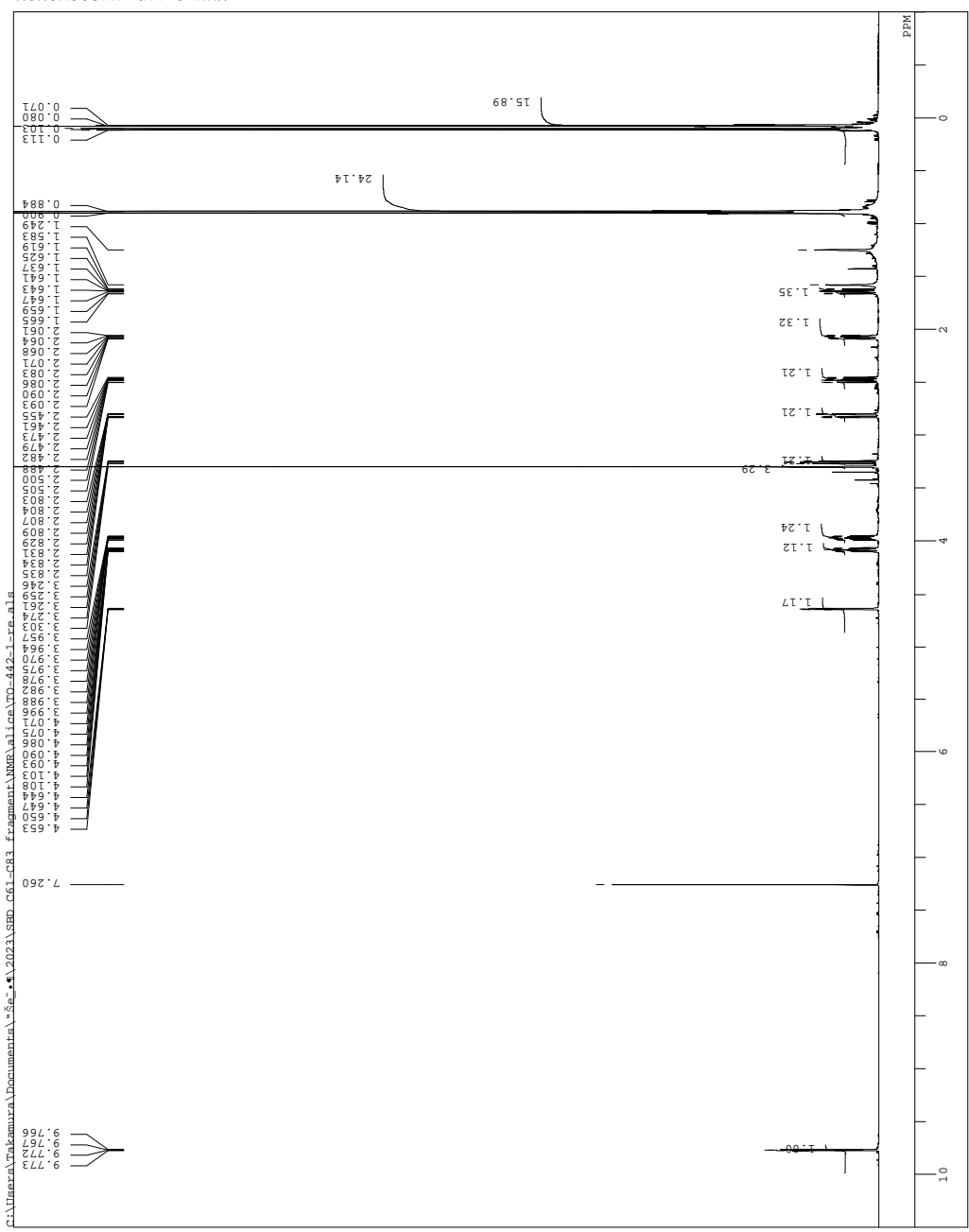
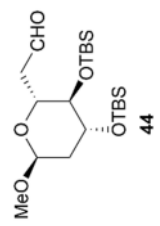
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 OBNUC 1H
 EXMOD NON
 OBSFO 399.65 MHz
 OBSFQ 124.00 MHz
 OBFIN 10500.00 Hz
 PRNUC 1H
 PRNUF 79337.68 Hz
 SCANS 8
 ACQTM 4.093 sec
 PRG 2.640 usec
 PW1
 IRNUC 1H 25.3 c
 SLMNT CDCL3 7.26 ppm
 EXREF 0.12 Hz
 RGAIN



PFI1 70-431-1 13C.sls
 COMPT Thu Nov 15 17:14:32 2018
 DATEM 13C
 DEMOC 13C
 SNAME B3C
 OBFRQ 100.40 MHz
 OBSFT 125.00 KHz
 OBSRG 100.00 Hz
 POINT 32768
 PRGQU 27173.90 Hz
 ACQNS 1.205 sec
 PDGTM 1.7940 sec
 PMA 6.80 usec
 PMA1 1H
 CTMP 27.3 c
 SLVNT CDCL3 77.00 ppm
 REF 2.00 Hz
 RGAIN 2.25

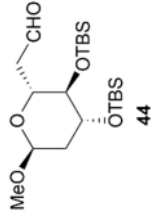
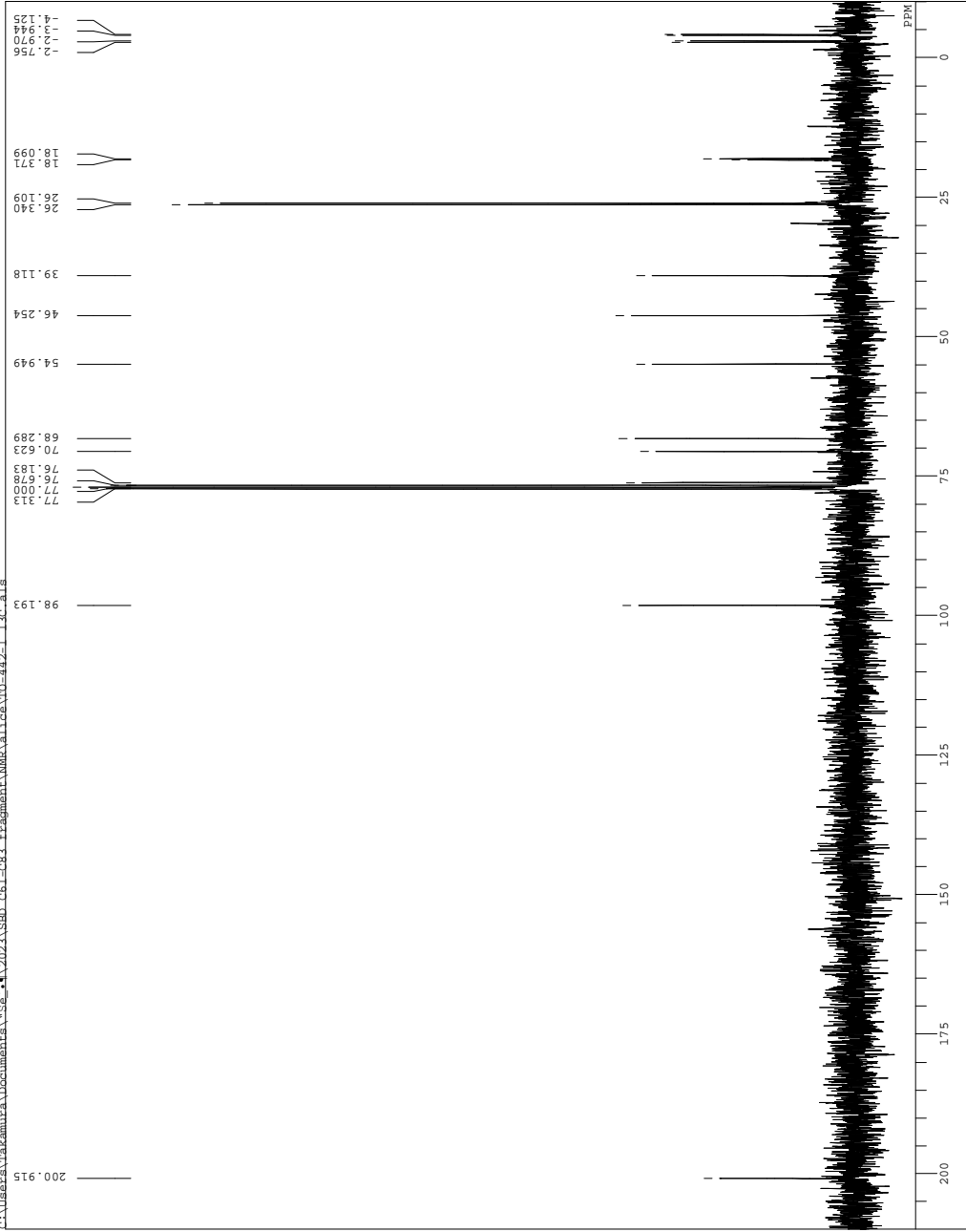


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 COMNT TO-442-1-re
 DATEM 2023-03-20 15:43:12
 PFM 1
 EXMOD 22pul
 OBERQ 599.76 MHz
 OBSFQ 0.90 Hz
 OBSFN 32768
 POINT 9615.3 Hz
 SLOWU 3.4079 sec
 ACQTM 1.5921 sec
 PD 5.63 usec
 IRNUC 83.0 c
 CTEMP cdcl3 7.26 Ppm
 EXREF BF 4.20 Hz
 RGAIN



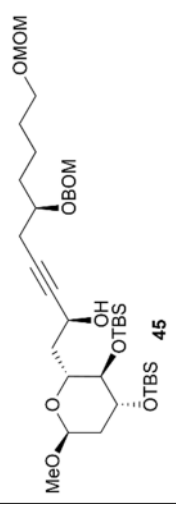
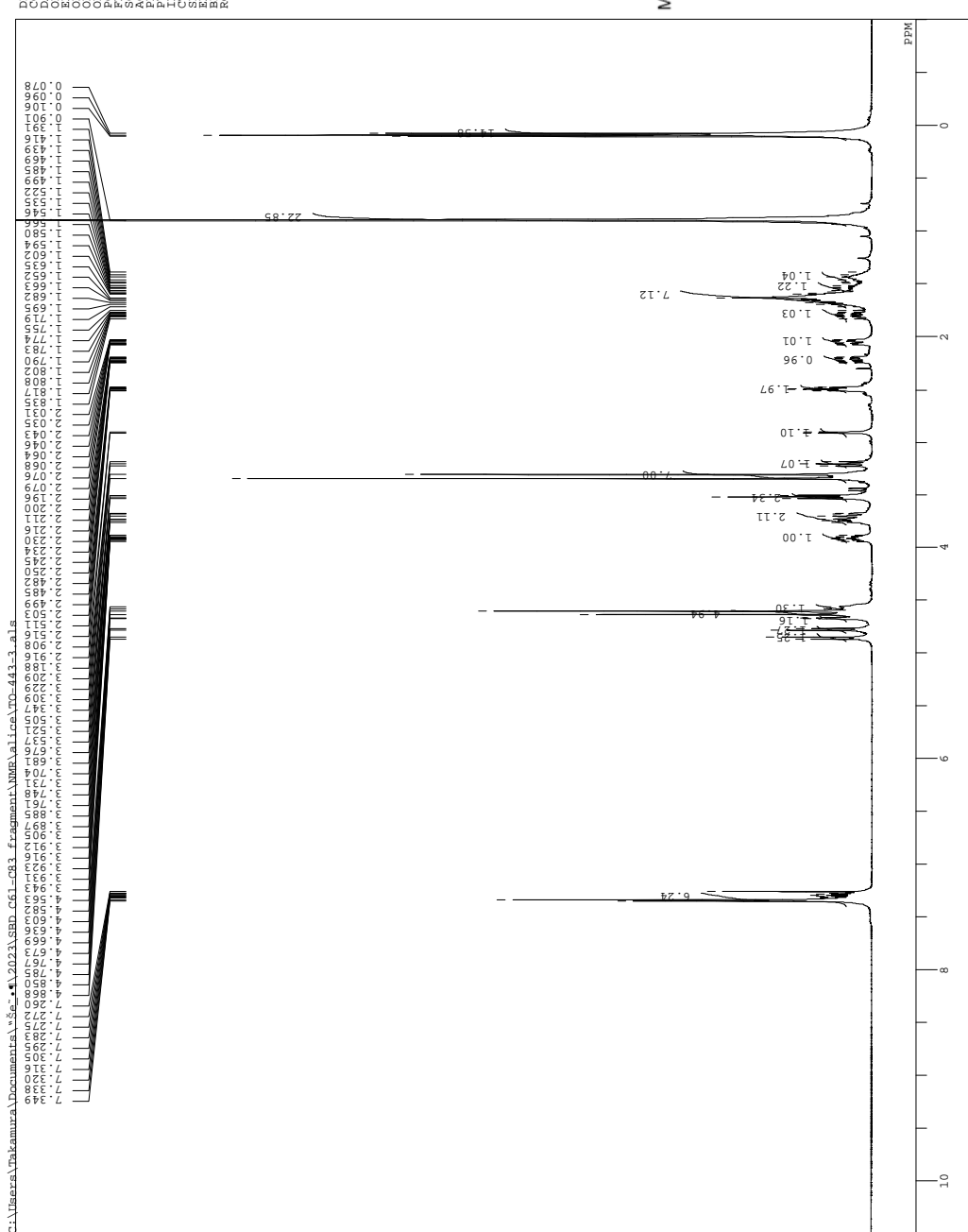
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EXPTN TD-442-1_13C_als
COMPT
DATE_ Fri Nov 16 22:57:45 2018
SOLVENT CDCL3
PULPROG zgpg30
OBPRG zgpg30
F2 100.40 MHz
SFO 125.00 MHz
AQ 1.00000000
RG 32768
RPOINT 27173.90 Hz
FREQ 27173.90 Hz
SCANS 2
ACQMS 1.2055 sec
PD 0.17940 sec
PULPROG zgpg30
PULSE 1H
CTEMP 27.3 c
SLVNT CDCL3
SFO 125.00 MHz
RG 32768
RGAIN 2.24

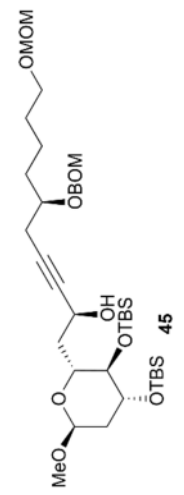
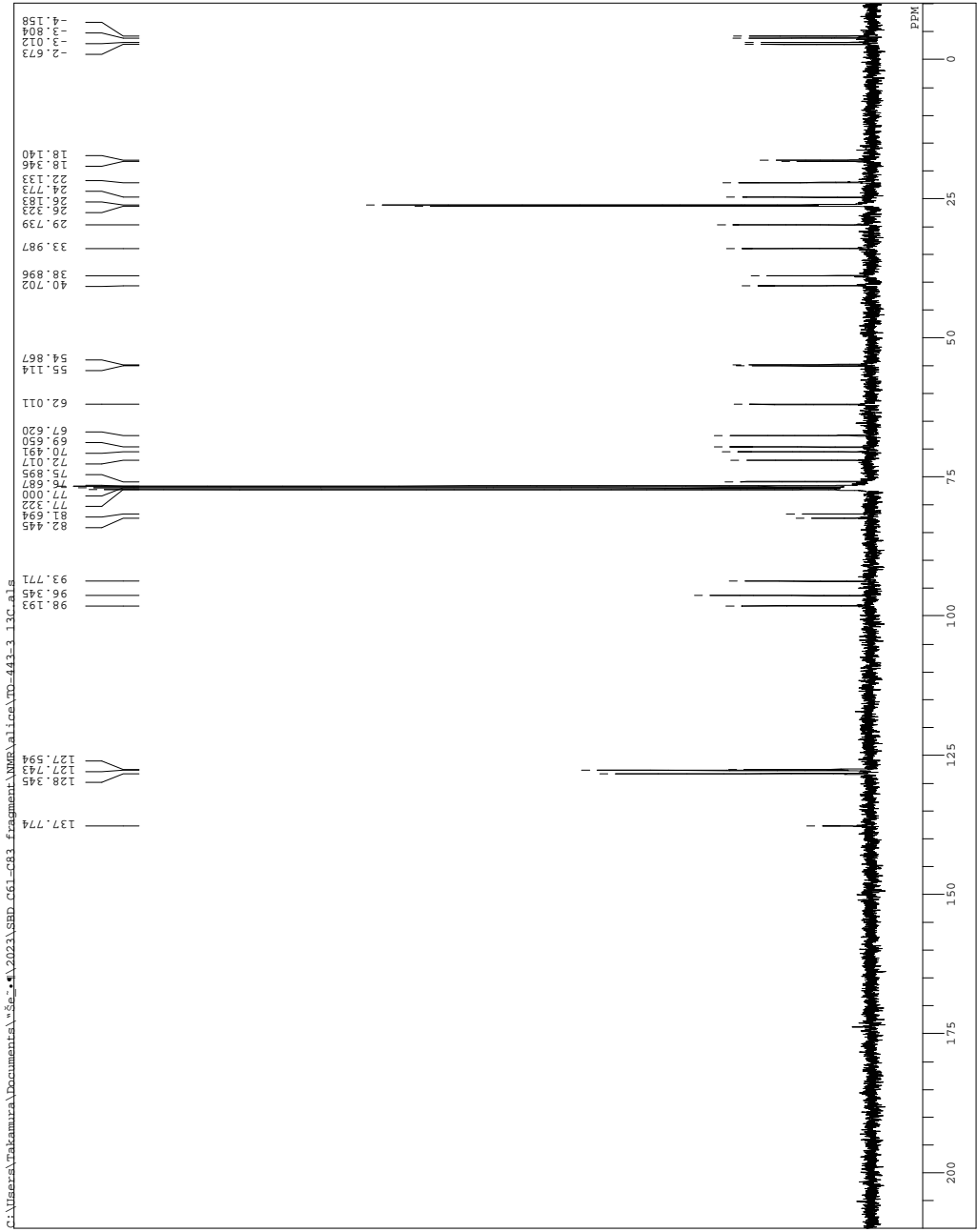


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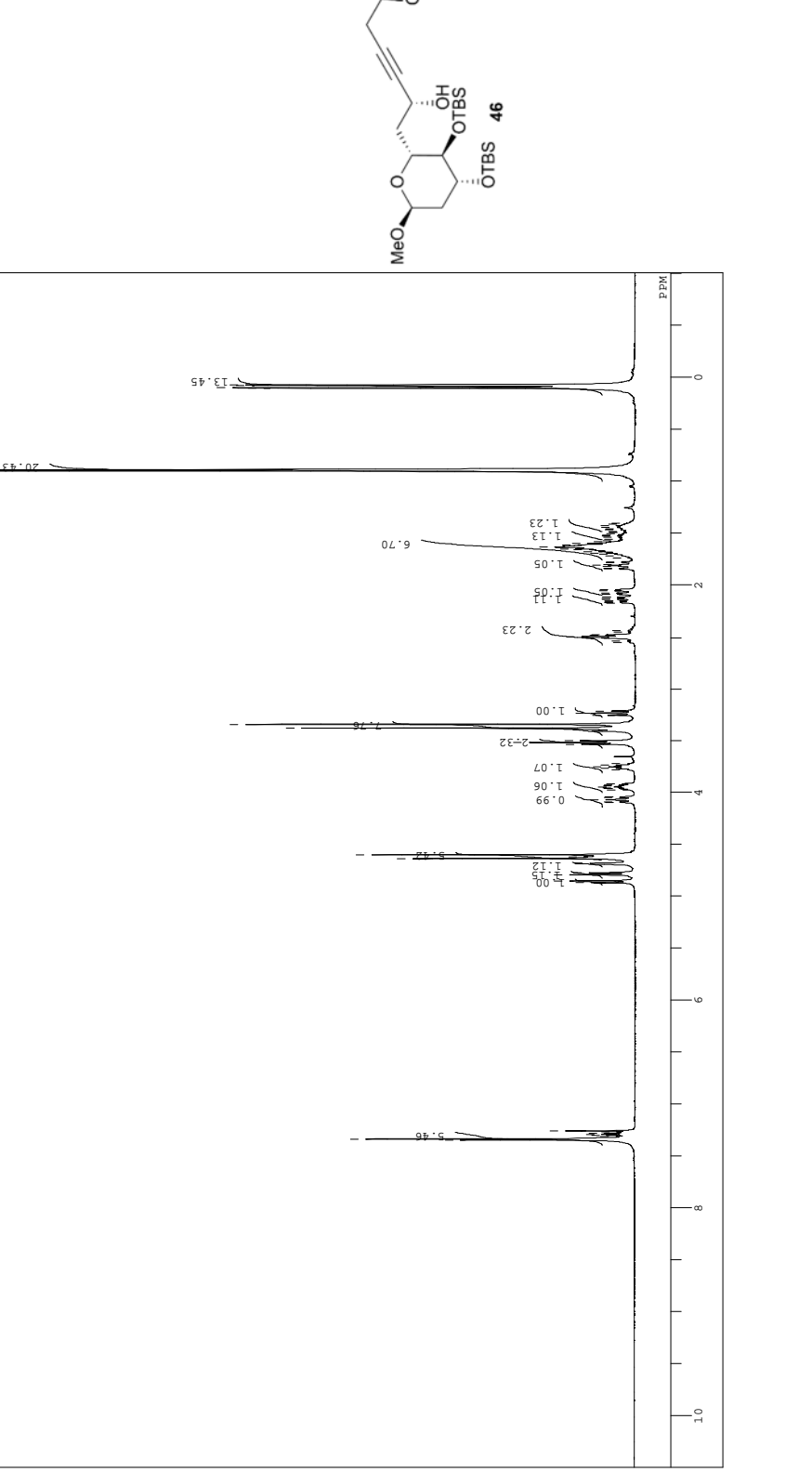
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 INSTR BMN
 EXMOD NON
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 OSETF 0
 OBFIN 10500.00 Hz
 FREQ 799.2760 Hz
 SCANS 8
 ACQTM 4.0973 sec
 AQT 2.640 usec
 PULPROG zgpg30
 IERNO 1H
 IERNC 1H
 IERNA 1H
 SLVMT CDCL3
 EXPRF 7.26 ppm
 REFIN 0.12 Hz
 REFIN



File TO-443-3 13C.als
 Date Thu Nov 29 19:41:26 2018
 Name 13C
 Observed 100.40 MHz
 Observed 125.00 KHz
 Observed 10500.00 Hz
 F2 27173.98 Hz
 F1 680
 SCANS 1.7540 sec
 PD 1.7540 sec
 PD QTM 6.80 usec
 PW 26.6 c
 IRMS 77.00 EPM
 SLANT CDCL3 2.20 Hz
 EXREF
 RGAIN

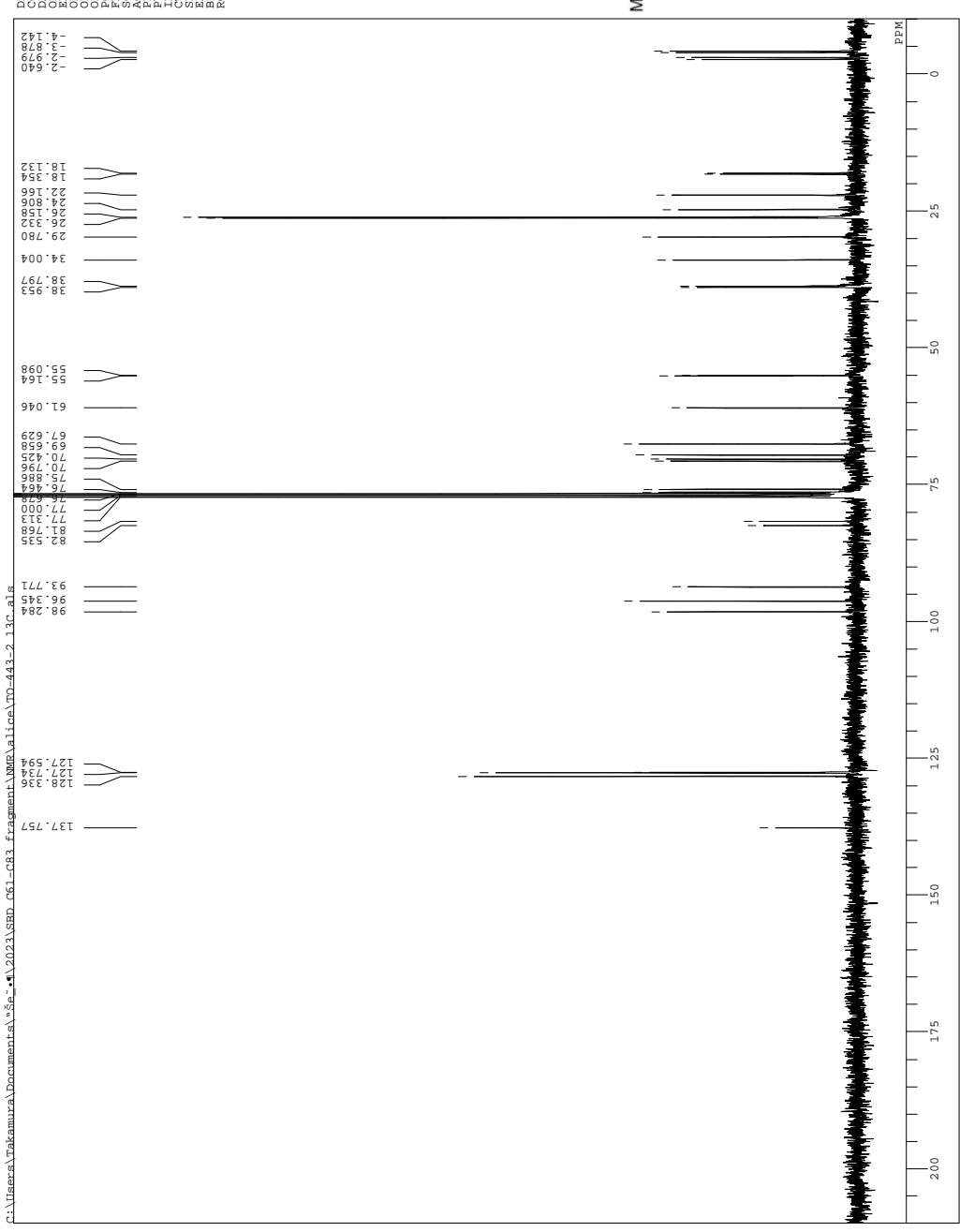


C:\Users\Takamura\Documents\Se*\2021\SHD_661-c83_fragments\NMR\1c\TO-443-2_als
 DEFILE TO-443-2_als
 DATE Thu Nov 29 12:06:27 2018
 DATTM Thu Nov 29 12:06:27 2018
 ORBVC 1H
 ORBVD NOM
 ORBVO 399.65 MHz
 ORBVF 124.00 KHz
 ORBVM 10500.00 Hz
 ORBVS 7931.60 Hz
 FREQU 4.0988
 SCANS 2.9010 sec
 PD CYM 6.40 usec
 PM1
 IRMVC 1H
 IRMVD 24.9 C
 IRMVF CDCL3
 IRMVM 7.26 PPM
 EXREF 0.14 Hz
 RGAIN



C:\Users\takamura\Documents\Se...2023\SED_061-c83_Fragment_NMR\data\TO-443-2_13C.nmr

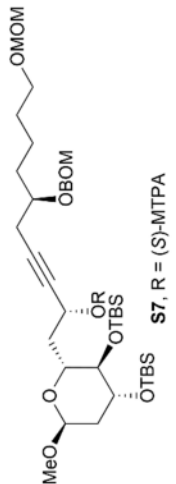
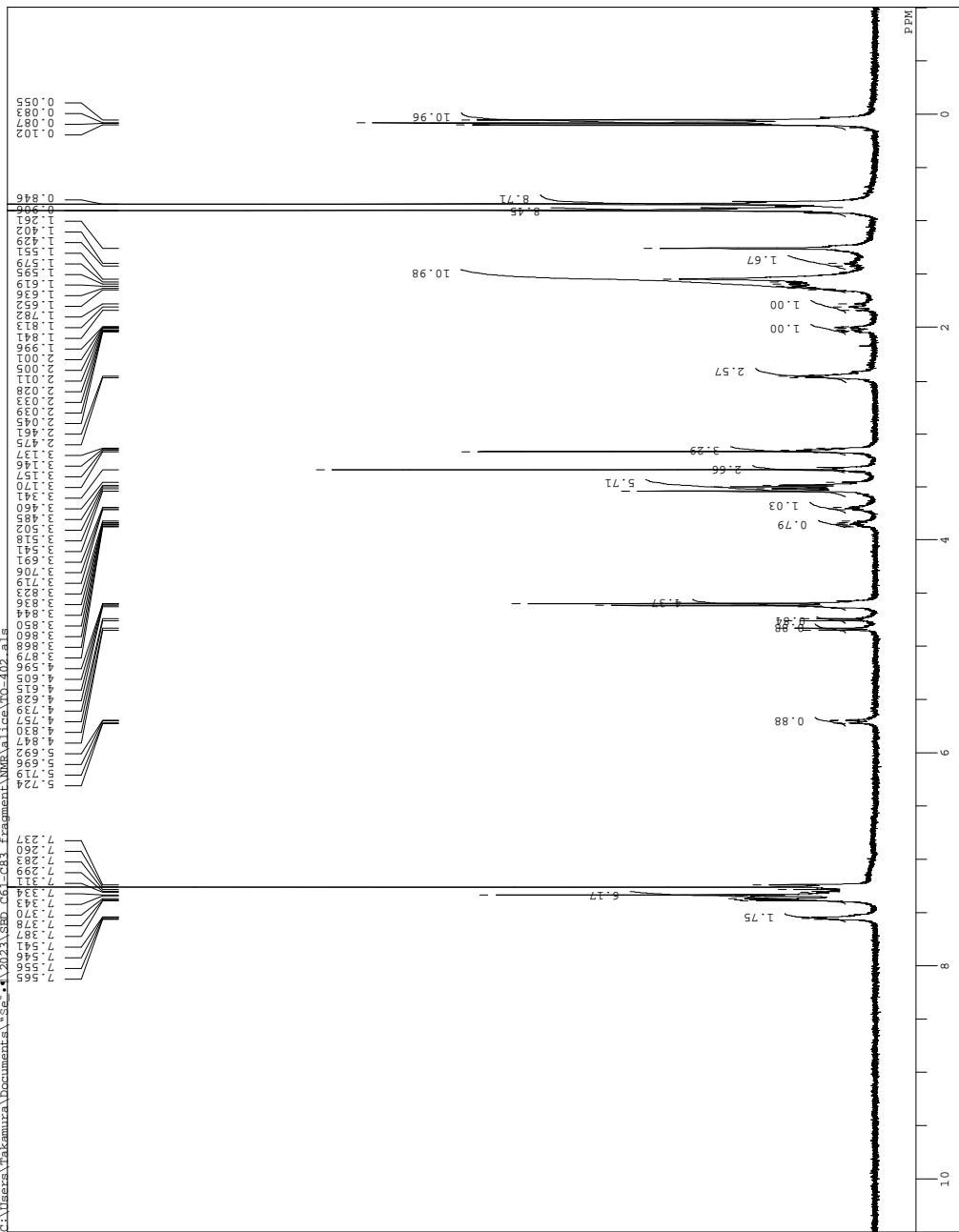
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NAME Se...
DATE Thu Nov 29 12:34:17 2018
PROCNO 13C
PROBHD 5mm
PULPROG zgpg30
AQ 1.488
RG 1.290
SFO 125.00
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.00
FREQ 100.62
NUC1 13C
NUC2 13C
SOLVENT CDCl3
RGAIN 2.24



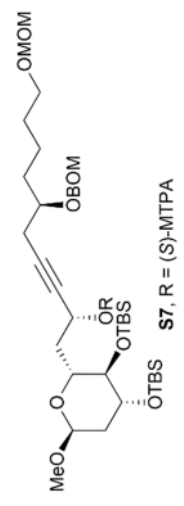
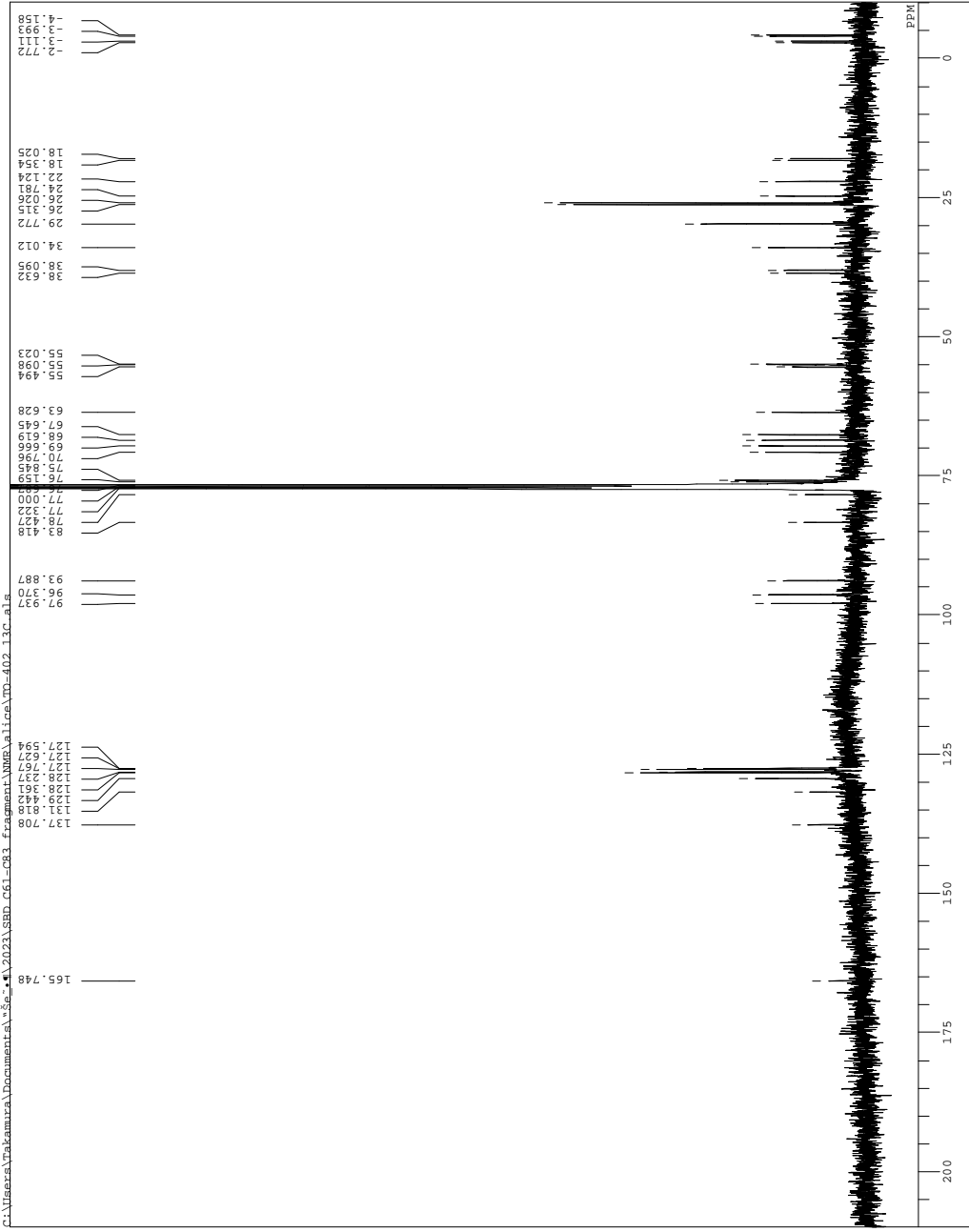
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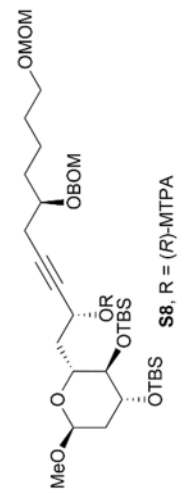
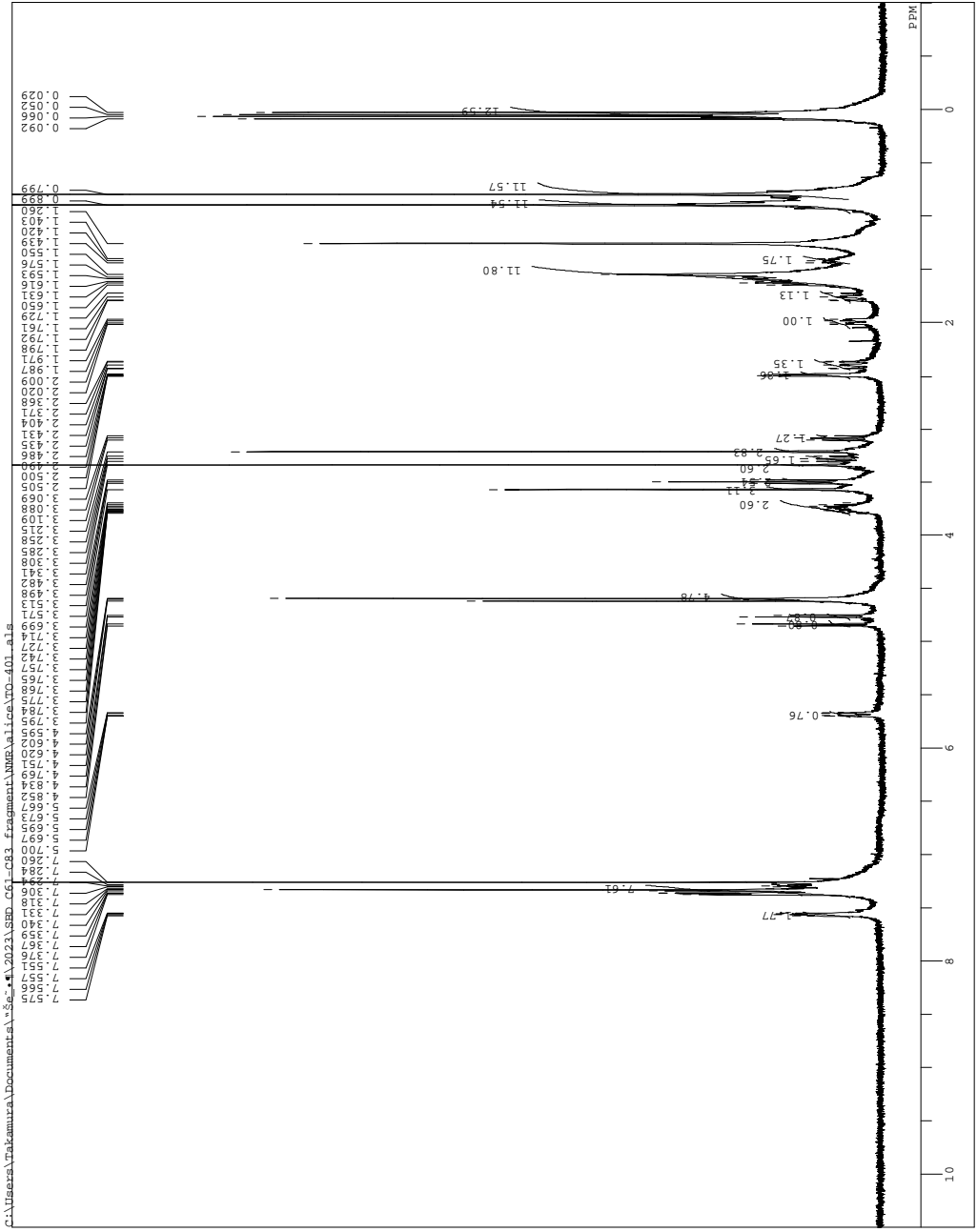
DRIF TO-402.als
COM1 Tue Nov 21 19:24:20 2017
DATE
PULSE 1H
ORBIT 1H
PROB 1H
PULPROG zgpg30
399.65 MHz
ORBIT 1H
PROB 1H
PULPROG zgpg30
124.00 KHz
FREQ 105327.68 Hz
SOLVENT CDCL3
SCANS 4
AQ 4.0893 sec
RG 2.9010 sec
PD 5.00 usec
P1 0.00 usec
P2 0.00 usec
P3 0.00 usec
P4 0.00 usec
P5 0.00 usec
P6 0.00 usec
P7 0.00 usec
P8 0.00 usec
P9 0.00 usec
P10 0.00 usec
PC 25.3 C
SOLVENT CDCL3
SOLNT CDCL3
REF 7.26 ppm
RGAIN 0.12 Hz
RGAIN 0.22
  
```



C:\Users\takamura\Documents\Sample\2021\8BD_C61-C93_Fragment\NMR\data\402_13C_als
 FILE TO-402_13C_als
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 DATEM 13C
 DEPTM 13C
 OBMOC 13C
 OBFPC 13C
 OBSST 100.40 MHz
 OBSST 125.00 KHz
 POINT 10532768 Hz
 FREQU 27173.90 Hz
 SCANN 1200
 PC 1.7940 sec
 PD 6.80 usec
 PULC 1H
 CTMP 26.3 C
 SLVNT CDCl3 77.00 ppm
 REFR 2.00 Hz
 RGAIN 2.24

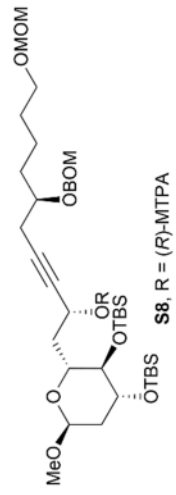
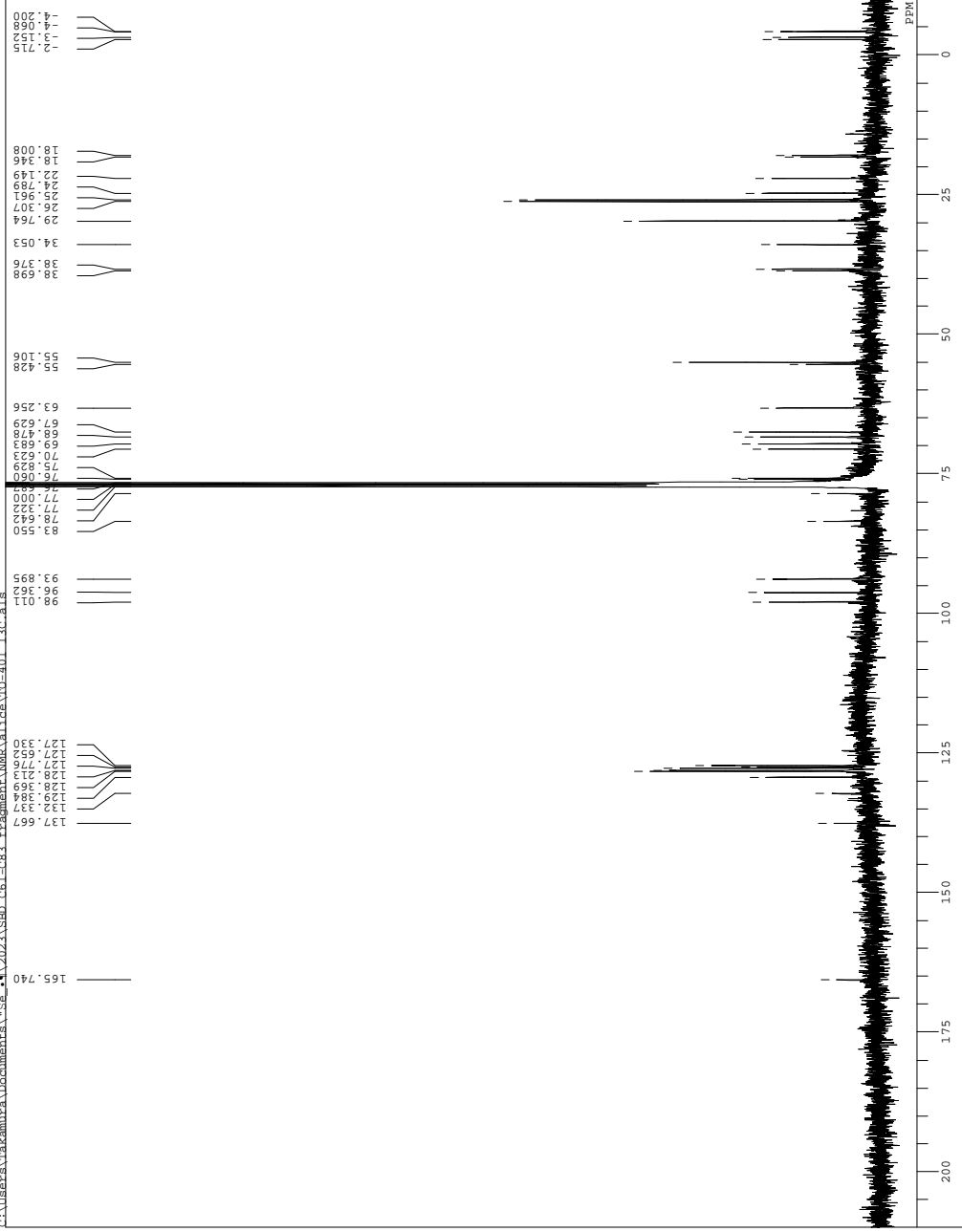


FILE TO-401.als
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 ORNTC LH
 OBSFQ NON
 OBSFQ 399.65 MHz
 OBSFQ 124.00 KHz
 OBSFQ 10590768 Hz
 PREQ 79831.60 Hz
 SCANS 4.0988
 PDVFM 2.9010 sec
 PDVFM 6.40 usec
 PULPROG zgpg30
 PC 25.3 c
 CPMPC 1H
 CPMPC CDCL3
 SILVNT CDCL3
 EXREF
 RGAIN 7.26 pfm
 0.22 Hz

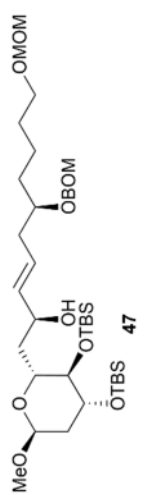
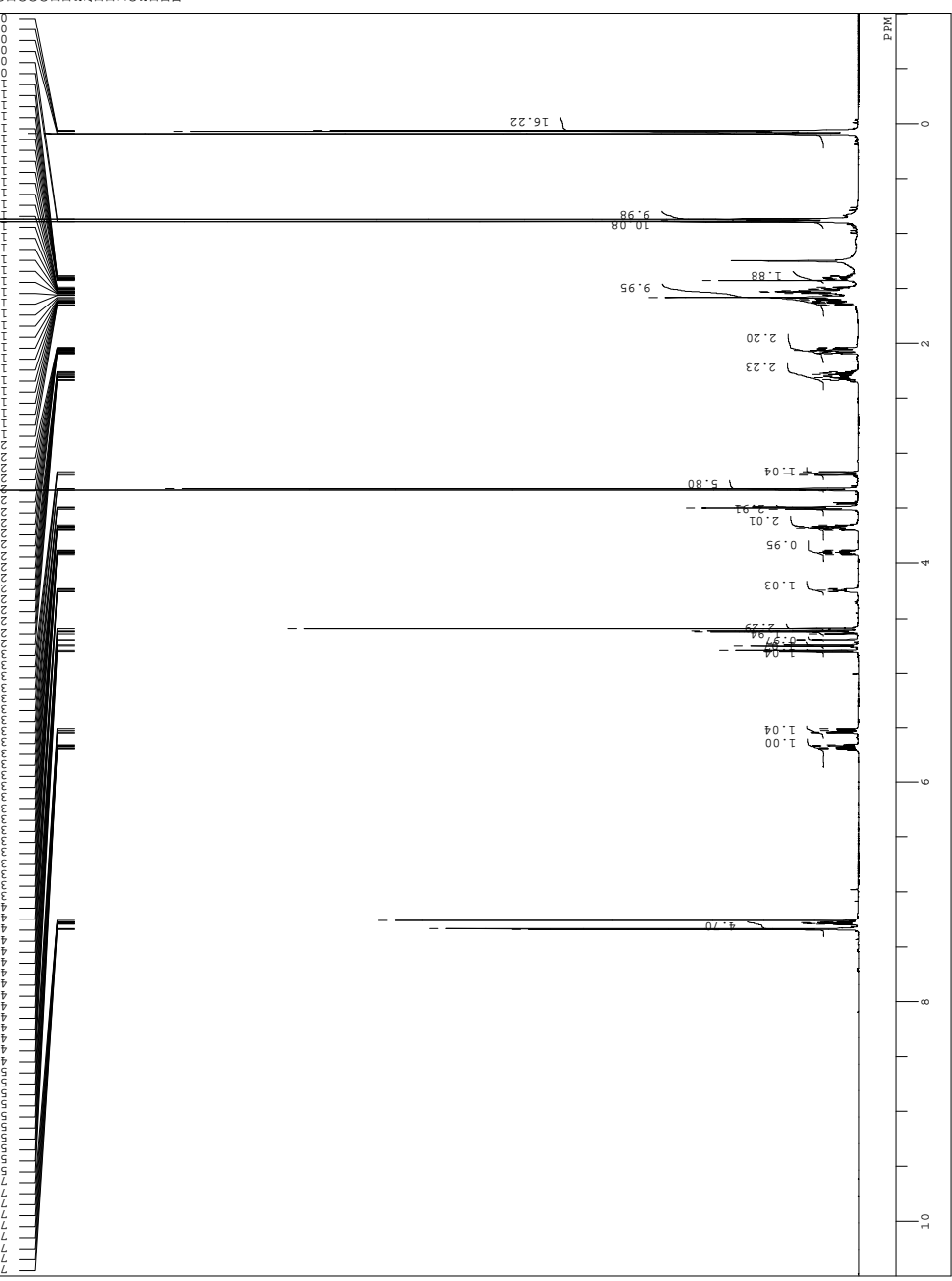


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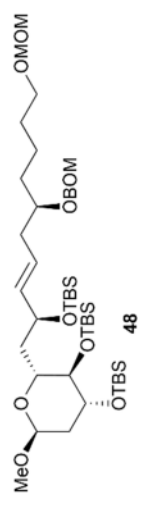
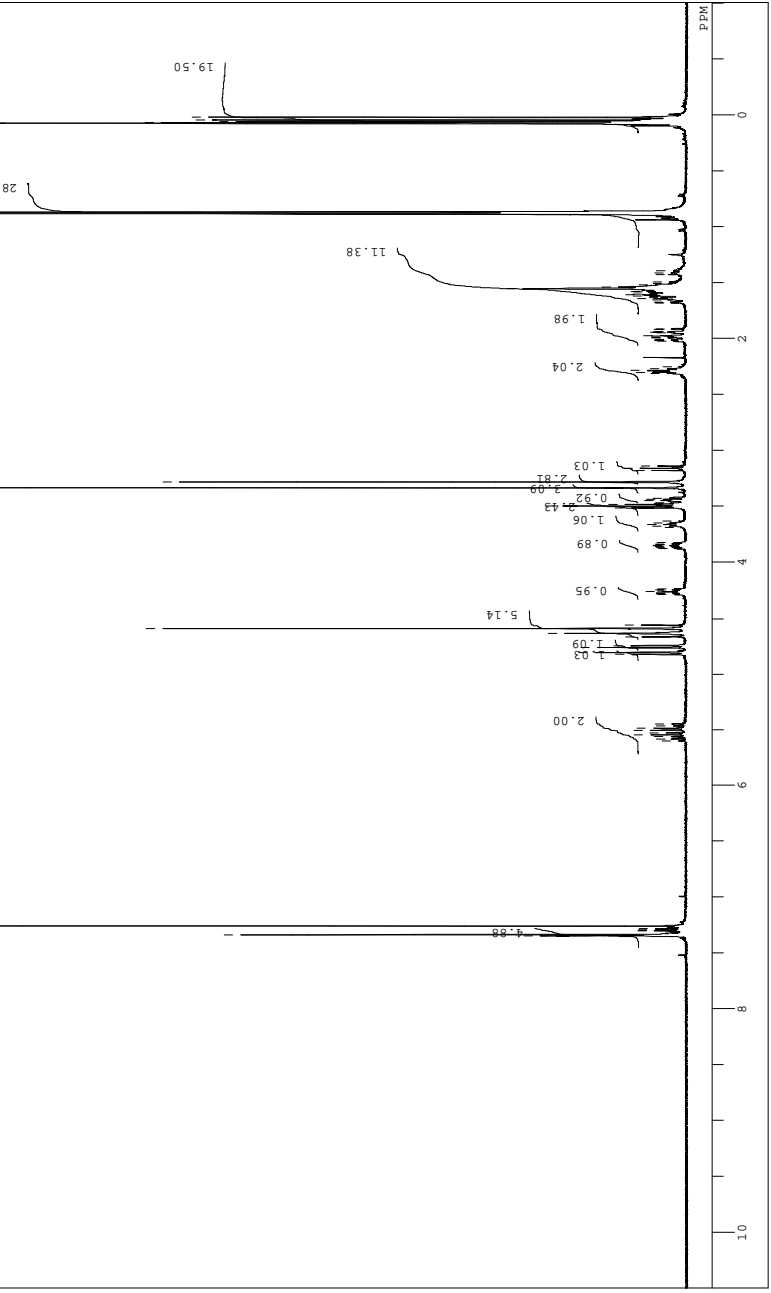
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 CONTM Fri Nov 30 06:26:00 2018
 ORBIT 13C
 EXMOD BCM
 OBSF 100.40 MHz
 OBSF2 125.00 MHz
 ORFN 10500.00 Hz
 PFG1 27137.90 Hz
 SCANS 10000
 ACQTM 1.7259 sec
 PUL 1.6780 usec
 INTC 1H
 SLEN 26.2 c
 SOLV CDCL3
 EXREF 77.00 PPM
 REIN 2.00 Hz
 RGAIN 2.24



C:\Users\Trakamura\Documents\Se...2021\GSD_661-c31_fragments\NMR\data\KH48-1H-re-als
 DEPT KH-48-1H-re-als
 F2 20210330 15:17:51
 DATE_ 20210330
 DTIME H1
 ORNVC H1
 PROC s2pul
 CPD 599.76 MHz
 RESOL 5.06 KHz
 ORFN 0.60 Hz
 FREQ 9615.38 Hz
 SCANS 32
 PD 3.48
 PCYTM 1.5521 sec
 PM1 5.65 usec
 PM2
 TEND 83.0 c
 SFTV cdc13
 SFTV 7.26 ppm
 EXRF 0.36 Hz
 RGAIN

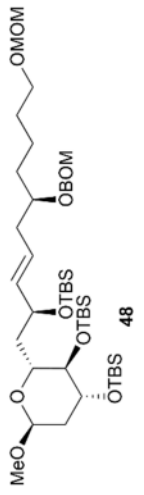
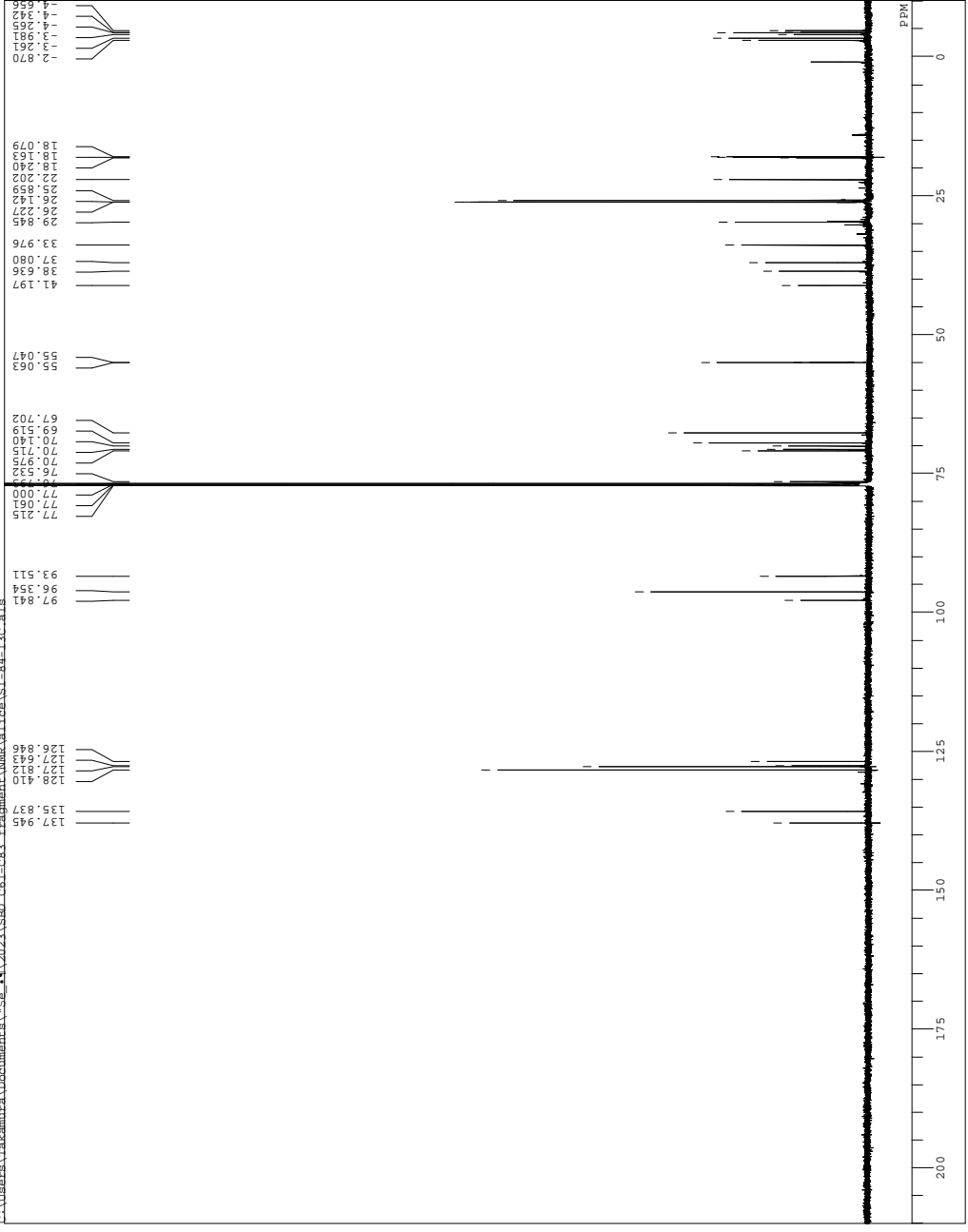


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 F2
 DATE KH-90-1H_als
 TIME 11:03:44
 INSTR 2013-12-14 11:03:44
 PROC H1
 PULPROG zgpg30
 SFO 399.91 MHz
 OBSF1 1.99 KHz
 OBSF2 32768 Hz
 P1 3.20 sec
 FREQ0 6410.26 Hz
 SCANS 32
 PD 1.5000 sec
 PL 0.00 dB
 PC 7.25 usec
 PGM1 c
 PRG1 c
 CTRM c
 CTRP c
 CTRD c
 SILENT c
 SILVER c
 EXPT 7.25 PPM
 EXPR 0.154 Hz
 RGAIN

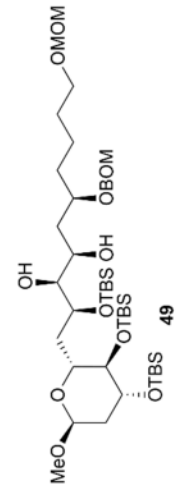
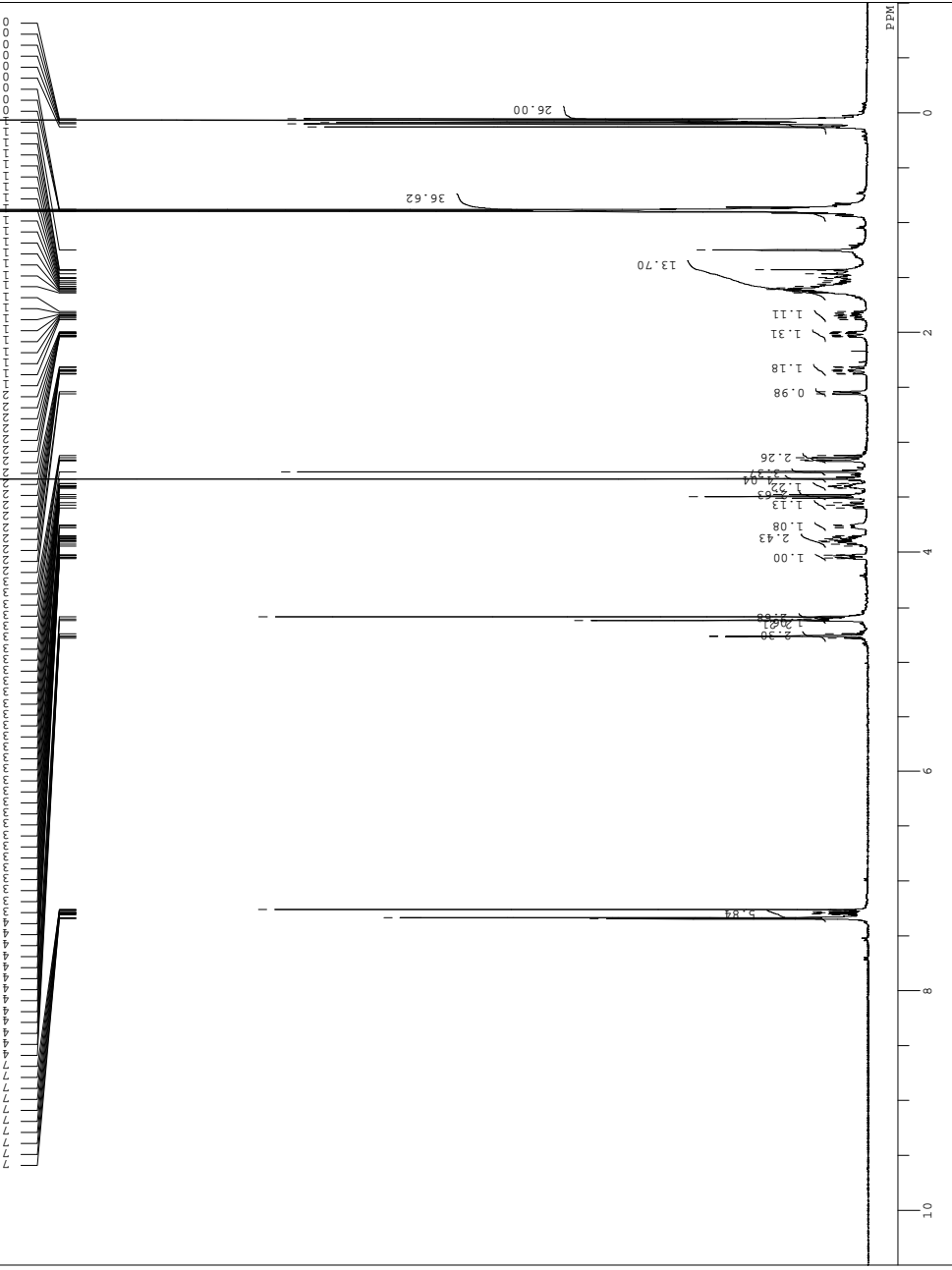


C:\Users\takamura\Documents\Se*\2023\8RD_C61-C83_fragment\NMR\all\ce\SI-84-13C.nls

DATE SI-84-13C.nls
 TIME 01:19
 DATE 2023-04-03 21:37:44
 INSTR C13
 PROC s2pul 150.82 MHz
 OBSCF 6.72 KHz
 OBSRG 32768 Hz
 PULPROG zgpg30
 FREQD 37878.79 Hz
 SCANS 64
 DS 4
 PD 2.1345 sec
 PDSF 6.10 usec
 PULP1
 PULPROG cdc13
 TEMPC 83.0 C
 PROT1
 SILVNT cac13
 EXPT 77.00 PPM
 EXRG 0.160 Hz
 RGAIN

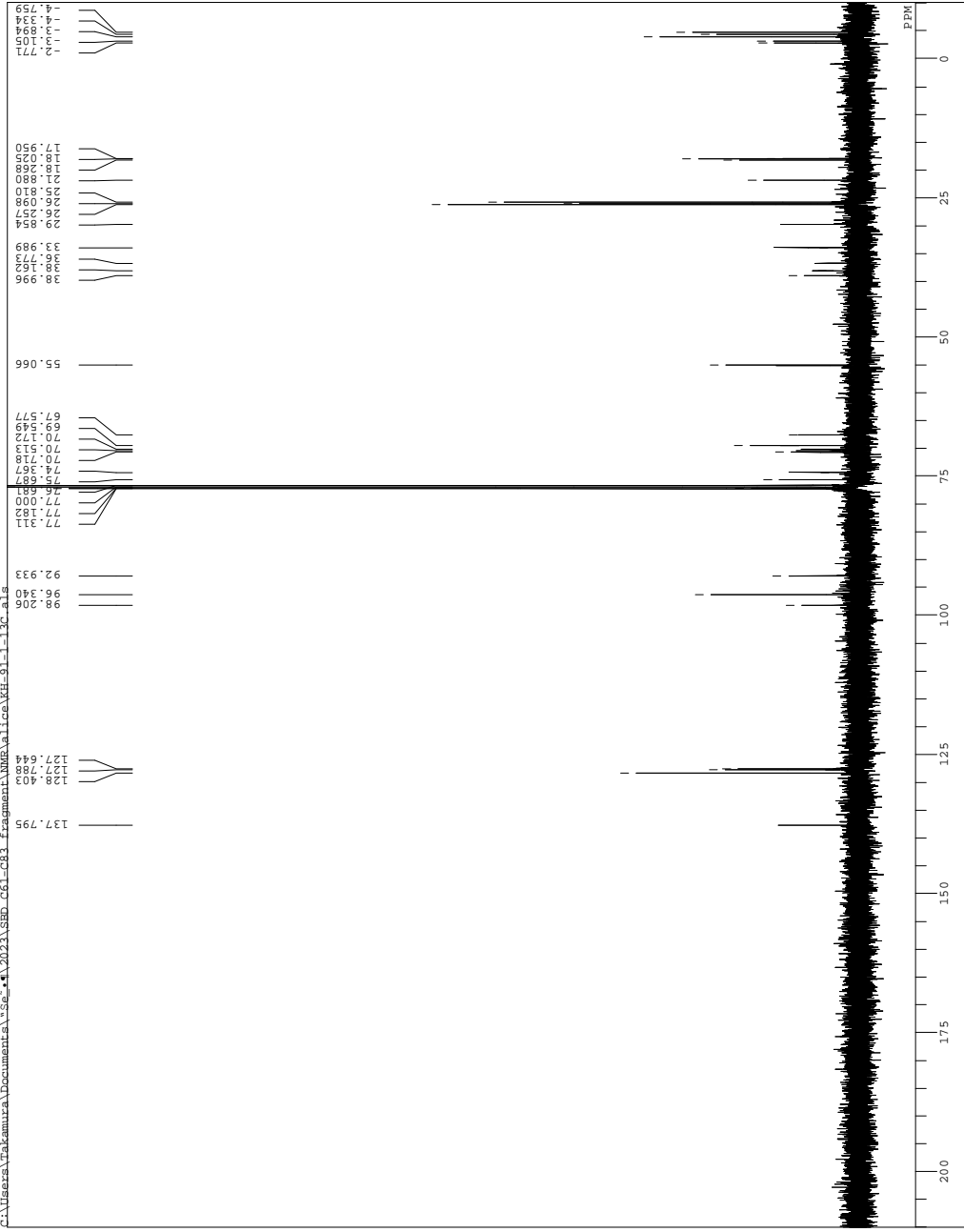


C:\Users\Takamura\Documents\Se...2021\SHD_661-c83_fragment\NMR\valica\KH-91-1-1-H_als
KH-91-1-1-H_als
Date_20121214_15:34:24
Name_H1
P1
PROC s2pul
EXMO 399.91 MHz
OBSF 1.95 KHz
OBPR 2.00 Hz
FREQ 6410.26 Hz
SCANS 32
AQTM 3.5000 sec
PULPROG zgpg30
PWL 1.7.25 usec
IRNUC
SOLNT cdcl3
SUNT
EXREF 7.26 ppm
RGAIN 0.12 Hz
RGAIN

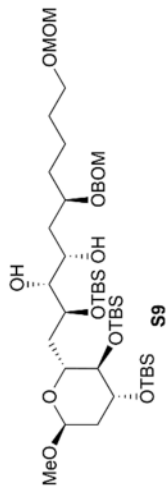
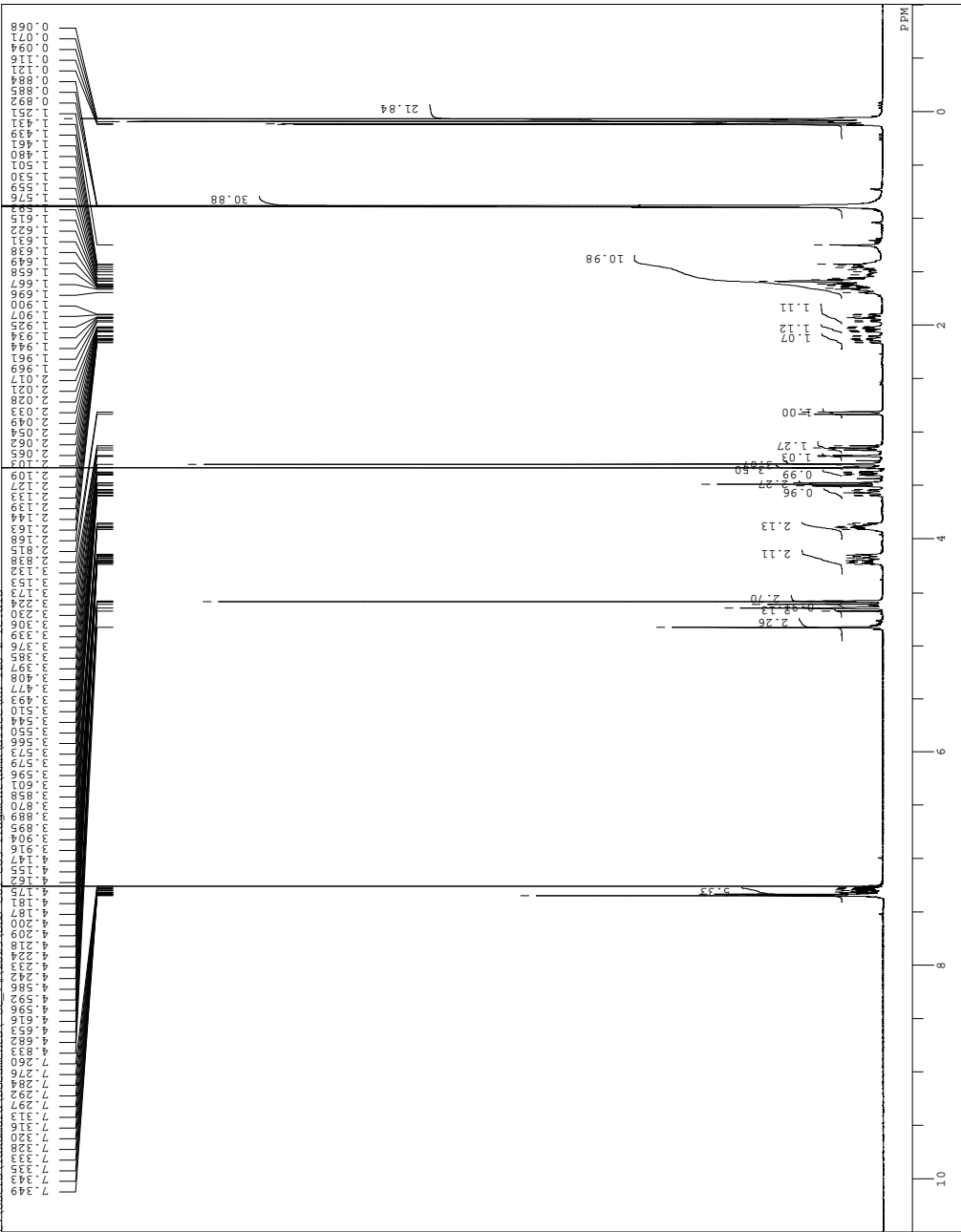


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DFILE KH-91-1-13c_als
COMPR KH-91-1-13c_Data
CQ19-12-14 15:39:08
NAME C19-12-14
EXPNO 2
PROCNO 1
EXMOD s2pul
OBSFQ 100.56 MHz
PULPROG zgpg30
OBPRG 8.30 Hz
OBSF1 8.30 Hz
POINT 32768 Hz
SCANS 25000.64
ACQTM 1.3107 sec
P1 1.6993 sec
P2 5.30 usec
IIRNUC
CENPC cdc13 30.0 c
CENRF
CENRF 77.00 ppm
EXPRF
BF 0.12 Hz
RGAIN 60



DATE KH-128-2-re-als
TIME 2023-03-06 11:37:43
ORNTC H1
PULPRO s2pul
ORSET 399.91 MHz
FREQ 1.99 KHz
PULPRG 32768 Hz
PCYEM 6410.26 Hz
SCANS 32
PD 1.5000 sec
PL 7.15 usec
PWI c
PRM c
TEMP 37.0 c
SILVNT cac13
EXREF 7.26 ppm
RGAIN 4.42

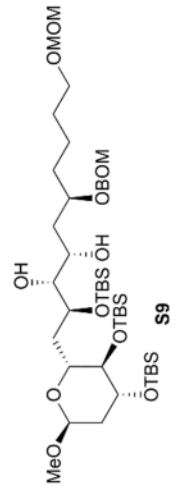
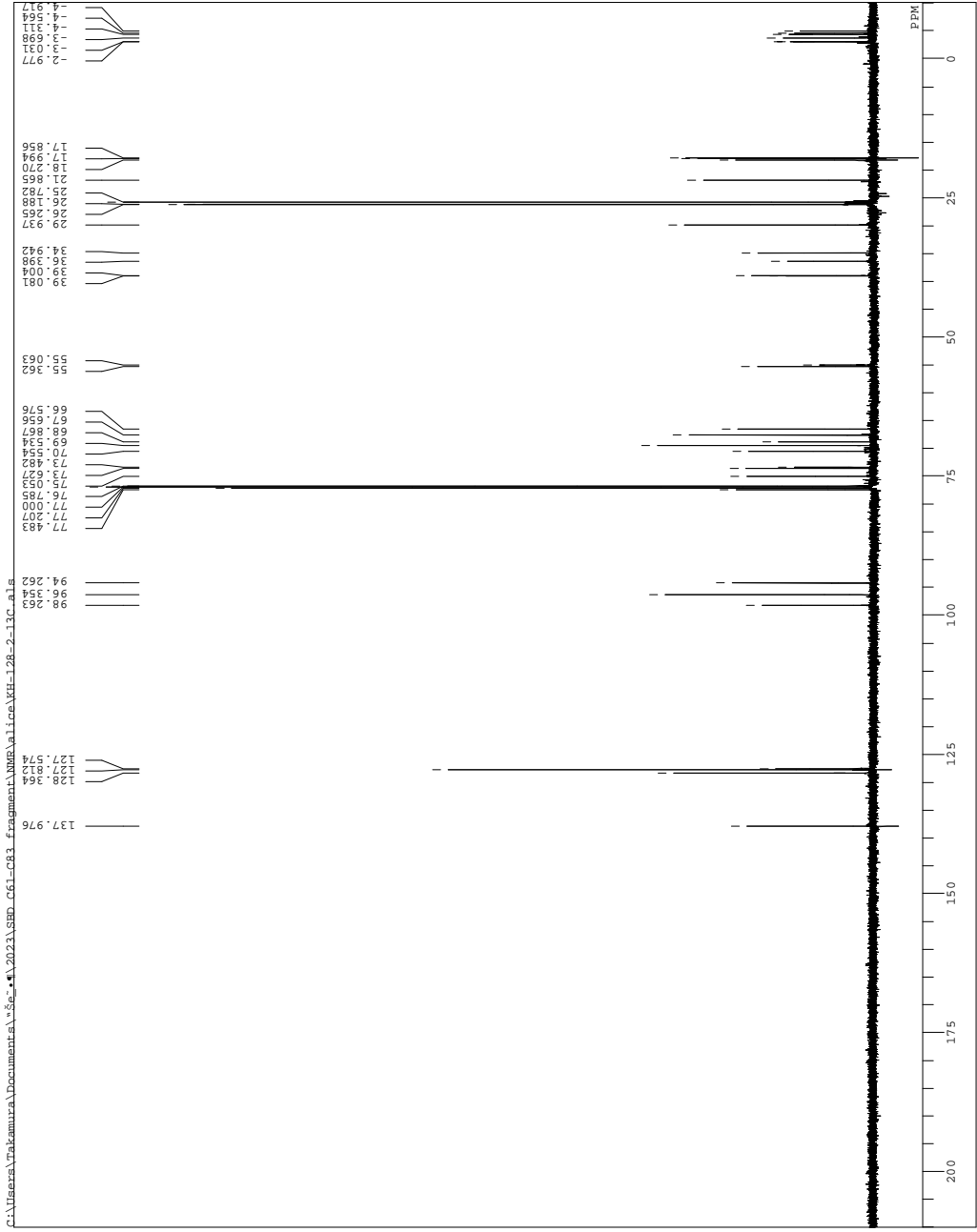


S9

C:\Users\Takahara\Documents\Se-4\2021\8HD_661-c83_fragment\NMR\all\ce\KH-128-2-13c_als

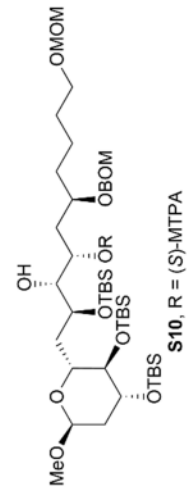
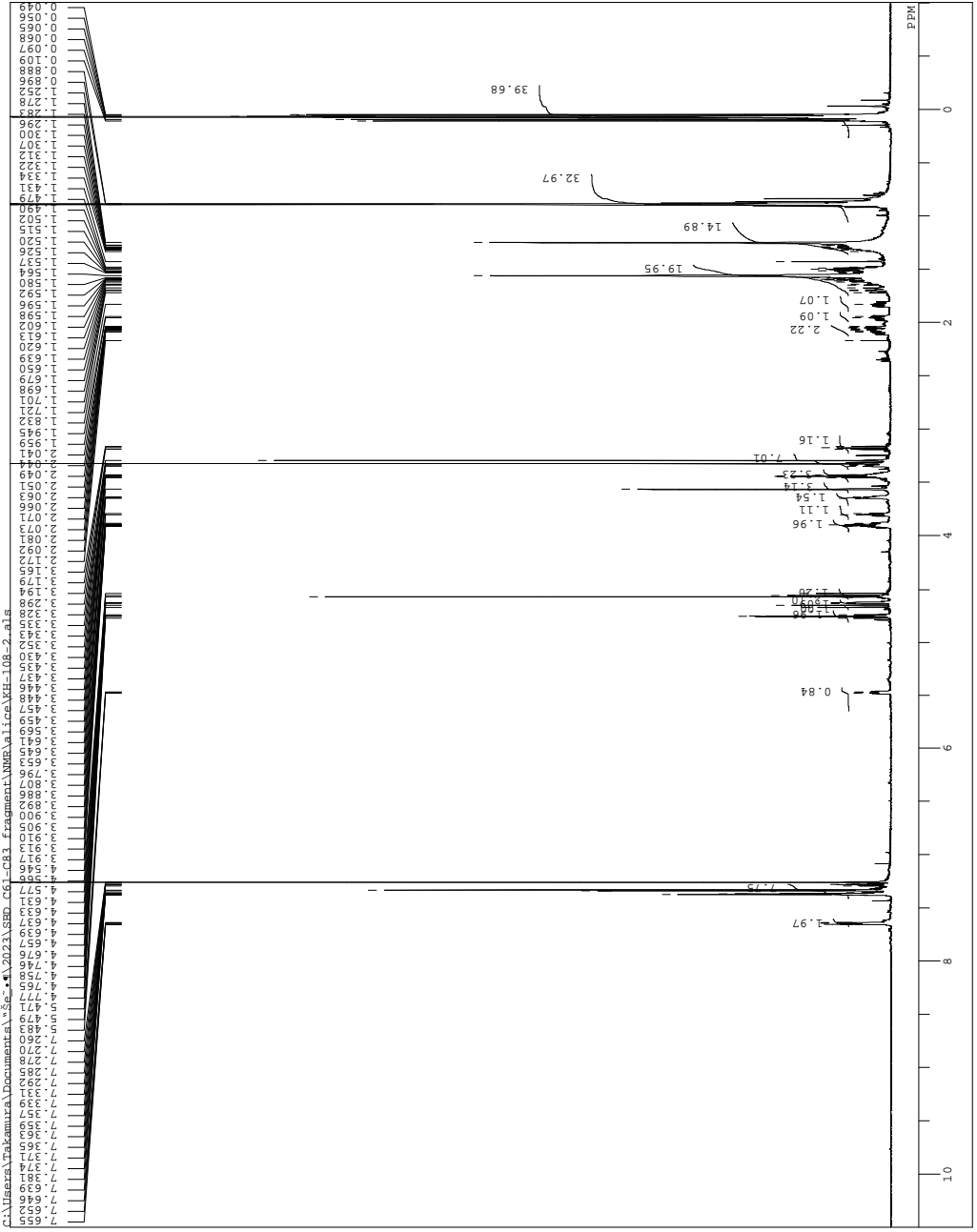
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DETE KH-128-2-13c_als
NAME 8HD_661-c83_fragment
DATE 2023-03-15 13:49
DIR C:\Users\Takahara\Documents\Se-4\2021\8HD_661-c83_fragment\NMR\all\ce\KH-128-2-13c_als
PROC 1
PULPROG zgpg30
PROBHD 5mm QNP 1H/13
PROB 1
P1 12.00
PC 0.64
PCYTM 2.1349 sec
PCYTD 6.05 usec
PCYTH 40.0 c
SFO 125.76 MHz
NUC1 13C
NUC2 1H
SOLVENT cdcl3
SOLNT 77.00 PPM
EXREF 0.13 Hz
RGAIN 1.60
  
```



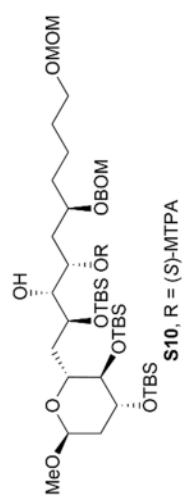
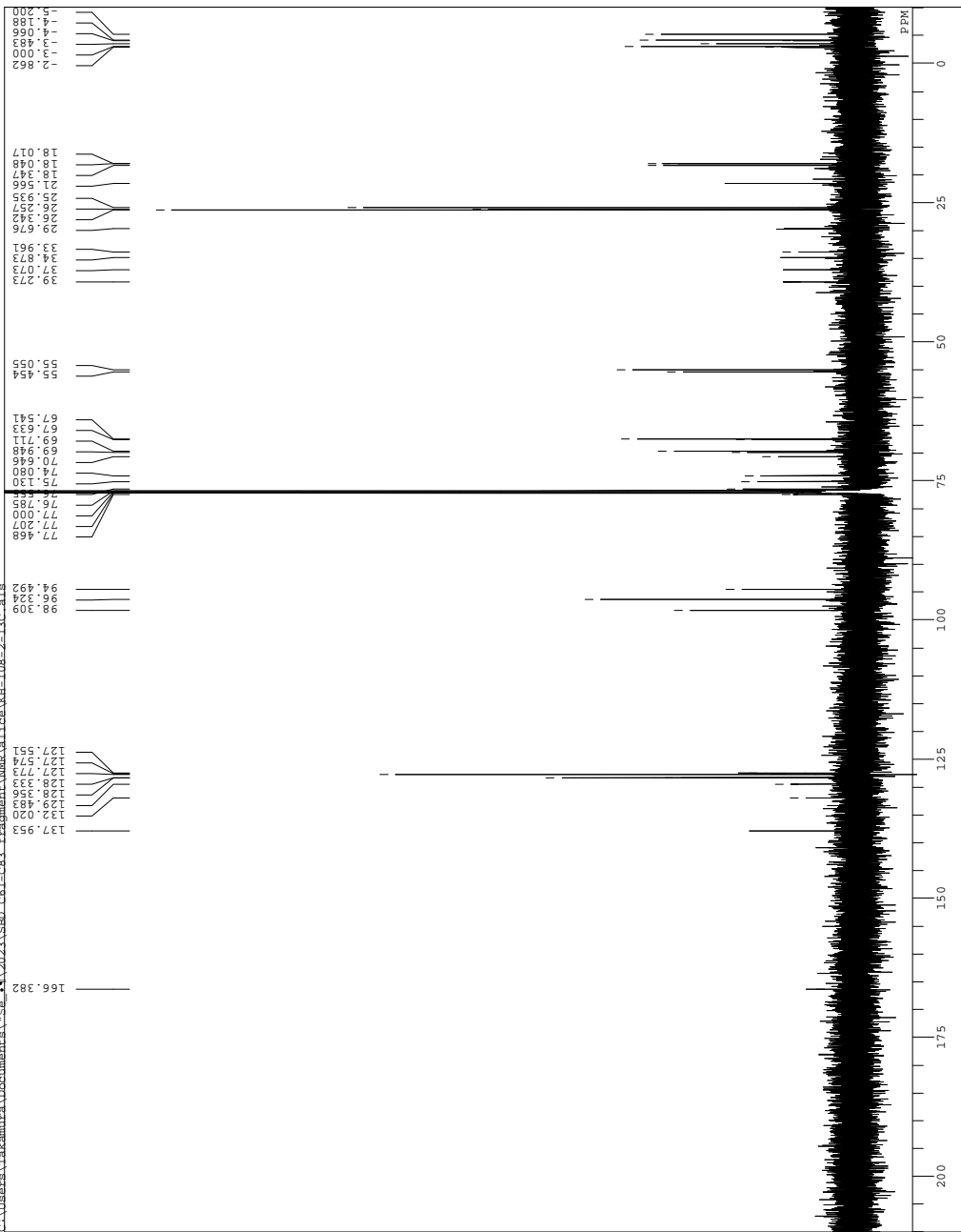
C:\Users\Takamura\Documents\Sample\2021\EBD_C61-C83_Fragment\NMR\valice\KH-108-2_als

DRIF KH-108-2_als
COMT KH-108-2
DATE 2019-10-09 19:21:58
DEMO H1
NAME H1
PULPRO s2pul
ORSET 599.76 MHz
FREQ 5.06 KHz
PROB 32068 Hz
PULPRO 9615.38 Hz
SCANS 3.4073 sec
PD 1.5921 sec
PFI 5.25 usec
CTEMP 25.0 C
SOLNT cdc13
SOLNT 7.26 ppm
RF 0.12 Hz
RGAIN 4.44



C:\Users\Takamura\Documents\Se-4\2023\SRD_C61-C83_fragments\NMR\all\c61\KH-108-2-13C_als

DATE KH-108-2-13C_als
 TIME 18:57:10
 DATE 2023-02-22 10:21:34
 INSTR C13
 PROC S2pul
 P1 150.82 MHz
 OBSF 6.72 MHz
 OBPC 32768 Hz
 DRT 37878.79 Hz
 FREQ 0.864 sec
 SCANS 2.1349 sec
 PD CYM
 PULPROG 5.75 usec
 PM1
 PRGNAME caci13
 PROC 25.0 c
 TRF
 SFT 77.00 ppm
 EX 0.160 Hz
 EPGF1
 SFTV1
 RGAIN

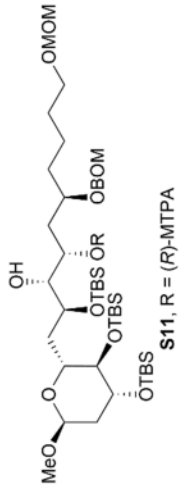
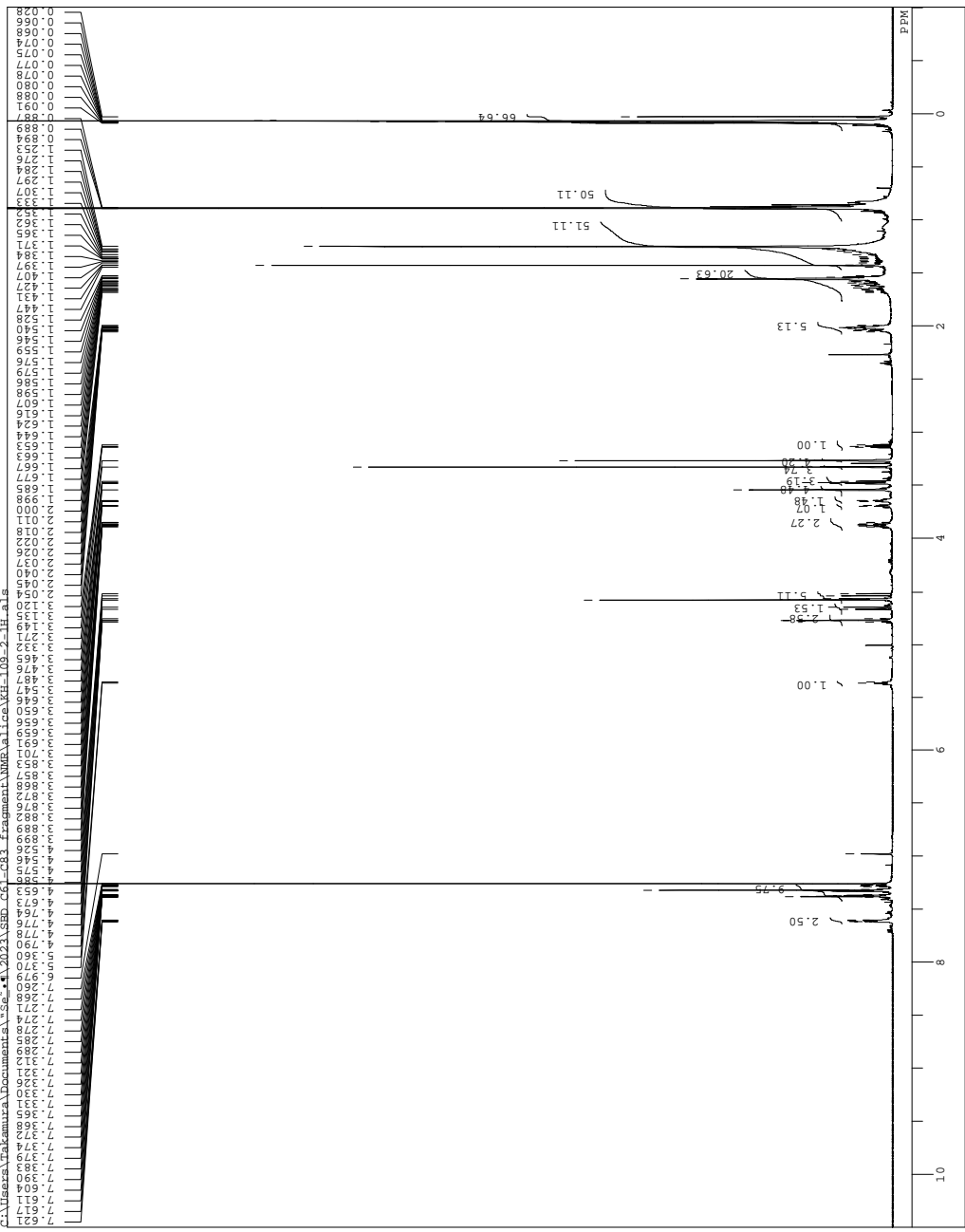


C:\Users\Takahara\Documents\4-8-2023\SED_061_C03_Fragment\MMR\all\ca\KH-109-2-1H_als

```

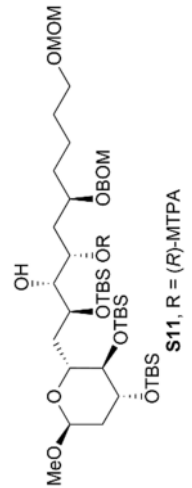
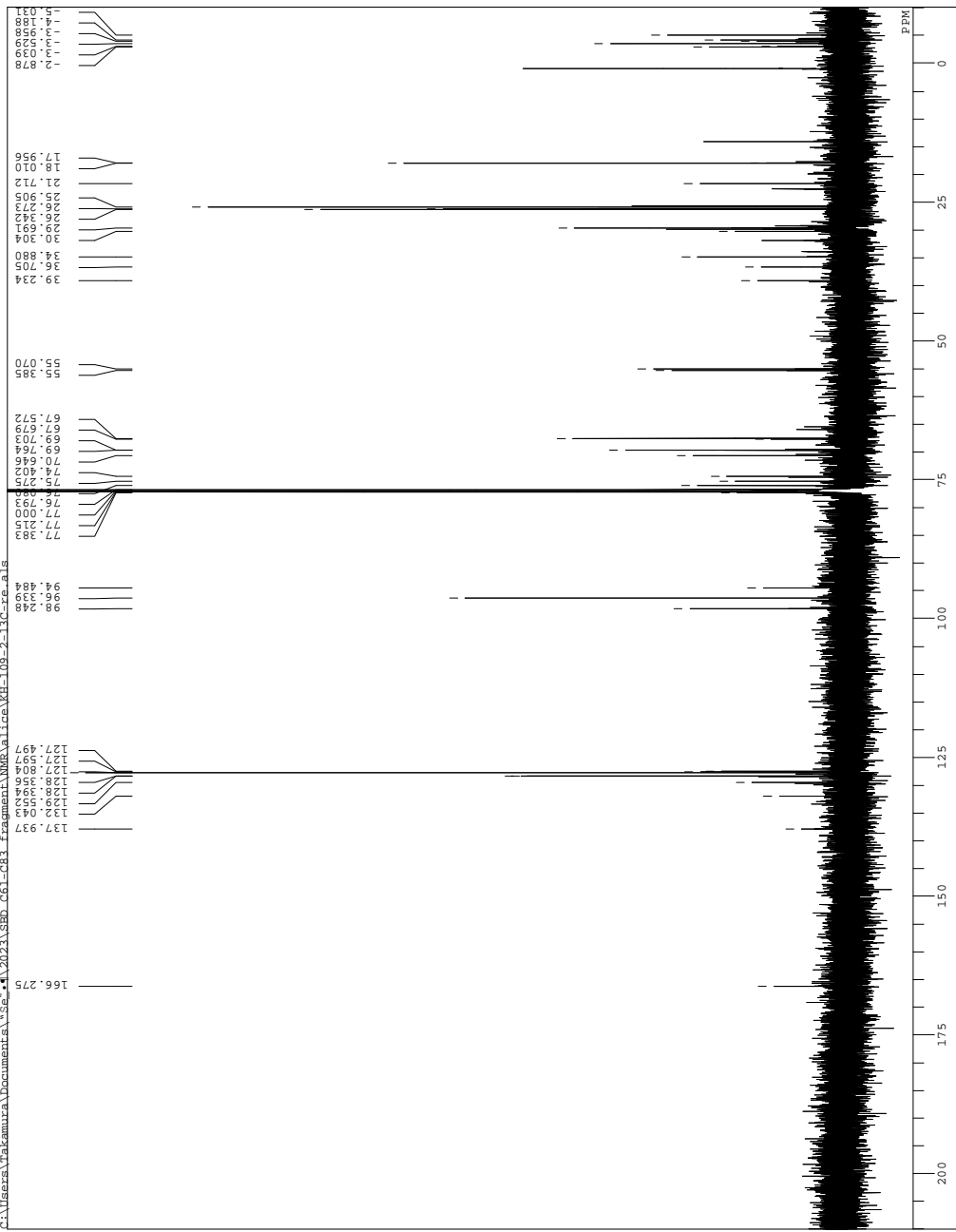
FILE KH-109-2-1H_als
COM1 KH-109-2-1H_Data
CONTC 020-02-15 10:09:25
PRG 2
EXMOD s2pul
OBPQ 599.76 MHz
OBP 0.60 Hz
OBF 0.60 Hz
POINT 9632768 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PUL 5.25 usec
IRNUC
CTEMP 25.0 c
EXPEF cdc13
BF 7.26 ppm
RGAIN 0.12 Hz
40

```

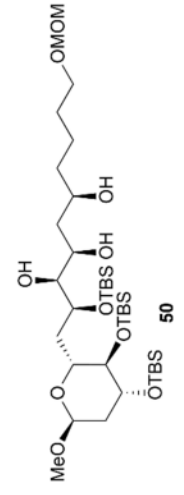
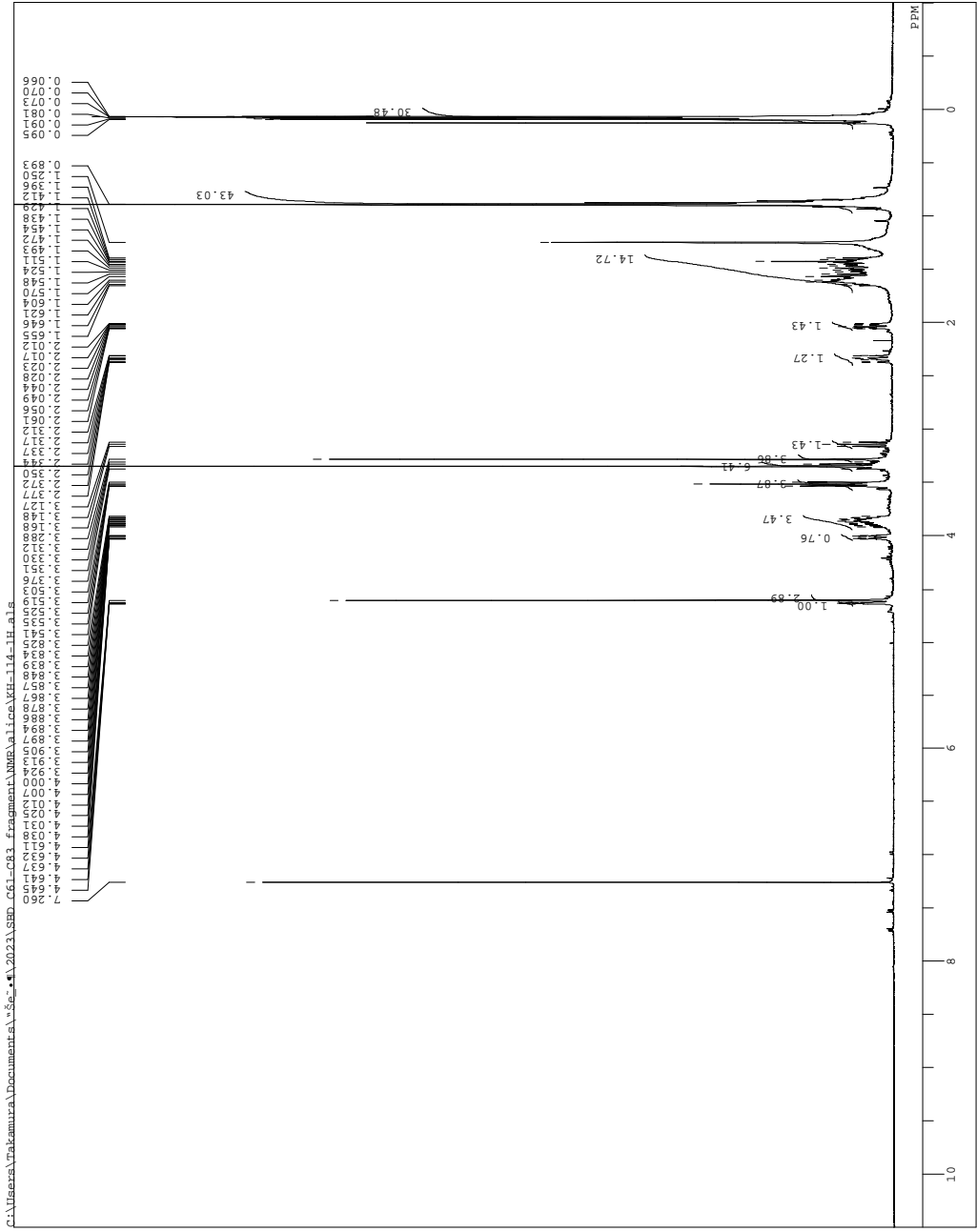


C:\Users\Takamura\Documents\Se*\2023\SRD_G61-G83_Fragment\NMR\all\ca\KH-109-2-13C-re-als

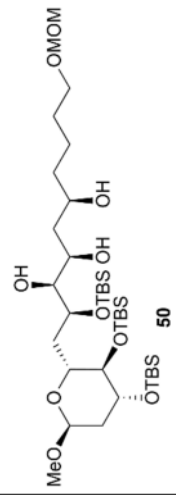
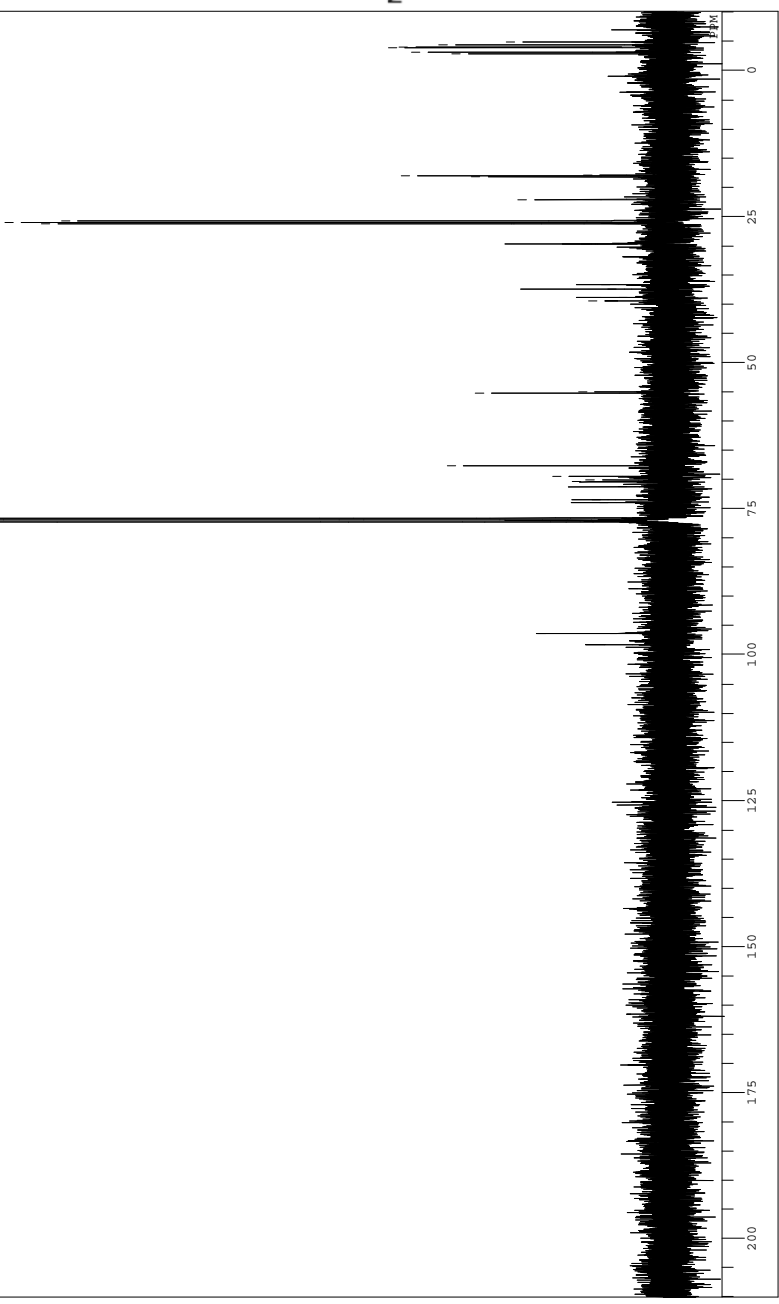
DEFILE KH-109-2-13C-re-als
 COMPT KH-109-2-13C
 ONVIC C13-03-31 23:26:24
 EXMOD s2pul 156.82 MHz
 OBSFO 8.70 Hz
 POINT 37876.64 Hz
 SCANS 0.8651 sec
 ACQTM 2.610 ssec
 PUL 6.10 ssec
 IRNUC cdcl3 83.0 c
 STPM 77.00 ppm
 EXREF 0.12 Hz
 RF 60
 RGAIN



C:\Users\Takamura\Documents\Se-4\2021\88D_661-c81_fragment\MSX\114-1H_als
 DEPT 135 114-1H_als
 F2 114-1H_als
 DATE_ 2019-12-13 12:13:28
 TIME 12:13:28
 ORNVC H1
 EXPNO 2
 PROCNO s2pul 399.91 MHz
 RESOL 1.99 KHz
 ORF1N 2.00 Hz
 FREQ0 6410.26 Hz
 SCANS 32
 PCYTM 1.5000 sec
 PM1 7.25 usec
 PM2
 PM3
 TENDC 30.0 c
 SLOPE
 SILVNT cdcl3
 EXREF 7.26 ppm
 RGAIN 0.42

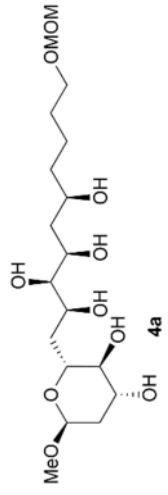
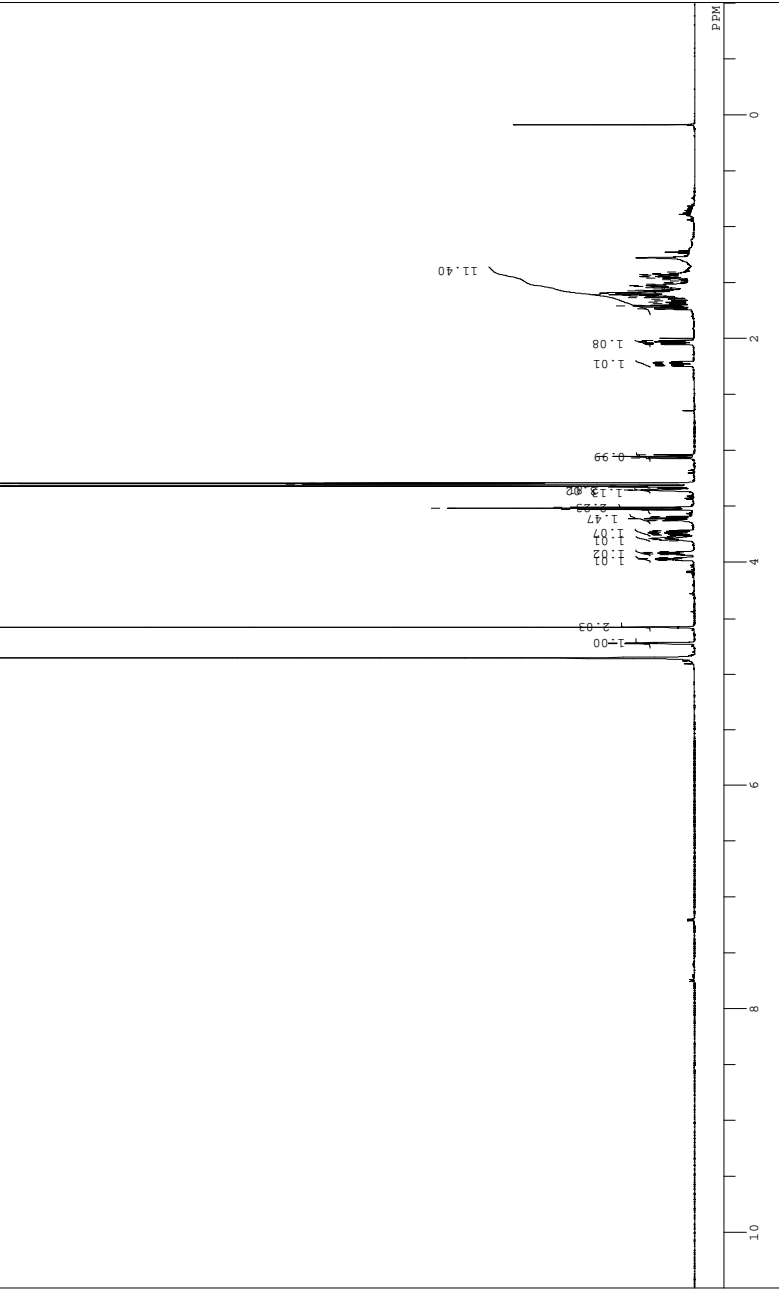


C:\Users\Yakamura\Documents\Se...2023\8BD_061_c83_fragment\NMR\data\KH-114-13C_als
 Date_ KH-114-13C_als
 Time 12:13:23
 Date_ 2019-12-13 12:21:49
 Name_ C13
 OBNC C13
 EXPNO 2
 PROCNO 2
 F2 100.62 MHz
 F3 100.62 MHz
 OBPRG 100.56 MHz
 OBSF1 8.40 KHz
 OBSF2 8.40 KHz
 OBSF3 8.40 KHz
 FREQD 250000.00 Hz
 FREQD2 250000.00 Hz
 SCANS 1
 PC 1.64
 PC2 1.6803 sec
 PC3 5.90 usec
 PULPROG zgpg30
 PWD 1.00
 PMW 1.00
 L1 100.62 MHz
 L2 100.62 MHz
 L3 100.62 MHz
 SFO 100.62 MHz
 SOLVENT cdcl3
 T1 77.00 sec
 T2 77.00 sec
 EXPT 77.00 sec
 ACQ 77.00 sec
 RGAIN 0.54 Hz



C:\Users\Takamura\Documents\Se-4\2021\SHD_661-G31_Fragment\NMR\1ca\KH-125-1H_als

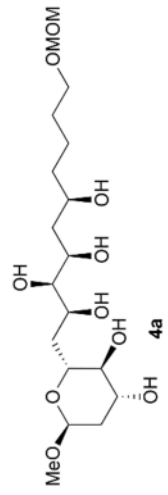
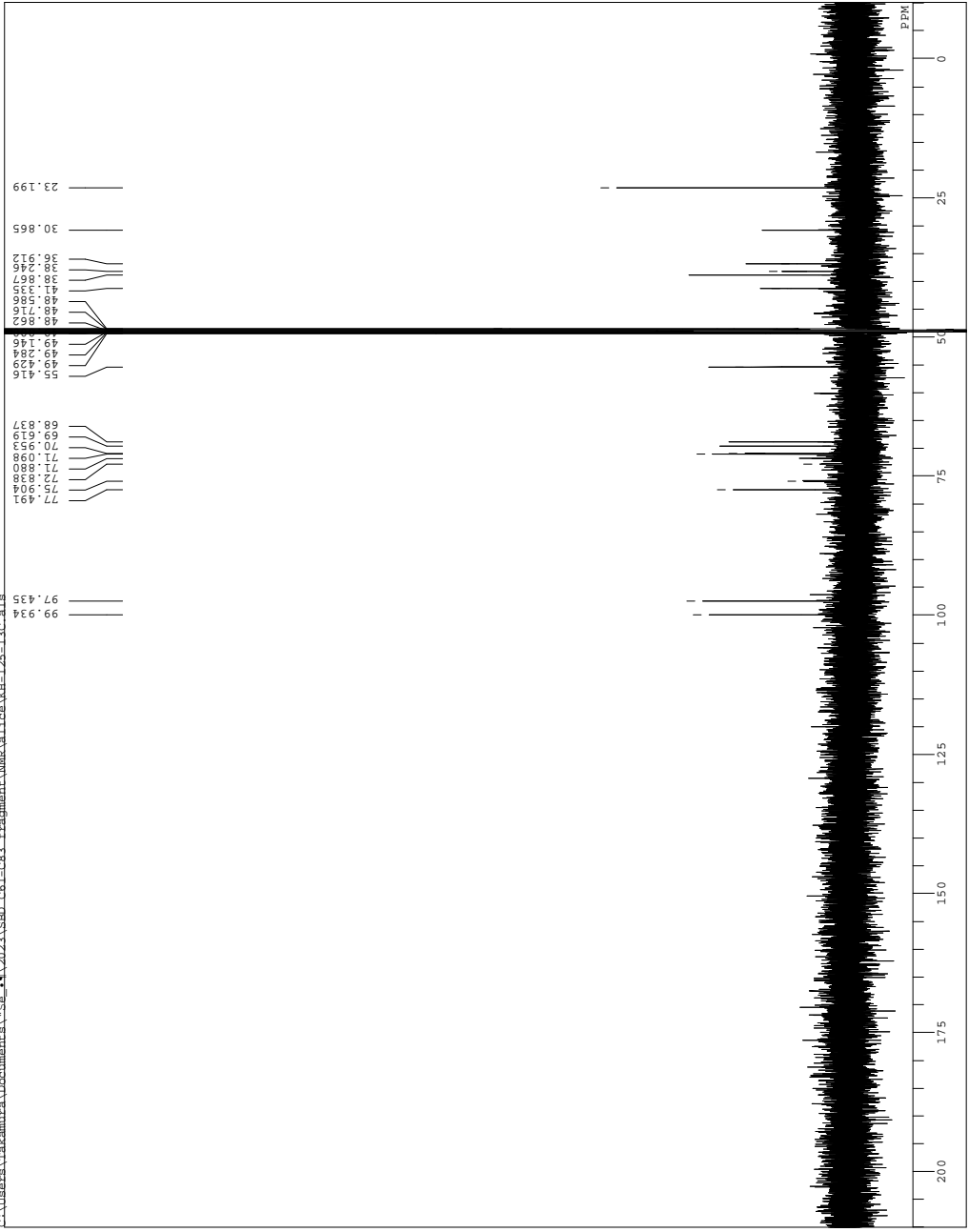
FILE KH-125-1H_als
 Conv 20201127 20:56:43
 COM 1
 ORNUC H1
 ES 2
 EXMOD s2pul
 OBSF1 599.76 MHz
 OBSF2 7.42 KHz
 OBSF3 3.60 Hz
 PFGM1 9635.38 Hz
 PFGM2
 SCANS 32
 ACQTM 3.45079 sec
 PUL 1.5.25 usec
 INTC
 IRTN 25.0 c
 SFTN
 SFTV cd3pd
 EXREF 3.30 ppm
 RGAIN 0.42 Hz
 RAIN



4a

C:\Users\Takamura\Documents\Se*\2023\8RD_061-C83_fragment\NMR\125-13C_als

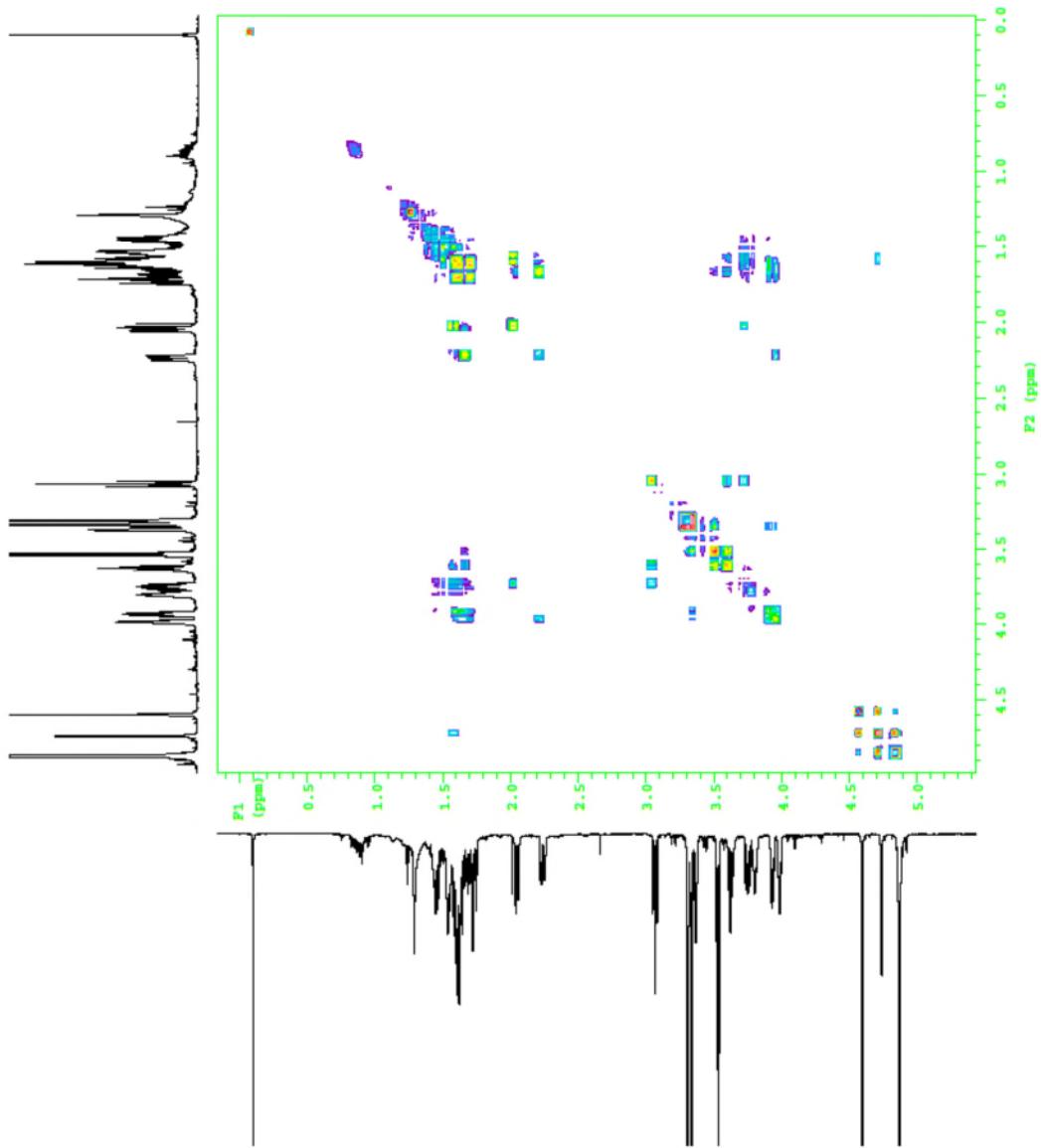
DATE KH-125-13C_als
 TIME 11:13:18
 DATE 2023-01-27 21:01:44
 ORNU C13
 PULPROG zgpg30
 ACF0 s2pul
 OBSFQ 150.82 MHz
 OBSFZ 7.32 KHz
 DWT 32768 Hz
 DWIN 32768 Hz
 FREQD 37878.79 Hz
 SCANS 64
 PD 0.864 sec
 PDCY 2.1345 sec
 PDEL 5.75 usec
 PML C
 TRM 25.0 C
 TRMPC
 TRMPP
 SILVNT cd3od
 EXPT 49.00 PPM
 EXREF 0.160 Hz
 RGAIN



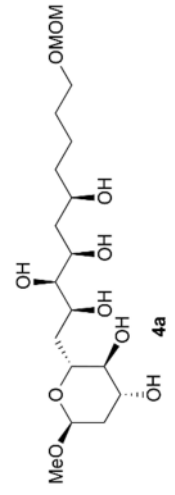
```

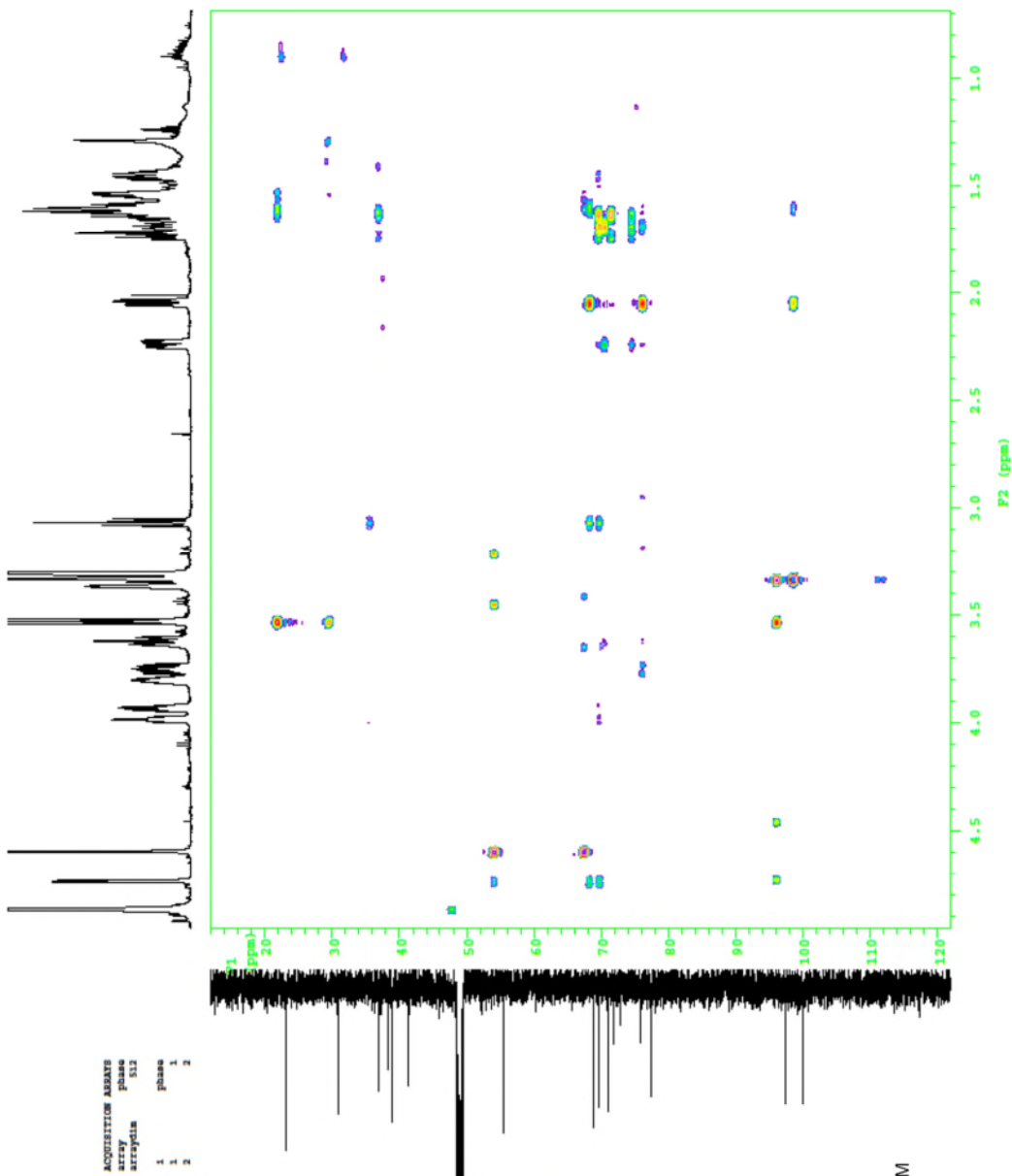
EX-125_Data
exp3 gCOSY
=====
NAME          PLAGE
date   Jan 27 2020   hr
solvent cdcl3
sample  6120
=====
ACQUISITION
pw          9115.4   temp      not used
pc          2155   shif1     not used
sp          2184   shif2     0
zb          4000   F2 PROGRMING  0
as          32   sb          -0.075
cl          1.000   sbw      not used
ct          14   fm          4096
=====
2D ACQUISITION
pw          9115.4   shif1     not used
pc          2155   shif2     not used
sp          2184   shif3     not used
=====
F2 F1
=====
F2 F1
=====
NAME          n          DISPLAY
-----
wt          -14.1
tm TRANSMITTER  n          sp          3075.1
w          599.787   wpl          3356.9
toF          599.7   rF1          3356.9
tpwr          59   rF2          3378.2
pw          10.500   rF3          3308.5
=====
GRABBER 1105
SOLVIE  0.001000   WC          351.9
KIDratio 1.000   WC          9.8
gpcTab  0.000500   wC3         208.9
=====
C13 VS
C13 VS          445
C13 VS          445
=====
SI   C13   4

```



$^1\text{H}-^1\text{H}$ COSY (600 MHz, CD_3OD)



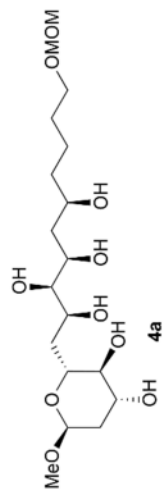


```

KE-135_Data
exp5 gsmc
ACQUISITION ARRAYS
date Jun 27 2020 hr 00 min
solvent cd3od
p1 7
arrayid 512
phase 1
array 1
phase 2
acq 9615.4 SPECIAL
at 0.150 temp not used
zb 2884 gain
zc 4000 ap1a
zd 1.00
ze 12 CHANNELS 500
zf 12 F1 0.001000
zg 12 F2 0.001000
2D ACQUISITION
sw1 36195.1 F1 1500
sw2 256 F2 256
phase arrayed
PROBHDATUM
nu1 -0.075
nu2 0.075
nu3 0.075
nu4 0.075
nu5 0.075
nu6 0.075
nu7 0.075
nu8 0.075
nu9 0.075
nu10 0.075
nu11 0.075
nu12 0.075
nu13 0.075
nu14 0.075
nu15 0.075
nu16 0.075
nu17 0.075
nu18 0.075
nu19 0.075
nu20 0.075
TRANSMITTER
tx 01 F1
sfrq 599.787 F1a1 not used
tuf 599.7 F1a1
tpr 59 F1a1
pwr 10.500 F1a1 DISPLAY 2048
P1 CHANNELS
dn 120000000 F1 413.9
dot 1542.4 F1a1 1800.9
dm 1542.4 F1a1 1800.9
dncvwrw M1a1 1305.9
dncf 31008 F1a1 2264.4
dncf 31008 F1a1 2264.4
p1a1 55 F1a1
pwr 12.100 F1a1 PLOT
j1a3 146.0 ac 9.8
j1a4 81.0 wcd 208.9
wcd 81.0
wcd 132
ts 12
a1 cd3 od 37

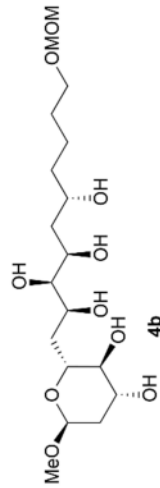
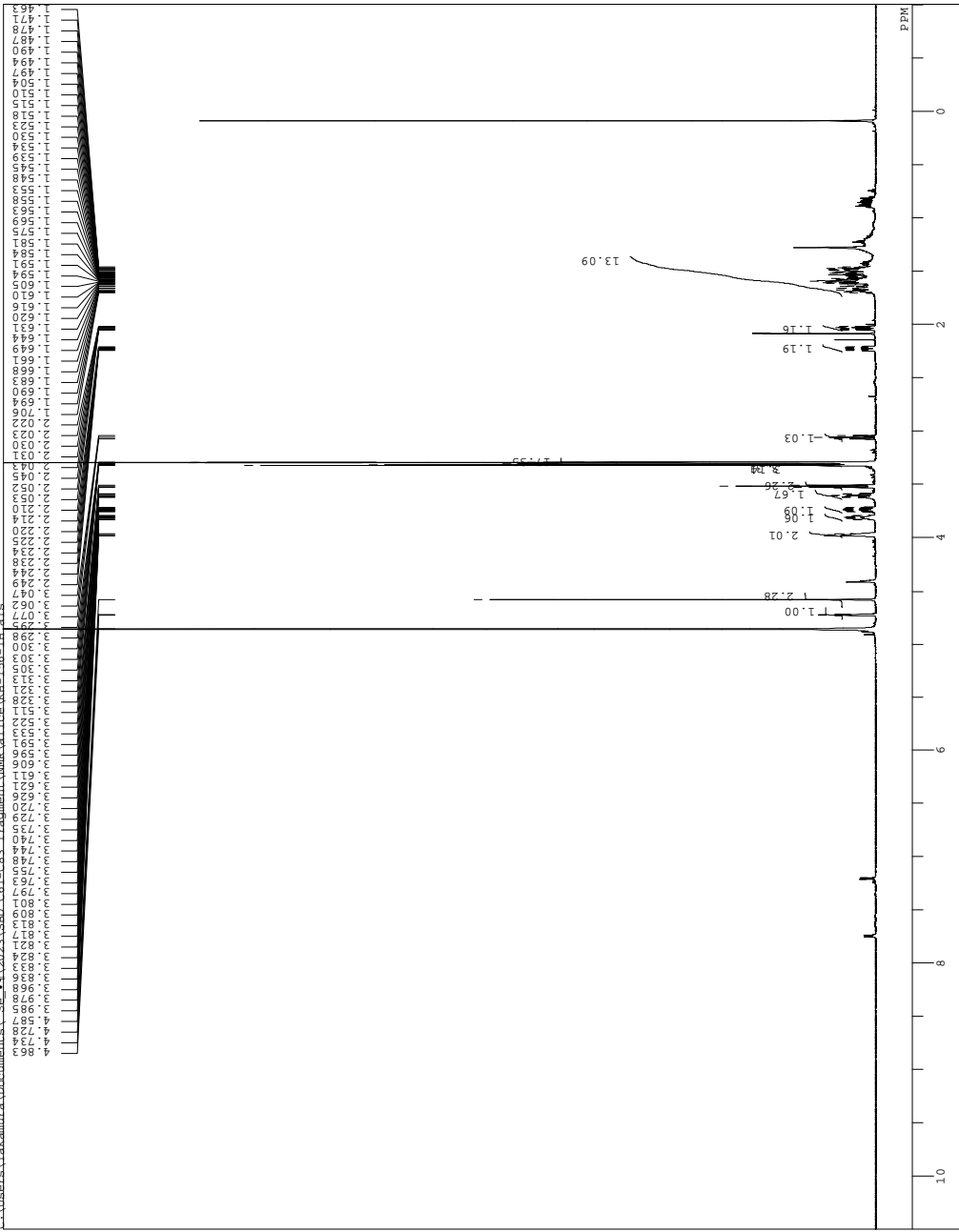
```

HMBC (600 MHz, CD₃OD)



C:\Users\Takamura\Documents\Se_*\2021\GSD_661-c83_fragment\NMR\1h\caXH-156-1H.als

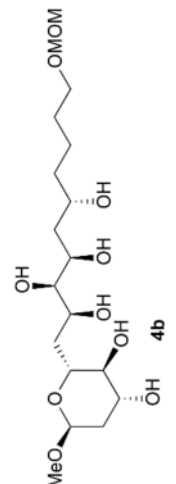
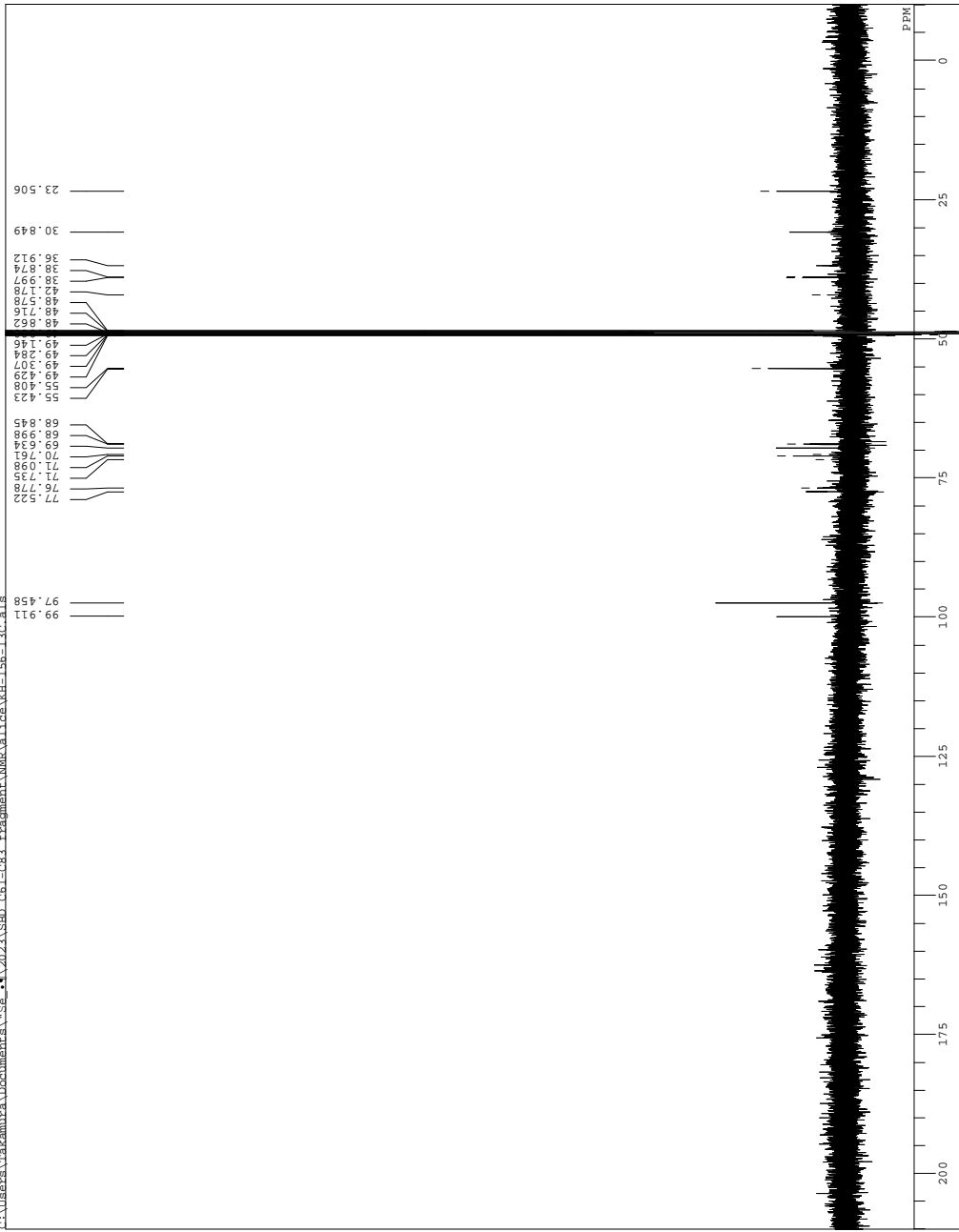
DETE KH-156-1H.als
VOP 2020-02-04 21:01:36
DATE 2020-02-04 21:01:36
DIR H1
NAME s2pul
PULPROG 599.76 MHz
PROBHD 7.42 KHz
PULPROG 3.60 Hz
PROCNO 9615.98 Hz
FREQ 9615.98 Hz
SCANS 32
PCYCLE 3.48 sec
PCYCLE 1.5921 sec
PCYCLE 5.25 usec
PWI 25.0 c
IRMSQ 3.30 pfm
SOLVENT cd3od
EXREF 0.46 Hz
RGAIN

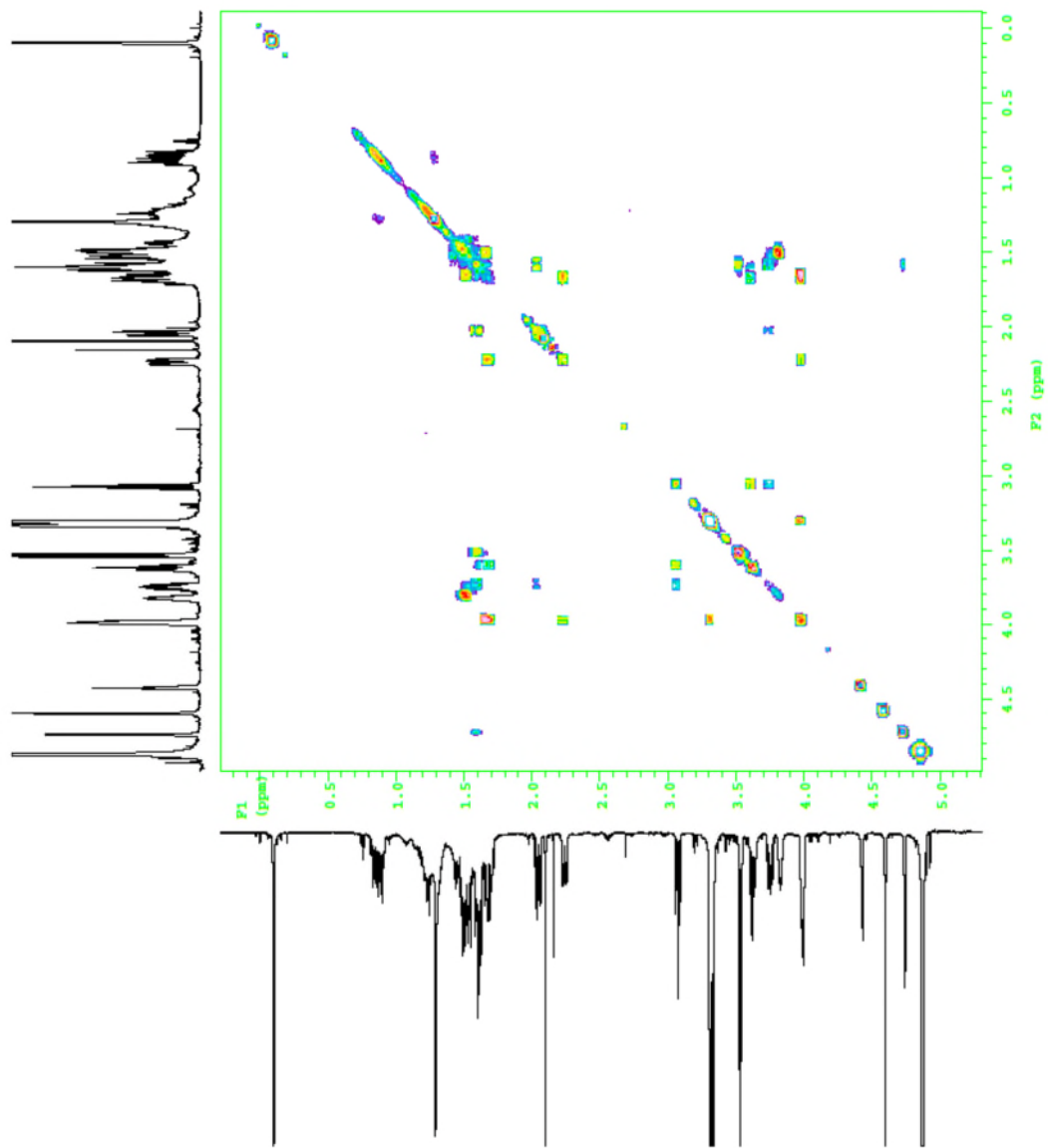


C:\Users\Takamura\Documents\Se_*\2021\SRD_061-c83_fragment\NMR\data\KH-156-13c_als

```

DEFILE KH-156-13c.als
COMP  20200204
ORIG  20200204 21:05:40
PROC  C13
EXMOD  s2pul
PULSE  150.82 KHz
PROG  3.00 Hz
OBFTN  3787879 Hz
PCPD  64
SCANS  0.8631 sec
ACQTM  2.575 usec
RES  0.12 Hz
PWL  25.0 c
IRMUC  49.00 PPM
SOLNT  cd3od
SUN  0.12 Hz
EXREF  0.00 PPM
RGAIN  0.00
  
```



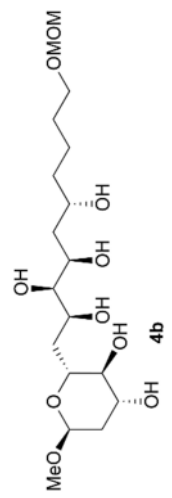


```

EX-156-1E_Data
exp) gcosy
=====
NAME      SAMPLE          FLAG
date     Feb  4 2015      m
solvent  CD3OD                m
sample   6130                 m
ACQUISITION
=====
acq       9415.4 temp not used
at        2884 spm          46
ap        4950             20
aq        12             0
al        1.000 sde       not used
dt        16             16
=====
2D ACQUISITION  F1 PROCESSED
=====
wv       9415.4  sol       -0.027
al        256  shsa1  not used
c1         0    f2proc  4094
=====
PREPARATION  n    DISPLAY
=====
wt        n    sp       -83.9
=====
TRANSMITTER  wp       3651.8
tx            RI     sp     -173.9
afiq       539.767  wpl     3356.3
tqc        579.9    fil     3379.1
pwr        10.500  ffil    3380.1
p#         GRADIENTS  fqa1    1979.2
=====
GALVAN     5102      PLOT   351.9
GBR        0.001000  WC
kdratio    1.000   ac       9.8
spread     #160500  wds    286.3
=====
ON          CLK  W         286.4
OM          MM  W         16.4
=====
SI  OBS   BY
=====

```

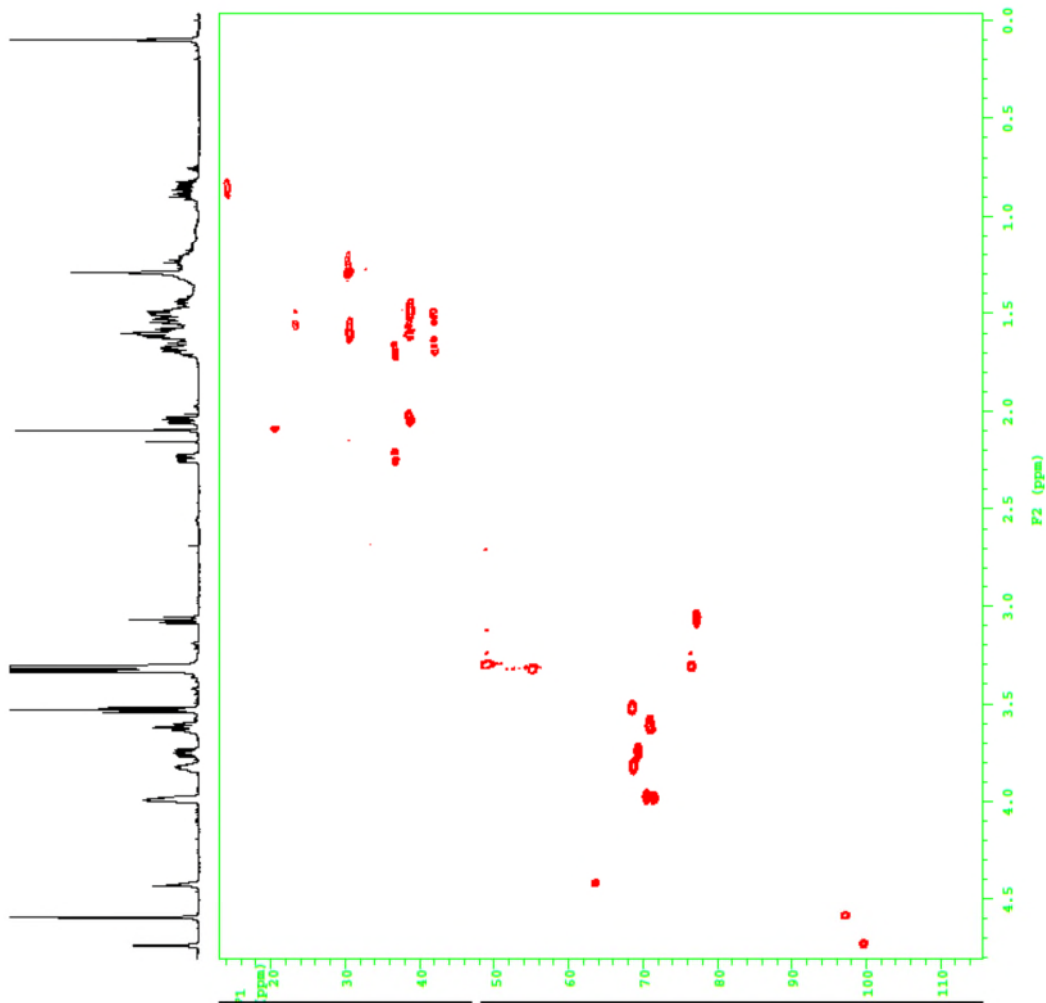
¹H-¹H COSY (600 MHz, CD₃OD)



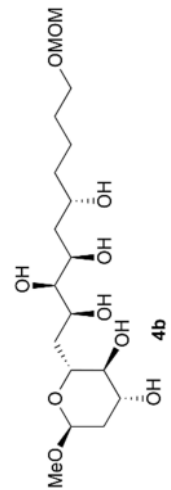
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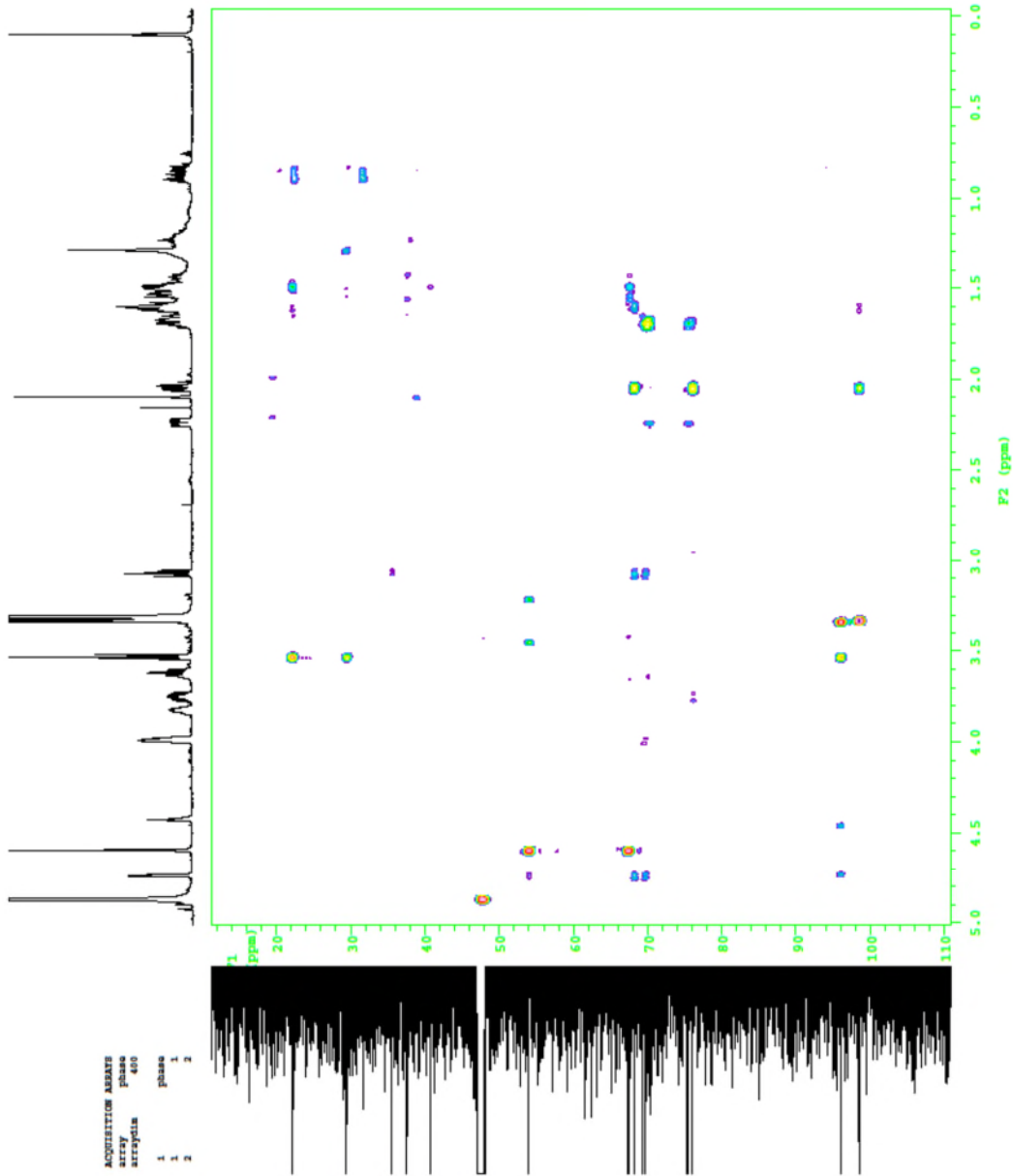
XR-156-1E_Data
emp3 gMQC
=====
Date_  Sub  4  2020  ha
Solvent_ cd3od
Sample_
Acquisition_ 6120
=====
ac  9433.4  SPCIAL  1  phase
sc  0.150  temp  not used  1  1
st  1200  SPC  20
rs  4000  SPC  20
=====
ss  32  GRADIENTS  0
dl  1.000  SVAIR  5102
nt  32  GC  0.002000
=====
2D ACQUISITION_  KRatio  3.977
wt  2166.0  SPC  0.16000
st  2100  SPC  20
rs  2100  SPC  20
=====
Phase_  arrayed  gf  0.069
Pulsation_  gfs  not used
suzsoda_  n  fn  4096
wt  10.500  sp  -19.1
=====
TRANSMITTER  n1  SFL  0.007
tx  598.747  SPC  20
=====
f1  599.7  F1  2048
=====
pw  10.500  sp  -19.1
=====
dc  1983.4  SPC  2901.5
de  -2192.0  SPC  1849.4
df  3188.9  SPC  13186.9
=====
deconvolve  W40  compare  rFD  1979.2
dat  31008  rFD  8731.6
=====
qpcw  48  rFD  7389.7
pccw  56
=====
poc  13.100  w  351.9
=====
j13c  146.0  W  208.0
sol13c  y  s2  0
mult  2  vs  286
=====
al  ods  ph  2

```



HMQC (600 MHz, CD₃OD)



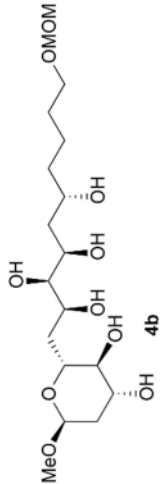


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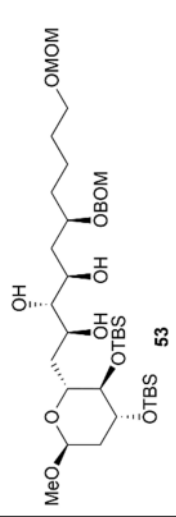
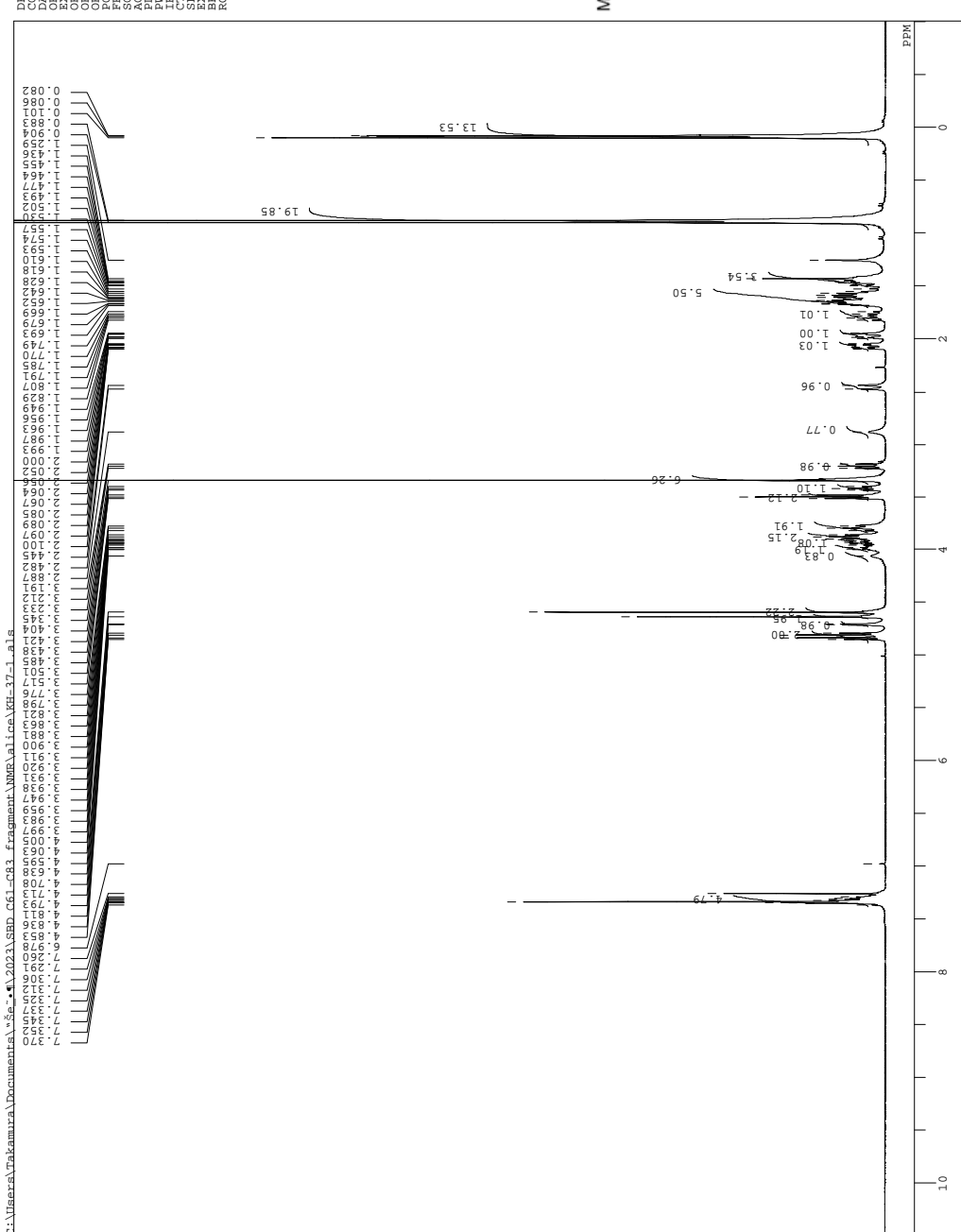
EX-186-18_Data
exp4 gsmc
ACQUISITION PARAMETERS
NAME 4 2020 ha
SOLVENT cd3od
ACQUISITION 6120
SPECIAL
TEMP not used
PULPROG zgpg30
DELTA 4.000
DELTA2 0
DELTA3 0
GRADIENTS 32
G1 1.800 g1v11 500
G2 32 g11 0.001000
2D ACQUISITION g1v13 1500
WEIGHT 36199.1 g1v13 0.001000
PROBHD 5mm QNP1H1
PHASE STRIP04 F2 PROCESSING
PREPARATION ad -0.075
SOLVENTS n ohc not used
WEIGHTS n in 4096
TRANSMITTER n f1 PROCESSING
PULPROG zgpg30
DELTA 5.997 del not used
DELTA2 5.997 g1v13 10
TYPE 59 f11 2048
P1 10.500
P2 DISPLAY
P3
P4
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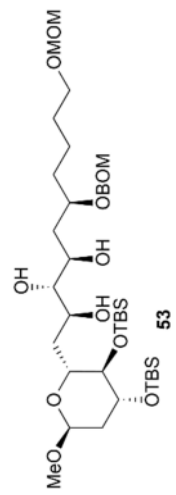
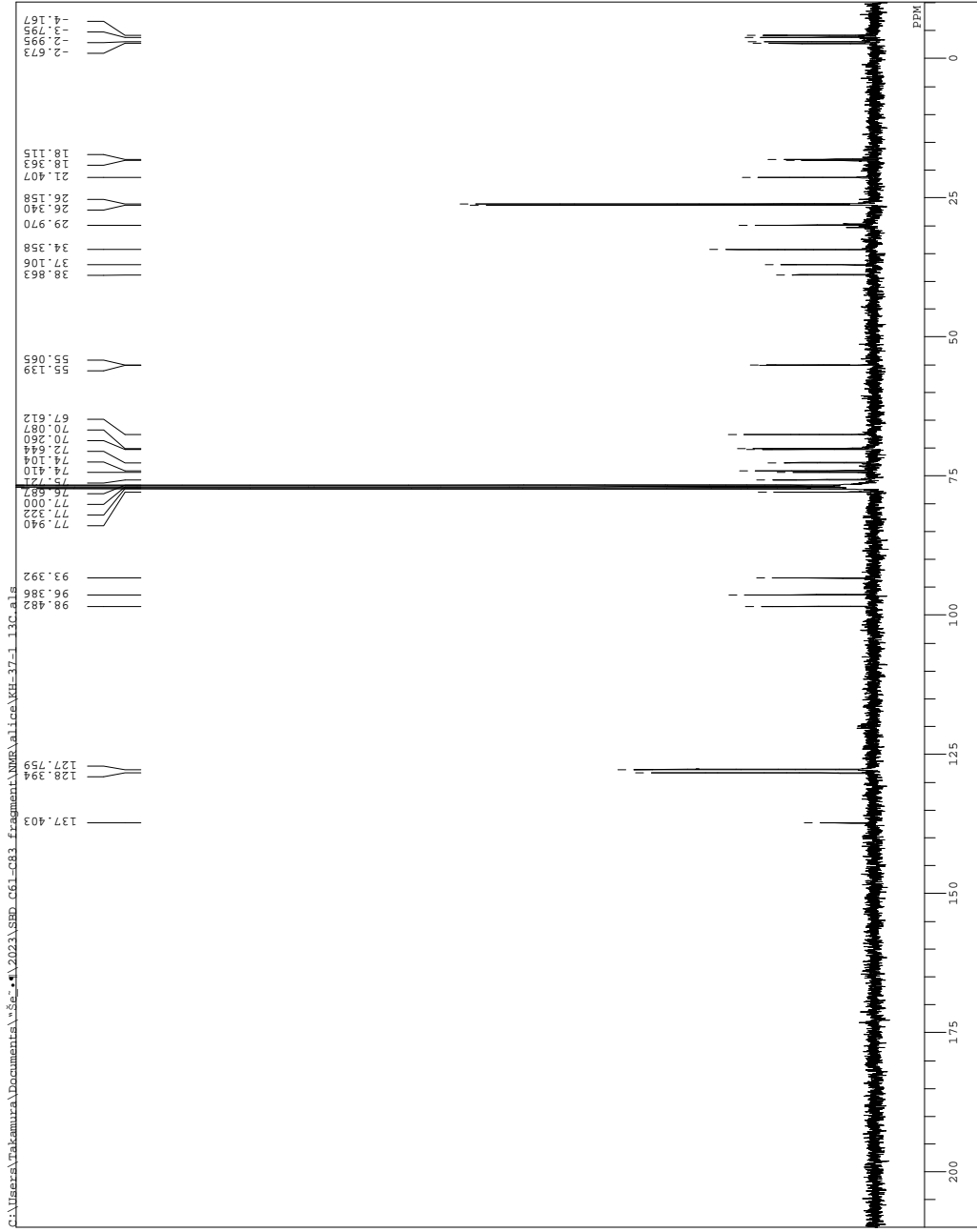
HMBC (600 MHz, CD₃OD)



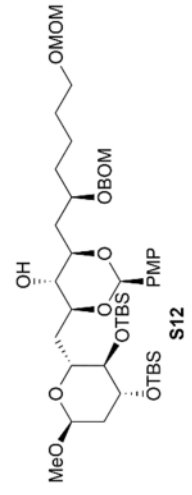
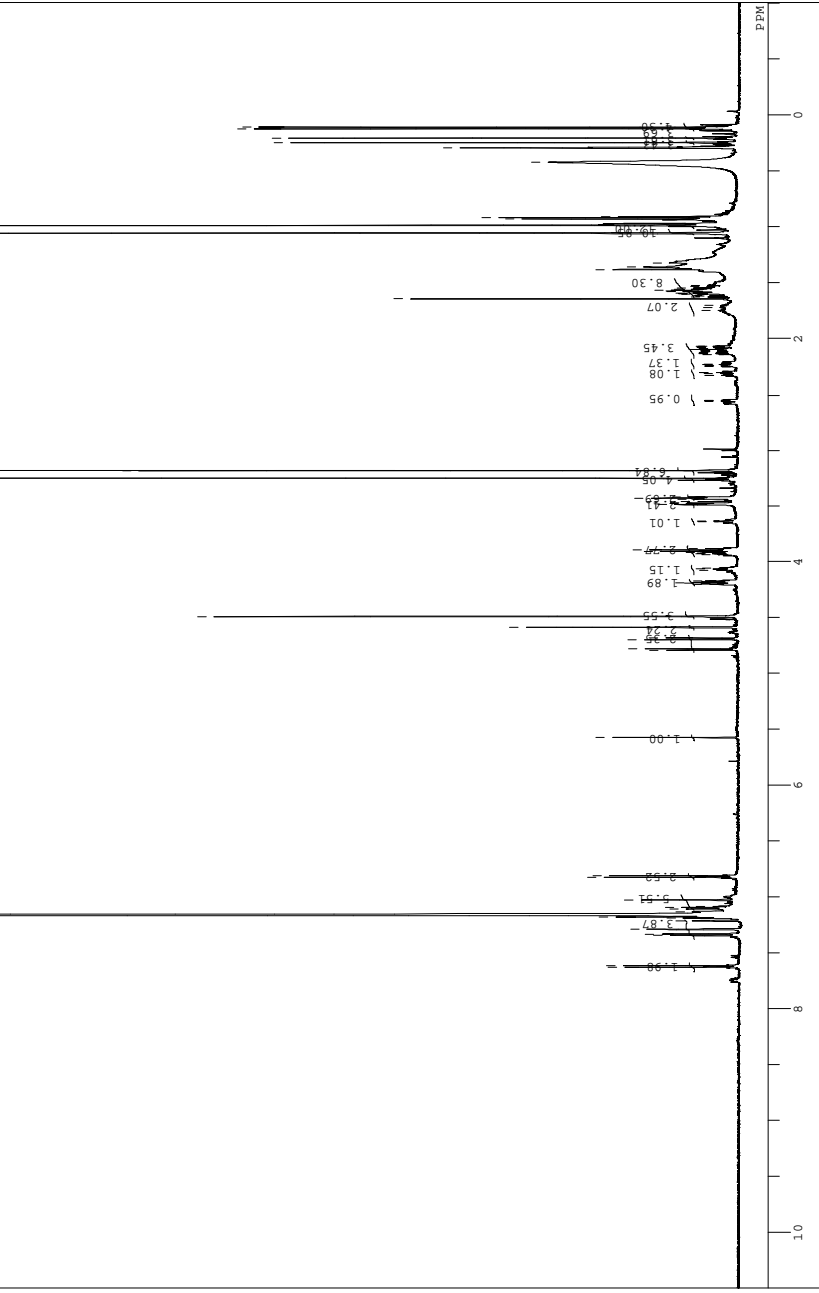
C:\Users\Takamura\Documents\Se...2023\8BD_661_cr3_fragment\NMR\data\KH-37-1_als
 FILE KH-37-1_als
 DATE Thu Feb 21 11:47:21 2019
 INSTR 1H
 PULPROG zgpg30
 PROCNO 1
 F2 399.65 MHz
 F1 124.00 MHz
 OBSERV 13C
 FREQ 79.9160 Hz
 F2 399.65 MHz
 F1 124.00 MHz
 OBSERV 1H
 FREQ 500.1360 Hz
 SCANS 8
 DS 4
 AQ 2.9070 sec
 PC 6.40 usec
 PM 1
 L1 23.6 C
 L2
 L3
 SOLT CDCl3
 SOLNT CDCl3
 EXPT 7.26 min
 EXRF 0.15 Hz
 RGAIN



C:\User\Takamura\Documents\Se_4\2021\SRD_561-C83_Fragment\NMR\alica\KH-37-1_13C_als
 FILE KH-37-1_13C_als
 CONTM Thu Feb 21 12:22:45 2019
 CPD 13C
 ORNOC 13C
 EXMOD BCM
 ESSE 100.40 MHz
 OFPIN 125.00 MHz
 FREQ 10500.00 Hz
 F2FREQ 27137.90 Hz
 SCANS 620
 ACQTM 1.2039 sec
 PUL 1.680 usec
 INTC 1H
 SLEN 25.7 c
 SLVN CDCL3
 EXRF 77.00 PPM
 REAN 2.00 Hz
 RGAIN 2.24

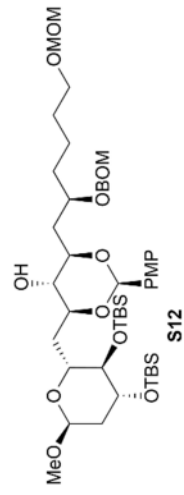
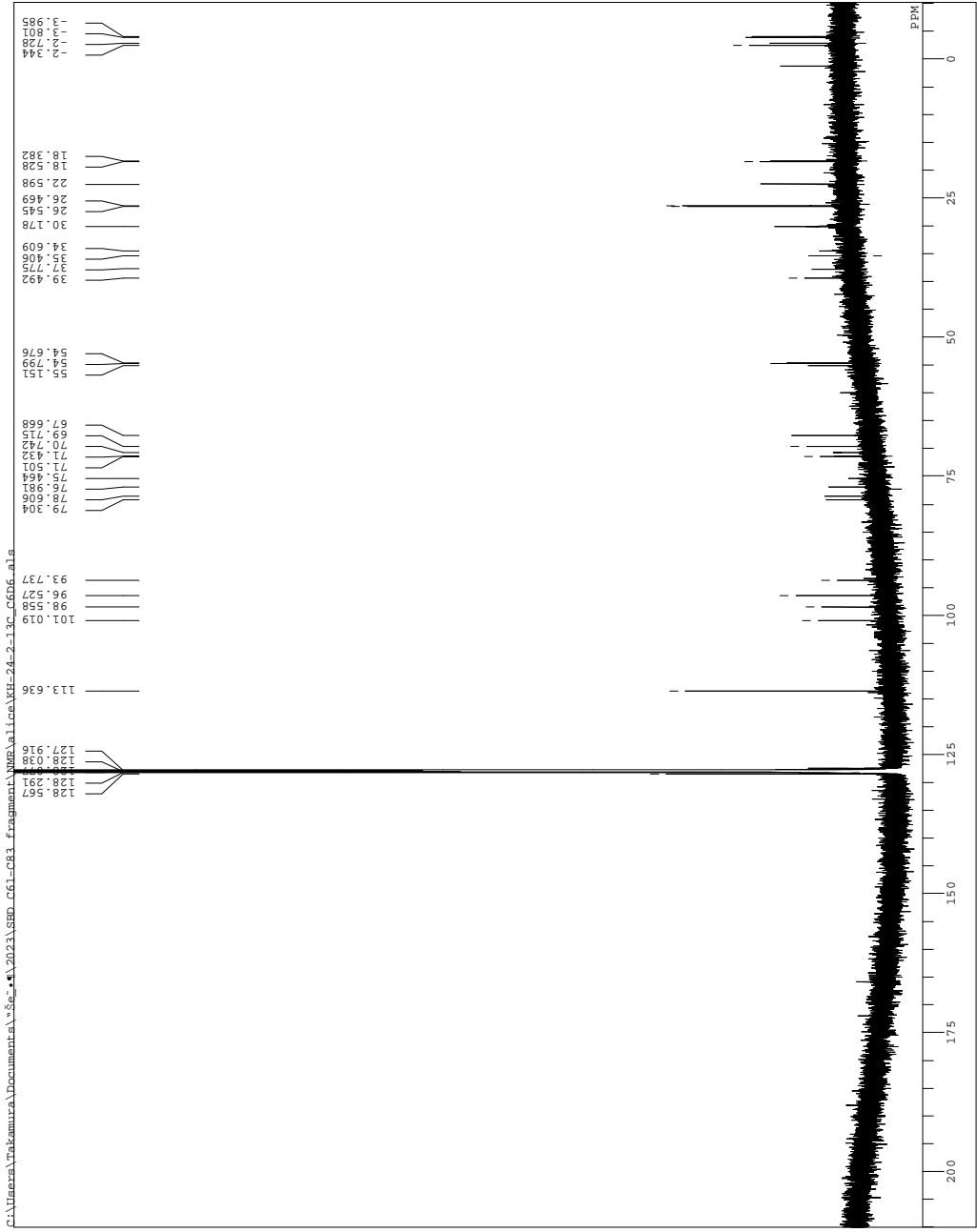


C:\Users\Tadamura\Documents\...2023\SED_061_C03_Fragment\MIR\alpha.Lico\KH-24-2-C6D6-Data.als
 DFILF KH-24-2-C6D6-Data.als
 COMF KH-24-2-1H-Data.als
 CONTC 2020-02-13 21:05:59
 EXMOC 1
 EXMOD S2pul
 OFPRQ 599.76 MHz
 OFPFI 4.50 Hz
 OFPIN 4.50 Hz
 POINT 962768 Hz
 SCANS 32
 ACQTM 3.4079 sec
 PD 1.5921 sec
 PUL 5.25 usec
 IENUC
 CTEMP 25.0 c
 EXPRF c6d6
 BF 7.16 ppm
 RGAIN 0.12 Hz
 42

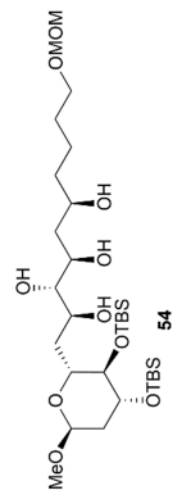
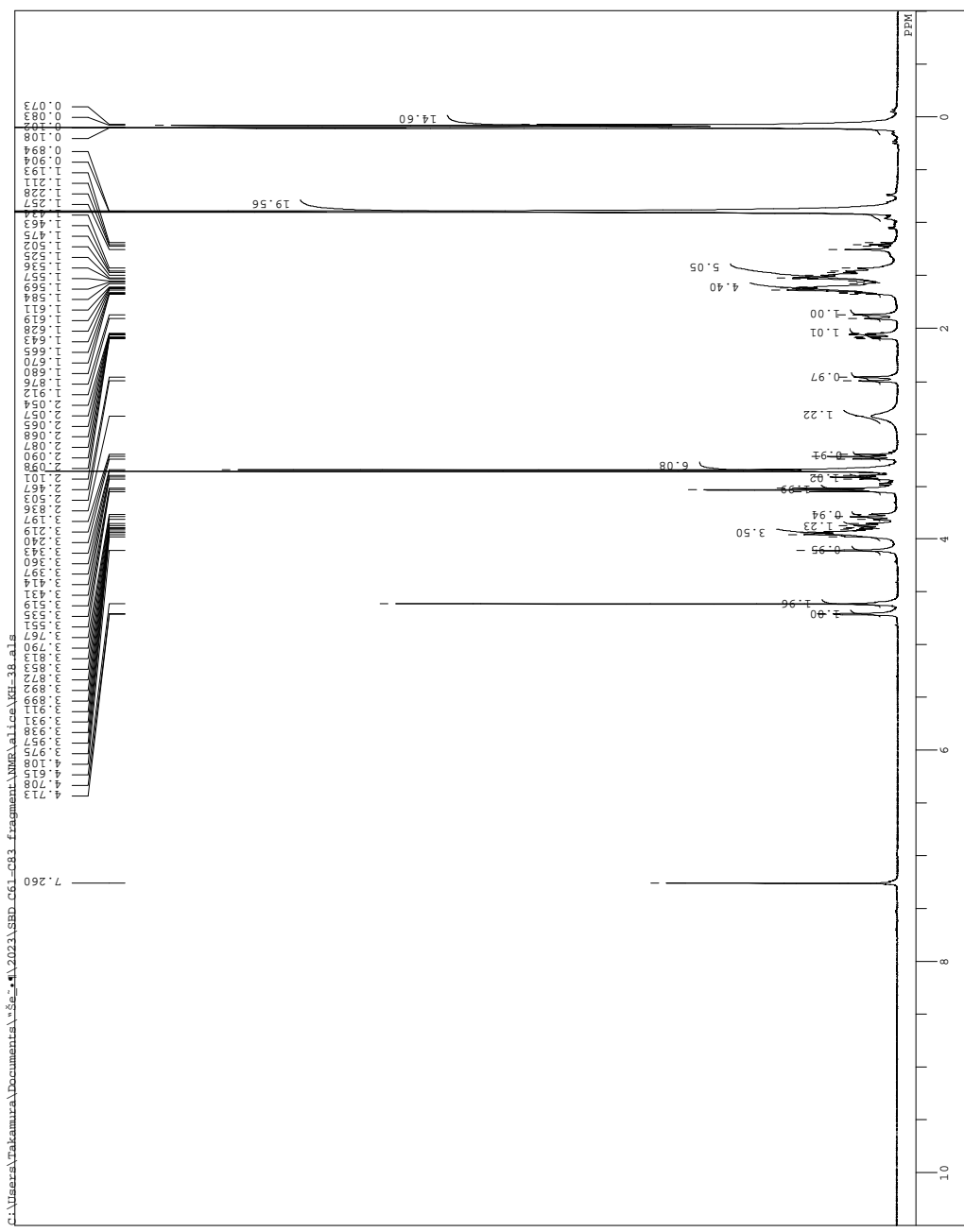


C:\Users\Takatsuma\Documents\Se_*\2021\86D_661-c83_fragment\NMR\all\ce\KH-24-2-13c_66D6_als

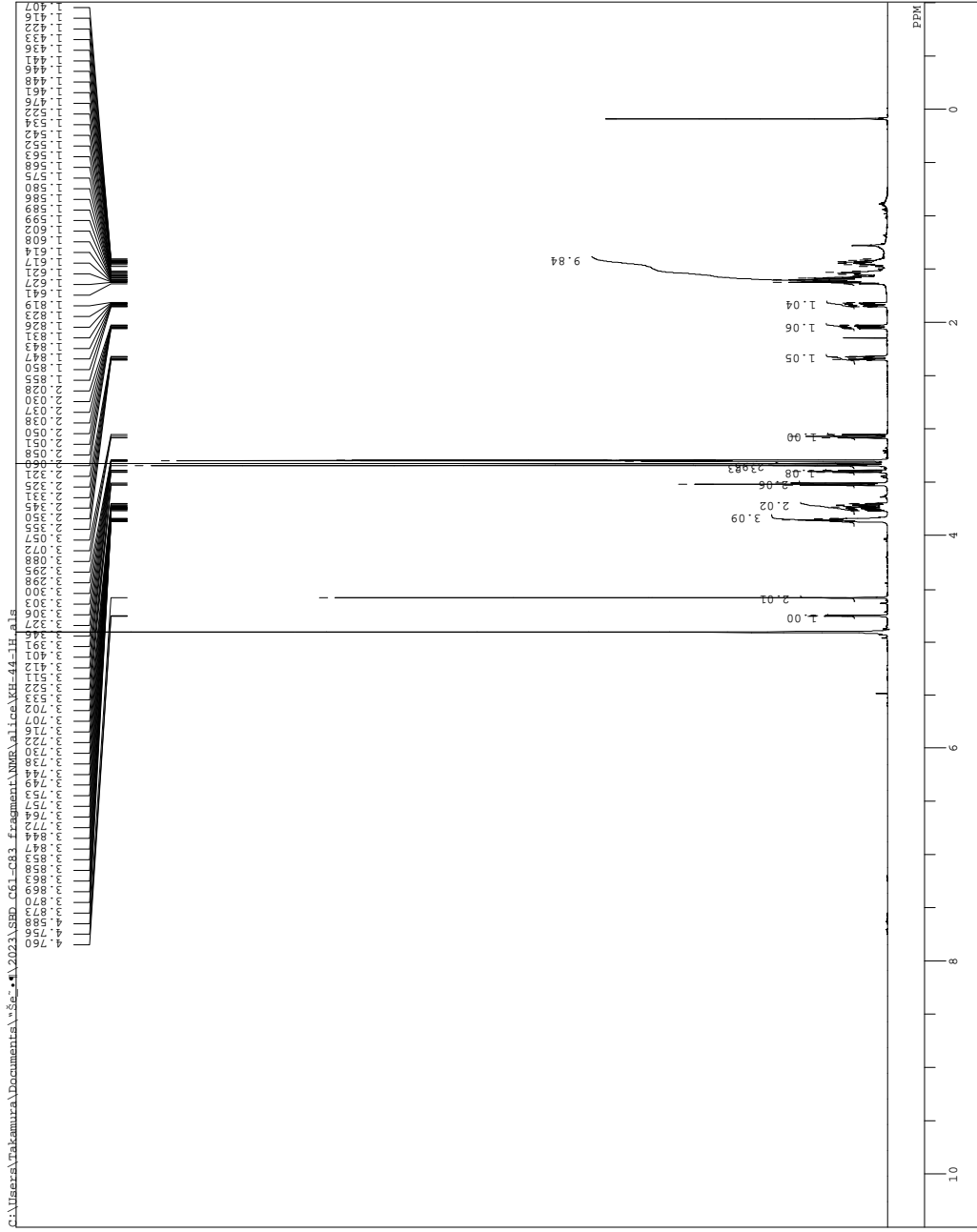
DEPT KH-24-2-13c_66D6_als
 INSTR spect
 DATE_ 2020-02-13 21:11:53
 ORNUC C13
 QRES 0.15
 PROCNO s2pul
 PULPROG zgpg30
 RESFREQ 150.82 MHz
 ORSET 6.74 KHz
 ORFEN 2.30 Hz
 FREQ0 37878.79 Hz
 SCANS 64
 PCQTM 0.834 sec
 PCQTA 2.134 sec
 PM1 5.75 usec
 PM2
 PM3
 TEMPC 25.0 c
 SFO 125.76 MHz
 SILVNT c6d6
 EXREF 128.00 PPM
 EXREF 0.160 Hz
 RGAIN



C:\Users\Takatuzaki\Documents\2021\SSD_C61-83_Fragment\NMR\data\KH-38.a1s
 FILE KH-38.a1s
 COMPT 1H
 DATE_ TIME Sat Feb 23 14:31:53 2019
 INSTR spect
 EXMOD NON
 OBPRO 398.65 MHz
 OBSFQ 10500.00 Hz
 POINT 32768
 SCANS 79931.6 Hz
 ACQTM 4.0953 sec
 PD 2.9010 sec
 P1 6.40 usec
 IRRUC 1H 24.2 C
 CTEMP CDCl3 7.26 ppm
 EXREF 0.12 Hz
 BF 1.4
 RGAIN

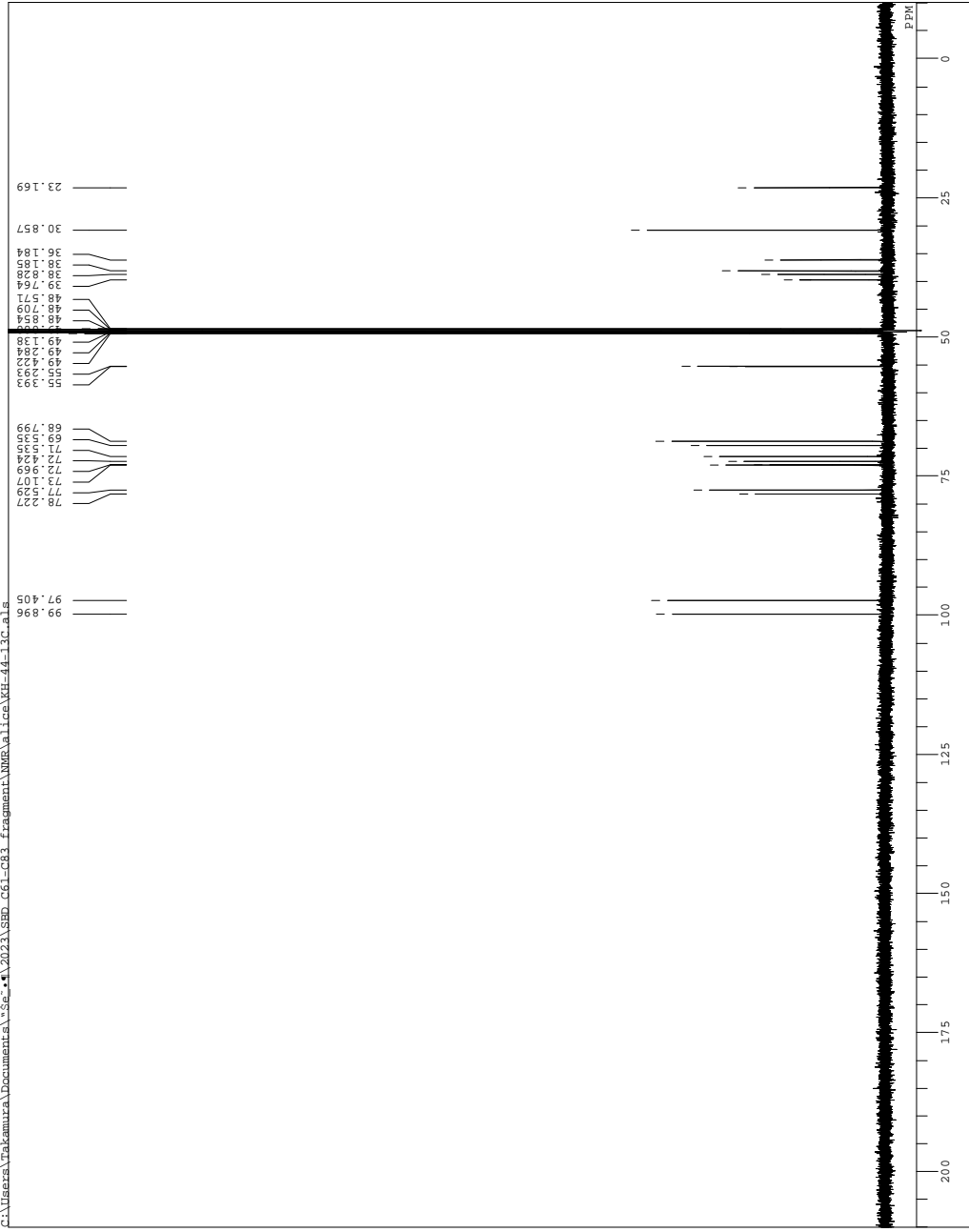


D:\User\Takamura\Documents\Se_4\2021\SHD_661_C83_Fragment\NMR\1ca\KH-44-1H_als
 Date_ 2019-03-07 21:08:45
 CONT H1
 ORNUC H1
 EXMOD s2pul
 OBSF1 599.76 MHz
 OBSF2 7.42 KHz
 PULPROG zgpg30
 PCYCLIC 3.60 Hz
 FREQ0 9635.38 Hz
 SCANS 32
 ACQTM 3.4509 sec
 PUL 1.5225 usec
 INJ 25.0 c
 INVT cd30d
 SFTN 3.30 PPM
 EXREF 0.32 Hz
 RGAIN



C:\Users\Takamura\Documents\Se_4\2021\SRD_061-083_Fragment\NMR\alica\KH-44-13C_als

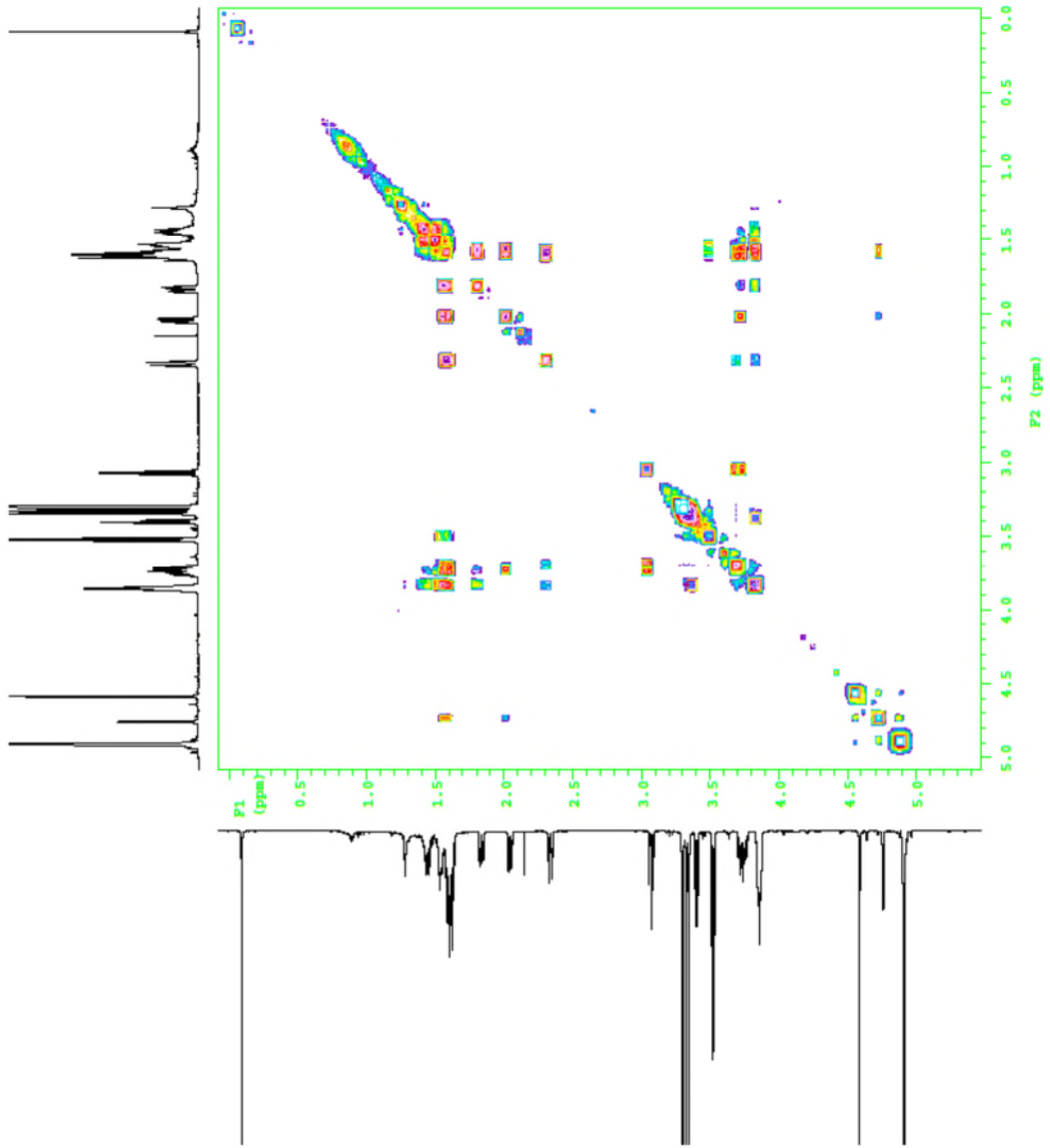
DFILE KH-44-13C_als
 CONV 2019-03-07 21:22:57
 C13
 EXMOD s2pul
 FREQ 150.82 MHz
 PULPROG zgpg30
 OBSF1 17.32 KHz
 OBFTN 3.00 Hz
 F2FREQ 37878.79 Hz
 SCANS 64
 ACQTM 0.8531 sec
 RELAX 2.575 usec
 PUL 25.0 c
 IRETC 49.00 pfm
 SLEW 0.12 Hz
 EXREF
 REFIN



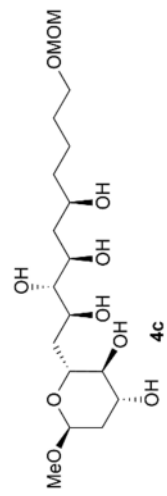
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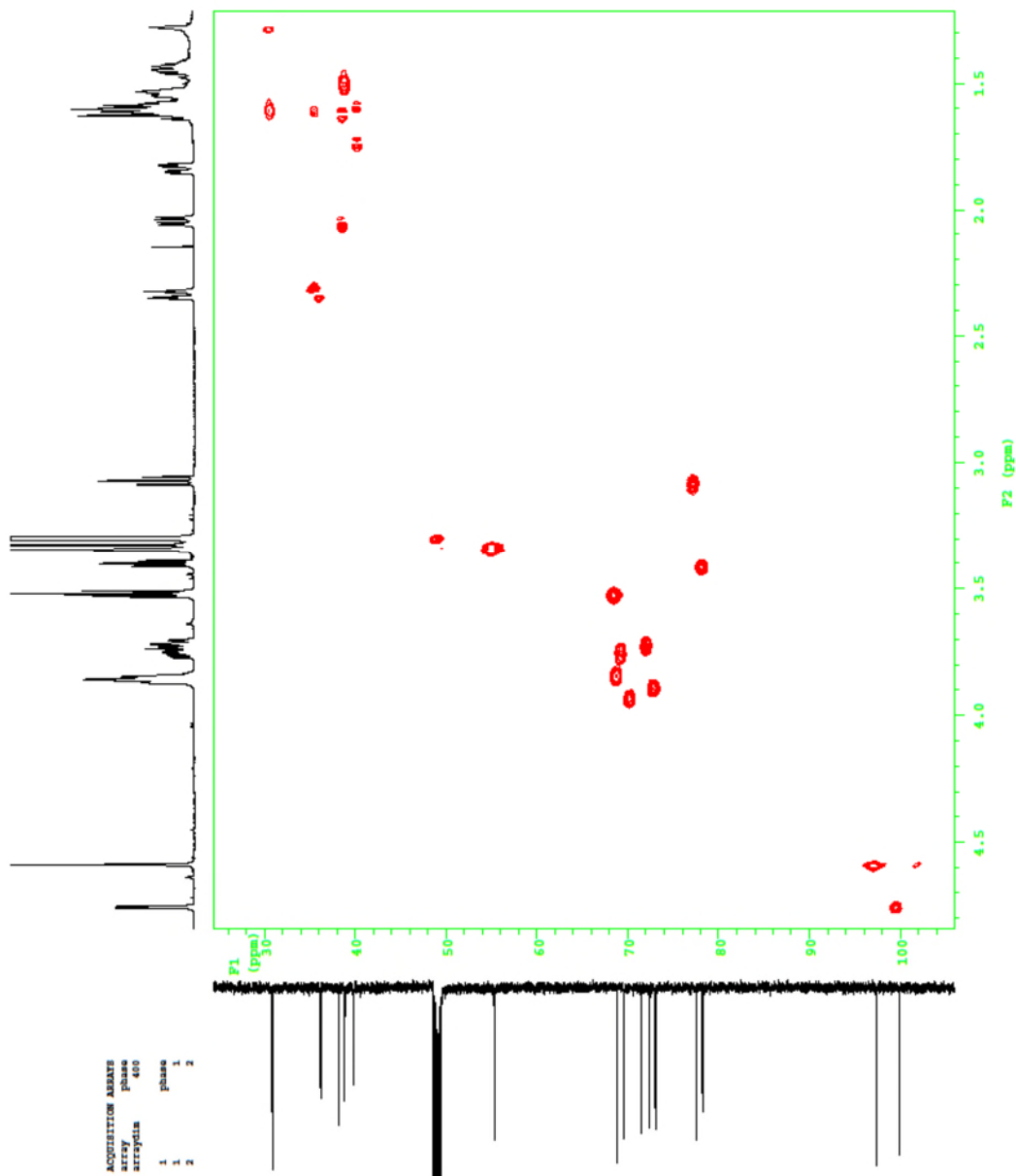
exp3 gcosy
=====
NAME      SAMPLE
date      REC# 8 2013   ba
solvent    cdh3o       7
sample     6120
=====
ACQUISITION
pr      9615.4  temp    not used
sc      0.159   gain     50
in      4096   f1qz     0
p2      4096   f2       0
az      32     ad      -0.075
cp      1.000   abse   not used
ct      4     fr      4096
=====
2D ACQUISITION  F1 PROCESSING
acq     9615.4  abn     -0.083
sc      0.159   gain     50
in      4096   f1qz     0
pr      0     proc1   2D
=====
SOLVENTATION  f1  4096
=====
acqmode      s      4096
=====
wrt          n      sp      -38.3
tx           s      wp      2084.6
tx2          s      wp      2084.6
tx3          s      wp      3248.1
tx4          s      wp      3248.1
tx5          s      wp      3248.1
tx6          s      wp      3248.0
tx7          s      wp      3248.0
tx8          s      wp      1979.2
tx9          s      wp      1979.2
tx10         s      wp      1979.2
=====
SOLVENT      s102
=====
GEN          0.001000  wc
=====
SAMPLING    0.001500  wq
=====
SPIN        0.001500  wq2
=====
SOLVENT     CL3  VR      169
=====
OR          mm  LR      5
=====
SI         5
=====
BR

```



¹H-¹H COSY (600 MHz, CD₃OD)



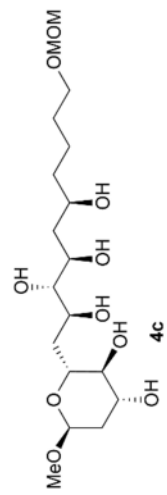


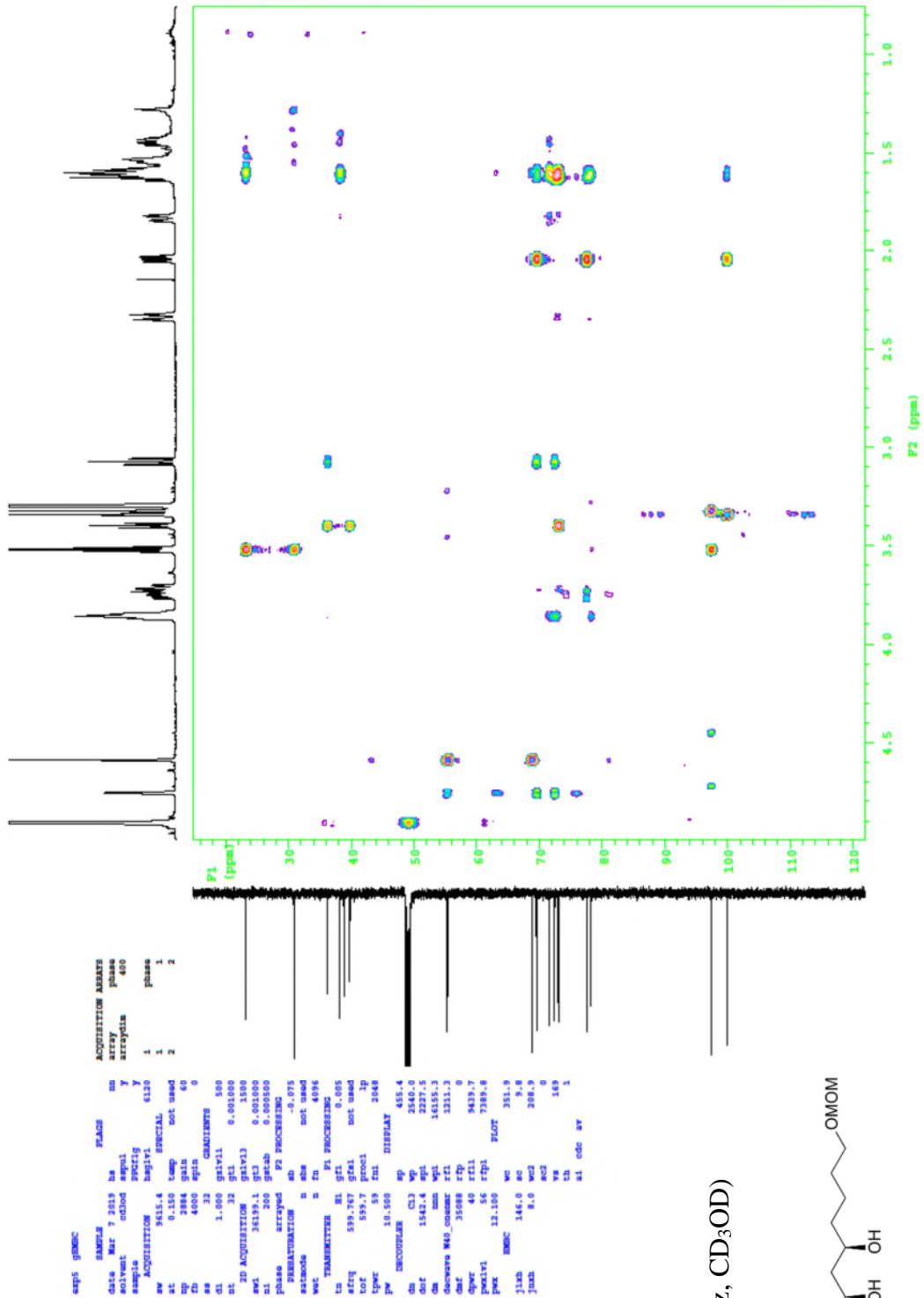
```

emp4 gMOC
=====
data   Mar 5 2019   ha   PLAGE
solvent  cdcl3      emp1   y
sample   4c          emp2   y
acq      400MHz     emp3   y
sw       9.411.4    emp4   6120
nt       0.184      emp5   not used
zb       4000      emp6   60
as       32        emp7   0
dl       1.000     emp8   5102
nt       32       emp9   0.003000
=====
2D ACQUISITION: 2D ratio 3.977
nt       361200    emp10  0.003000
sw       361200   emp11  F2 PROCESSING
phase   arrayed   emp12  not used
PRESATURATION gfs not used
satmode n       emp13  4096
wet     TRANSMITTER n F2 PROCESSING
nt       0.005
nt       0.005
nt       0.005
nt       599.787   emp14  not used
nt       599.7   emp15  2048
tpwr    59   emp16  DISPLAY
pw       10.800   emp17  736.2
=====
INCOUPLAR:
du       643      emp18  3078.7
du       780.5    emp19  3078.7
du       780.5    emp20  3188.3
du       840       emp21  3078.2
du       35088     emp22  10255.9
du       40       emp23  7389.7
=====
pval1   40       emp24  PLOT
pwr     12.100   emp25  351.9
=====
flsh   gMOC
=====
multisig 146.0   emp26  308.9
multisig 2       emp27  67
mult     2       emp28  67
=====
al     odc     ph
=====

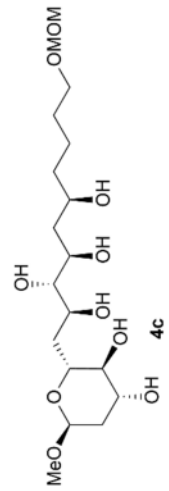
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HMOC (600 MHz, CD₃OD)

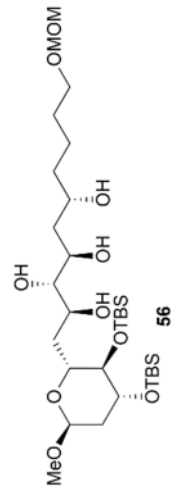
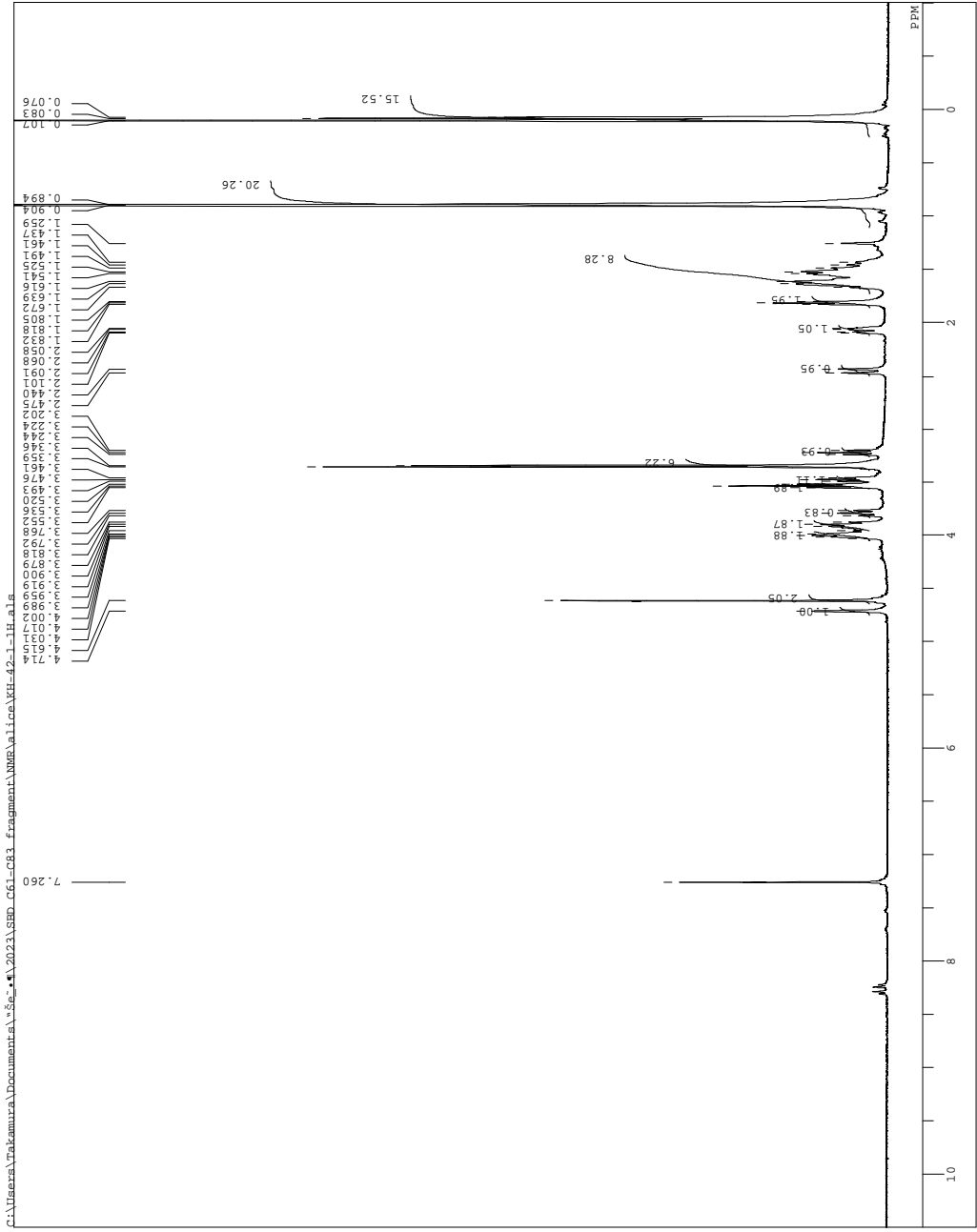




HMBC (600 MHz, CD₃OD)

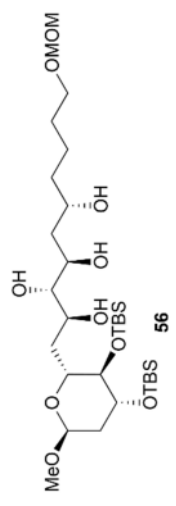
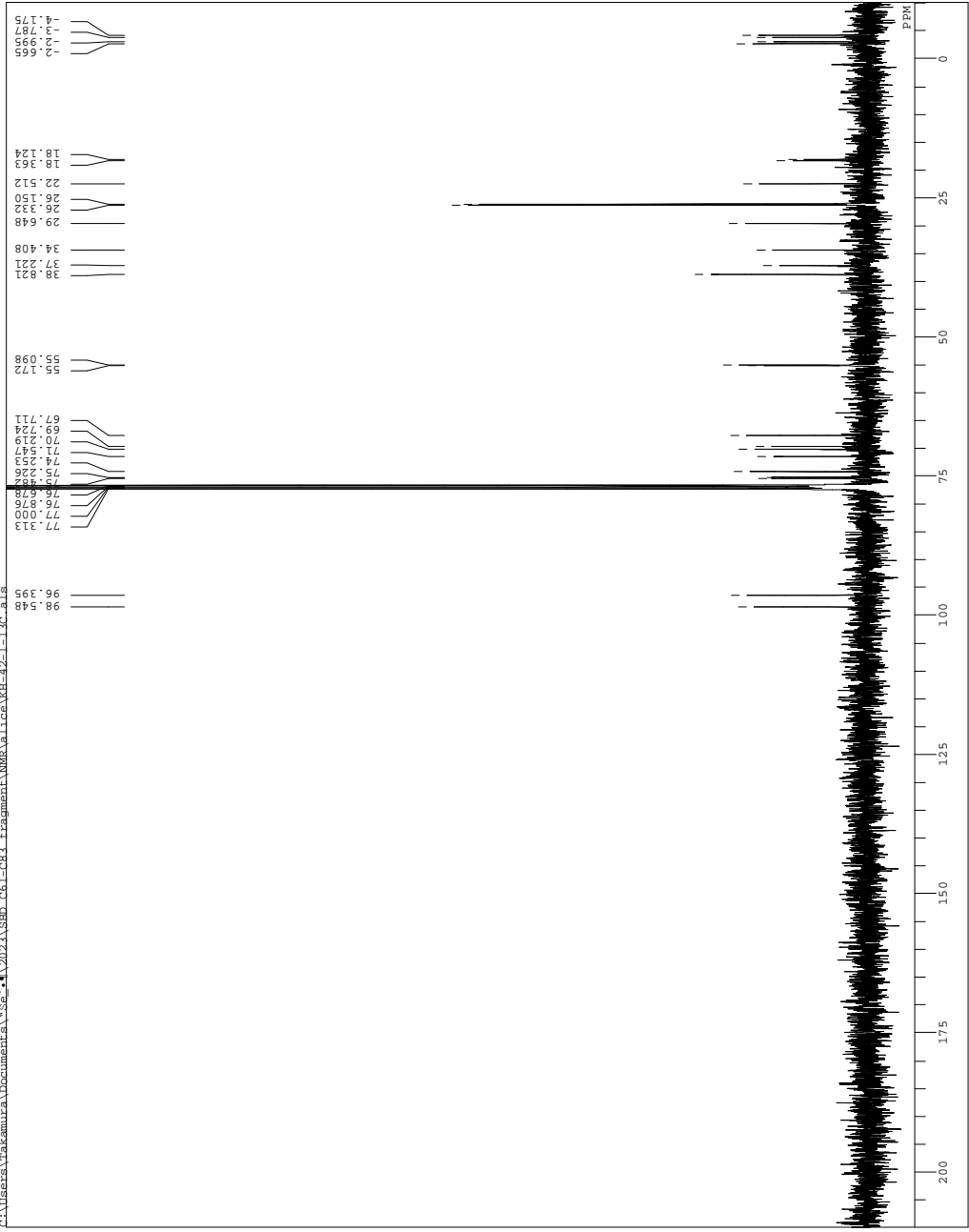


DEFILE KH-42-1-1H.als
 DATE_ Acq Fri Mar 01 13:13:30 2019
 DATM_ 19
 ORNVC 1H
 ORNVD NOM
 ORNVO 399.65 MHz
 ORSET 124.00 KHz
 ORFTN 10500.00 Hz
 ORFECU 79831.60 Hz
 SCANS 4.00000
 PCQTM 2.9010 sec
 PM1 6.40 usec
 IRMNC 1H
 SINTV 23.9 C
 SILVNT CDCL3
 EXREF 7.26 PPM
 RGAIN 0.16

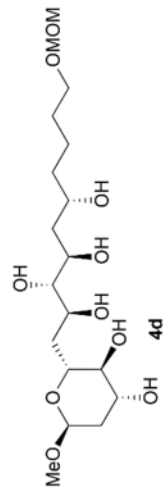
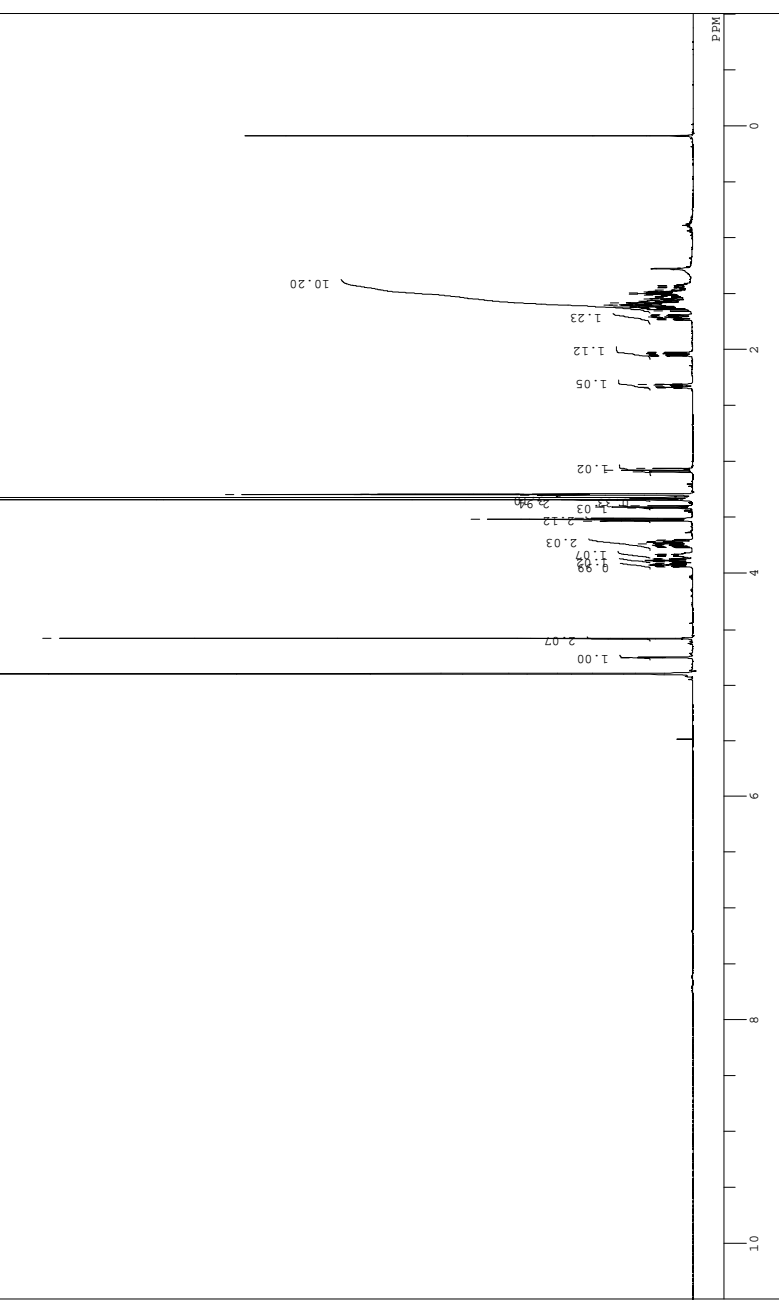


C:\Users\Takatsuma\Documents\Se_*\2021\SHD_561-c83_Fragment\NMR\13c\KH-42-1-13c_als

DEFILE KH-42-1-13c_als
 DATE_ 20190321
 DATIM Fri Mar 01 18:06:21 2019
 ORBIT 13C
 PULPROG zgpg30
 PROCNO 1
 QPCONV 100.40 MHz
 QRESOL 125.00 KHz
 ORFEN 10500.00 Hz
 FREQ0 27173.90 Hz
 FREQ1
 SCANS 1.320
 PCYCLE 1.7240 sec
 PULPROG 6.80 usec
 PM1
 INVC 1H
 TEMPC 26.3 C
 SOLVENT CDCL3
 SREF 77.00 PPM
 EXREF 2.24 Hz
 RGAIN

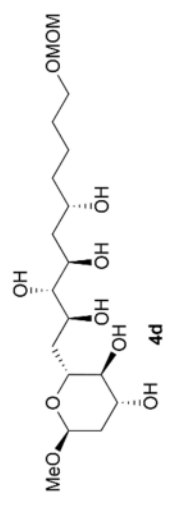
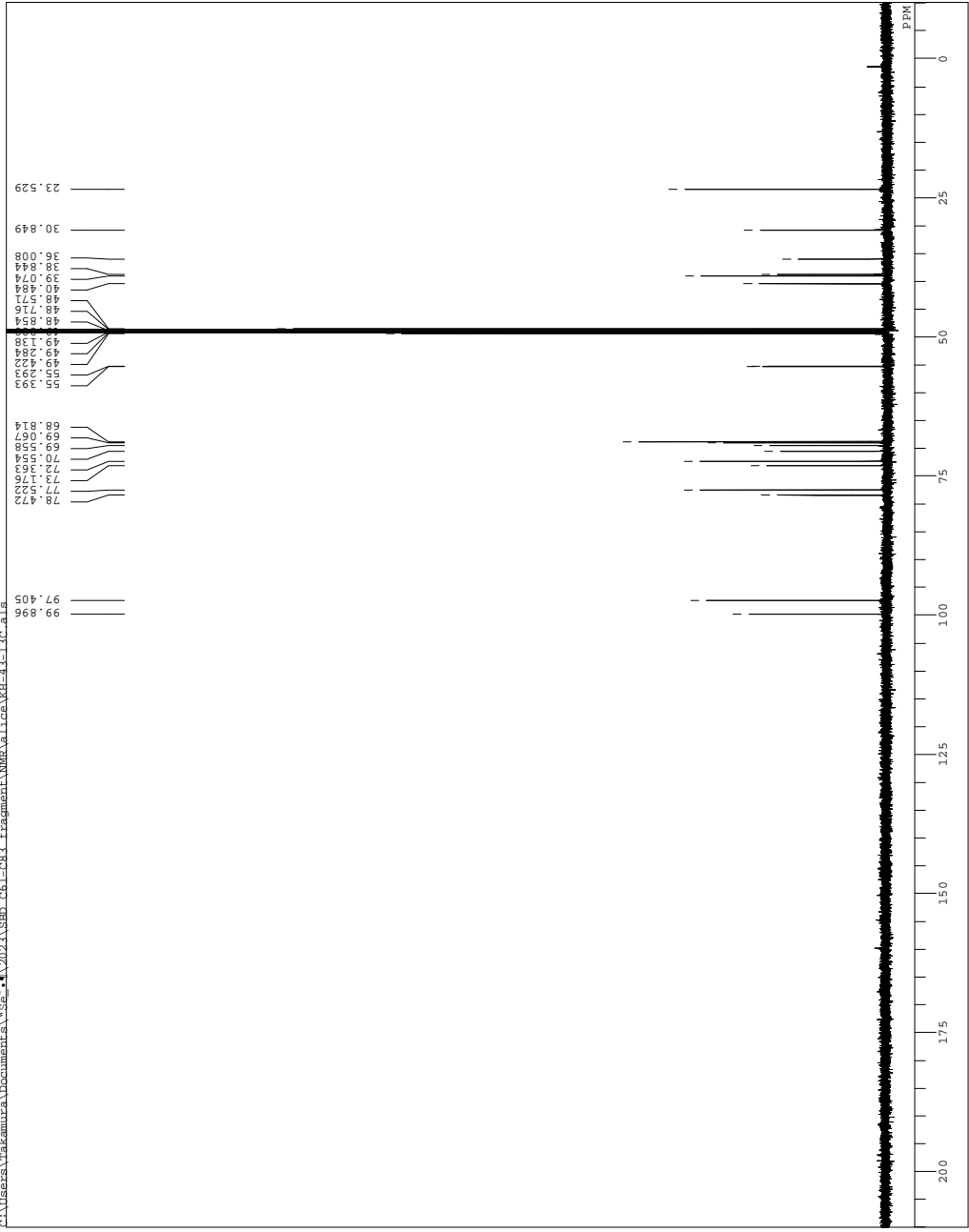


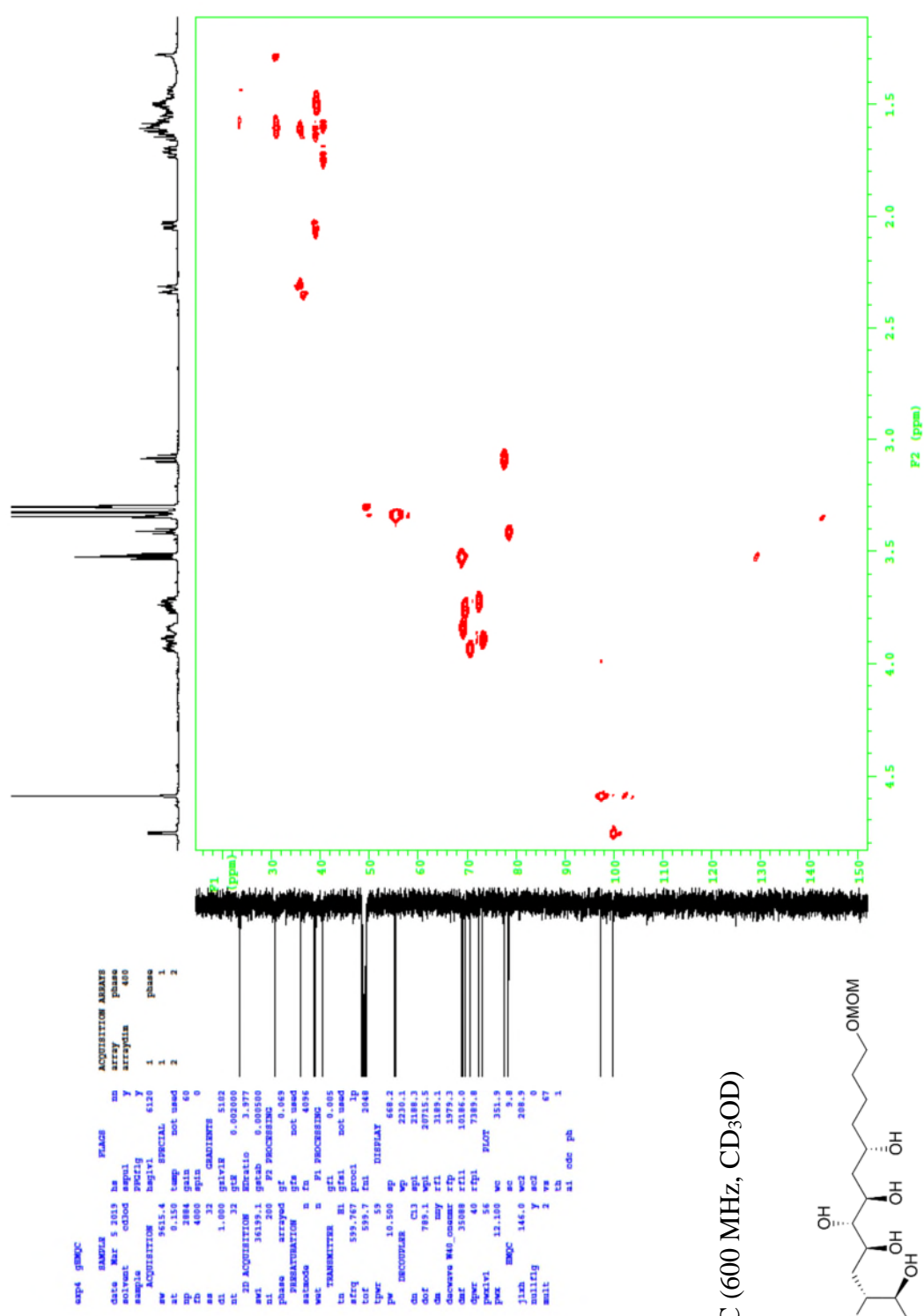
C:\Users\Takamura\Documents\Se_*\2021\SHD_561-C83_Fragment\NMR\1ca\KH-43-1H_als
 DFILE KH-43-1H_als
 COM1 2019-03-05 21:06:06
 CONTC H1
 ORNUC H1
 EXMOD s2pul
 OBSF1 599.76 MHz
 OBSF2 7.42 KHz
 OBF1N 3.60 Hz
 OBF2N 0.00 Hz
 FREQ1 9635.38 Hz
 FREQ2 0.00 Hz
 SCANS 32
 ACQTM 3.4509 sec
 PULPROG zgpg30
 PVI 1.525 usec
 IRENUC 25.0 c
 IRTN 1000
 SFTN cd30d
 SIUNIT 3.30 ppm
 EXREF 0.12 Hz
 RGAIN



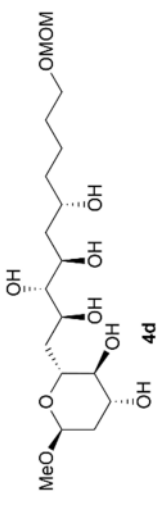
C:\Users\Takatsuma\Documents\Se*\2021\SHD_661-c83_Fragment\NMR\1c\KH=43-13C_als

DEFILE KH-43-13C_als
 DATE 2019-03-05 21:18:38
 DTIME 21:18:38
 ORNVC C13
 ORNVD s2pul
 ORNVO 150.82 MHz
 ORNVT 71.32 KHz
 ORNVS 32.00 Hz
 ORNVA 37878.79 Hz
 ORNVC 64
 SCANS 0.8349 sec
 PCQTM 2.1349 sec
 PM1 5.75 usec
 TRNVC 25.0 c
 SFLVNT cd3od
 EXREF 49.00 ppm
 RGAIN 0.60





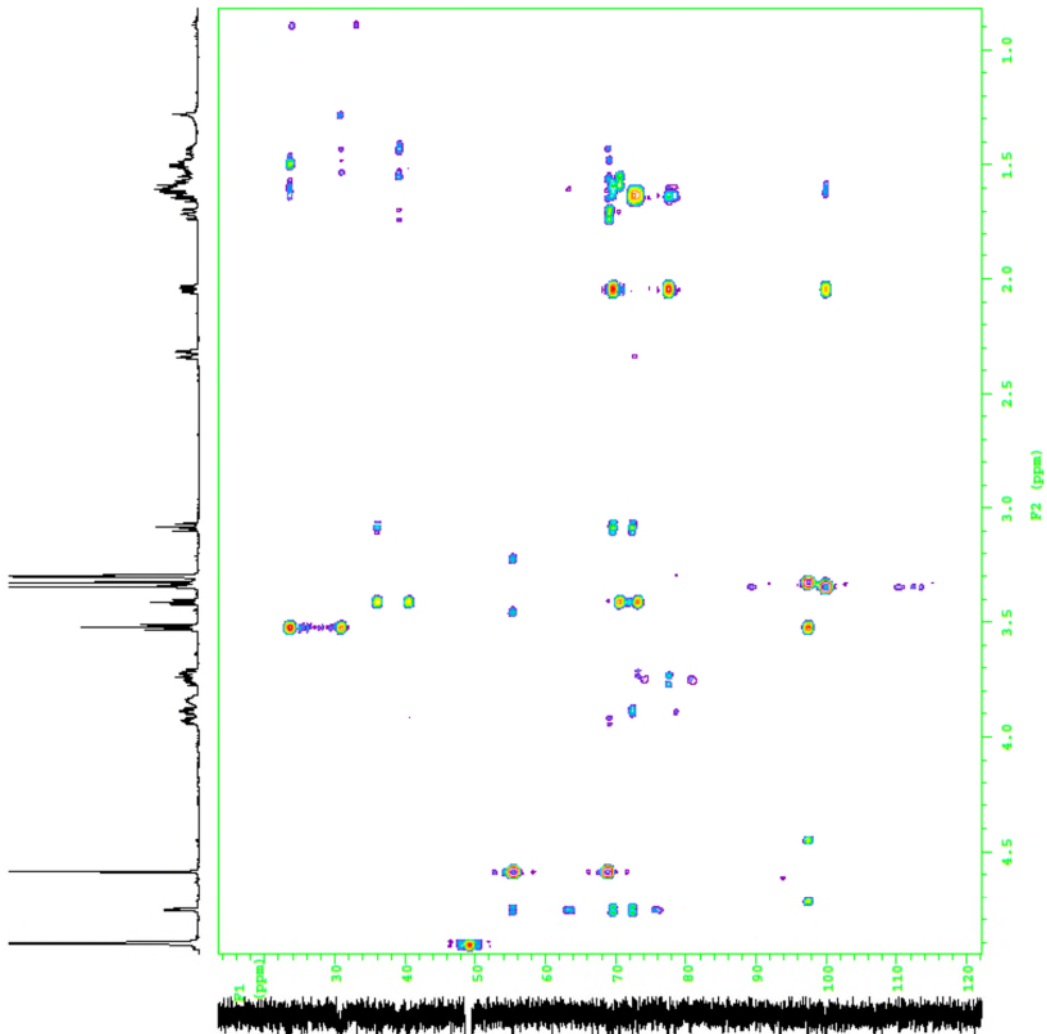
HMQC (600 MHz, CD₃OD)



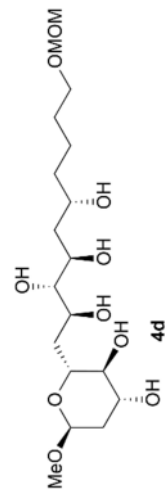
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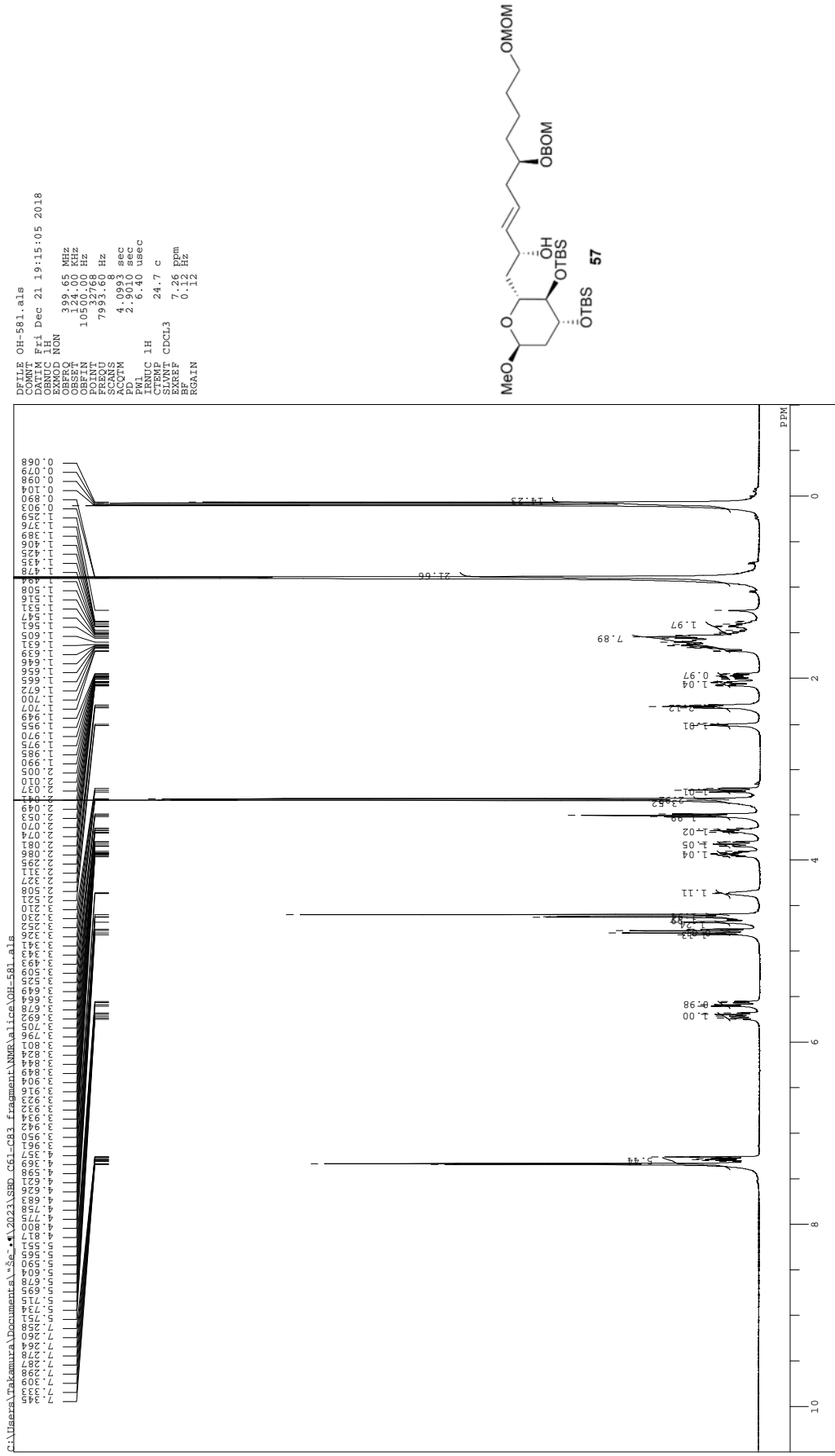
exp5 gMBC
=====
SAMPLE          NAME          PLATE
Date    Mar 5 2019   hs
solvent  cd3od      y
sample   array      y
=====
ACQUISITION     SERIAL    6110
=====
acq        1616.4  begin1
ns         1310    temp    not used
ns         3884    spins   not used
ns         4000    spins   0
=====
CH1         1.000  g1v11  500
=====
2D ACQUISITION  32  g11  0.001000
=====
acq        31199.1  g1v11  0.001000
ns         31199.1  g1v11  0.001000
ns         200  g1v16  0.000500
=====
phase  arrayed  F2 PROCESSING
=====
PARAMETER      VALUE
-----
satmode  n  shw  not used
wet       n  shw  not used
=====
INSTRUMENT      n  shw  not used
=====
TRANSMITTER     n  shw  not used
=====
freq          599.767  g1a1  not used
=====
proc          599.7  proc1  1p
=====
type         59  fml  1048
=====
pw           10.500  DISPLAY
=====
=====
DECOUPLER       n  shw  not used
=====
ch1            493.4  CP  493.4
ch2            1542.3  WP  1542.3
=====
ds            16403.7  W1  16403.7
=====
decouple MAG  constant  r1l  3190.1
=====
dof          31988  r1l  31979.3
=====
dqr         40  r1l1  9437.5
=====
pqr         56  r1l1  7389.8
=====
pwr         13.100  W1  351.9
=====
flah        146.0  ac  9.8
=====
jash         8.0  w2  208.9
=====
vs          67  w2  0
=====
ts          67  w2  0
=====
al  cdc  av  1
=====

```

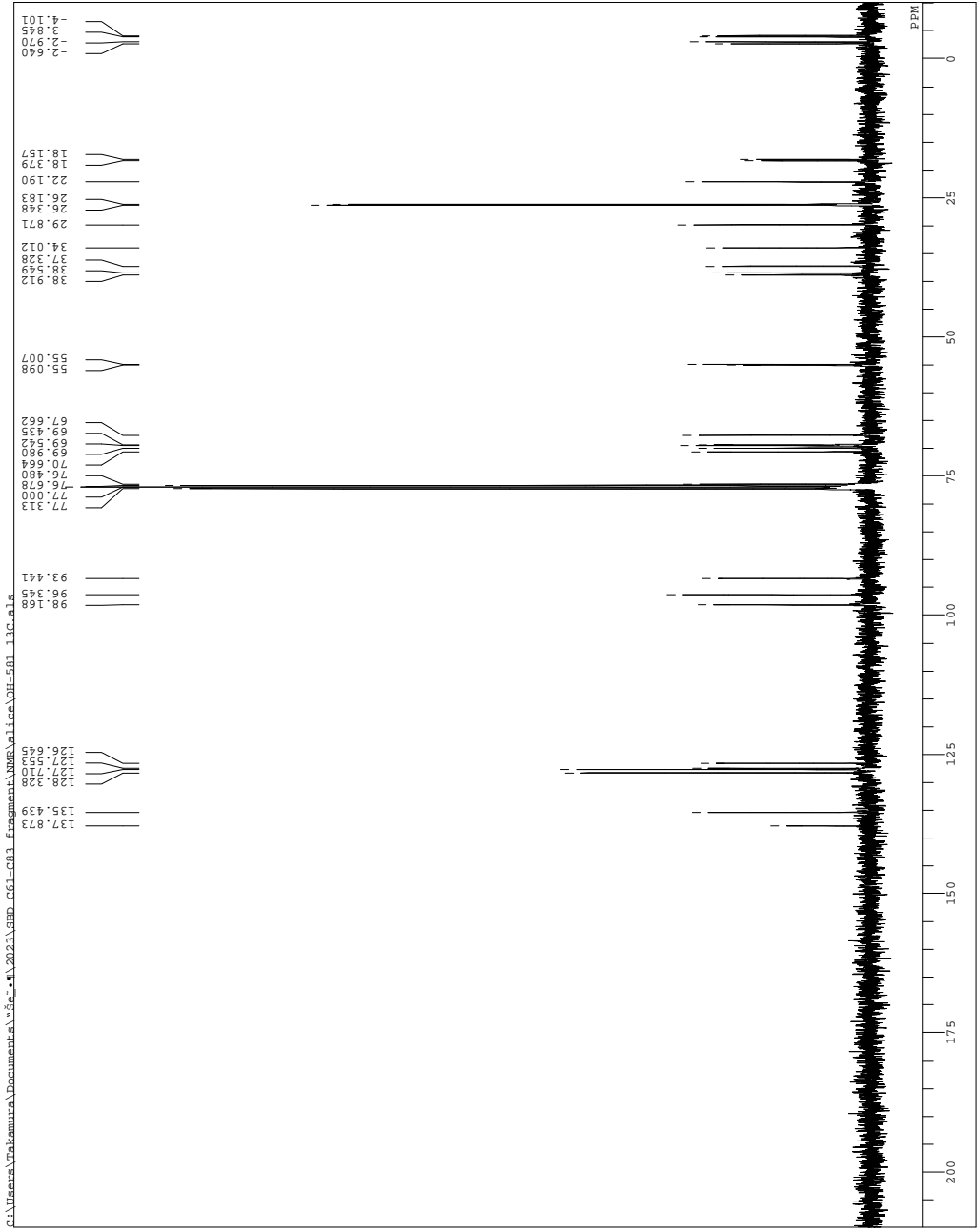


HMBC (600 MHz, CD₃OD)

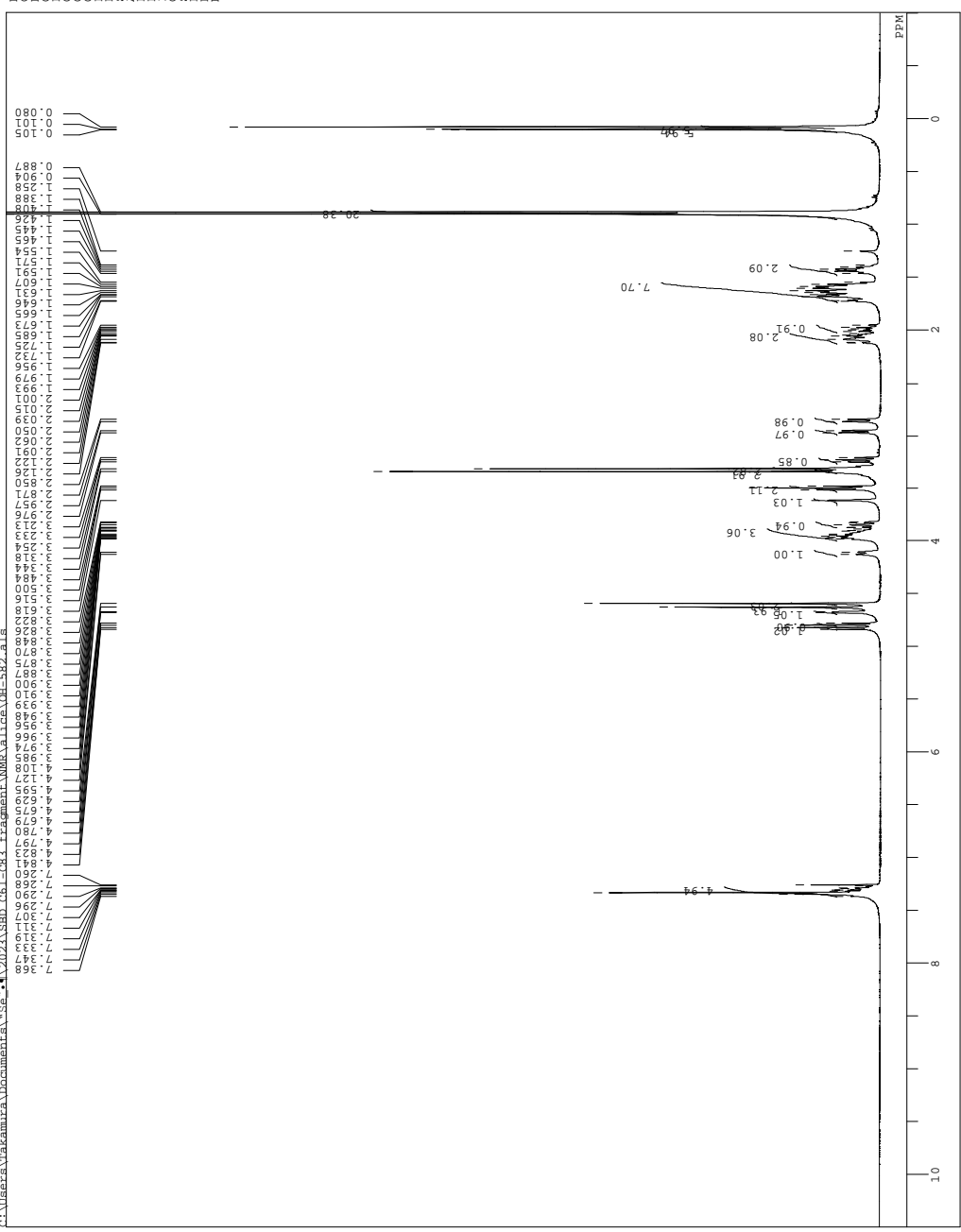
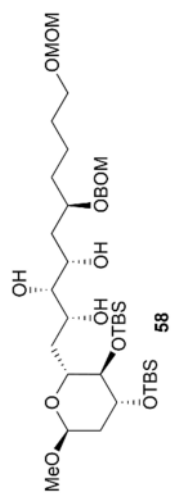




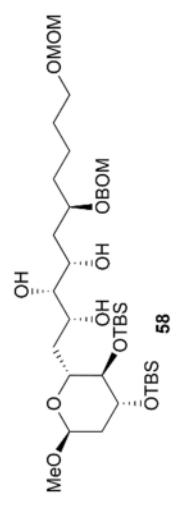
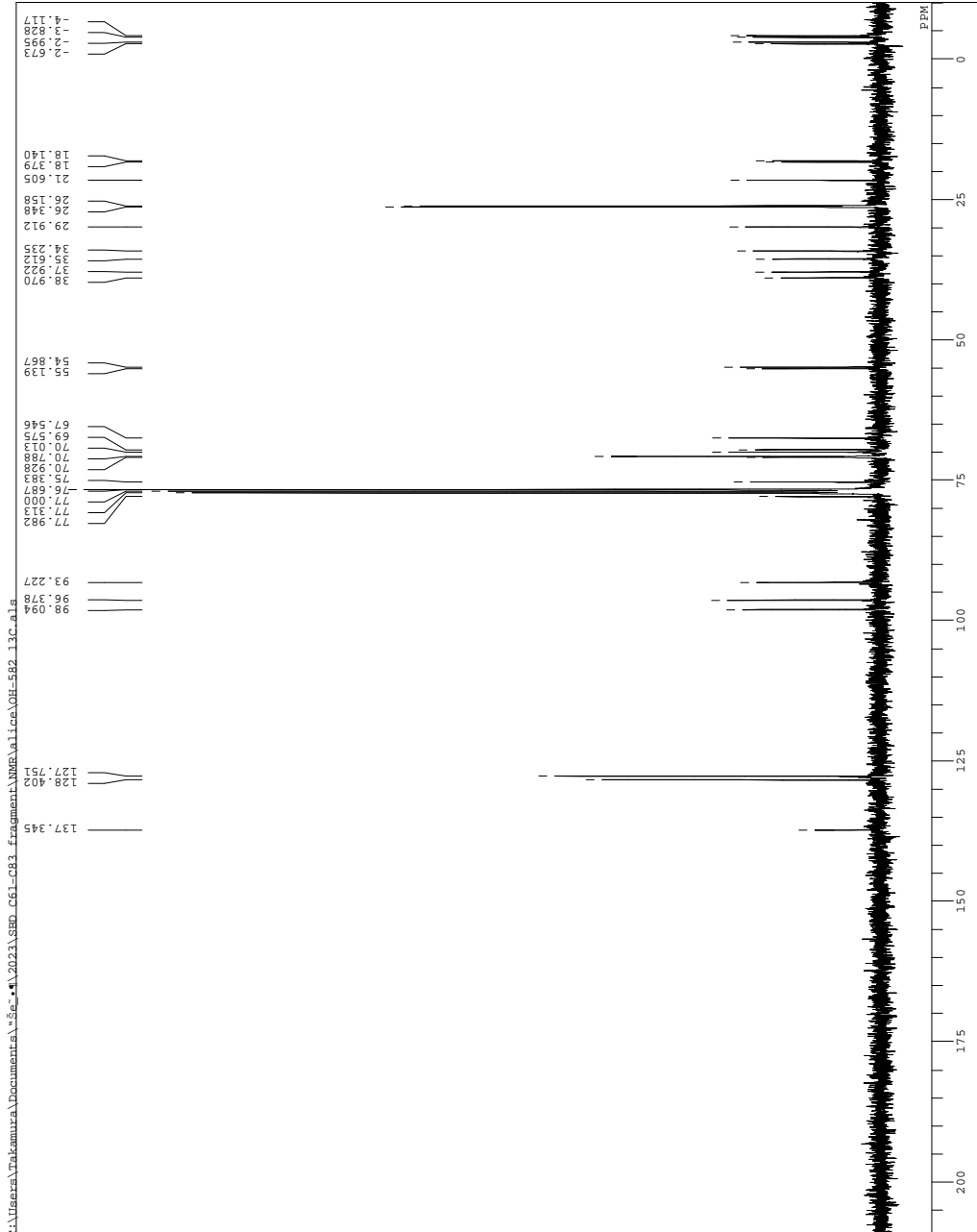
DFILF OH-581_13c.als
 COMNT
 DATM Fri Dec 21 19:27:56 2018
 EXMID BOM
 EXMID BOM
 OFREQ 100.40 MHz
 OFS 0.00 Hz
 OFSIN 10540.00 Hz
 POINT 32768
 FREQ 27173900 Hz
 SFO 8
 ACQTM 1.2859 sec
 PD 1.7940 usec
 INUC 1H
 INUC 6.80 usec
 CTMP CDCL3 26.5 c
 EXMID BOM
 EXMID BOM
 BF 77.00 PPM
 BF 2.00 Hz
 RGAIN 24



C:\Users\Ynakamura\Documents\Se...2023\SHD_661_c83_Fragment\NMR\data\OH-582_als
 FILE OH-582_als
 DATE The Dec 25 17:57:08 2018
 INSTR 1H
 PULPROG zgpg30
 PROCNO 1
 AQ 1.00
 ORBIT 1H
 F2 399.65 MHz
 F1 124.00 KHz
 OFFSET 10500.00 Hz
 A2 1.00
 FREQ2 79831.60 Hz
 SCANS 4.0000
 PC 2.9010 sec
 PD 6.40 usec
 PM1 1H
 PM2 1H
 FIDRES 24.5 C
 SFO 124.00 MHz
 SOLVENT CDCl3
 EXREF 7.26 PPM
 RGAIN 0.14

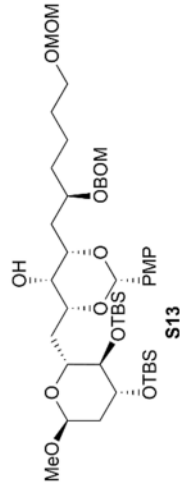
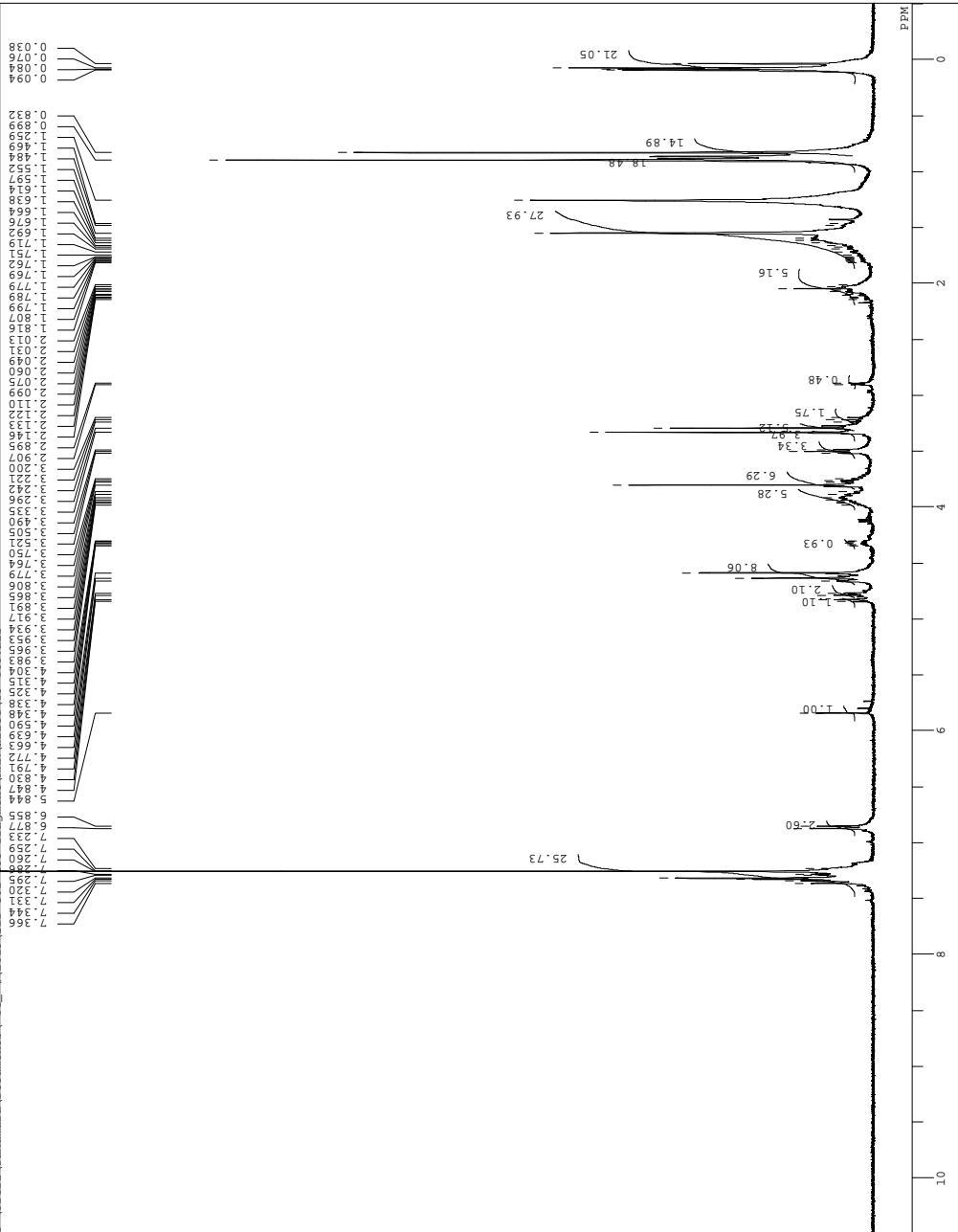


DFILE OH-582 13c.als
 CONTM The Dec 25 18:13:15 2018
 EXMTC 13C
 EXMOD BCM
 OBSF1 100.40 MHz
 OBSF2 125.00 KHz
 OBSF3 10500.00 Hz
 PULPROG zgpg30
 PCYCL 27137.90 Hz
 SCANS 400
 ACQTM 1.7039 sec
 PUL 1.6780 usec
 INTC 1H
 SNU 26.4 c
 SOLV CDCL3
 EXREF 77.00 PPM
 REFIN 2.00 Hz
 RGAIN



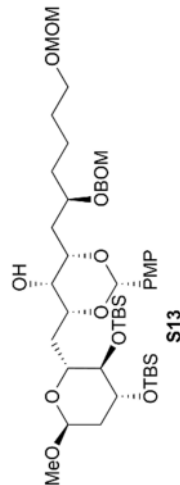
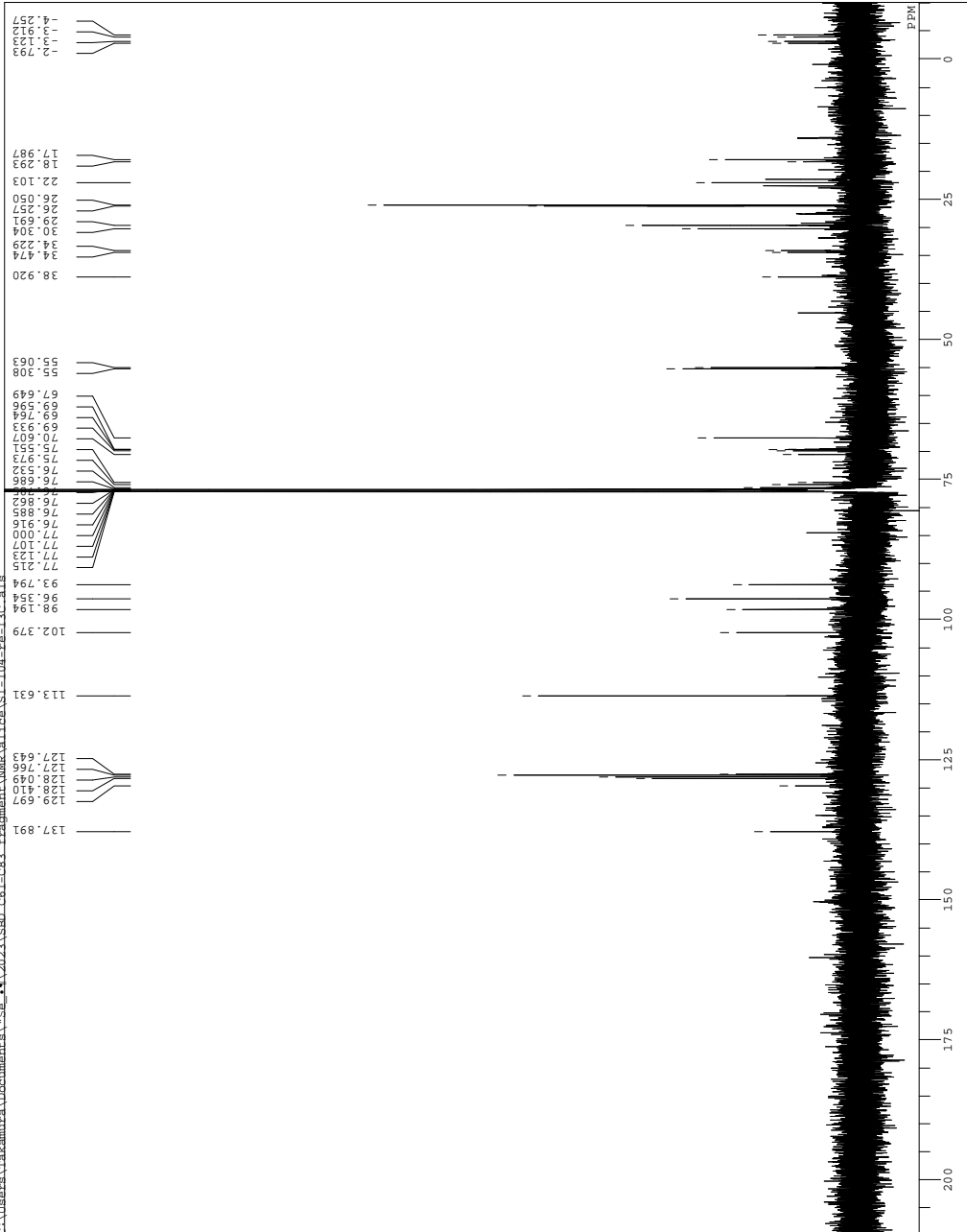
C:\Users\Trakamura\Documents\20231_SBD_C61_093_Fragment\NMR\1h\1h\TO_448.a1z

DFILE TO-448.a1z
COMPT 1h Mar 02 21:41:28 2018
NAME
PULSE 1h
EXMOD NON
OBPRQ 399.65 MHz
OBPRQ 105500.00 Hz
POINT 32768
SCAN 7993.32 Hz
ACQTM 4.0983 sec
PUL 2.507 sec
PULP 5.00 usec
IENUC 1h 23.9 c
CTEMP CDCL3 7.26 PPM
EXREF BF 0.12 Hz
RGAIN 23



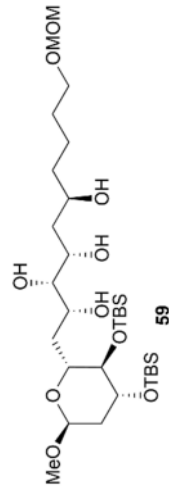
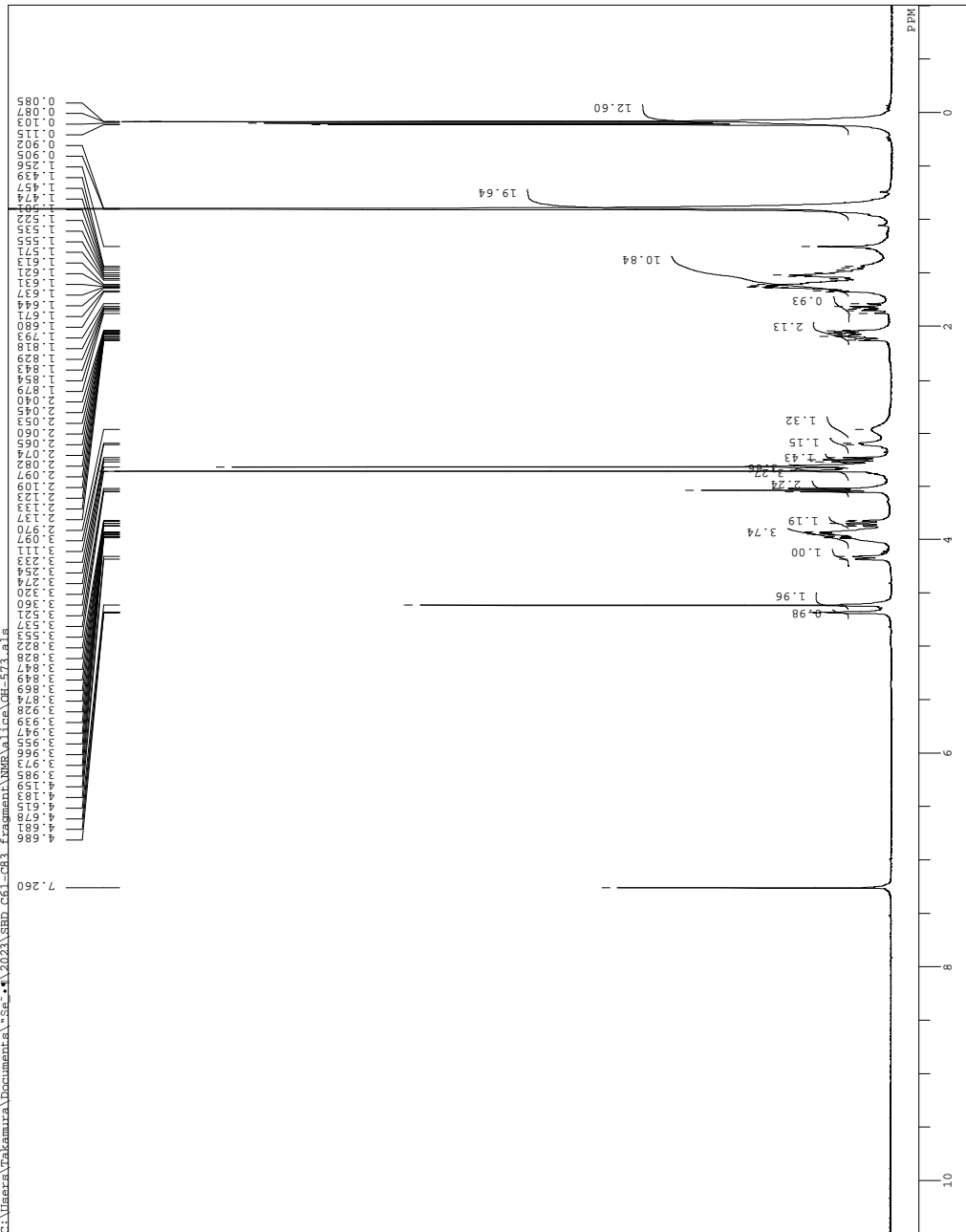
C:\Users\Tpkemura\Documents\... \2023\SED_C61-C81_Fragment\NMR\data\SI-104-re-13c_als

DFILE SI-104-re-13c_als
 COMPI SI-104-re-13c
 DATE 23-05-29 21:16:48
 OPR C13
 EXMOD s2pul
 OBSFO 150.82 MHz
 OBS 8.70 Hz
 OFETM 8.70 Hz
 POINT 32768 Hz
 SCANS 37878.64 Hz
 ACQTM 0.8651 sec
 PD 2.1349 sec
 PD 0.10 usec
 IRENUC 10.0 c
 CTEMP cdc13 77.00 ppm
 EXPRF BF 0.12 Hz
 RGAIN 60



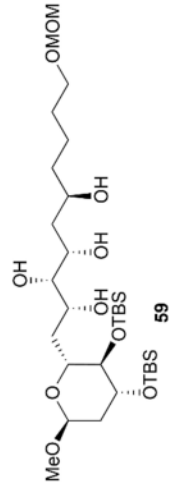
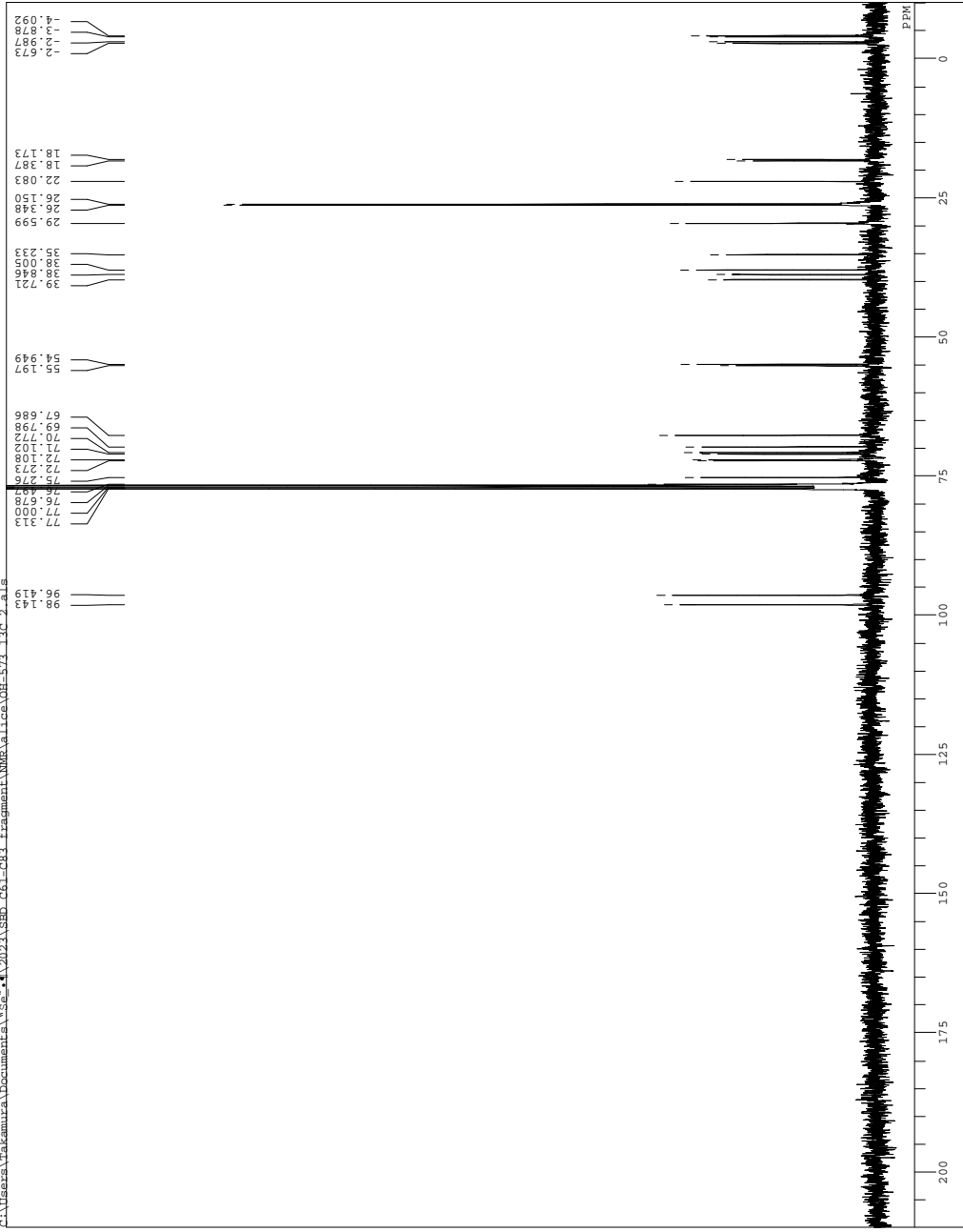
C:\Users\Takamura\Documents\Sei-4\2021\SED_c61-cr3-Fragment\NMR\alic\OH-573_als

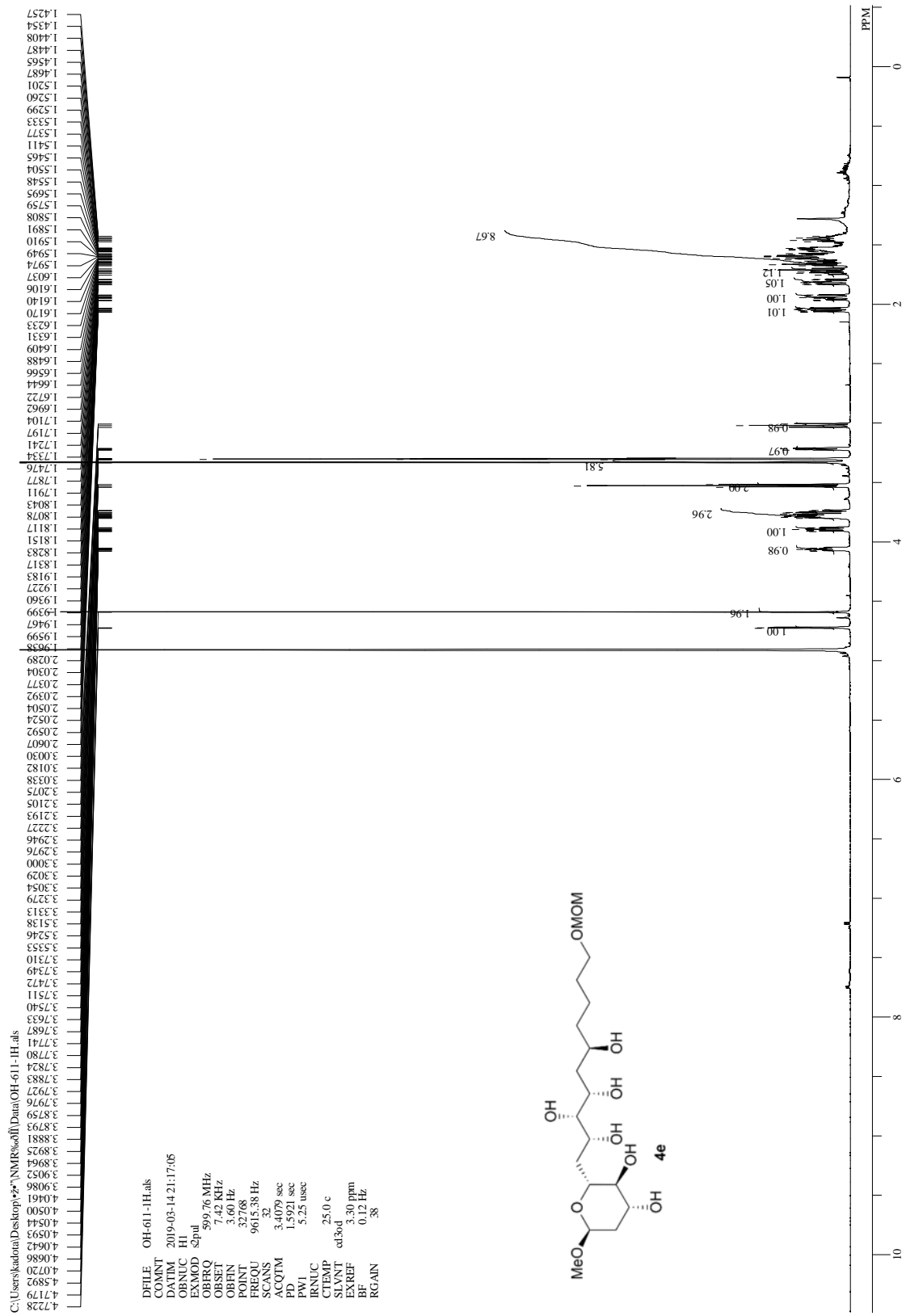
DRFILE OH-573_als
 COMMT
 DATIN Mon Dec 17 14:36:27 2018
 EXMOD NON
 OBRQ 398.65 MHz
 OBRF 105204.00 Hz
 POINT 32768 Hz
 SREQ 7993.60 Hz
 ACORN 4.0993 sec
 PD 2.2010 sec
 IEMUC 1H 6.40 usec
 IEMUC 24.4 c
 CTEMP CDCL3 24.4 c
 EXPRF 7.26 ppm
 BF 0.12 Hz
 RGAIN 1.4



C:\Users\Takamura\Documents\Se*\2023\8RD_C61-C83_Fragment\NMR\all\ce\OH=573_13C_2_als

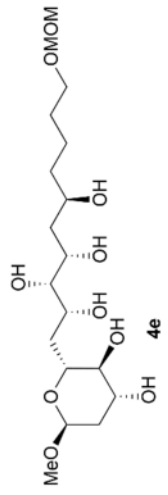
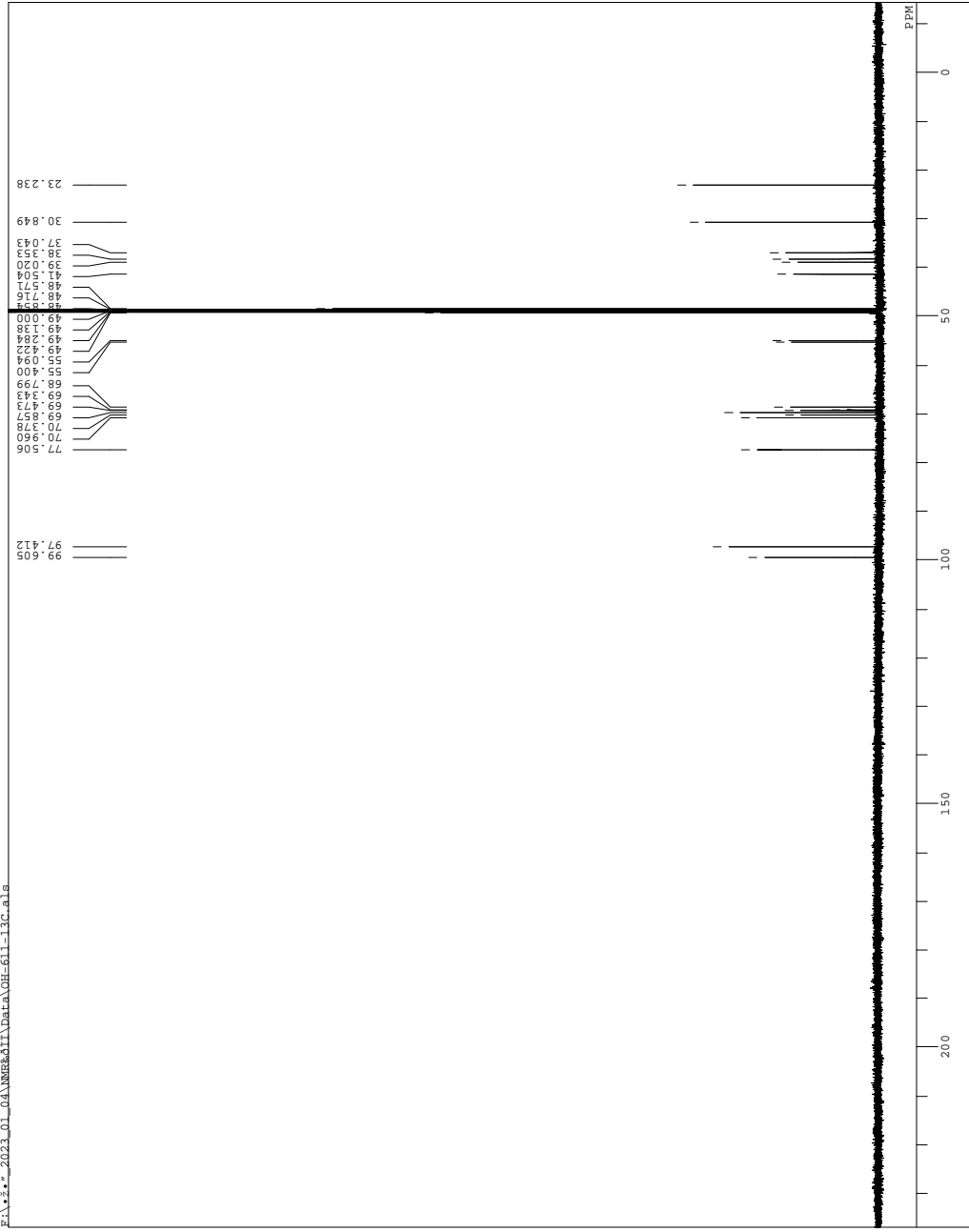
DATE OH-573 13C 2.als
TIME 17:11:11
DATE Mon Dec 17 15:48:03 2018
DIR C:\Users\Takamura\Documents\Se*\2023\8RD_C61-C83_Fragment\NMR\all\ce\OH=573_13C_2_als
NAME OH-573_13C_2.als
PROC 13C
PULPROG zgpg30
SFO 100.625
AQ 0.50000000
RG 0.00000000
ORBIT 100.40 MHz
ORSET 125.00 KHz
NUC1 13C
NUC2 13C
P1 1.05000000 Hz
P2 27133.90 Hz
FREQ 27133.90 Hz
SCANS 3372
SOLVENT CDCL3
PD 1.7940 sec
PC 6.80 usec
PM 1.00000000
PR 26.3 C
TE 300.2 K
SOLVENT CDCL3
SILVER 77.00 ppm
EXPT 2.24 Hz
RGAIN





F:\3*_*_2023_01_04\NMR\data\OH-611-13c.als

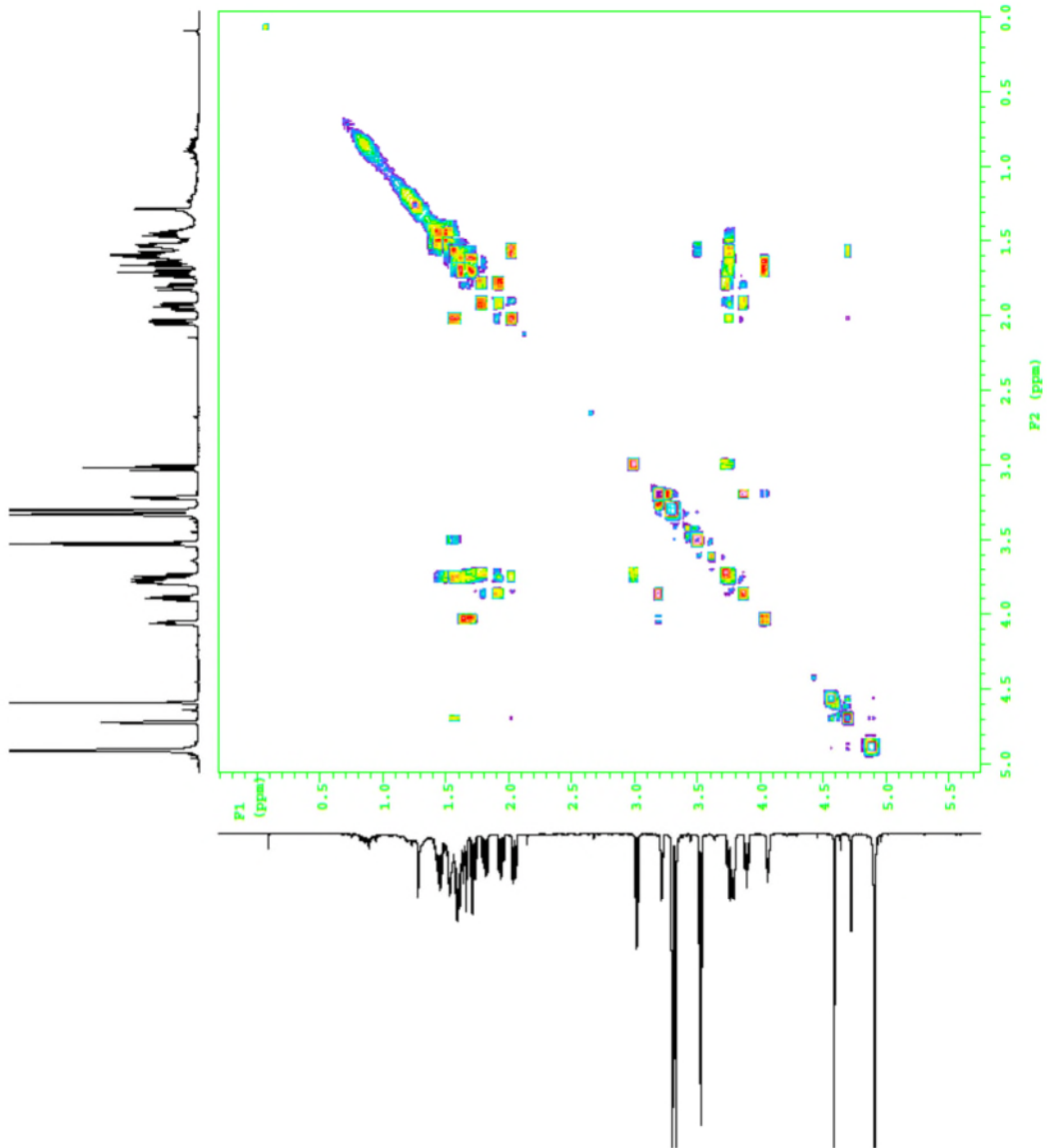
DFILE OH-611-13c.als
 CONT 2019-03-14 21:30:23
 OBNUC C13
 EXMOD s2pul
 ES 150.82 MHz
 OBSF 77.32 KHz
 OFPIN 3.00 Hz
 OFS 0.00 Hz
 FREQ 378787.9 Hz
 SCANS 64
 ACQTM 0.8651 sec
 PUL 2.575 usec
 INTC 25.0 c
 LN 1
 SOLV cd3od
 EXREF 49.00 PPM
 REFIN 0.12 Hz
 RGAIN 0.0



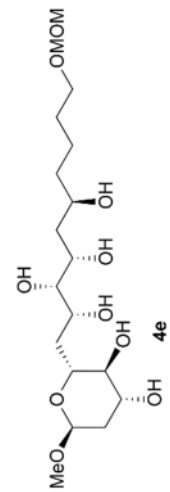
```

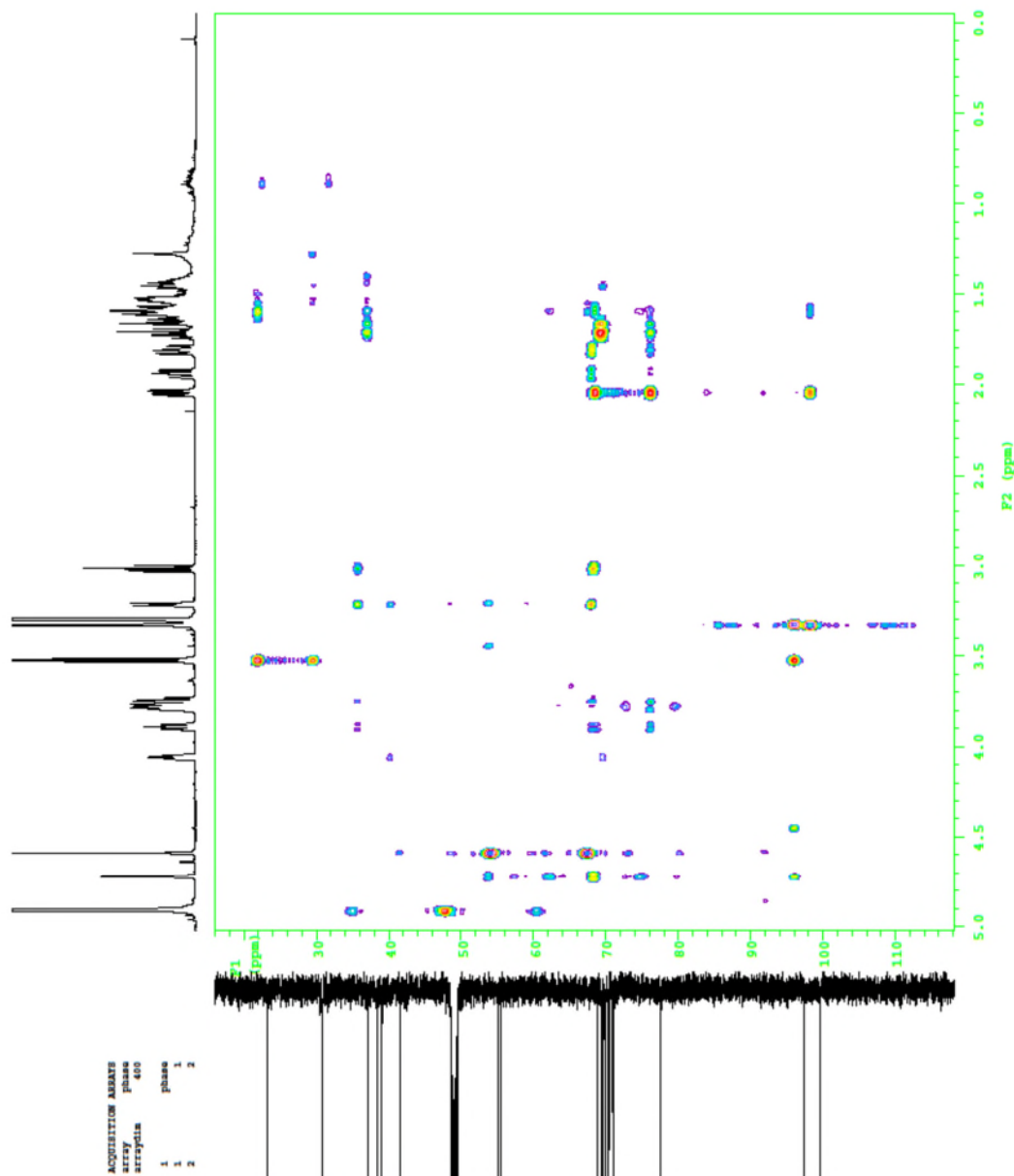
exp3 gCOSY
=====
DATA   MER 15 2019   IN          PEAK#   IN
SOLVENT CD3OD       SPT#1     6120
SAMPLR  4000       SPT#1     4096
ACQUISITION  SERIAL          SPECIAL
AV      9415.4   temp   not used
AT      0.150   gain    38
TP      2884   SPT#1
ED      4000       F2 PROCESSING 0
SI      15       F2          0.001
SI      1.000   SPT#1   not used
SI      8       F2          not used
SI      4096   SPT#1
=====
2D ACQUISITION  F1 PROCESSING
SI      9415.4   SPT#1   -0.013
SI      128   SPT#1   not used
SI      128   SPT#1   not used
SI      4096   SPT#1
=====
PARAMETERIZATION  SPT#1   DISPLAY  4096
=====
PARAMETERIZATION  SPT#1   DISPLAY  4096
=====
NAME      SPT#1   DISPLAY  4096
=====
TRANSMITTER  WP      3051.8
LN      RL   SPT#1   -185.7
SFRq    599.787   SPT#1   3633.9
tor     599.7   F1L    3207.9
tpw     10.500   F1L    3211.2
P#      CHANNEL#2   F1L    1879.2
=====
SPT#1#2   S102   PLOT  351.9
SFR      0.001000   WC
SFRatio  1.000   AC   9.8
gstab   0.000500   WCD 208.9
=====
INCOUPLER  CL3   WCD  53.9
=====
SPT#1   SPT#1   SPT#1   4
=====

```



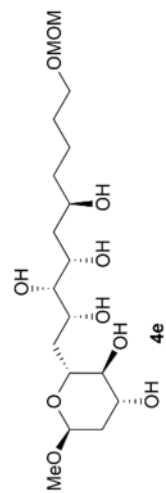
^1H - ^1H COSY (600 MHz, CD_3OD)



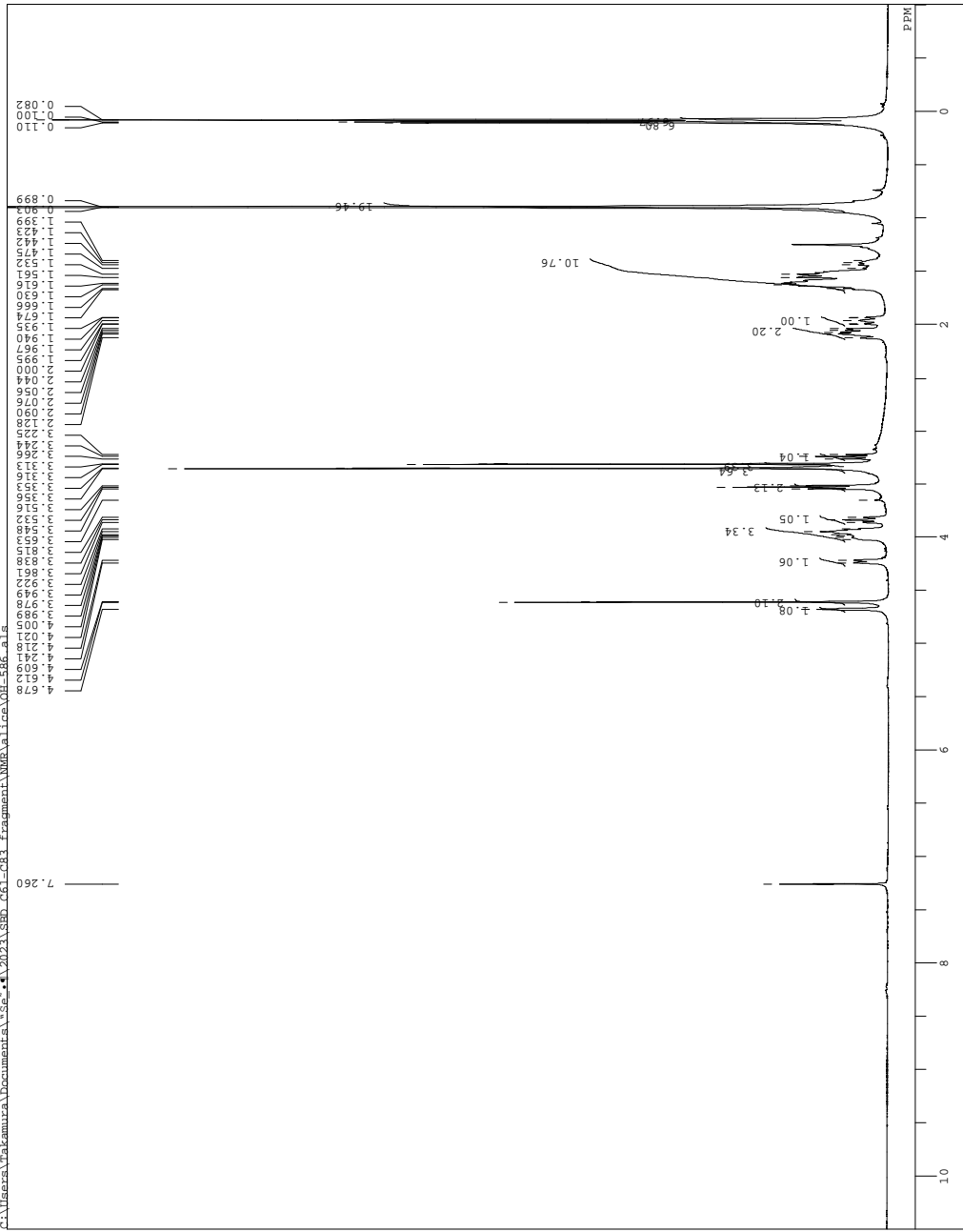
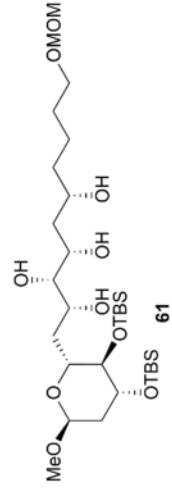


exp5 gsmc
 date Mar 14 2019 hr
 name_0000000000
 sample_0000000000
 acq 9615.4 temp not used
 at 0.150 lamp not used
 sp 2884 gain
 fr 4000 spin
 as 1.00
 ds 32
 ss 0.001000
 us 32
 us 0.001000
 2D ACQUISITION 9615.4 1500
 sw 36199.1 f2 0.001000
 ut 200 gscad 0.000500
 phase arrayed f2 PROCESSING
 PREPARATION 9615.4
 acq 0.150
 wsc 4894
 TRANSMITTER 9615.4
 tx 0.005
 atfq 599.767 g5a1 not used
 tor 599.7 g5a1 hp
 tpr 10.000 fill DISPLAY 2048
 P ENCOUNTER -28.2
 ds 2037.7
 dsz 1542.4 gpa 2483.9
 ds mm wpl 15432.9
 ds dszwa wa0_consumer rfl 1311.3
 dsz 31008 f2 0
 dsz 146 gpa 2344.0
 dsz 56 f2p1 2344.0
 pow 13.100 PLDT 381.9
 11ch 146.0 ac 5.8
 12ch 8.0 wsc 208.9
 ac2 0
 ac3 133
 ac4 133
 al odb av

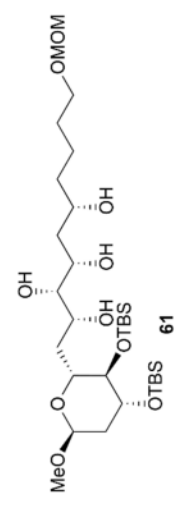
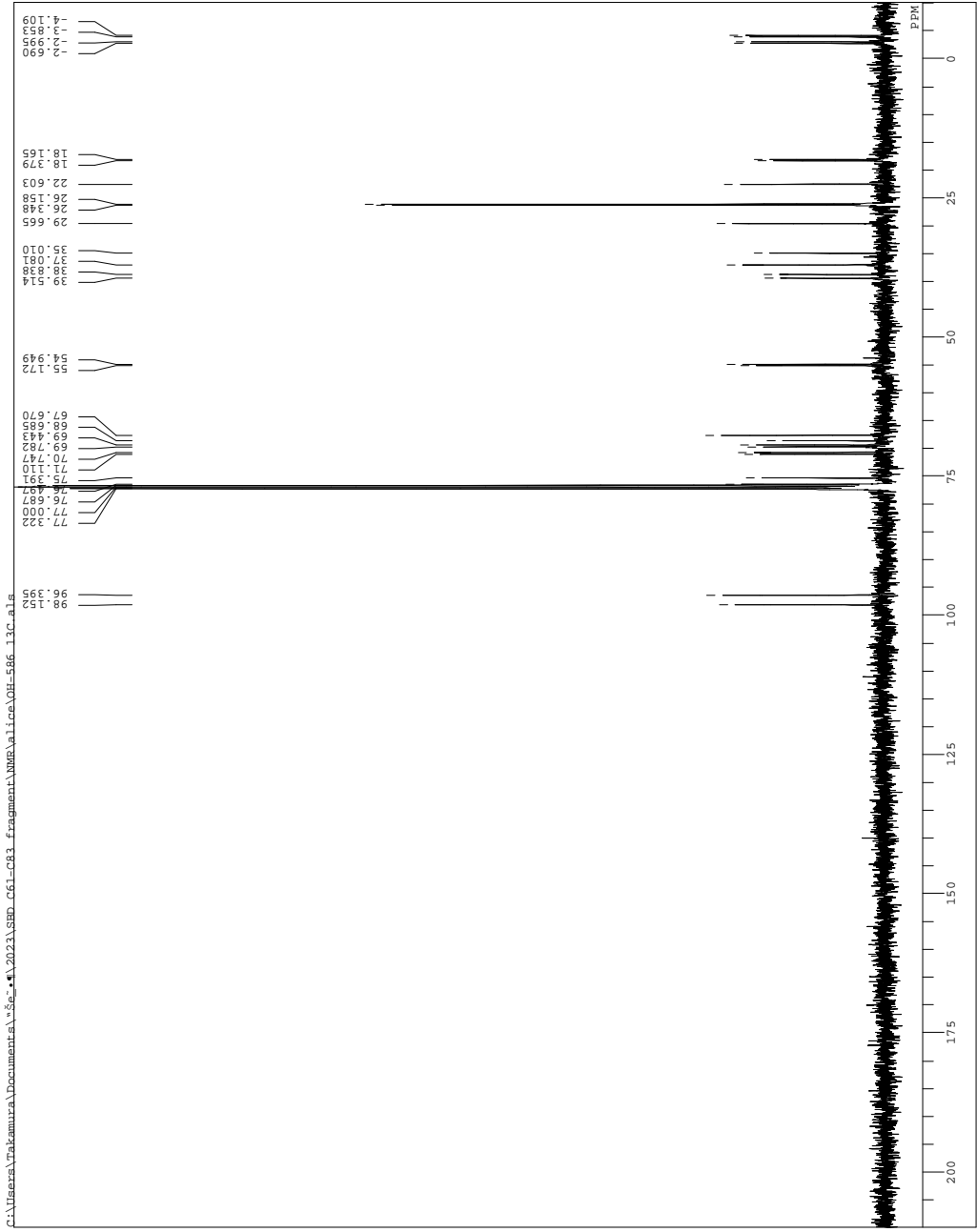
HMBC (600 MHz, CD₃OD)



C:\Users\TakaMura\Documents\se_4\2023\SRM_061-C83_Fragment\NMR\Alice\OH-586_a1s
 FILE OH-586_a1s
 COMPT Thu Dec 27 21:02:21 2018
 CONV 1H
 ORNTC 1H
 EXMOD NON
 OBSFQ 398.65 MHz
 OBSF1 134.00 MHz
 ORFIN 10500.00 Hz
 POINT 793768 Hz
 SCANS 32
 ACQTM 4.0993 sec
 PUL 2.640 msec
 PW 6.40 msec
 IRNUC 1H
 STNUC 24.7 c
 STREF CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 14



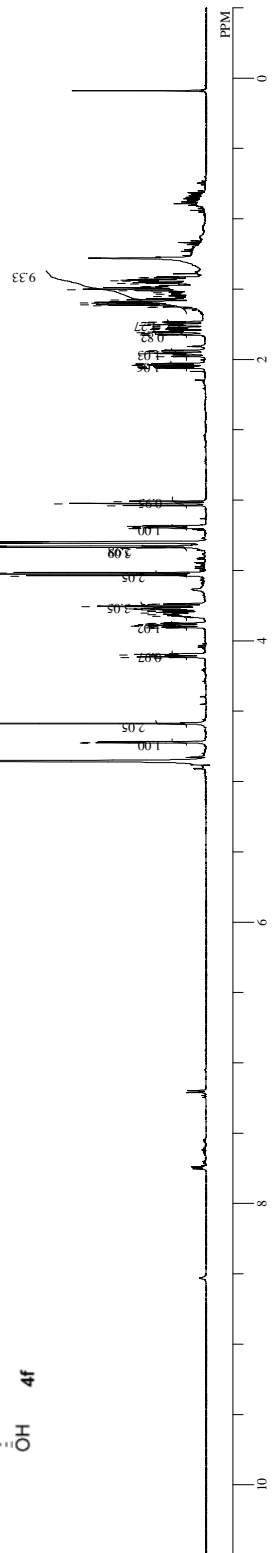
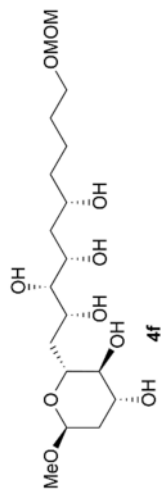
DEFILE OH-586 13C.als
 DATE_ TIME Thu Dec 27 21:22:39 2018
 ORNVC 13C
 ORNVC BCM
 ORNVC 100.40 MHz
 ORNVC 125.00 KHz
 ORNVC 10500.00 Hz
 FREQ0 271731.90 Hz
 SCANS 1.3884
 PCQTM 1.7240 sec
 PM1 6.80 usec
 IRMVC 1H
 IRMVC 26.3 C
 SOLVT CDCl3 77.00 PPM
 EXREF 2.24 Hz
 RGAIN



C:\Users\kadom\Desktop\2*\NMR\%off\Data\KH-53-1H.xls

4.7242
4.7188
4.8877
4.1900
4.1141
4.1097
4.1019
4.0975
3.9062
3.9028
3.8944
3.8910
3.8886
3.8873
3.8773
3.8739
3.8201
3.8113
3.7976
3.7888
3.7829
3.7780
3.7741
3.7716
3.7692
3.7633
3.7580
3.7516
3.7394
3.7349
3.5368
3.5260
3.5153
3.3378
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
3.0837
3.0231
3.0079
2.0612
2.0592
2.0524
2.0504
2.0392
2.0309
2.0289
1.9761
1.9565
1.9521
1.9389
1.9350
1.8254
1.8215
1.8073
1.8014
1.7975
1.7848
1.7815
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
1.4139

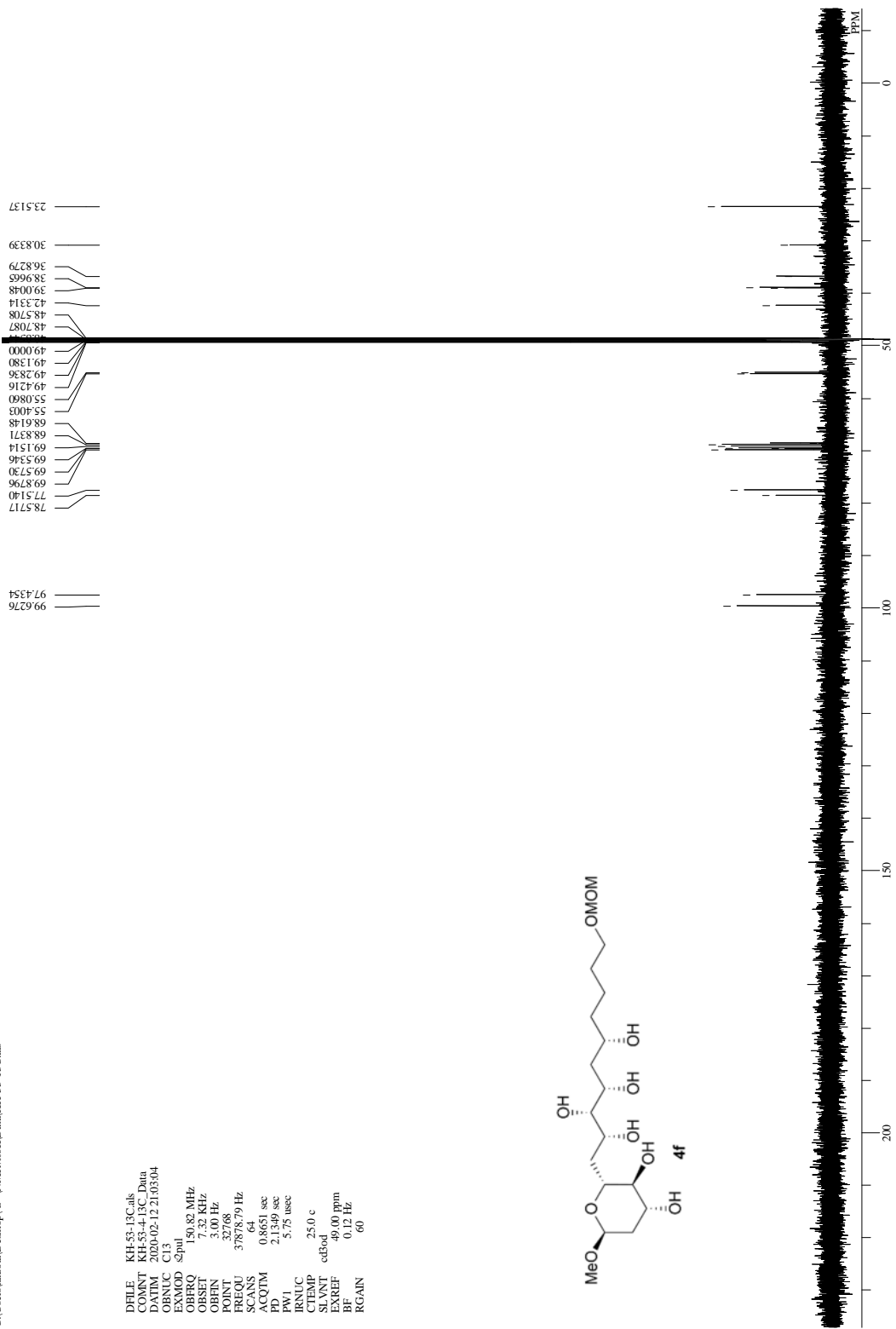
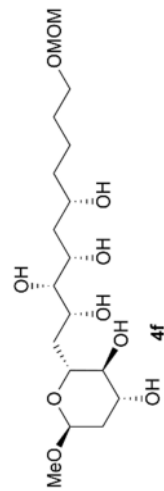
DEFILE KH-53-1H.xls
COMINT KH-53-4-1H_Data
DATIM 2020-02-12 20:58:40
ORNTUC HI
EXMOD S2p
PULPROG zgpg30
FREQ 99.6276 MHz
ORSET 7.42 kHz
ORFIN 3.60 Hz
POINT 32768
FREQ 9615.38 Hz
SCANS 32
ACQTM 3.4079 sec
PD 1.5921 sec
PWL 5.25 usec
SOLVENT cd3od
CTEMP 25.0 c
SLVNT cd3od
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 42



C:\Users\katom\Desktop\4f-1\NMR\%d\1\Dat\KH-53-13C.xls

```

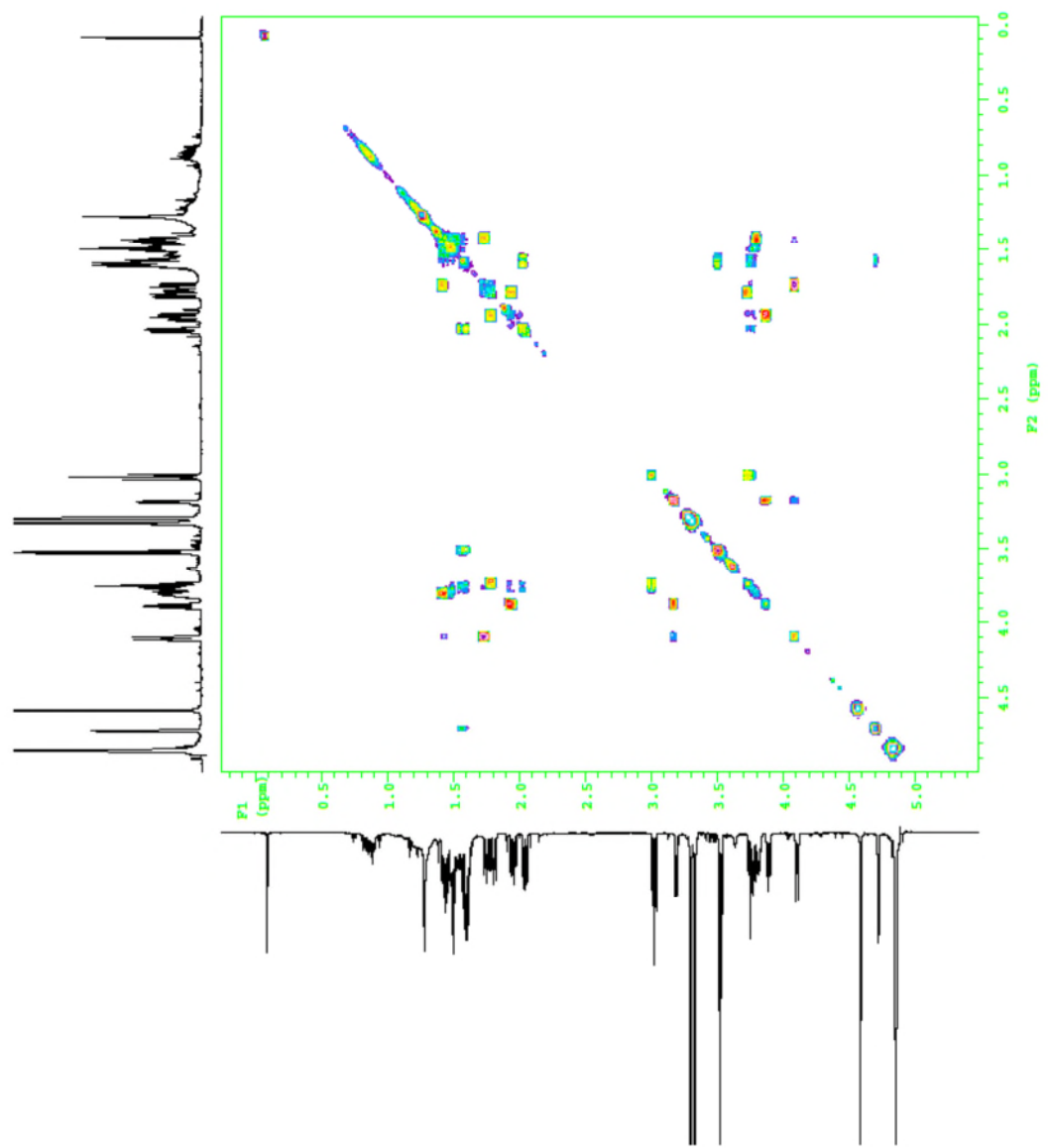
DTITLE KH-53-13C.xls
COMINT KH-53-13C Data
DATIM 2020-02-12 21:03:04
OBRNUC C13
EXMOD s2pul
PULPROG zgpg30
PROBHD 5mm QNP 1H/13
PULPROG 150.82 MHz
OBSET 7.32 KHz
OBFIN 3.00 KHz
POINT 32768
SOLVENT DMSO-d6
F2 378.7879 Hz
AQ 6.0000000 sec
RG 0.8651 sec
ACQTM 2.1349 sec
PD 5.75 usec
PW1 6.0000000 usec
IRNUC 13C
CTEMP 25.0 c
SLANT cdBod
EXREF 49.00 ppm
BF 0.12 Hz
RGAIN 60
  
```



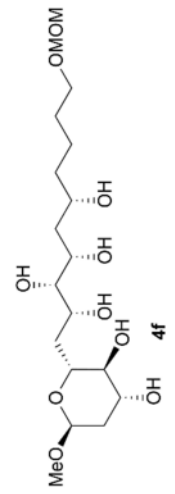
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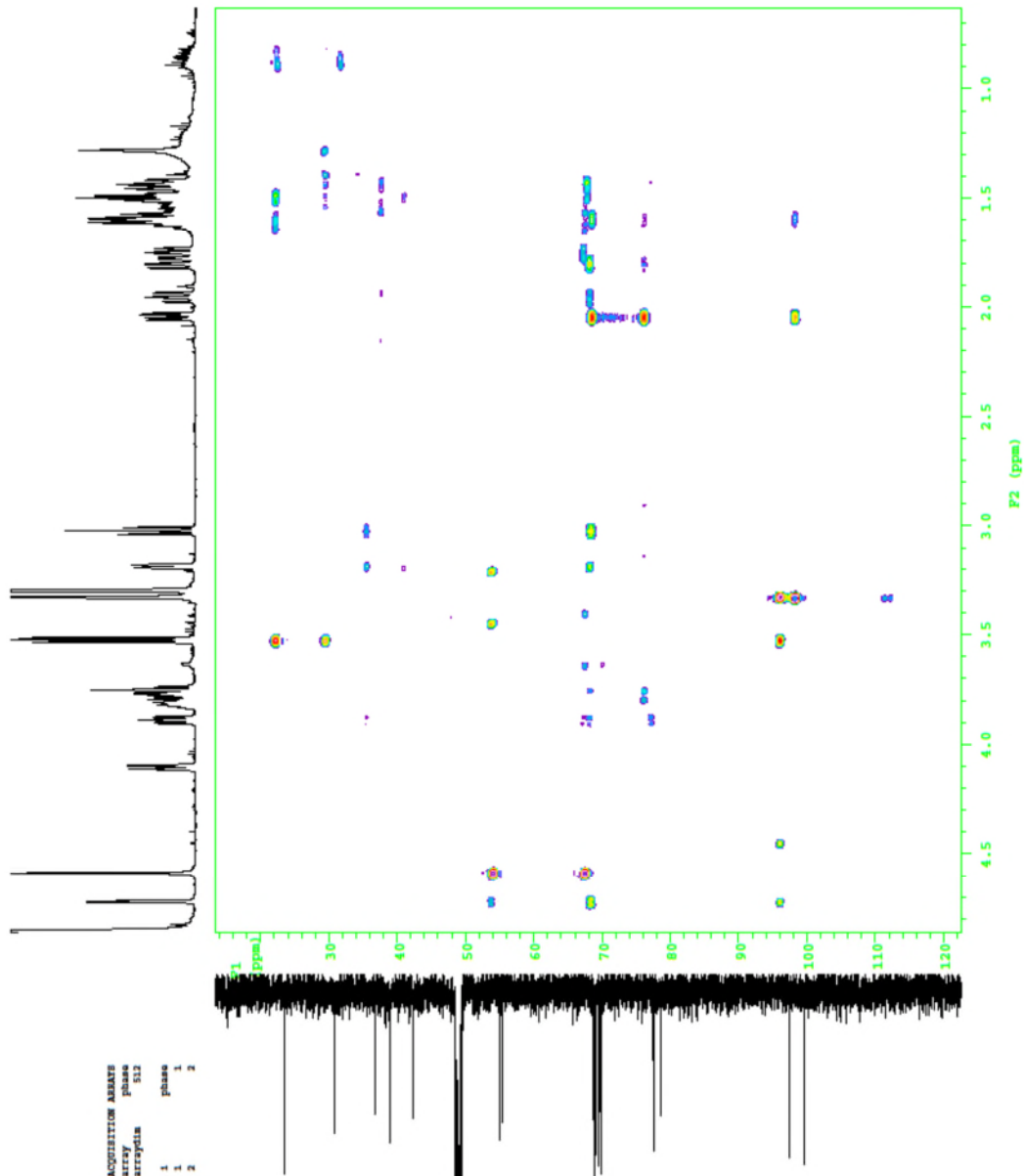
EX-13-4-gcomf_data
exp3 gcomf
=====
SAMPLE          PLACE
Date Feb 12 2020 1a
solvent cd3od
sample          bagivi
=====
ACQUISITION
nu  3415.4  name  not used
sc  1500  op1a  36
sp  2884  op1a  36
fr  4000  F2 PROCESSING  0
as  32  ab  -0.075
cl  1.000  abs  not used
dl  1.000  abs  not used
=====
2D ACQUISITION
nu  3415.4  ab1  F1 PROCESSING  0
sc  256  ab1a  not used
sp  256  ab1a  not used
dl  0  p1001  lp
=====
PREPARATION
nu  4096
strmode  n  f1  DISPLAY
wt  n  sp  -28.7
=====
TRANSMITTER
nu  4096  w1  2135.9
fr  4000  w1  2135.9
afreq  599.767  w1  3441.4
tof  599.7  r1l  3390.5
lpre  59  rfp  3379.2
pw  10.500  rfl1  3389.6
=====
GRAVIMETRY
nu  4096  w1  PLOT 351.9
sp  256  w1  256
stratio  1.000  w2  9.8
grlab  0.000500  w23  208.9
=====
ENCODING
nu  4096  w1  131
sc  256  w1  131
sp  256  w1  131
=====

```



¹H-¹H COSY (600 MHz, CD₃OD)



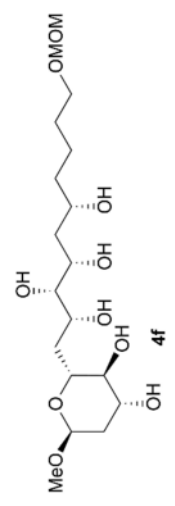


```

EX-31-4_18_Data
exp1 gsmc
=====
SAMPLE                               FLAGS
date Feb 13 2020  hs
solvent cd3od  solv
sample 4f         y
acq 1            y
=====
ACQUISITION PARAMETERS
pr 16615.4  hz
ac 0.150  temp  not used
tp 3884  gain  20
zb 4000  spin  0
as 32
cs 1.000  gr1vl  500
dl 32  gr1  0.00100
dl 32  gr2  0.00100
dl 32  gr3  0.00100
sw 16399.1  gr3  0.001000
nl 256  gr4b  0.001500
phase arrayed  p2  PROCRING2
PERRATION ab  -0.075
antenna n  sbs  not used
wct TRANSMITTER n  in  PROCRING2 4076
ts 599.767  gr1  0.097
srfy 599.767  gr1a  not used
tot 599.7  proc1  1p
tqwr 59  fml  2048
pw 10.500
=====
DC INCOUPLER  cp  306.0
dm  2035.0
grf 1542.4  wrl  2013.0
dm  mm  wpl  14473.4
decouple r40_consumer  r1l  1311.6
dar 31088  rfp  0
dpr 40  r1l1  2164.4
pmsvl 56  rfp1  0
pwr 12.100  wct  PLOT 351.9
j1xh 146.0  ac  9.8
juxh 8.0  wct  208.9
vs 131
vl 131
al obs av  2
=====
ACQUISITION ARRAYS
array y  phase  S12
array y  phase  1
array y  phase  2
=====

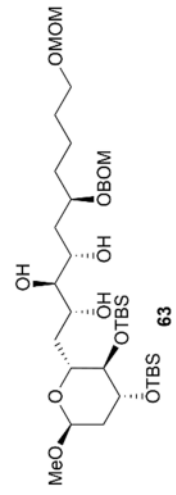
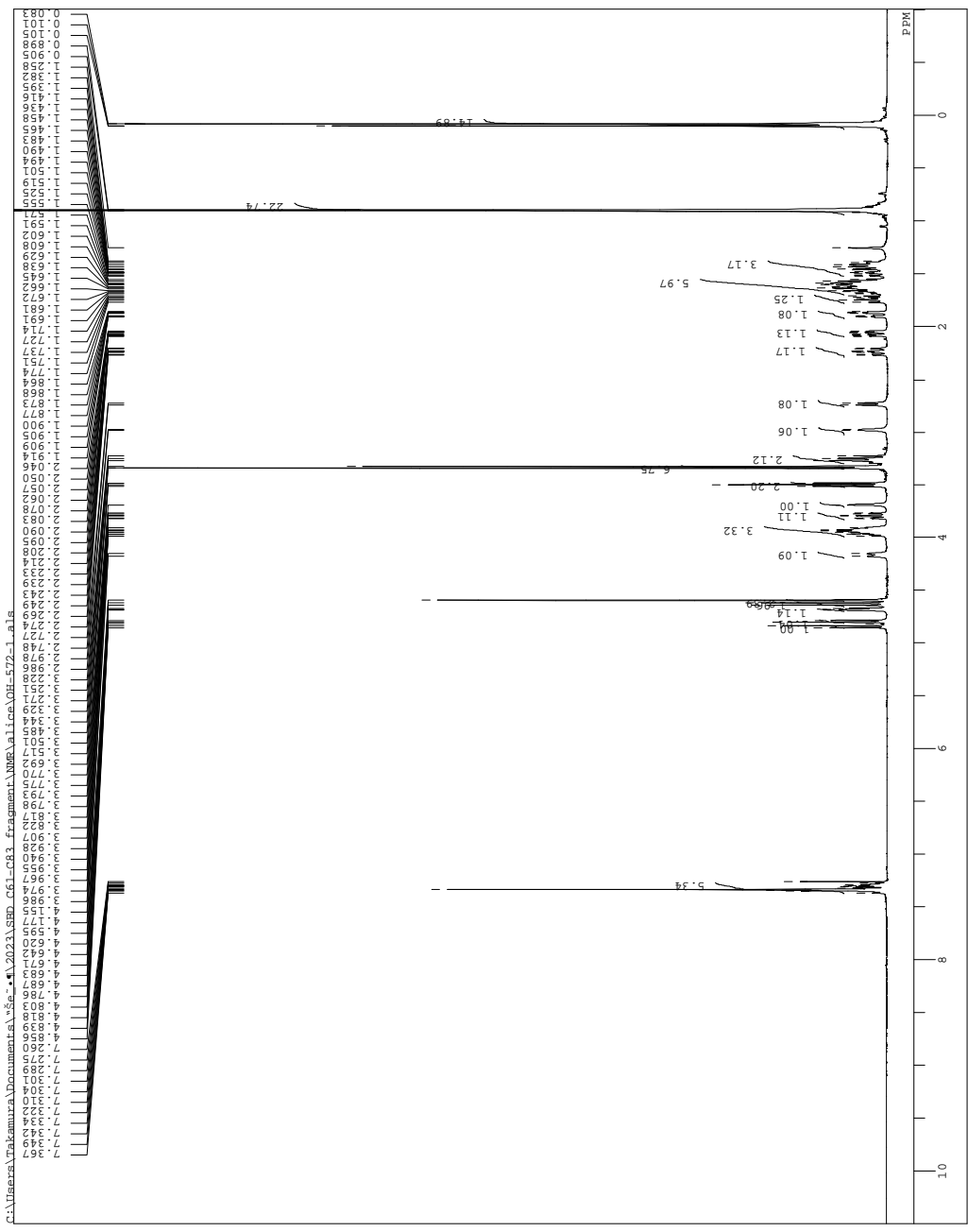
```

HMBC (600 MHz, CD₃OD)

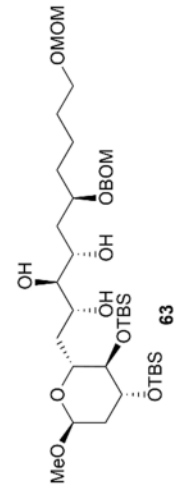
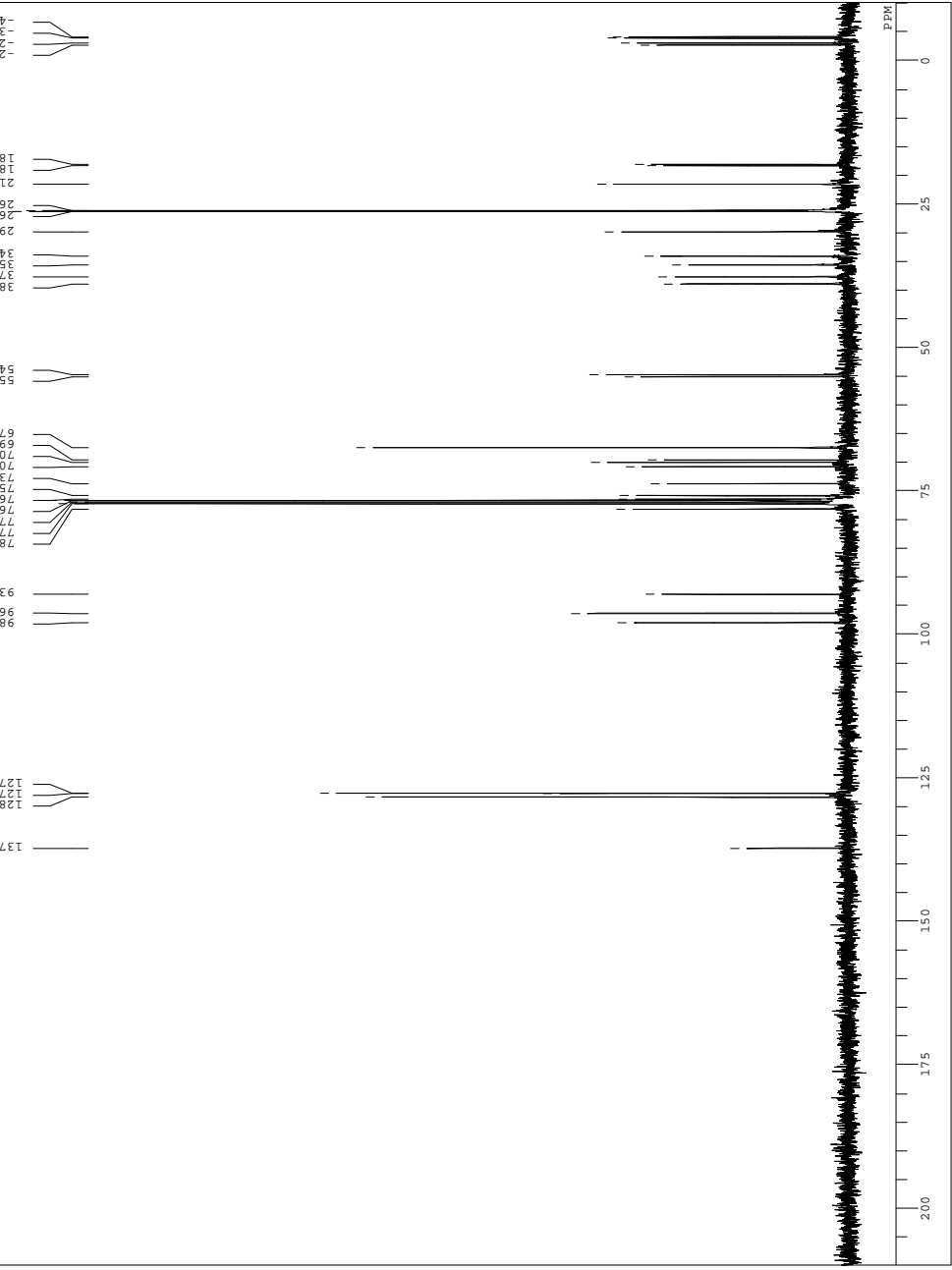


```

FILE      OH-572-1.ais
NAME      OH-572-1
DATE_    Fri Dec 14 20:29:30 2018
DIR      C:\Users\Takamura\Documents\Se...
PROBHD   5mm
PULPROG  zgpg30
DPR      399.65 MHz
AQ       124.00 kHz
RG       1050.00 Hz
FIDRES   7993.60 Hz
SOLVENT  CDCL3
NS       8
DS       4
SWH      4.000 sec
F2       2.900 sec
AQ2      2.640 usec
PC       24.7 C
PWL      1.000 sec
PRG      ARMG LH
SOLVENT  CDCL3
SOLNT    CDCL3
EXREF   7.26 ppm
RGAIN    0.11 Hz
  
```

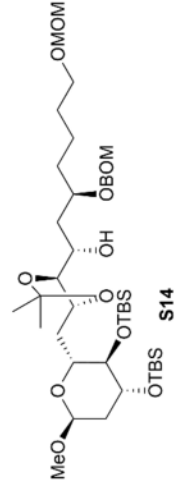
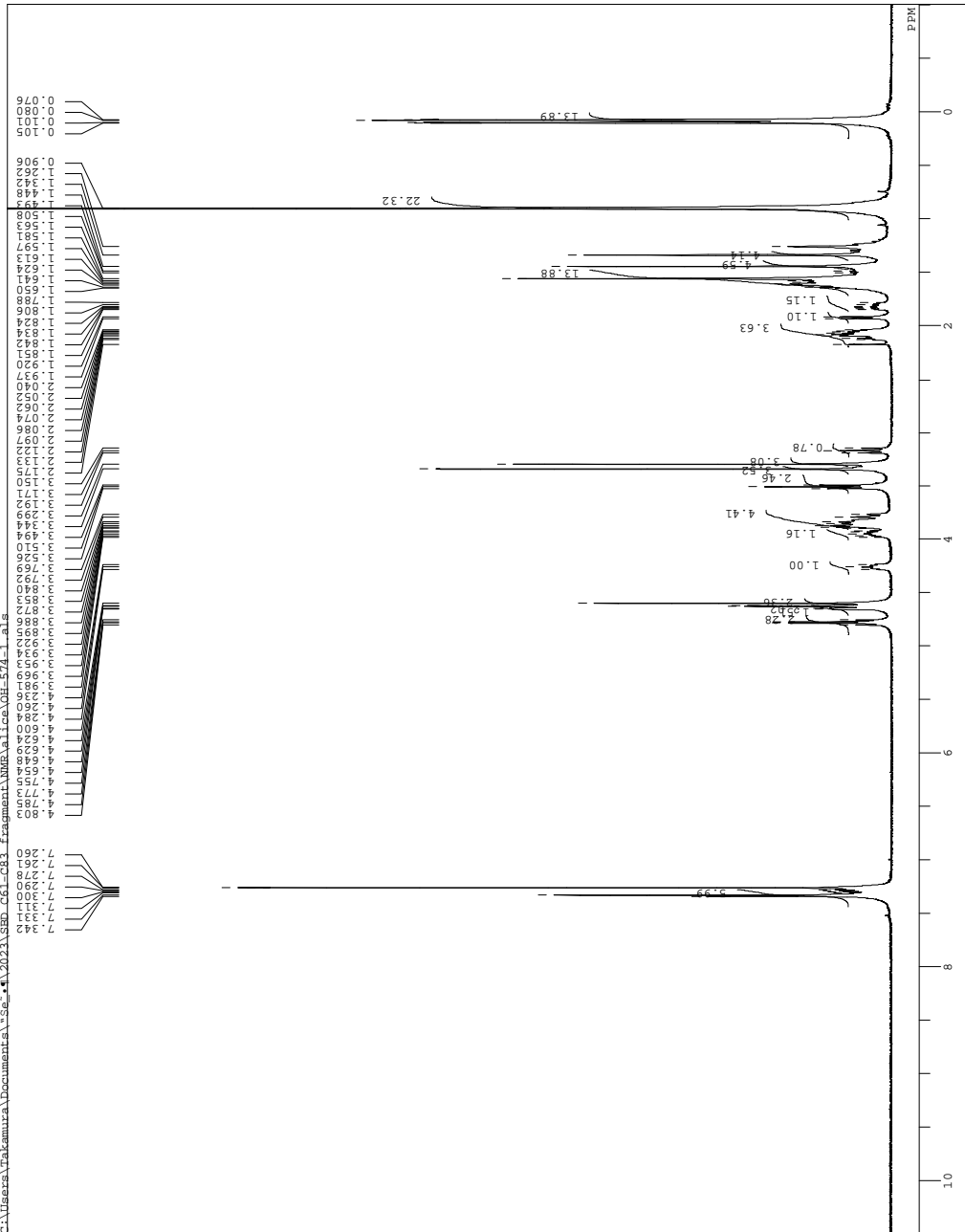


C:\Users\Takatsuma\Documents\Se*\2021\86D_661-c83_fragment\NMR\all\ce\OH=572-1_13c_als
 DEFILE OH-572-1_13c.als
 DATE_13C
 DATIM Fri Dec 14 20:46:22 2018
 ORNVC 13C
 ORNVD BCM
 ORNVO JC
 ORSET 100.40 MHz
 ORFEN 125.00 KHz
 ORFEN 10500.00 Hz
 FREQU 271731.90 Hz
 SCANS 1.280
 PCQTM 1.7240 sec
 PM1 6.80 usec
 IRMVC 1H
 SINTV 26.6 C
 SILV1 CDCL3
 EXREF 77.00 PPM
 RGAIN 2.25

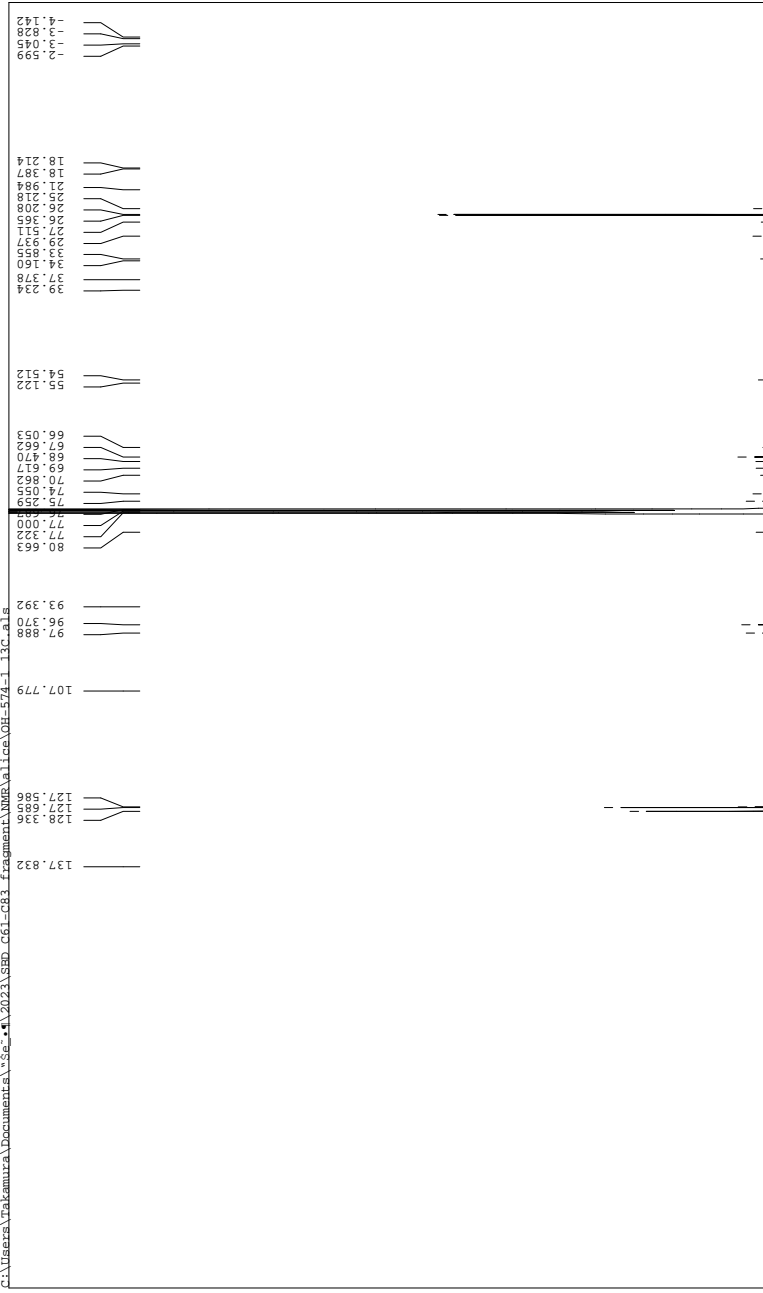
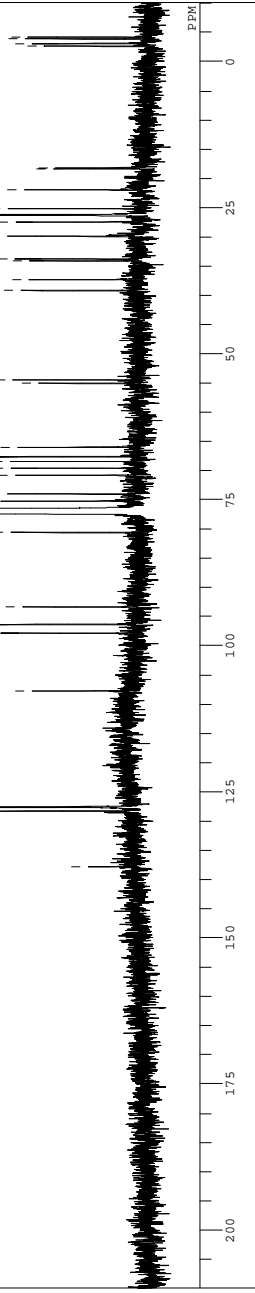
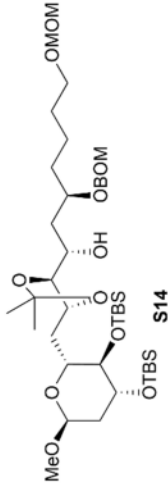


C:\Users\Tpkemura\Documents\1_36_4\2023\Fragment\MMX\Valica\OH-574-1_als

DFILE OH-574-1_als
 COMPT Thu Dec 20 00:22:14 2018
 DATE 11
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSW 10500.00 Hz
 POINT 10500.00 Hz
 SCANS 79931.32
 ACQTM 4.0893 sec
 PD 2.5010 sec
 PUL 6.40 usec
 IPRNUC 1H
 IPRNUC 1H 24.8 c
 CTEMP
 EXREF CDCL3 7.26 ppm
 BF 0.12 Hz
 RGAIN 21

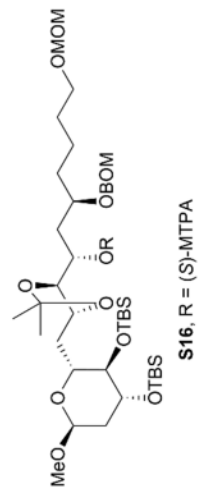
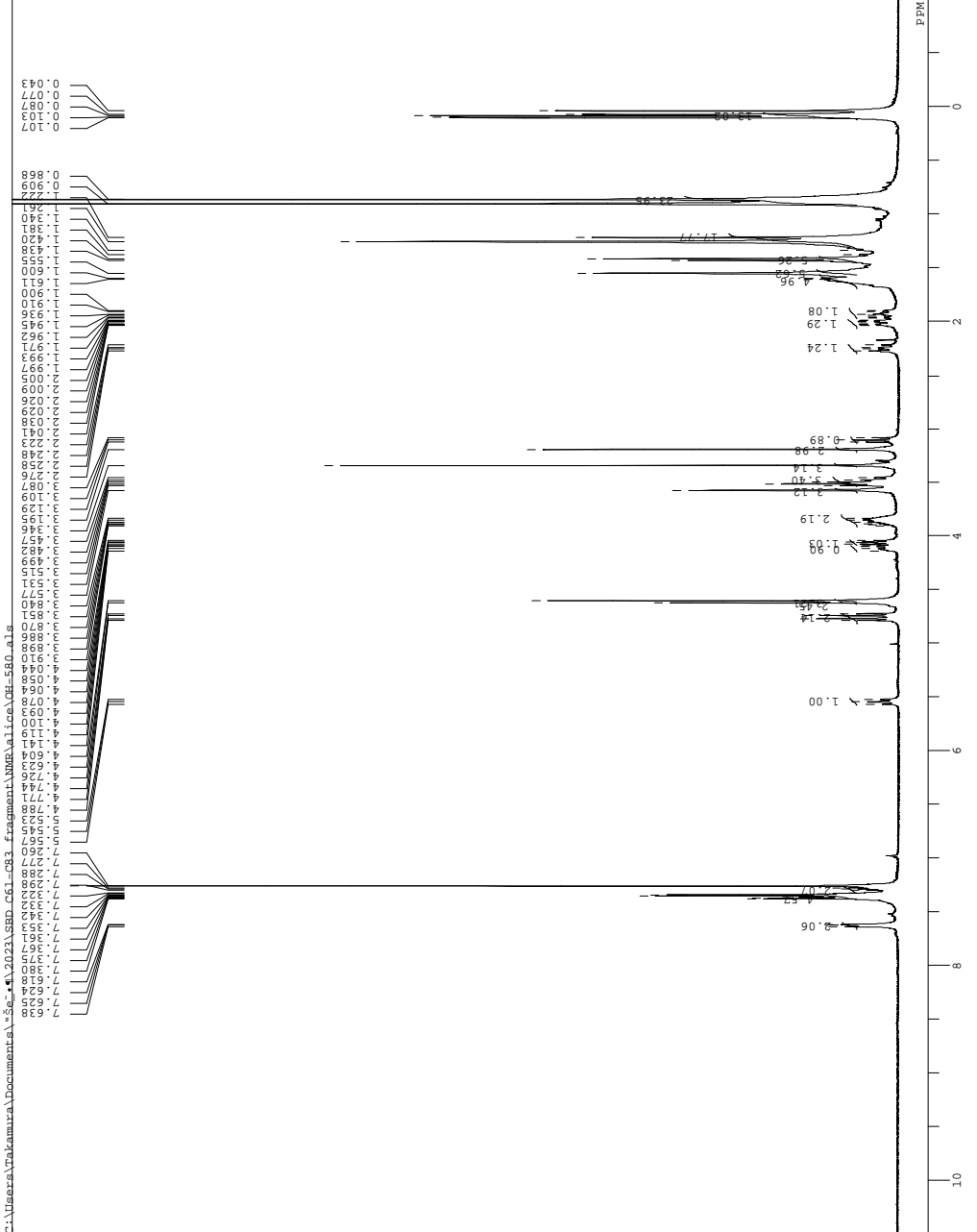


C:\Users\Takamura\Documents\Se_4\2021\SRD_561-c83_frgment\NMR\data\OH-574-1_13c_als
 DEFILE OH-574-1_13c.als
 CQM Thu Dec 20 08:44:21 2018
 COM 13C
 ENMC 13C
 EXMOD BCM
 EXPT 1
 F1 100.40 MHz
 F2 125.00 MHz
 ORF1N 10500.00 Hz
 PCEN 27137.90 Hz
 SCANS 10000
 ACQTM 1.7059 sec
 PM 1.6780 usec
 INTC 1H
 INTN 26.1 c
 SOLV CDCL3
 EXRF 77.00 PPM
 RAIN 2.00 Hz
 RGAIN 2.24



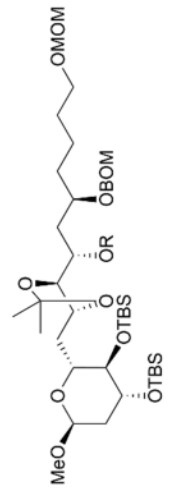
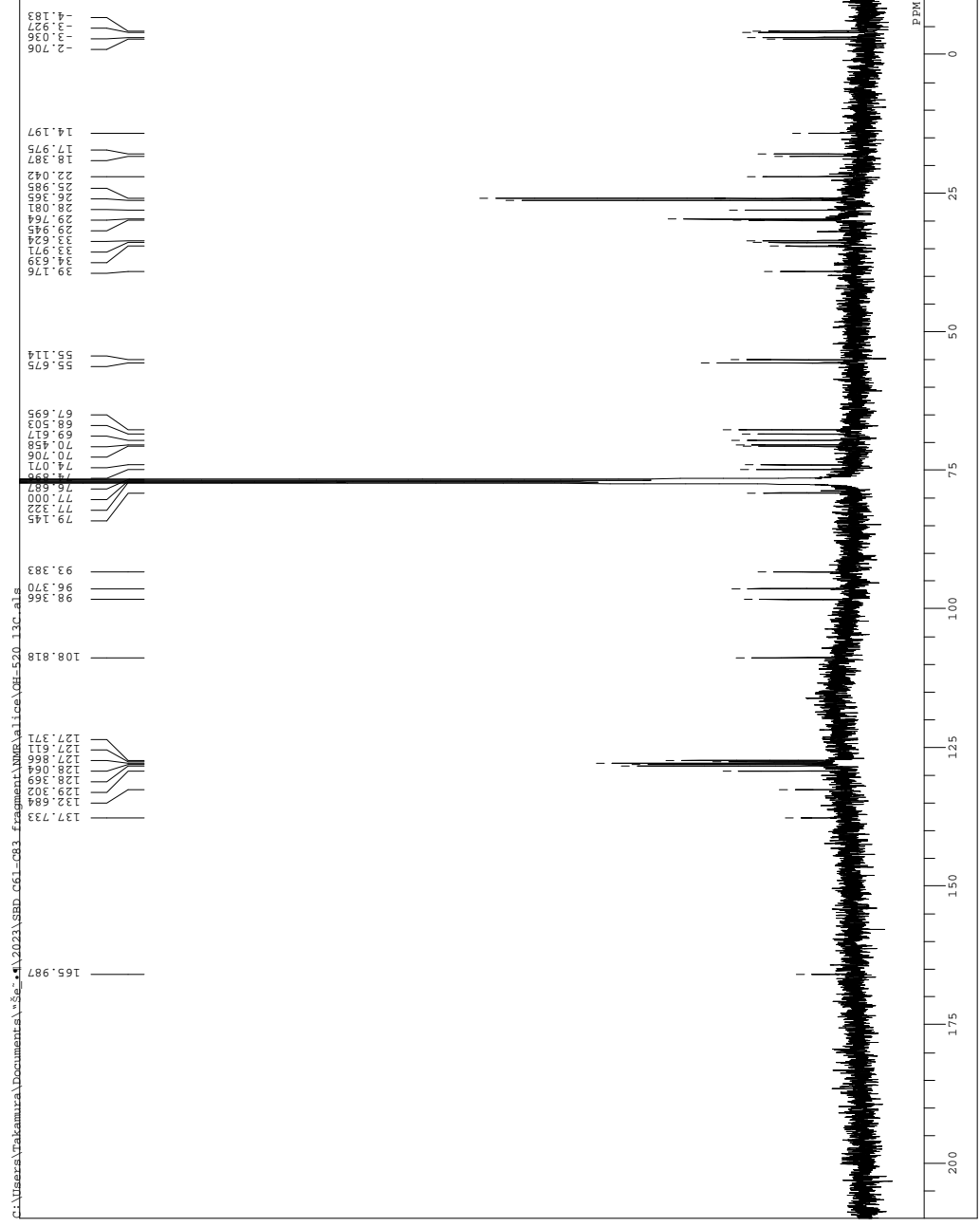
C:\Users\Takamura\Documents\2021_SSD_C61_083_Fragment\NMR\1D\OH-580.als

```
DFILE OH-580.als  
COMPT F01 Dec 21 00:34:45 2018  
ORIGIN 1H  
EXMOD NON  
OBPRQ 399.65 MHz  
OBPRQ 105500.00 Hz  
POINT 32768  
SCANS 7993.32 Hz  
ACQTM 4.0993 sec  
PUL 2.50 sec  
PI 6.10 usec  
IERNUC 1H 24.9 c  
CTEMP 25.00  
EXREF CDCL3 7.26 ppm  
BF 0.12 Hz  
RGAIN 20
```

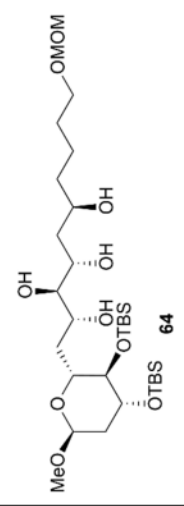
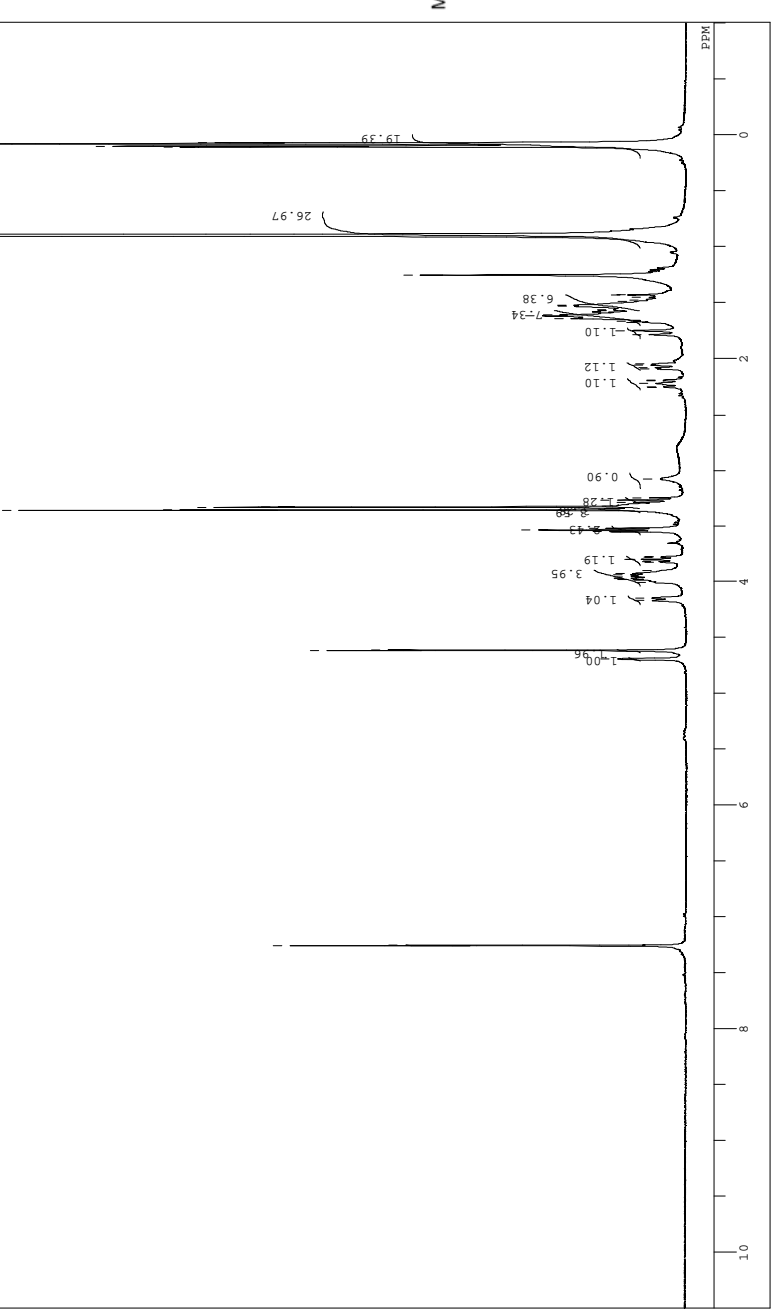


C:\Users\Tarakumura\Documents\13c\20231_SBD_C61_C83_Fragment\NMR\13c\CH-520_13c_als

DFILE OH-520_13c_als
 COMPT Tue Dec 18 06:46:07 2018
 ORMC 13C
 EXMOD BCK
 OBPRQ 100.40 MHz
 OBSFO 105500.00 Hz
 POINT 32768 Hz
 SCANS 271
 ACOFM 1.2059 sec
 PD1 1.790 sec
 PULP 6.00 usec
 IRRUC 1H 26.0 c
 CTMP CDCL3 77.00 PPM
 EXREF BF 2.00 Hz
 RGAIN 24

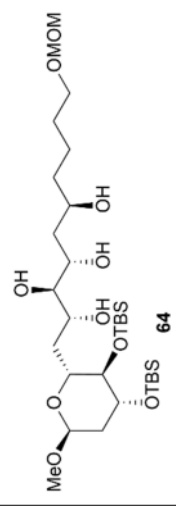
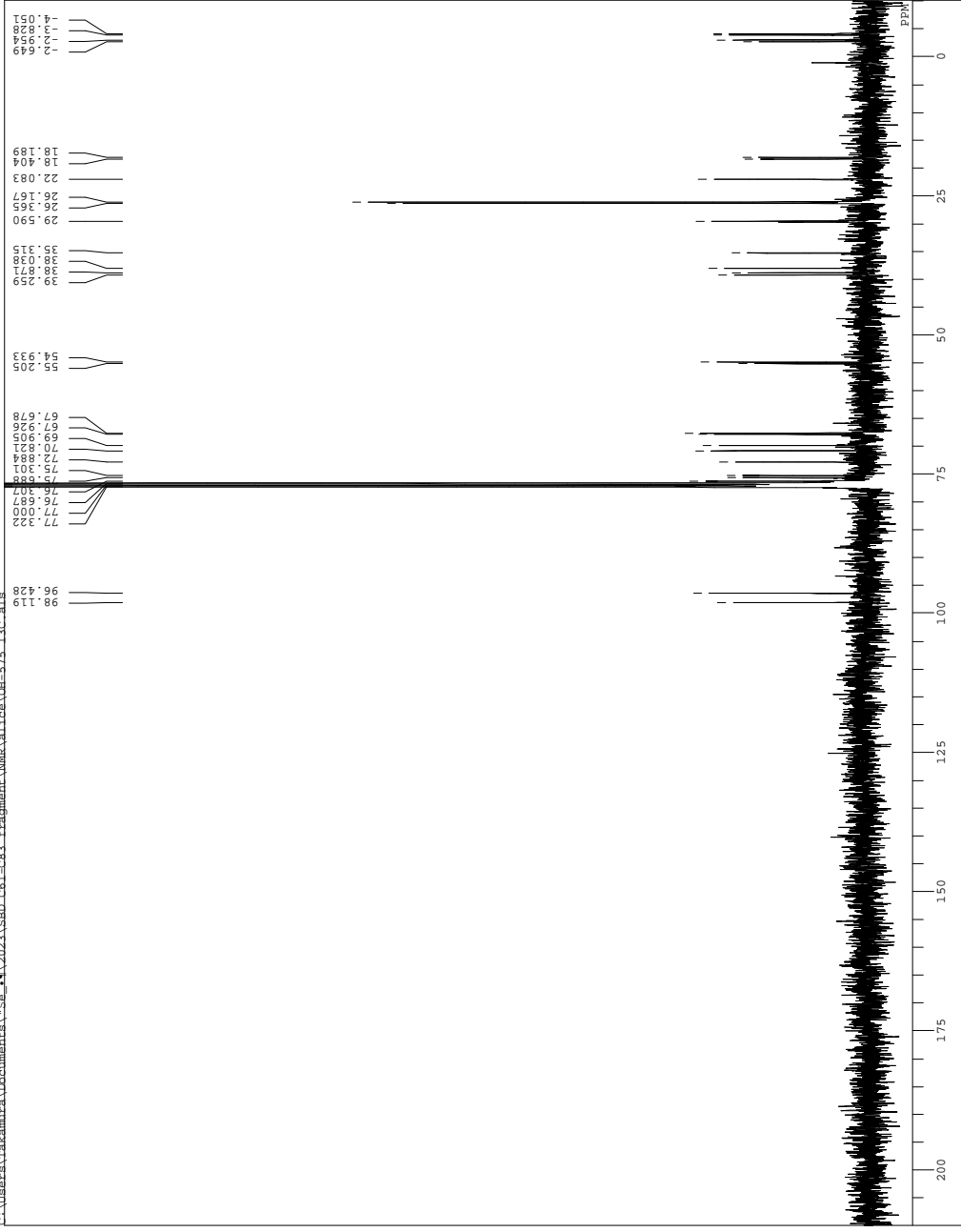


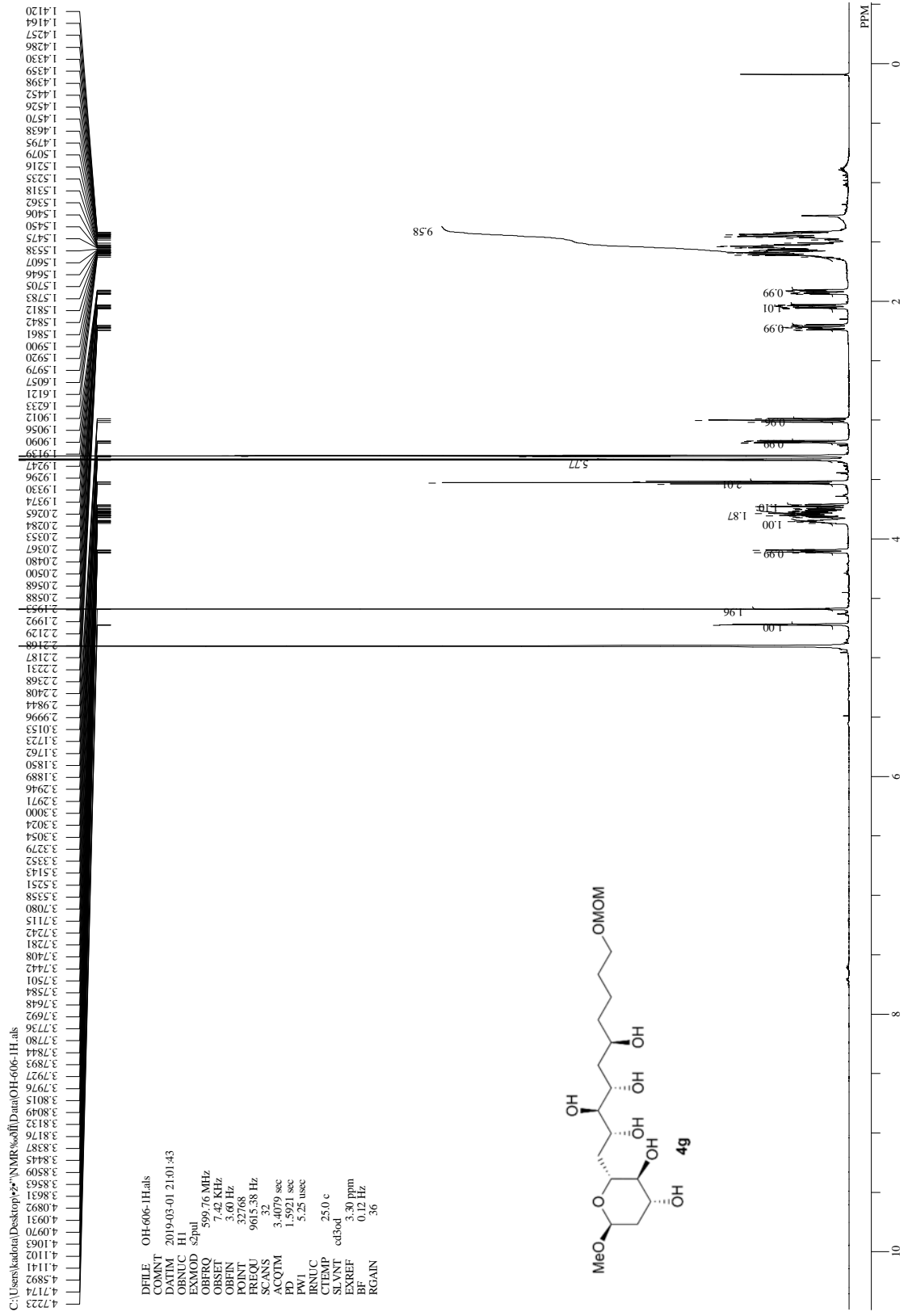
C:\Users\Trakamura\Documents\Se...2023\8BD_061_c83_Fragment\MNH\OH-575_als
 FILE OH-575_als
 DATE Tue Dec 18 19:05:03 2018
 INSTR 1H
 ORBIT 399.65 MHz
 PULPROG zgpg30
 EXPTNO 1
 OBSERV 124.00 KHz
 OBFTN 10500.00 Hz
 FREQ 7953.60 Hz
 F2 -
 SCANS 4.000
 DS 2
 EQ 2.903 sec
 PC 6.40 usec
 PM 1
 L1 24.8 C
 L2
 L3
 SOLT CDCl3
 EXPT 7.26 min
 ACQ 0.17 Hz
 RGAIN



C:\Users\Takahara\Documents\2023\SSD_C61-C83_Fragment\NMR\data\OH-575_13C_als

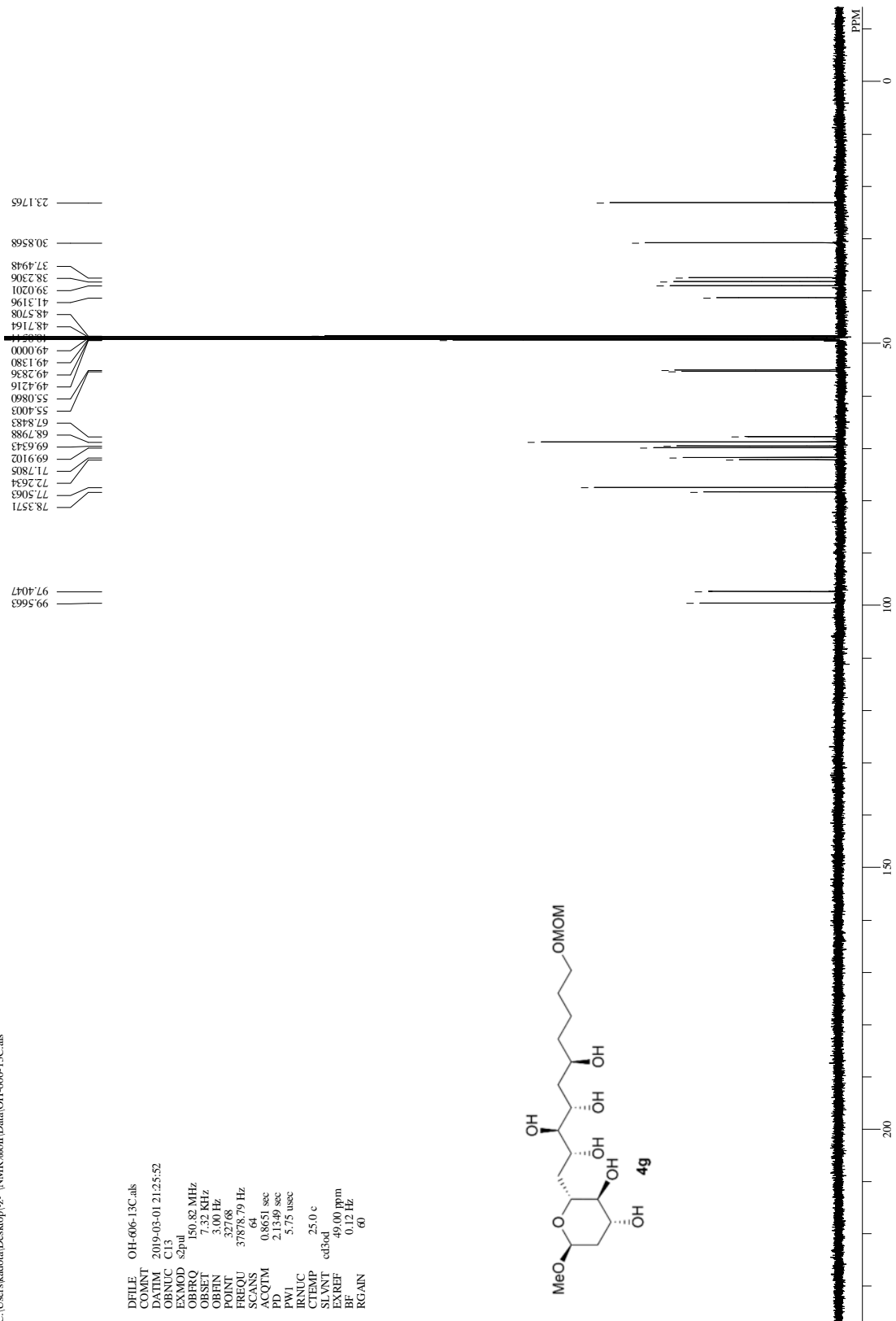
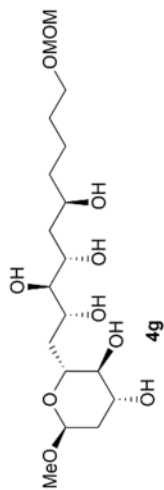
DFILE OH-575_13C_als
COMPT Tue Dec 18 20:12:48 2018
NAME 13C
EXMOD BCK
ORF50 100.40 MHz
ORF51 10500.00 Hz
POINT 32768
SCAN 2711
SCANS 1184
ACQTM 1.2059 sec
PD 1.7940 usec
P1 6.00 usec
IRNUC 1H
CTEMP 26.2 c
EXSOL CDCl3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24





C:\Users\kadota\Desktop\22-1\NMR\%01\Dat\OH-606-13C.als

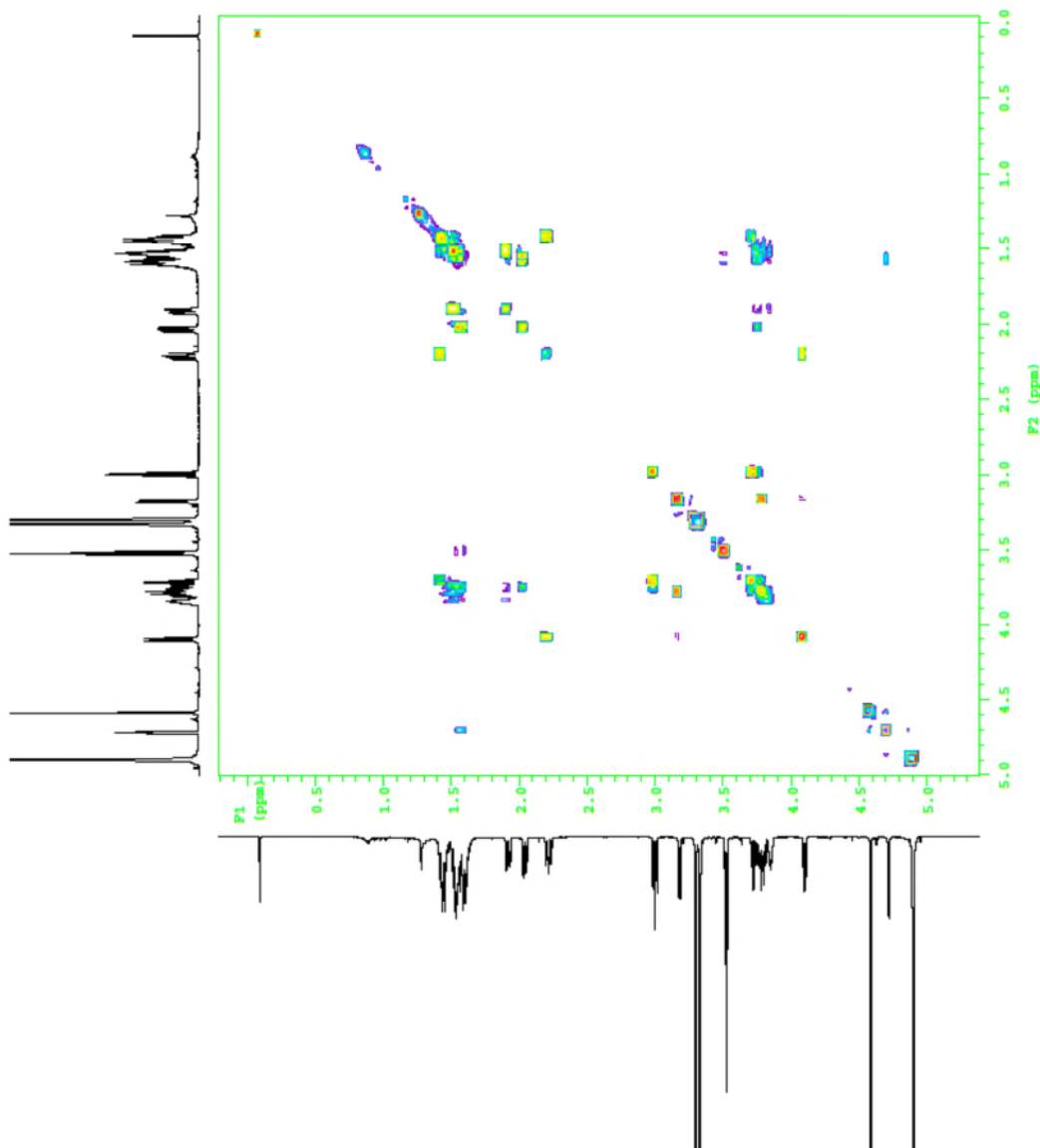
DFILE OH-606-13C.als
COMNT
DATIM 2019-03-01 21:25:52
ORNUC C13
EXMOD s2pul
OBFRQ 150.82 MHz
OBSET 7.32 KHz
OBFIN 3.00 Hz
POINT 327.68
FREQU 37878.79 Hz
SCANS 64
ACQTM 0.8651 sec
PD 2.1349 sec
PWLIC 5.775 usec
SOLVNT
CTEMP 25.0 c
EXREF ed3ad
SLENT 49.00 ppm
BF 0.12 Hz
RGAIN 60



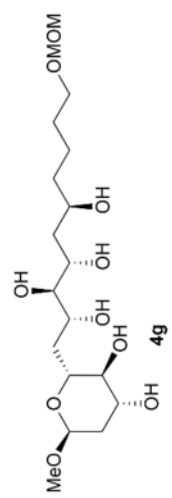
```

exp3 gcosy
=====
SAMPLE                   FLAG#   nm
Date Mar 2 2019         ha
Solvent cd3od           solui   y
Sample                 mgtivi  6120
Acquisition            m      y
=====
acq 0615.4             not used
acq 0615.4             not used
=====
aw 0.150              gain 36
aw 2884                spins 0
aw 4000                f2 processing 0
aw 32                  ad -0.075
aw 1.000               adw not used
aw 0.000               adx not used
aw 0.000               ady not used
aw 0.000               adz not used
aw 0.000               adxx not used
aw 0.000               adyy not used
aw 0.000               adzz not used
=====
f1 0615.4             not used
f1 138              not used
=====
cs PREPARATION 0 prool   hp
cs PREPARATION 0      full  4096
=====
NAME#      n   sp   DISPAR#  -23.4
NAME#      n   sp   DISPAR#  -23.4
=====
wv TRANSMITTER      ns   3023.4
wv TRANSMITTER      ns   -127.2
wv TRANSMITTER      ns   -127.2
=====
afreq 539.767       wpl  2386.9
afreq 539.767       wpl  2386.9
=====
tqc 599.7          rrl  2386.5
tqc 599.7          rrl  2386.5
=====
tpr 59            rfp  1979.2
tpr 59            rfp  1979.2
=====
pw 16.500         rfil  2099.7
pw 16.500         rfil  2099.7
=====
pwr CHANNEL#  0102   rfd  1979.2
pwr CHANNEL#  0102   rfd  1979.2
=====
pf1 0.001000       wt  351.9
pf1 0.001000       wt  351.9
=====
stratio 1.000      ac   9.8
stratio 1.000      ac   9.8
=====
grabb 0.000500     wsc  208.9
grabb 0.000500     wsc  208.9
=====
ds ENCOUPLE      ac2  0
ds ENCOUPLE      ac2  0
=====
ds     min    31    cod  87  3

```



^1H - ^1H COSY (600 MHz, CD_3OD)



```

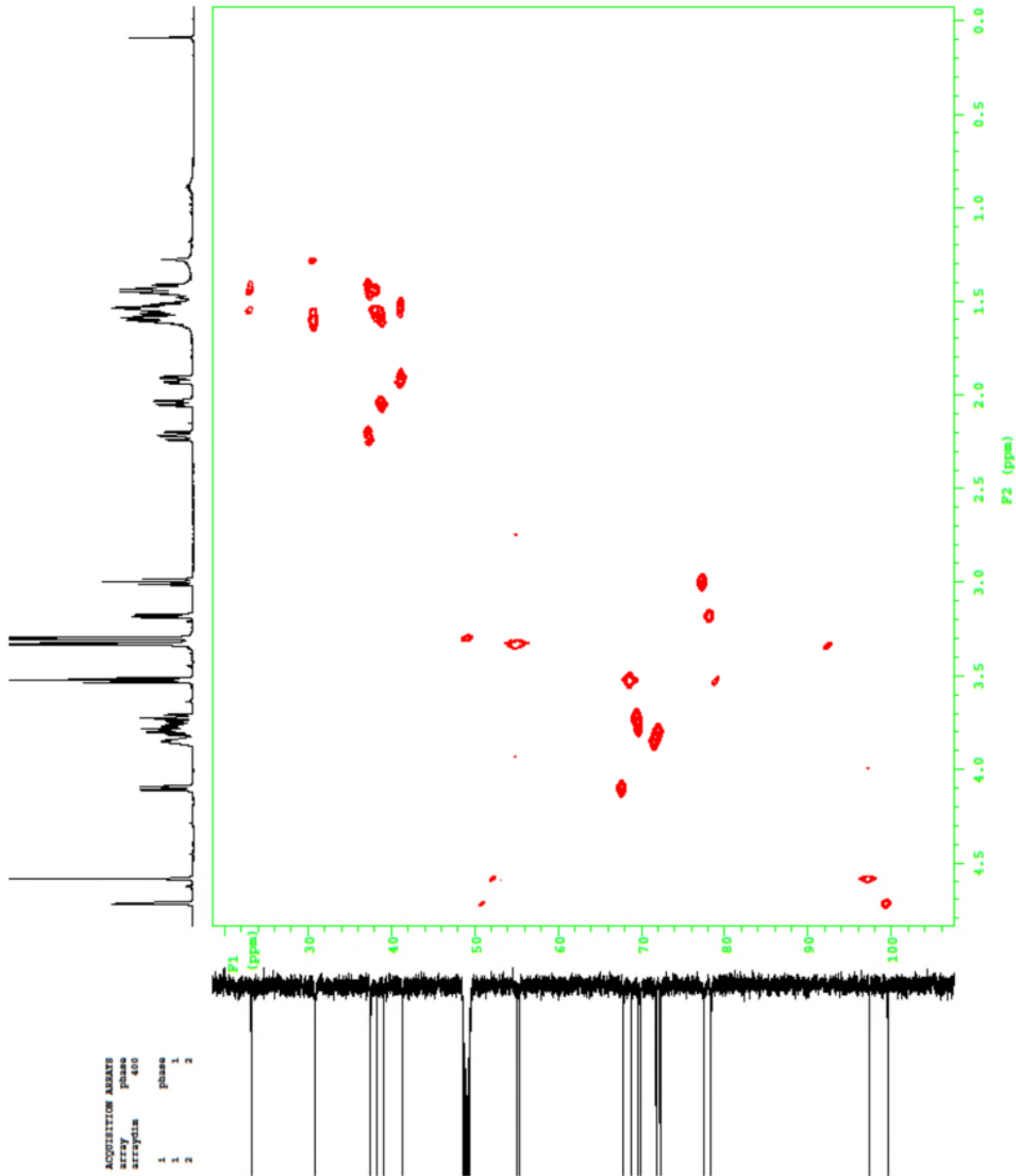
exp4 gmqc
=====
date_   Mar  1 2019   hr   FLAG
time    0000         y
=====
NAME    0000         y
EXPNO   7
PROCNO  1
PROCPS  1
AQ      0.150      temp not used
RG      2884      gain
DS      4000      spin
AQ      1.400      ps/line
SI      0.002000
US      32      gzb
2D ACQUISITION ENRatio 3.977
F1 25441.0 gzbab 0.000100
F2 200      F2 PROCESSING
=====
phase  arrayed f1 not used
PREPARATION  f2 not used
NAME      0000
WAX       8      F1 PROCESSING
=====
TRANSMITTER 8      F1 0.007
tx          tx f1a1 not used
afreq      599.767 ppsol hp
tort       599.7   thl  DIBPAM 2048
t1pr       10.100  sp
P1 ENCOUPLE  Wp      2843.8
ds          CL3  wpa  2793.8
corz       -2982.0 wpa  13421.5
om         omv  r1l  3190.1
=====
Oscova W40_consumer rfp 1979.2
Osc 31000 r1l 1977.5
Osc 31000 r1l 1979.7
pbcv1      56 rfp 1979.7
pwr        12.100 wv
=====
j1ub      gmqc ac      5.8
j1ub      146.0 wv2  208.9
malicig   y acz      0
mit       2 va      436
=====
SI  ods pb  1

```

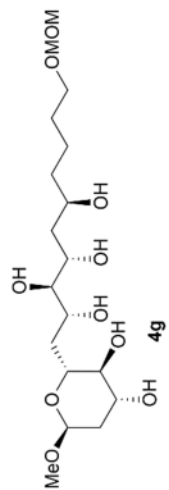
```

=====
ACQUISITION ARRAYS
array      phase
arrcp1a1  400
1          1
2          2

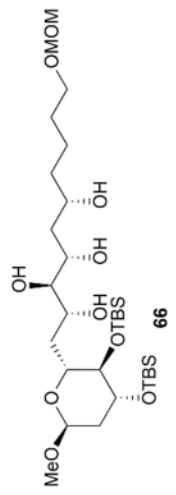
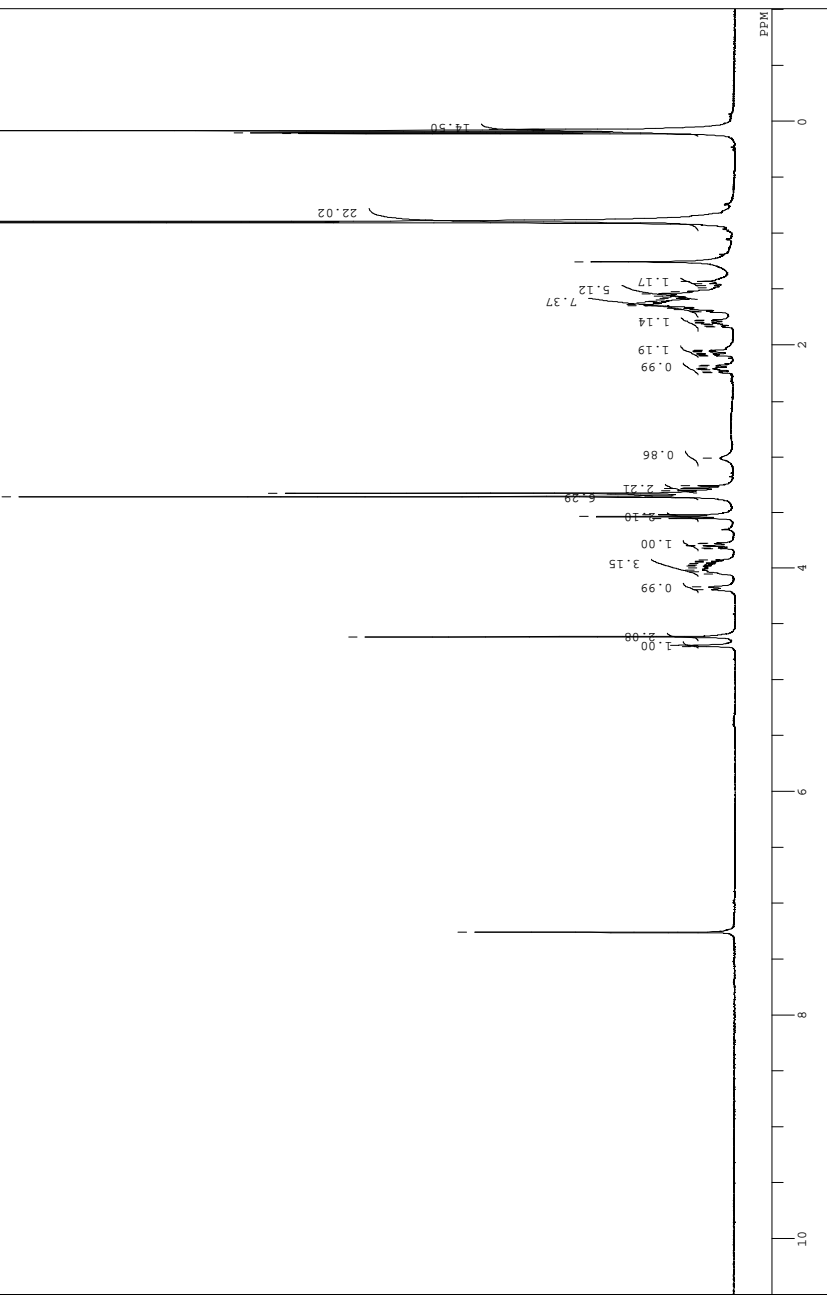
```



HMQC (600 MHz, CD₃OD)

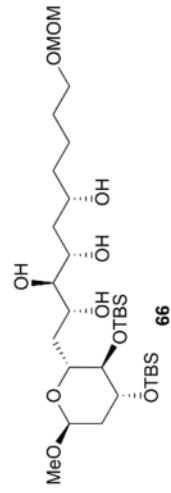
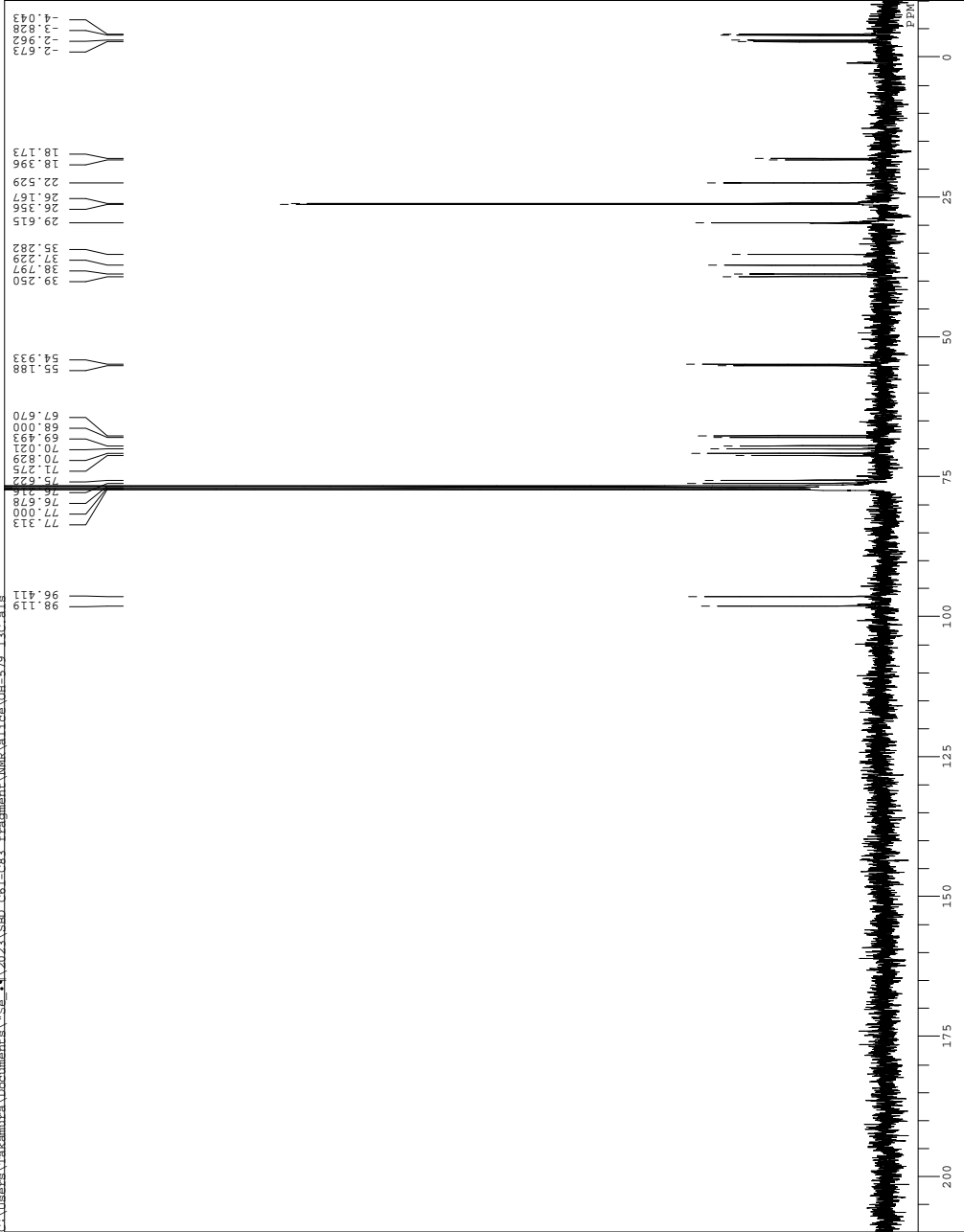


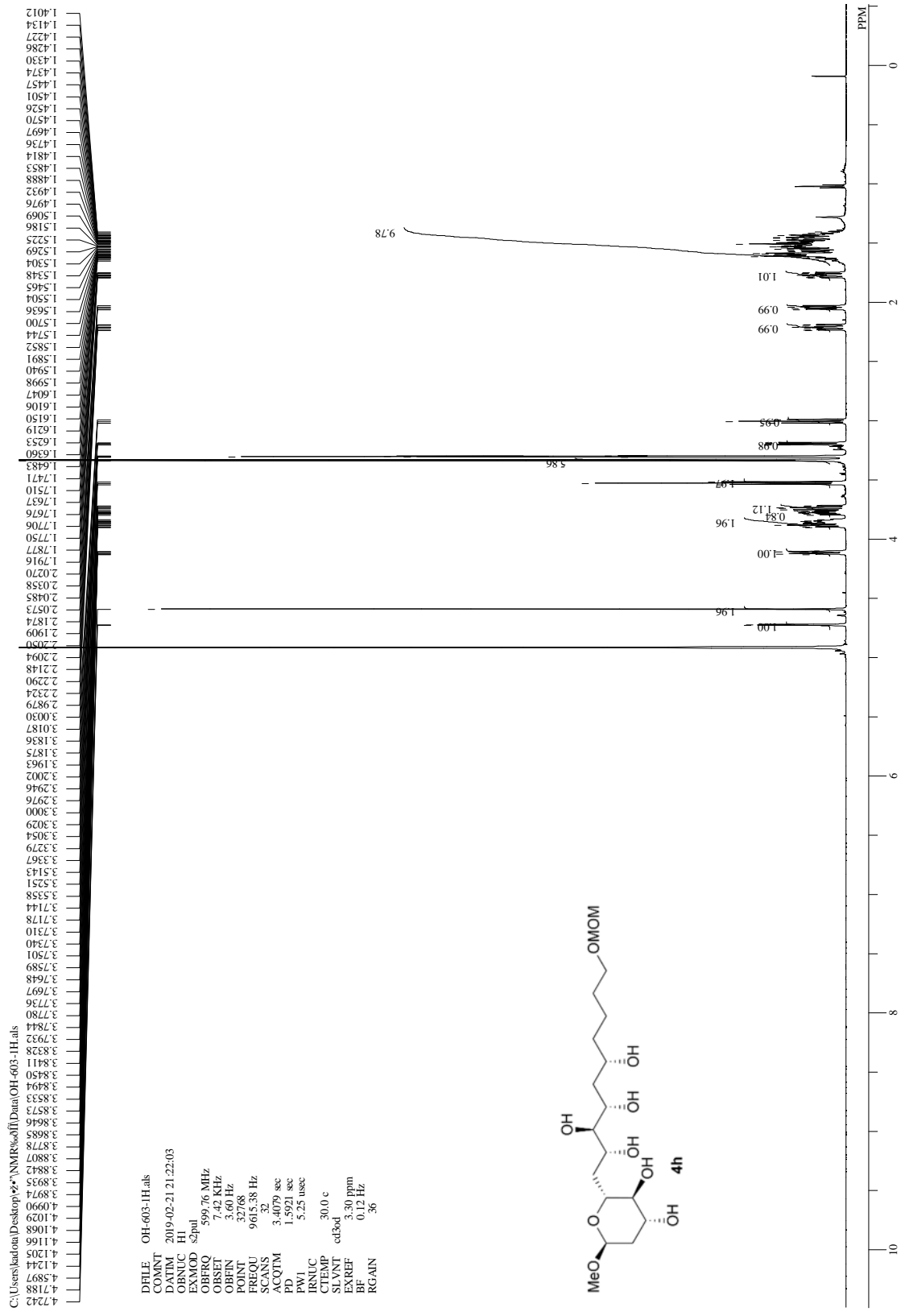
C:\Users\takamura\Documents*_s*_4\2023\SED_C61-C83_Fragment\NMR\alic\OH-579_a1s
 DF FILE OH-579_a1s
 DOPM Thu Dec 20 17:07:24 2018
 ORNUC 1H
 EXMOD NON
 OSET 399.55 MHz
 OBFIN 124.00 KHz
 OFREQ 10500.00 Hz
 PREP1 7992.76 Hz
 SCANS 4
 ACQTM 4.0973 sec
 PUL 2.640 usec
 IERNUC 1H
 IERNUC 25.5 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 REFIN 0.12 Hz
 REFIN



C:\Users\Tpkemura\Documents\sa_s*\2023\Fragment\NMR\alpha\OH-579_13c.a1s

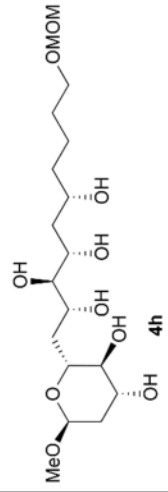
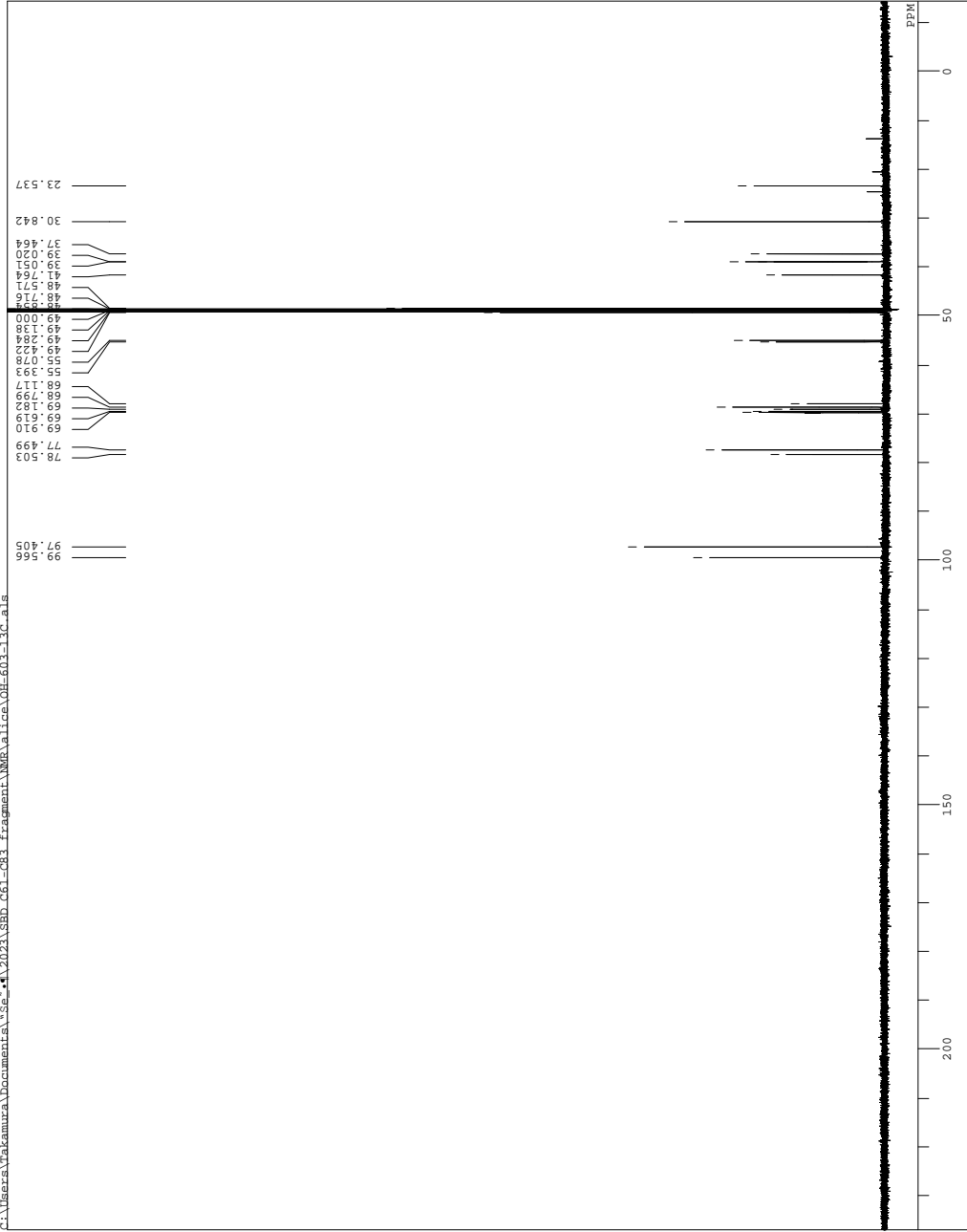
DFILE OH-579_13c.a1s
COMPT Thu Dec 20 17:03:17 2018
PROC 13C
EXMOD BCM
OBPFO 100.40 MHz
OBPFI 10500.00 Hz
OBFIN 10500.00 Hz
POINT 27132768 Hz
SCANS 1445
ACQTM 1.2059 sec
PD 1.7940 sec
PUL 6.50 usec
INNUC 1H
IRNUC 1H 26.2 c
CTEMP
EXREF CDCL3 77.00 PPM
BF 2.00 Hz
RGAIN 24





C:\Users\Takamura\Documents\562-4\2021\SBD_C61_CB3_fragment\NMR\alice\OH-603-13C.a1s

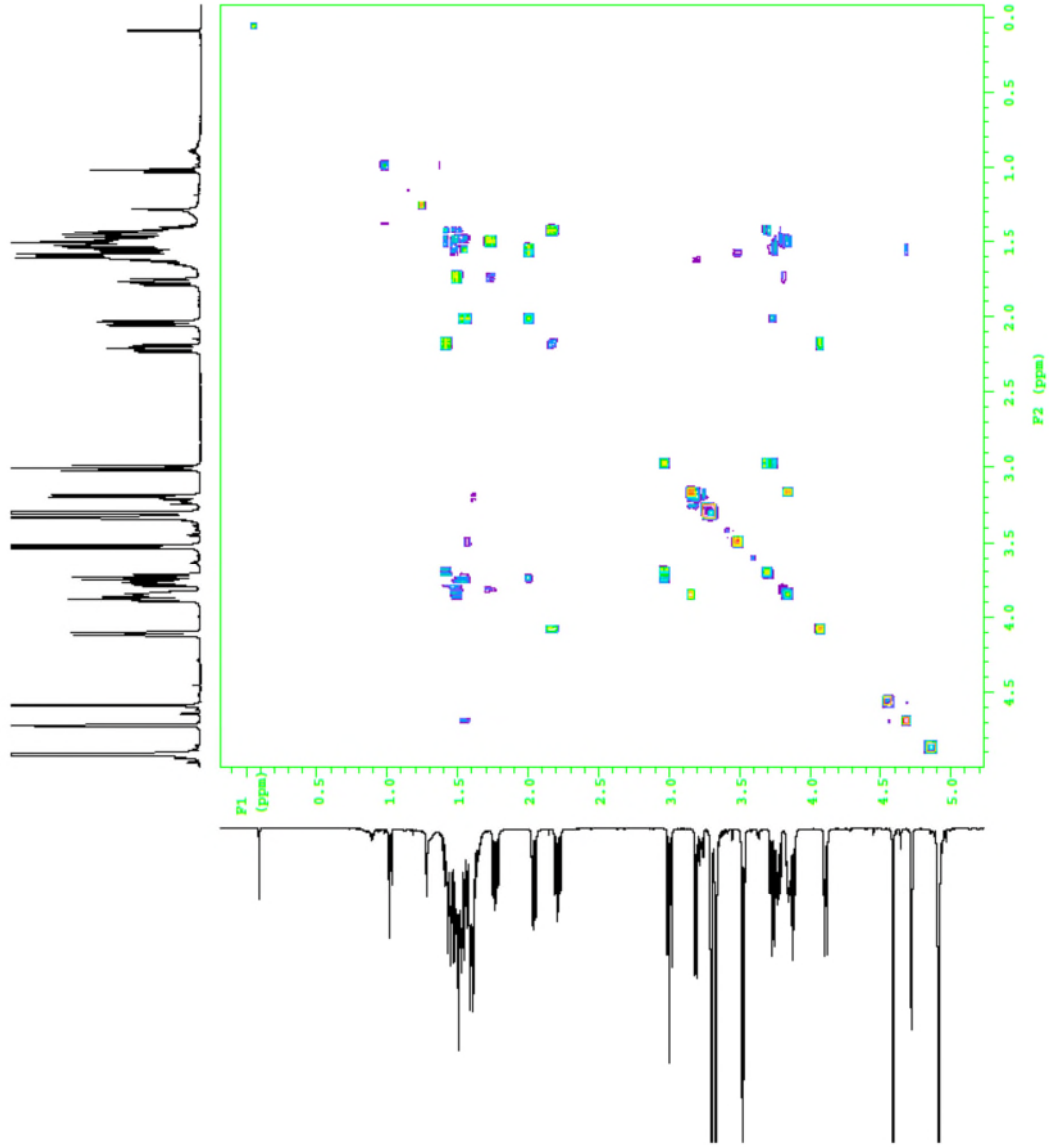
DFILE OH-603-13C.a1s
 COMNT 0019-02-21 21:34:39
 ORNAM C13
 EXMOD s2pul
 OBFRQ 150.92 MHz
 OBFREQ 32768 Hz
 POINT 37878.64 Hz
 SCANS 2
 ACQTM 0.8651 sec
 PD 2.1349 sec
 PD1 5.73 usec
 IRNUC cd3od
 CTMP 30.0 c
 EXREF 49.00 Ppm
 BF 0.12 Hz
 RGAIN 60



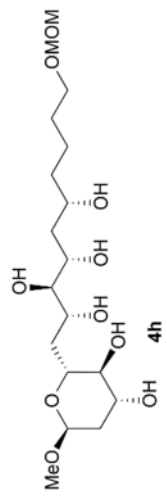
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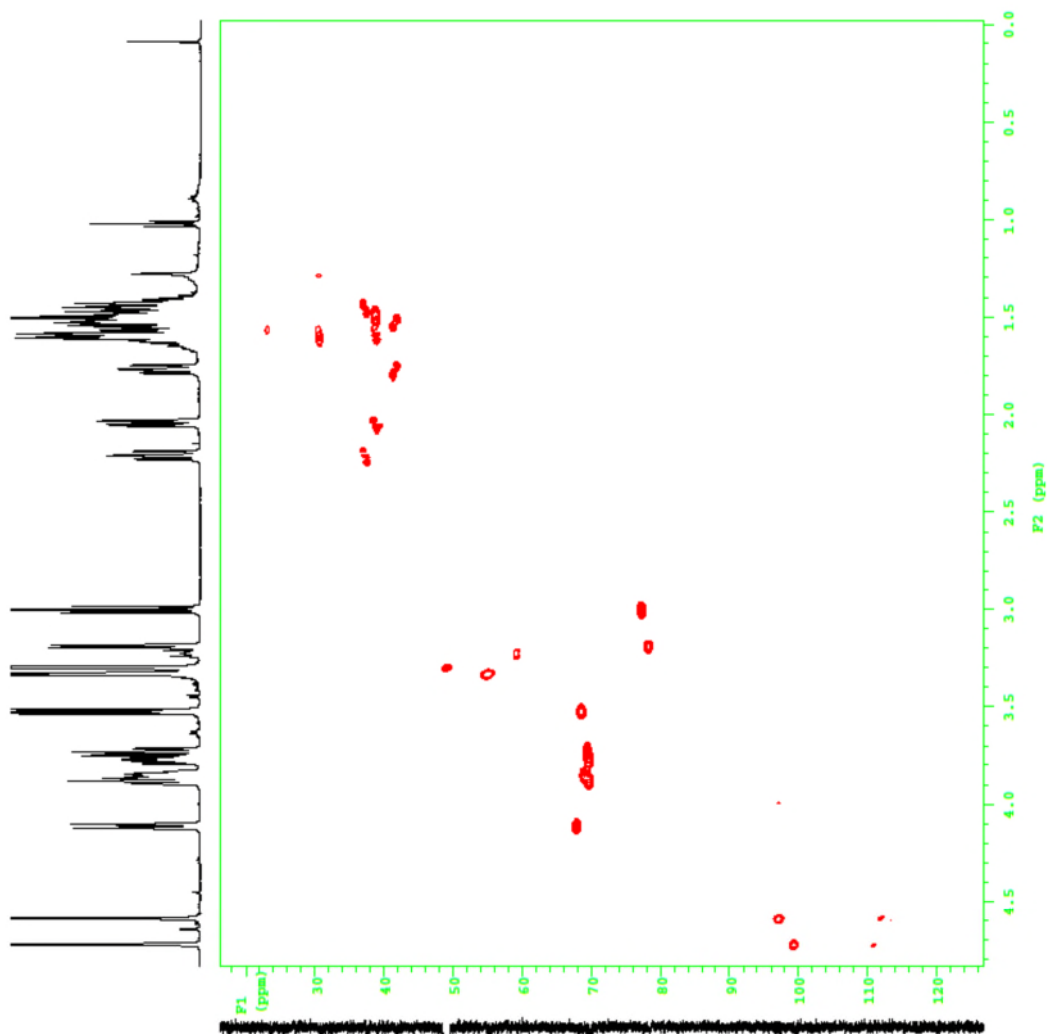
mp3 500T
=====
NAME          SAMPLE
DATE_ TIME    21 2018   ba
SOLVENT       CD3OD
SAMPLE        6120
=====
ACQUISITION  9615.4 temp not used
PC           0.150 gain
PP           4000
SS           32 ad
TT           0.075
CL           1.000 abs not used
SC           4 fa
=====
2D ACQUISITION F1 PROCESSING
MW1          9615.4 acq -0.013
SI           120
SN           0
PR            0
PERMANENT    4896
=====
NAME         ba
WVC          0
TX           0
TRANSMITTER 0
TX           0
FREQ         599.97
LTYPE       59 FID
PW           10.500
P1           1979.2
P2           1979.2
=====
SILVER      5102
GUN         0.001000 wt
METHALCO   1.000 wt
SPINRATIO   0.000000
=====
ON          0
ENCODER     CL3
=====
OM          0
RES         13
SI          0
CGS         4

```



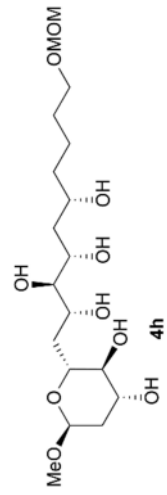
¹H-¹H COSY (600 MHz, CD₃OD)





exp1 gsmc
 date Feb 22 2019 hr
 solvent cd3od
 sample 4h
 acqno 9411.4
 acq 0.150 temp not used
 p1 1800 sp1s 60
 p2 4000 sp2s 80
 p3 0
 p4 32 GRADIENTS
 p5 1.000 gain 5162
 p6 32 GE 0.002000
 ID ACQUISITION 3.977
 ac 3460.1 S/N 0.34500
 at 200 P2 PROCESSING
 phase arrayed gf 0.069
 PRESATURATION gfs not used
 sitaxs n fn 4096
 wt TRANSMITTER n FI PROCESSING
 tx 0.005
 rfc not used
 4fz 599.747 frcol 10
 tot 599.7 fsi 2048
 tpr 59 59 DISPLAY
 pw 18.500 sp -8.9
 INCOUPLER wp 2986.2
 da CL3 sp 2451.2
 de 154.6 fsi 1388.0
 deconv W40 convmr ftd 1978.2
 dat 35088 rfil 8732.9
 qpr 40 rtp1 7389.7
 pcvl 56
 psc 12.100 wt 351.9
 jlab 146.0 wds 208.9
 nullif y 803
 mult 2 vs 222
 at cde pb 1

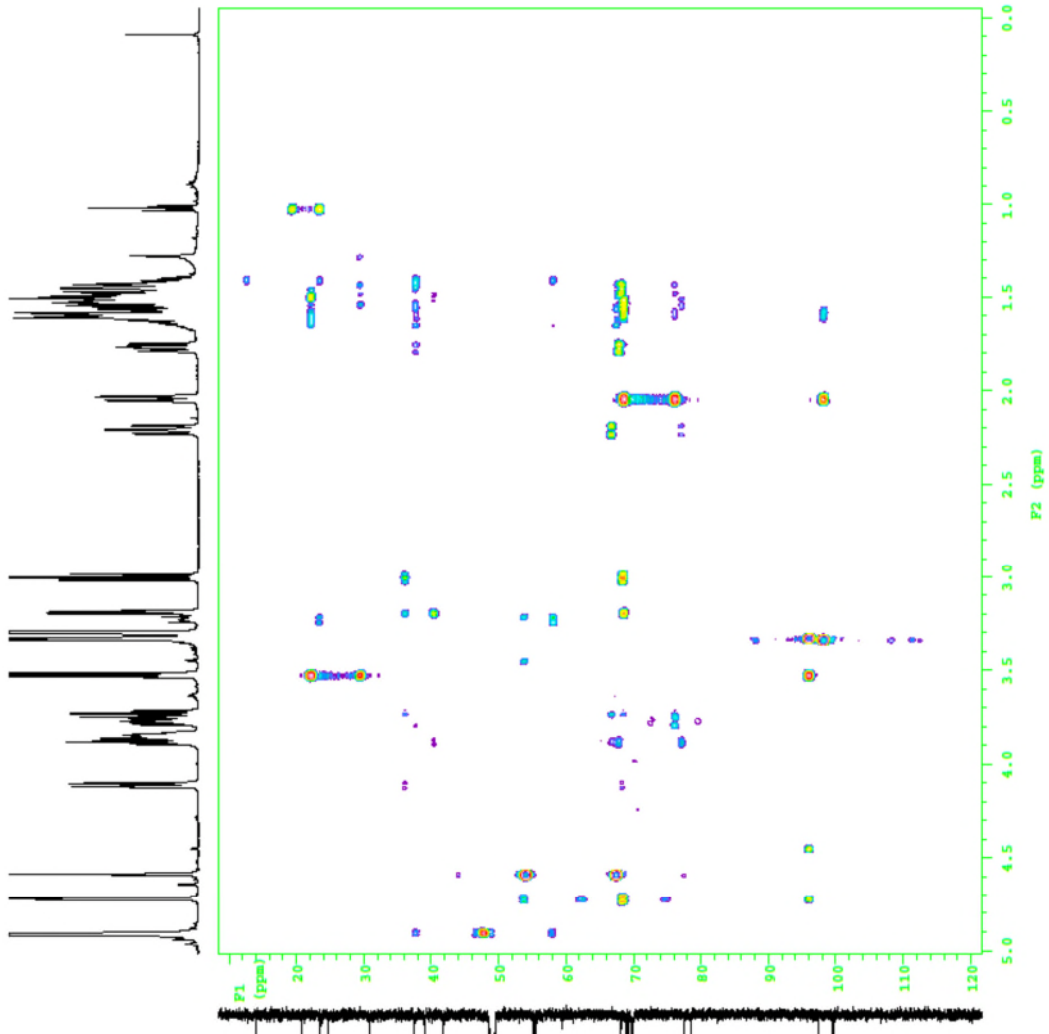
HMQC (600 MHz, CD₃OD)



```

exp5 gsmc
=====
NAME: 20130322_013
DATE_: 20130322
TIME: 13:00
PROC: 1
SOLVENT: CD3OD
SAMPLE: 4
ACQUISITION: 1
P1: 1.000
P2: 0.01000
P3: 0.01000
P4: 0.01000
P5: 0.01000
P6: 0.01000
P7: 0.01000
P8: 0.01000
P9: 0.01000
P10: 0.01000
P11: 0.01000
P12: 0.01000
P13: 0.01000
P14: 0.01000
P15: 0.01000
P16: 0.01000
P17: 0.01000
P18: 0.01000
P19: 0.01000
P20: 0.01000
P21: 0.01000
P22: 0.01000
P23: 0.01000
P24: 0.01000
P25: 0.01000
P26: 0.01000
P27: 0.01000
P28: 0.01000
P29: 0.01000
P30: 0.01000
P31: 0.01000
P32: 0.01000
P33: 0.01000
P34: 0.01000
P35: 0.01000
P36: 0.01000
P37: 0.01000
P38: 0.01000
P39: 0.01000
P40: 0.01000
P41: 0.01000
P42: 0.01000
P43: 0.01000
P44: 0.01000
P45: 0.01000
P46: 0.01000
P47: 0.01000
P48: 0.01000
P49: 0.01000
P50: 0.01000
P51: 0.01000
P52: 0.01000
P53: 0.01000
P54: 0.01000
P55: 0.01000
P56: 0.01000
P57: 0.01000
P58: 0.01000
P59: 0.01000
P60: 0.01000
P61: 0.01000
P62: 0.01000
P63: 0.01000
P64: 0.01000
P65: 0.01000
P66: 0.01000
P67: 0.01000
P68: 0.01000
P69: 0.01000
P70: 0.01000
P71: 0.01000
P72: 0.01000
P73: 0.01000
P74: 0.01000
P75: 0.01000
P76: 0.01000
P77: 0.01000
P78: 0.01000
P79: 0.01000
P80: 0.01000
P81: 0.01000
P82: 0.01000
P83: 0.01000
P84: 0.01000
P85: 0.01000
P86: 0.01000
P87: 0.01000
P88: 0.01000
P89: 0.01000
P90: 0.01000
P91: 0.01000
P92: 0.01000
P93: 0.01000
P94: 0.01000
P95: 0.01000
P96: 0.01000
P97: 0.01000
P98: 0.01000
P99: 0.01000
P100: 0.01000
=====

```



HMBC (600 MHz, CD₃OD)

