

## Supplementary Information

Total synthesis and structure–antifouling activity relationship of scabrolide F

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**General Methods.** Optical rotations were recorded on JASCO DIP-1000. IR spectra were recorded on JASCO FT/IR-460 plus or JASCO FT/IR-FT-001. NMR spectra were recorded on JEOL JNM-AL400 or Varian NMR System PS600. Chemical shifts in the NMR spectra are reported in ppm with reference to the internal residual solvent (for  $^1\text{H}$  NMR,  $\text{CDCl}_3$ : 7.26 ppm,  $\text{C}_6\text{D}_6$ : 7.16 ppm; for  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ : 77.0 ppm,  $\text{C}_6\text{D}_6$ : 128.0 ppm). The following abbreviations are used to designate the multiplicity: s = singlet, d = doublet, t = triplet, 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). Analytical thin layer chromatography (TLC) was performed using aluminum TLC plates (Merck TLC silica gel 60F<sub>254</sub>). Column chromatography was performed on Fuji Silysia silica gel BW-300 or Kanto Chemical silica gel 60N. 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.

**Epoxy Alcohol 17.** To a suspension of powdered MS4Å (797 mg) in  $\text{CH}_2\text{Cl}_2$  (45 mL) were added (+)-DIPT (0.30 mL, 1.49 mmol),  $\text{Ti}(\text{O}i\text{-Pr})_4$  (0.30 mL, 1.01 mmol), and TBHP (ca. 5.0 M in 2,2,4-trimethylpentane, 4.0 mL, 20.0 mmol) at  $-30\text{ }^\circ\text{C}$ . The mixture was stirred at the same temperature for 30 min. To the mixture was added allylic alcohol **16** (3.85 g, 9.90 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL + 6.0 mL + 5.0 mL) at  $-40\text{ }^\circ\text{C}$ . The mixture was stirred at the same temperature for 6 h. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{O}$  and brine, and concentrated. To the mixture were added  $\text{Et}_2\text{O}$  and 3 M aqueous NaOH. The mixture was stirred at  $0\text{ }^\circ\text{C}$  for 30 min. The mixture was diluted with  $\text{EtOAc}$ , washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/ $\text{EtOAc}$  = 11:1, 1:1) gave epoxy alcohol **17** (3.88 g, 97%): colorless oil;  $R_f$  = 0.35 (hexane/ $\text{EtOAc}$  = 4:1);  $[\alpha]_{\text{D}}^{26}$  +2.0 ( $c$  0.48,  $\text{CHCl}_3$ ); IR (neat) 3434, 2954, 2929, 2892, 2856  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09–4.03 (m, 1 H), 3.89 (dd,  $J$  = 11.3, 2.3 Hz, 1 H), 3.67–3.63 (m, 3 H), 3.00 (dd,  $J$  = 3.6, 1.8 Hz, 1 H), 1.87 (dd,  $J$  = 14.0, 5.2 Hz, 1 H), 1.76 (brs, 1 H), 1.73–1.68 (m, 2 H), 1.57 (dd,  $J$  = 14.0, 6.8 Hz, 1 H), 1.33 (s, 3 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  66.7, 63.4, 61.3, 59.7, 59.4, 46.4, 40.7, 26.0, 25.9, 18.3, 18.0, 17.3,  $-4.3$ ,  $-4.3$ ,  $-5.3$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{44}\text{O}_4\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  427.2676, found 427.2671.

**Diol 18.** To a solution of epoxy alcohol **17** (3.88 g, 9.59 mmol) in THF (137 mL) was added Red-Al (65% in toluene, 7.3 mL, 24.0 mmol) at  $-40\text{ }^\circ\text{C}$ . The mixture was warmed up to  $-20\text{ }^\circ\text{C}$  and stirred at the same temperature for 8 h. The reaction was quenched with saturated aqueous

sodium potassium tartrate. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1, 1:1) gave diol **18** (1.58 g) and epoxy alcohol **17** (2.28 g).

To a solution of epoxy alcohol **17** recovered above (2.28 g) in THF (80 mL) was added Red-Al (65% in toluene, 4.3 mL, 14.1 mmol) at -40 °C. The mixture was warmed up to -20 °C and stirred at the same temperature for 23 h. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1, 1:1) gave diol **18** (1.20 g) and epoxy alcohol **17** (1.02 g).

To a solution of epoxy alcohol **17** recovered above (1.02 g) in THF (36 mL) was added Red-Al (65% in toluene, 1.9 mL, 6.23 mmol) at -40 °C. The mixture was warmed up to -20 °C and stirred at the same temperature for 23 h. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1, 1:1) gave diol **18** (408 mg, totally 3.19 g, 82% in three cycles) and epoxy alcohol **17** (553 mg). For **18**: colorless oil; *R<sub>f</sub>* = 0.49 (hexane/EtOAc = 1:1); [ $\alpha$ ]<sub>D</sub><sup>20</sup> -29.6 (*c* 0.46, CHCl<sub>3</sub>); IR (neat) 3388, 2954, 2929, 2888, 2857 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.35–4.32 (m, 1 H), 4.01 (td, *J* = 10.6, 3.3 Hz, 1 H), 3.77 (dt, *J* = 10.6, 4.8 Hz, 1 H), 3.65 (dd, *J* = 7.1, 4.9 Hz, 2 H), 2.06–1.99 (m, 1 H), 1.97–1.89 (m, 1 H), 1.79 (dd, *J* = 14.4, 4.0 Hz, 1 H), 1.69–1.65 (m, 2 H), 1.48 (dt, *J* = 14.4, 4.0 Hz, 1 H), 1.27 (s, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.16 (s, 3 H), 0.14 (s, 3 H), 0.05 (s, 3 H), 0.05 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  73.7, 68.8, 59.9, 59.3, 47.3, 41.2, 41.0, 27.5, 25.9, 18.3, 18.0, -3.5, -4.3, -5.3; HRMS (ESI-TOF) calcd for C<sub>20</sub>H<sub>46</sub>O<sub>4</sub>Si<sub>2</sub>Na [M + Na]<sup>+</sup> 429.2832, found 429.2831.

**$\alpha,\beta$ -Unsaturated Ester 19.** To a solution of alcohol **18** (2.92 g, 7.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (144 mL) were added PhI(OAc)<sub>2</sub> (2.78 g, 8.62 mmol) and TEMPO (168 mg, 1.08 mmol) at room temperature. The mixture was stirred at the same temperature for 6 h. To the mixture was added Ph<sub>3</sub>P=CHCO<sub>2</sub>Me (4.94 g, 14.4 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h. The mixture was filtered through short column chromatography (EtOAc). The mixture was concentrated, washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, saturated aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O, and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1) gave  $\alpha,\beta$ -unsaturated ester **19** (3.02 g, 91%): colorless oil; *R<sub>f</sub>* = 0.49 (hexane/EtOAc = 4:1); [ $\alpha$ ]<sub>D</sub><sup>23</sup> -16.4 (*c* 0.51, CHCl<sub>3</sub>); IR (neat) 3497, 2954, 2929, 2892, 2856, 1729, 1657 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.03–6.96 (m, 1 H), 5.86 (d, *J* = 15.6 Hz, 1 H), 4.30–4.26 (m, 2 H), 3.72 (s, 3 H), 3.64 (dd, *J* = 7.1, 4.9 Hz, 2 H), 2.48 (dd, *J* = 13.6, 7.2 Hz, 1 H), 2.36 (dd, *J* = 13.6, 8.7 Hz, 1 H), 1.96–1.89 (m, 1 H), 1.75–1.67 (m, 3 H) 1.17 (s, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.05 (s, 3 H), 0.05 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 145.4, 123.5, 72.0, 69.0, 59.2, 51.4, 45.8, 44.6, 41.0, 28.3, 25.9, 25.9, 18.3, 18.0, -3.4, -

4.5, -5.4; HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>48</sub>O<sub>5</sub>Si<sub>2</sub>Na [M + Na]<sup>+</sup> 483.2938, found 483.2939.

**Diol 20.** To a solution of  $\alpha,\beta$ -unsaturated ester **19** (37.0 mg, 80.3  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL) was added DIBAL-H (1.03 M in hexane, 0.27 mL, 0.278 mmol) at -78 °C. The mixture was stirred at the same temperature for 40 min. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was filtered through a Celite pad and washed with EtOAc. Concentration and column chromatography (hexane/EtOAc = 2:1) gave diol **20** (33.4 mg, 96%): colorless oil;  $R_f$  = 0.29 (hexane/EtOAc = 2:1);  $[\alpha]_D^{23}$  -20.5 (*c* 1.09, CHCl<sub>3</sub>); IR (neat) 3399, 2954, 2928, 2892, 2856, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.82–5.75 (m, 1 H), 5.63 (dt, *J* = 15.3, 5.4 Hz, 1 H), 4.38–4.32 (m, 1 H), 3.92 (d, *J* = 5.4 Hz, 2 H), 3.60 (t, *J* = 6.1 Hz, 2 H), 3.53 (brs, 1 H), 2.40 (dd, *J* = 13.6, 7.1 Hz, 1 H), 2.24 (dd, *J* = 13.6, 7.7 Hz, 1 H), 1.95–1.87 (m, 1 H), 1.79–1.69 (m, 3 H) 1.26 (s, 3 H), 0.99 (s, 9 H), 0.98 (s, 9 H), 0.17 (s, 3 H), 0.14 (s, 3 H), 0.07 (s, 3 H), 0.07 (s, 3 H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  133.4, 127.9, 72.0, 68.8, 63.5, 59.8, 47.2, 45.8, 41.9, 28.2, 26.2, 26.2, 18.5, 18.3, -3.4, -4.1, -5.1; HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>48</sub>O<sub>4</sub>Si<sub>2</sub>Na [M + Na]<sup>+</sup> 455.2989, found 455.2984.

**Alcohol 21.** To a solution of diol **20** (50.7 mg, 0.117 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3.9 mL) were added imidazole (55.8 mg, 0.820 mmol), TMSCl (75.6  $\mu$ L, 0.586 mmol), and DMAP (7.1 mg, 58.1  $\mu$ mol) at 0 °C. The mixture was stirred at room temperature for 4 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with Et<sub>2</sub>O, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 40:1, 10:1) gave alcohol **21** (10.7 mg) and the corresponding tetrakis-silyl ether (52.8 mg). To a solution of the corresponding tetrakis-silyl ether obtained above (52.8 mg) in MeOH (3.0 mL) was added K<sub>2</sub>CO<sub>3</sub> (14.9 mg, 0.108 mmol) at 0 °C. The mixture was stirred at the same temperature for 20 min. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl. The mixture was diluted with Et<sub>2</sub>O, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1) gave alcohol **21** (45.3 mg, totally 56.0 mg, 95% in two steps): colorless oil;  $R_f$  = 0.20 (hexane/EtOAc = 10:1);  $[\alpha]_D^{24}$  +0.9 (*c* 1.28, CHCl<sub>3</sub>); IR (neat) 3348, 2955, 2927, 2897, 2856 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.73–5.66 (m, 1 H), 5.54 (dt, *J* = 15.4, 5.6 Hz, 1 H), 4.27–4.21 (m, 1 H), 3.87 (d, *J* = 5.6 Hz, 2 H), 3.84–3.73 (m, 2 H), 2.35–2.22 (m, 2 H), 2.13–2.05 (m, 1 H), 1.91–1.75 (m, 3 H), 1.29 (s, 3 H), 1.03 (s, 9 H), 1.02 (s, 9 H), 0.21 (s, 9 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  133.2, 127.7, 75.8, 67.3, 63.5, 60.1, 50.2, 48.0, 42.4, 27.8, 26.4, 26.3, 18.6, 18.4, 3.1, -3.7, -3.8, -4.9, -5.0; HRMS (ESI-TOF) calcd for C<sub>25</sub>H<sub>56</sub>O<sub>4</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup> 527.3384, found 527.3387.

**Epoxy Alcohol 24 (entry 2 in Table 1).** To a suspension of powdered MS4Å (104 mg) in CH<sub>2</sub>Cl<sub>2</sub> (6.7 mL) were added (+)-DET (54.0  $\mu$ L, 0.287 mmol) and Ti(O*i*-Pr)<sub>4</sub> (67.0  $\mu$ L, 0.226

mmol) at  $-30\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 10 min. To the mixture was added allylic alcohol **21** (104 mg, 0.205 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.5 mL + 1.5 mL + 1.0 mL) at  $-30\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 30 min. To the mixture was added TBHP (ca. 6.3 M in 2,2,4-trimethylpentane, 65.0  $\mu\text{L}$ , 0.410 mmol) at  $-40\text{ }^{\circ}\text{C}$ . The mixture was warmed up to  $-20\text{ }^{\circ}\text{C}$  and stirred at the same temperature for 13 h. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and concentrated. To the mixture were added  $\text{Et}_2\text{O}$  and 3 M aqueous NaOH. The mixture was stirred at  $0\text{ }^{\circ}\text{C}$  for 30 min. The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1) gave epoxy alcohol **24** (107 mg, quant): colorless oil;  $R_f = 0.62$  (hexane/EtOAc = 7:1);  $[\alpha]_{\text{D}}^{21} -13.7$  ( $c$  1.64,  $\text{CHCl}_3$ ); IR (neat) 3436, 2955, 2927, 2897, 2856  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.26–4.20 (m, 1 H), 3.84–3.72 (m, 2 H), 3.56 (dd,  $J = 12.4$ , 2.0 Hz, 1 H), 3.35 (dd,  $J = 12.4$ , 4.1 Hz, 1 H), 3.09 (td,  $J = 5.6$ , 2.2 Hz, 1 H), 2.64–2.62 (m, 1 H), 2.08–1.99 (m, 2 H), 1.91–1.80 (m, 2 H), 1.73 (d,  $J = 5.6$  Hz, 2 H), 1.36 (s, 3 H), 1.03 (s, 9 H), 1.01 (s, 9 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.18 (s, 9 H), 0.11 (s, 3 H), 0.11 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  75.5, 67.4, 61.9, 60.1, 58.4, 52.6, 50.3, 46.9, 42.4, 28.4, 26.3, 26.3, 18.6, 18.4, 3.0,  $-3.7$ ,  $-5.0$ ; HRMS (ESI–TOF) calcd for  $\text{C}_{25}\text{H}_{56}\text{O}_5\text{Si}_3\text{Na}$   $[\text{M} + \text{Na}]^+$  543.3333, found 543.3328.

**Epoxy Diol 22 (entry 3 in Table 1).** To a solution of allylic alcohol **15** (4.76 g, 11.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (110 mL) was added *m*CPBA (69–75%, 3.30 g, 13.1–14.3 mmol) at  $-40\text{ }^{\circ}\text{C}$ . The mixture was warmed up to  $0\text{ }^{\circ}\text{C}$  and stirred at the same temperature for 2 h. The reaction was quenched with 2-methyl-2-butene. The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with saturated aqueous  $\text{NaHCO}_3$  twice,  $\text{H}_2\text{O}$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 2:1) gave epoxy diol **22** (5.05 g, quant): colorless oil;  $R_f = 0.41$  (hexane/EtOAc = 1:1);  $[\alpha]_{\text{D}}^{23} -27.8$  ( $c$  0.54,  $\text{CHCl}_3$ ); IR (neat) 3298, 2950, 2927, 2883, 2856  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.35–4.29 (m, 1 H), 3.69 (s, 1 H), 3.60 (t,  $J = 6.1$  Hz, 2 H), 3.53 (d,  $J = 12.0$  Hz, 1 H), 3.39 (d,  $J = 12.0$  Hz, 1 H), 3.17 (td,  $J = 5.9$ , 2.1 Hz, 1 H), 2.65–2.64 (m, 1 H), 1.95–1.87 (m, 2 H), 1.86–1.69 (m, 3 H), 1.61 (brs, 1 H), 1.53 (dd,  $J = 13.9$ , 5.9 Hz, 1 H), 1.32 (m, 3 H), 0.98 (s, 9 H), 0.98 (s, 9 H), 0.16 (s, 3 H), 0.13 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  71.8, 68.7, 62.1, 59.7, 58.9, 53.1, 47.7, 44.6, 41.8, 28.8, 26.2, 26.2, 18.5, 18.3,  $-3.5$ ,  $-4.2$ ,  $-5.1$ ; HRMS (ESI–TOF) calcd for  $\text{C}_{22}\text{H}_{48}\text{O}_5\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  471.2938, found 471.2934.

**Alcohol 24 (Scheme 4).** To a solution of diol **22** (4.94 g, 11.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (110 mL) were added imidazole (2.62 g, 38.5 mmol),  $\text{TMSCl}$  (3.5 mL, 27.5 mmol), and DMAP (403 mg, 3.30 mmol) at  $0\text{ }^{\circ}\text{C}$ . The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous  $\text{NaHCO}_3$ . The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{O}$  and

brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration gave the corresponding tetrakis-silyl ether (6.35 g), which was used for the next step without further purification.

To a solution of the tetrakis-silyl ether obtained above (6.35 g) in MeOH (110 mL) was added K<sub>2</sub>CO<sub>3</sub> (1.82 g, 13.2 mmol) at 0 °C. The mixture was stirred at the same temperature for 20 min. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl. The mixture was diluted with Et<sub>2</sub>O, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 4:1) gave alcohol **24** (5.44 g, 95% in two steps).

**Vinyl Epoxide 27.** To a solution of alcohol **24** (33.8 mg, 64.9 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) were added PhI(OAc)<sub>2</sub> (23.3 mg, 72.3 μmol) and TEMPO (1.4 mg, 6.49 μmol) at 0 °C. The mixture was stirred at room temperature for 20 h. The reaction was quenched with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The mixture was diluted with Et<sub>2</sub>O, washed with saturated aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O, and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and short column chromatography (hexane/EtOAc = 25:1) gave the corresponding aldehyde (35.4 mg), which was used for the next step without further purification.

To a suspension of Ph<sub>3</sub>P<sup>+</sup>CH<sub>3</sub>Br<sup>-</sup> (85.4 mg, 0.227 mmol) in THF (1.1 mL) was added NaHMDS (1.0 M in THF, 0.16 mL, 0.160 mmol) at 0 °C. The mixture was stirred at the same temperature for 20 min. To the mixture was added the aldehyde obtained above (35.4 mg) in THF (0.3 mL + 0.3 mL + 0.3 mL) at 0 °C. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl. The mixture was diluted with Et<sub>2</sub>O, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 30:1) gave vinyl epoxide **27** (37.0 mg, quant in two steps): colorless oil; *R*<sub>f</sub> = 0.54 (hexane/EtOAc = 10:1); [α]<sub>D</sub><sup>21</sup> -1.4 (*c* 1.03, CHCl<sub>3</sub>); IR (neat) 2955, 2927, 2856, 1646 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 5.53 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1 H), 5.32 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.03 (dd, *J* = 10.2, 1.6 Hz, 1 H), 4.26–4.20 (m, 1 H), 3.84–3.71 (m, 2 H), 2.99–2.96 (m, 2 H), 2.04–2.01 (m, 2 H), 1.91–1.71 (m, 4 H), 1.36 (s, 3 H), 1.02 (s, 9 H), 1.01 (s, 9 H), 0.19 (s, 3 H), 0.17 (s, 3 H), 0.17 (s, 9 H), 0.11 (s, 3 H), 0.11 (s, 3 H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 136.6, 118.2, 75.5, 67.3, 60.1, 58.5, 57.3, 50.4, 47.2, 42.4, 28.4, 26.3, 26.3, 18.6, 18.4, 3.0, -3.7, -3.7, -5.0; HRMS (ESI-TOF) calcd for C<sub>26</sub>H<sub>56</sub>O<sub>4</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup> 539.3384, found 539.3388.

**Alcohol S1.** To a solution of TMS ether **27** (3.49 g, 6.75 mmol) in MeOH (68 mL) was added citric acid monohydrate (1.42 g, 6.75 mmol) at 0 °C. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane, hexane/EtOAc = 40:1, 10:1) gave alcohol **S1** (1.76 g) and TMS ether **27** (1.13 g).

To a solution of TMS ether **27** recovered above (1.13 g) in MeOH (22 mL) was added citric

acid monohydrate (460 mg, 2.19 mmol) at 0 °C. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane, hexane/EtOAc = 40:1, 10:1) gave alcohol **S1** (582 mg) and TMS ether **27** (368 mg).

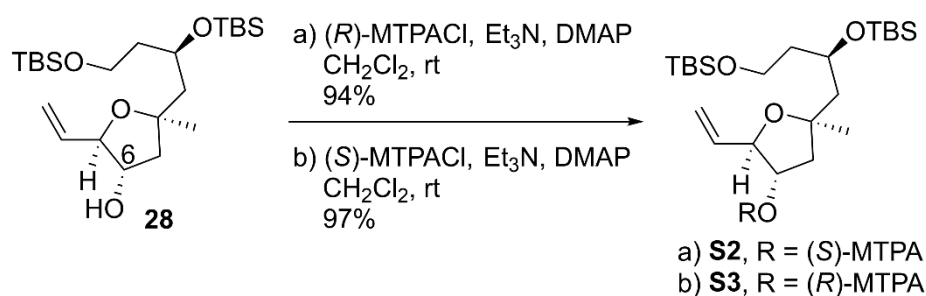
To a solution of TMS ether **27** recovered above (368 mg) in MeOH (7.0 mL) was added citric acid monohydrate (150 mg, 0.712 mmol) at 0 °C. The mixture was stirred at the same temperature for 5 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane, hexane/EtOAc = 40:1, 10:1) gave alcohol **S1** (140 mg, totally 2.48 g, 83% in three cycles) and TMS ether **27** (176 mg). For **S1**: colorless oil; *R<sub>f</sub>* = 0.53 (hexane/EtOAc = 4:1); [ $\alpha$ ]<sub>D</sub><sup>21</sup> -26.5 (*c* 0.55, CHCl<sub>3</sub>); IR (neat) 3485, 2954, 2929, 2856, 1641 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.58 (ddd, *J* = 17.1, 10.2, 8.0 Hz, 1 H), 5.46 (dd, *J* = 17.1, 1.5 Hz, 1 H), 5.26 (dd, *J* = 10.2, 1.5 Hz, 1 H), 4.29–4.27 (m, 1 H), 4.21 (brs, 1 H), 3.66 (dd, *J* = 7.1, 5.1 Hz, 2 H), 3.08 (dd, *J* = 7.3, 2.0 Hz, 1 H), 3.03 (td, *J* = 5.9, 2.0 Hz, 1 H), 1.98–1.92 (m, 2 H), 1.84 (dd, *J* = 14.2, 3.9 Hz, 1 H), 1.74–1.65 (m, 2 H), 1.57 (dd, *J* = 14.2, 6.3 Hz, 1 H), 1.25 (s, 3 H), 0.90 (s, 9 H), 0.89 (s, 9 H), 0.15 (s, 3 H), 0.13 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.6, 119.0, 71.7, 68.9, 59.3, 57.4, 46.4, 43.7, 41.1, 28.6, 26.0, 25.9, 18.3, 18.0, -3.5, -4.4, -5.3; HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>48</sub>O<sub>4</sub>Si<sub>2</sub>Na [M + Na]<sup>+</sup> 467.2989, found 467.2986.

**Tetrahydrofuran 28.** To a solution of alcohol **S1** (1.32 g, 2.97 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (99 mL) was added CSA (69.0 mg, 0.297 mmol) at -40 °C. The mixture was warmed up to -10 °C and stirred at the same temperature for 5 h. The reaction was quenched with Et<sub>3</sub>N. The mixture was diluted with Et<sub>2</sub>O, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1) gave tetrahydrofuran **28** (1.29 g, 98%): colorless oil; *R<sub>f</sub>* = 0.32 (hexane/EtOAc = 4:1); [ $\alpha$ ]<sub>D</sub><sup>23</sup> +1.0 (*c* 0.99, CHCl<sub>3</sub>); IR (neat) 3434, 2954, 2929, 2888, 2857, 1644 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.84 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.34 (d, *J* = 17.2 Hz, 1 H), 5.18 (d, *J* = 10.4 Hz, 1 H), 4.14–4.07 (m, 2 H), 4.05–3.99 (m, 1 H), 3.65–3.63 (m, 2 H), 2.37 (dd, *J* = 12.9, 7.3 Hz, 1 H), 1.82–1.66 (m, 6 H), 1.37 (s, 3 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.3, 116.8, 85.1, 81.8, 67.1, 59.6, 50.0, 46.7, 41.8, 26.7, 26.1, 26.0, 18.3, 18.1, -4.0, -4.1, -5.2; HRMS (ESI-TOF) calcd for C<sub>23</sub>H<sub>48</sub>O<sub>4</sub>Si<sub>2</sub>Na [M + Na]<sup>+</sup> 467.2989, found 467.2987.

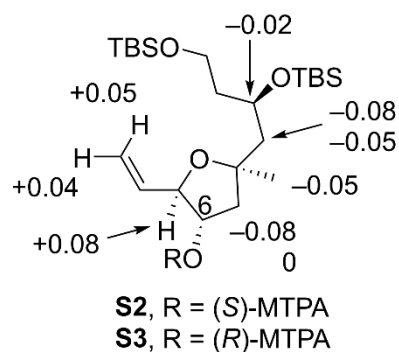
**Stereochemical Determination of 28.** The absolute configuration at the C6 position of **28** was elucidated by the modified Mosher method.<sup>1</sup> Treatment of alcohol **28** with MTPACl (MTPA =  $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetyl)/Et<sub>3</sub>N/DMAP provided (*S*)-MTPA ester **S2** and

(*R*)-MTPA ester **S3**, respectively as shown in Scheme S1. The calculated results on the chemical shift differences ( $\Delta\delta_{S-R}$ ) of **S2** and **S3** are described in Figure S1. The signs at the left side of the C6 position were positive and those at the right side of the C6 position exhibited negative. Therefore, the absolute stereochemistry at the C6 position of **28** was determined to be *S* as shown in Figure S1. In addition, the observed NOEs of H-4/H-6 and H-5/Me-8 in **28** revealed that these were oriented in the *syn* relationship to each other, respectively (Figure S2). Therefore, the absolute stereochemistry of **28** was unambiguously established.

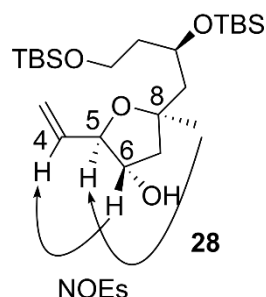
**Scheme S1.** Transformation of alcohol **28** for its stereochemical determination. MTPA =  $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetyl).



**Figure S1.** Chemical shift differences ( $\Delta\delta_{S-R}$ ) of MTPA esters **S2** and **S3**.



**Figure S2.** Observed NOEs in tetrahydrofuran **28**.



**(*S*)-MTPA Ester S2.** To a solution of alcohol **28** (3.0 mg, 6.74  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) were added DMAP (1.6 mg, 13.5  $\mu$ mol), Et<sub>3</sub>N (1.3  $\mu$ L, 9.44  $\mu$ mol), and (*R*)-MTPACl (1.5  $\mu$ L, 7.92  $\mu$ mol) at room temperature. The mixture was stirred at the same temperature for 10 min. The



reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ . The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/ $\text{EtOAc}$  = 40:1) gave (*S*)-MTPA ester **S2** (4.2 mg, 94%): colorless oil;  $R_f$  = 0.66 (hexane/ $\text{EtOAc}$  = 4:1);  $[\alpha]_{\text{D}}^{21}$   $-20.0$  ( $c$  0.18,  $\text{CHCl}_3$ ); IR (neat) 2954, 2929, 2856, 1751, 1646  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51–7.50 (m, 2 H), 7.42–7.39 (m, 3 H), 5.99 (ddd,  $J$  = 16.4, 10.4, 6.0 Hz, 1 H), 5.36 (d,  $J$  = 16.4 Hz, 1 H), 5.22–5.19 (m, 2 H), 4.44–4.43 (m, 1 H), 4.04–3.98 (m, 1 H), 3.67–3.61 (m, 2 H), 3.55 (s, 3 H), 2.34 (dd,  $J$  = 14.0, 7.2 Hz, 1 H), 1.87–1.80 (m, 2 H), 1.77–1.70 (m, 3 H), 1.18 (s, 3 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.08 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 136.2, 132.0, 129.6, 128.4, 127.1, 117.0, 83.1, 82.4, 81.3, 67.0, 59.5, 55.5, 49.7, 43.7, 41.6, 29.8, 26.0, 26.0, 24.9, 18.3, 18.1,  $-4.0$ ,  $-4.1$ ,  $-5.2$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{33}\text{H}_{55}\text{F}_3\text{O}_6\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  683.3387, found 683.3382.

**(R)-MTPA Ester S3.** To a solution of alcohol **28** (2.9 mg, 6.52  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (0.3 mL) were added DMAP (1.6 mg, 13.5  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (1.3  $\mu\text{L}$ , 9.44  $\mu\text{mol}$ ), and (*S*)-MTPACl (1.5  $\mu\text{L}$ , 7.92  $\mu\text{mol}$ ) at room temperature. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ . The mixture was diluted with  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/ $\text{EtOAc}$  = 40:1) gave (*R*)-MTPA ester **S3** (4.2 mg, 97%): colorless oil;  $R_f$  = 0.68 (hexane/ $\text{EtOAc}$  = 4:1);  $[\alpha]_{\text{D}}^{24}$   $+19.3$  ( $c$  0.21,  $\text{CHCl}_3$ ); IR (neat) 2954, 2929, 2856, 1751, 1646  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51–7.49 (m, 2 H), 7.41–7.38 (m, 3 H), 5.90 (ddd,  $J$  = 17.1, 10.4, 6.0 Hz, 1 H), 5.31 (dt,  $J$  = 17.1, 1.5 Hz, 1 H), 5.24–5.21 (m, 1 H), 5.17 (dt,  $J$  = 10.4, 1.5 Hz, 1 H), 4.36–4.33 (m, 1 H), 4.06–4.00 (m, 1 H), 3.68–3.63 (m, 2 H), 3.54 (s, 3 H), 2.34 (dd,  $J$  = 14.0, 7.4 Hz, 1 H), 1.94 (dd,  $J$  = 14.0, 3.0 Hz, 1 H), 1.86 (dd,  $J$  = 14.0, 5.0 Hz, 1 H), 1.78–1.71 (m, 3 H), 1.23 (s, 3 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.09 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 136.0, 132.0, 129.6, 128.4, 127.2, 116.7, 83.1, 82.5, 81.2, 67.0, 59.5, 55.4, 49.6, 43.7, 41.6, 29.8, 26.0, 26.0, 24.8, 18.3, 18.1,  $-4.0$ ,  $-4.1$ ,  $-5.2$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{33}\text{H}_{55}\text{F}_3\text{O}_6\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  683.3387, found 683.3390.

**MOM Ether 29.** To a solution of alcohol **28** (1.08 g, 2.43 mmol) in  $\text{CH}_2\text{Cl}_2$  (24 mL) were added *i*- $\text{Pr}_2\text{NEt}$  (2.5 mL, 14.6 mmol), MOMCl (0.55 mL, 7.29 mmol), and TBAI (180 mg, 0.486 mmol) at 0  $^\circ\text{C}$ . The mixture was stirred at 35  $^\circ\text{C}$  for 22 h. The reaction was quenched with saturated aqueous  $\text{NaHCO}_3$ . The mixture was diluted with  $\text{EtOAc}$ , washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/ $\text{EtOAc}$  = 9:1) gave MOM ether **29** (1.19 g, quant): colorless oil;  $R_f$  = 0.49 (hexane/ $\text{EtOAc}$  = 7:1);  $[\alpha]_{\text{D}}^{22}$   $+5.4$  ( $c$  1.00,  $\text{CHCl}_3$ ); IR (neat) 2954, 2930, 2888, 2857, 1641  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.86 (ddd,  $J$  = 17.1, 10.4, 6.4 Hz, 1 H), 5.33 (dt,  $J$  = 17.1, 1.4 Hz, 1 H), 5.14 (dt,  $J$  =

10.4, 1.4 Hz, 1 H), 4.64 (d,  $J = 6.8$  Hz, 1 H), 4.62 (d,  $J = 6.8$  Hz, 1 H), 4.27 (dd,  $J = 6.5, 5.5$  Hz, 1 H), 4.05–3.94 (m, 2 H), 3.69–3.60 (m, 2 H), 3.34 (s, 3 H), 2.29 (dd,  $J = 13.1, 7.4$  Hz, 1 H), 1.83–1.67 (m, 5 H), 1.35 (s, 3 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 116.2, 95.9, 83.2, 82.3, 82.2, 67.1, 59.6, 55.4, 49.8, 44.8, 41.7, 26.0, 26.0, 18.3, 18.1, -4.0, -4.1, -5.2; HRMS (ESI-TOF) calcd for  $\text{C}_{25}\text{H}_{52}\text{O}_5\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  511.3251, found 511.3248.

**Alcohol S4.** Ozone was bubbled into a solution of alkene **29** (49.8 mg, 0.102 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.7 mL) and MeOH (1.7 mL) at  $-78$  °C for 10 min until the solution turned to blue color. Excess ozone was removed with an oxygen stream at  $-78$  °C. To the solution was added  $\text{NaBH}_4$  (38.6 mg, 1.02 mmol) at  $-78$  °C. The mixture was warmed up to  $0$  °C and stirred at the same temperature for 1 h. The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 6:1) gave alcohol **S4** (46.2 mg, 92%): colorless oil;  $R_f = 0.24$  (hexane/EtOAc = 4:1);  $[\alpha]_{\text{D}}^{22} +15.8$  ( $c$  1.48,  $\text{CHCl}_3$ ); IR (neat) 3435, 2954, 2929, 2888, 2857  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.65 (d,  $J = 6.8$  Hz, 1 H), 4.63 (d,  $J = 6.8$  Hz, 1 H), 4.12 (dt,  $J = 8.0, 4.4$  Hz, 1 H), 4.07–4.01 (m, 1 H), 3.96 (dd,  $J = 8.4, 4.8$  Hz, 1 H), 3.74 (dd,  $J = 11.5, 3.4$  Hz, 1 H), 3.66 (td,  $J = 6.3, 1.8$  Hz, 2 H), 3.60 (dd,  $J = 11.6, 4.3$  Hz, 1 H), 3.36 (s, 3 H), 2.19 (dd,  $J = 13.2, 7.8$  Hz, 1 H), 2.01 (brs, 1 H), 1.86 (dd,  $J = 13.2, 4.1$  Hz, 1 H), 1.81–1.72 (m, 3 H), 1.67 (dd,  $J = 14.1, 6.6$  Hz, 1 H), 1.35 (s, 3 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.05 (s, 3 H), 0.05 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  96.3, 82.9, 82.6, 79.1, 67.0, 63.1, 59.6, 55.5, 49.3, 45.7, 41.4, 26.0, 25.6, 18.3, 18.1, -4.0, -4.1, -5.2; HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{52}\text{O}_6\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  515.3200, found 515.3203.

**Alkyl Iodide 30.** To a mixture of alcohol **S4** (76.3 mg, 0.155 mmol),  $\text{Ph}_3\text{P}$  (105 mg, 0.387 mmol), and imidazole (52.8 mg, 0.775 mmol) in THF (3.1 mL) was added  $\text{I}_2$  (98.2 mg, 0.387 mmol) at  $0$  °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  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane, hexane/EtOAc = 25:1) gave alkyl iodide **30** (90.8 mg, 97%): colorless oil;  $R_f = 0.60$  (hexane/EtOAc = 4:1);  $[\alpha]_{\text{D}}^{23} +2.6$  ( $c$  0.93,  $\text{CHCl}_3$ ); IR (neat) 2954, 2929, 2888, 2856  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.67 (d,  $J = 6.8$  Hz, 1 H), 4.64 (d,  $J = 6.8$  Hz, 1 H), 4.05–4.00 (m, 2 H), 3.87–3.84 (m, 1 H), 3.68–3.63 (m, 2 H), 3.38 (s, 3 H), 3.31 (dd,  $J = 10.0, 4.0$  Hz, 1 H), 3.25 (dd,  $J = 10.0, 6.0$  Hz, 1 H), 2.22 (dd,  $J = 13.4, 7.3$  Hz, 1 H), 1.87 (dd,  $J = 13.4, 3.4$  Hz, 1 H), 1.83–1.67 (m, 4 H), 1.34 (s, 3 H), 0.89 (s, 9 H), 0.89 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.05 (s, 3 H), 0.05 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  96.0, 83.4, 82.6, 81.7, 67.0, 59.7, 55.6, 49.9, 45.0, 41.7, 26.0, 26.0, 25.8, 18.3, 18.1, 9.2, -4.0, -4.1, -5.2, -5.2; HRMS (ESI-TOF) calcd for  $\text{C}_{24}\text{H}_{51}\text{IO}_5\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  625.2217, found 625.2215.

**Diol 33.** To a solution of diol **31** (205 mg, 1.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (14 mL) was added silica gel-supported NaIO<sub>4</sub> (0.693 mmol/g, 2.63 g, 1.83 mmol) at room temperature. The mixture was stirred at the same temperature for 10 min. To the mixture was added silica gel-supported NaIO<sub>4</sub> (0.693 mmol/g, 528 mg, 0.366 mmol) at room temperature. The mixture was stirred at the same temperature for 10 min. The mixture was filtered through short column chromatography (EtOAc). Concentration gave aldehyde **32** (190 mg), which was used for the next step without further purification.

To a solution of aldehyde **32** obtained above (190 mg) in THF (12 mL) was added LiAlH<sub>4</sub> (92.5 mg, 2.44 mmol) at 0 °C. The mixture was stirred at the same temperature for 20 min. The reaction was quenched with ice water. The mixture was diluted with EtOAc and washed with 1.0 M aqueous HCl. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 2:1) gave diol **33** (190 mg, 91% in two steps): colorless oil;  $R_f = 0.11$  (hexane/EtOAc = 2:1);  $[\alpha]_D^{26} +25.4$  ( $c$  0.60, CHCl<sub>3</sub>); IR (neat) 3324, 2968, 2920, 2878, 1645 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.26 (t,  $J = 7.2$  Hz, 1 H), 4.93 (t,  $J = 1.6$  Hz, 1 H), 4.78 (s, 1 H), 4.17 (d,  $J = 12.0$  Hz, 1 H), 4.01 (d,  $J = 12.0$  Hz, 1 H), 3.58–3.56 (m, 2 H), 2.37–2.30 (m, 1 H), 2.26–2.20 (m, 1 H), 2.13–2.11 (m, 1 H), 2.04 (brs, 2 H), 1.81 (d,  $J = 1.0$  Hz, 3 H), 1.73 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.3, 136.1, 125.8, 112.5, 62.8, 61.5, 48.9, 27.6, 21.9, 20.9; HRMS (ESI-TOF) calcd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>Na [M + Na]<sup>+</sup> 193.1205, found 193.1209.

**Bis-PMB Ether 34.** To a suspension of NaH (60%, 946 mg, 23.6 mmol) in THF (10 mL) was added diol **33** (671 mg, 3.94 mmol) in THF (3.5 mL + 3.5 mL + 3.0 mL) at room temperature. The mixture was stirred at the same temperature for 20 min. To the mixture were added PMBCl (1.3 mL, 9.46 mmol) and TBAI (291 mg, 0.788 mmol) at 0 °C. The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 12:1) gave bis-PMB ether **34** (1.59 g, 99%): yellow oil;  $R_f = 0.73$  (hexane/EtOAc = 1:1);  $[\alpha]_D^{26} -2.4$  ( $c$  1.21, CHCl<sub>3</sub>); IR (neat) 2933, 2852, 1646, 1612 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24–7.22 (m, 4 H), 6.87–6.85 (m, 4 H), 5.31 (t,  $J = 7.3$  Hz, 1 H), 4.82 (t,  $J = 1.6$  Hz, 1 H), 4.73 (t,  $J = 0.9$  Hz, 1 H), 4.44 (d,  $J = 12.0$  Hz, 1 H), 4.40 (d,  $J = 12.0$  Hz, 1 H), 4.36 (s, 2 H), 3.97 (s, 2 H), 3.80 (s, 3 H), 3.80 (s, 3 H), 3.41–3.32 (m, 2 H), 2.41–2.33 (m, 1 H), 2.27–2.20 (m, 1 H), 2.10–2.03 (m, 1 H), 1.77 (d,  $J = 1.2$  Hz, 3 H), 1.65 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 145.5, 133.0, 130.7, 130.6, 129.2, 129.0, 127.1, 113.7, 113.7, 111.9, 72.6, 72.0, 71.4, 68.4, 55.3, 47.2, 28.4, 21.7, 20.2; HRMS (ESI-TOF) calcd for C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>Na [M + Na]<sup>+</sup> 433.2355, found 433.2357.

**Diol 35.** To a solution of alkene **34** (403 mg, 0.980 mmol) in *t*-BuOH (1.6 mL) and H<sub>2</sub>O (1.6

mL) were added MeSO<sub>2</sub>NH<sub>2</sub> (95.3 mg, 1.00 mmol) and AD-mix- $\alpha$  (1.37 g) at 0 °C. The mixture was stirred at room temperature for 20 h. The reaction was quenched with saturated aqueous Na<sub>2</sub>SO<sub>3</sub>. The mixture was diluted with EtOAc and washed with saturated aqueous NaHCO<sub>3</sub> and brine. The aqueous phase was extracted with EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 12:1, 3:1) gave diol **35** (189 mg, 43%) as a 2.3:1 diastereomeric mixture and alkene **34** (144 mg, 36% recovery). For **35**: colorless oil;  $R_f$  = 0.43 (hexane/EtOAc = 1:1); IR (neat) 3466, 2934, 2856, 1641, 1612 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26–7.22 (m, 4 H), 6.88–6.85 (m, 4 H), 4.86–4.80 (m, 2 H), 4.50–4.43 (m, 4 H), 3.80 (s, 3 H), 3.80 (s, 3 H), 3.61–3.57 (m, 1 H), 3.47–3.43 (m, 2 H), 3.37–3.33 (m, 2 H), 2.73–2.67 (m, 0.7 H), 2.62–2.57 (m, 0.3 H), 1.79–1.60 (m, 4 H), 1.48–1.39 (m, 0.7 H), 1.31–1.21 (m, 0.3 H), 1.09 (s, 0.9 H), 1.08 (s, 2.1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 159.0, 147.5, 145.2, 130.3, 129.8, 129.3, 129.2, 113.8, 113.7, 112.7, 111.4, 75.2, 75.1, 75.0, 73.5, 73.4, 73.4, 73.2, 72.7, 72.6, 72.1, 55.3, 44.2, 44.0, 32.9, 32.7, 20.7, 20.7, 20.5, 19.8; HRMS (ESI–TOF) calcd for C<sub>26</sub>H<sub>36</sub>O<sub>6</sub>Na [M + Na]<sup>+</sup> 467.2410, found 467.2412.

**Dithiane 38.** To a solution of diol **35** (575 mg, 1.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (13 mL) was added silica gel-supported NaIO<sub>4</sub> (0.693 mmol/g, 2.80 g, 1.94 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min. To the mixture was added silica gel-supported NaIO<sub>4</sub> (0.693 mmol/g, 1.40 mg, 0.970 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The mixture was filtered through short column chromatography (EtOAc). Concentration gave aldehyde **36** (285 mg), which was used for the next step without further purification.

To a solution of aldehyde **36** obtained above (285 mg) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) were added 1,3-propanedithiol (**37**, 0.17 mL, 1.73 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (29  $\mu$ L, 0.230 mmol) at 0 °C. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 20:1) gave dithiane **38** (317 mg, 72% in two steps): colorless oil;  $R_f$  = 0.48 (hexane/EtOAc = 4:1); [ $\alpha$ ]<sub>D</sub><sup>23</sup> –8.9 (*c* 1.08, CHCl<sub>3</sub>); IR (neat) 3072, 2932, 2900, 2852, 1612 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (d,  $J$  = 8.4 Hz, 2 H), 6.87 (d,  $J$  = 8.4 Hz, 2 H), 4.90 (t,  $J$  = 1.6 Hz, 1 H), 4.86 (s, 1 H), 4.46 (d,  $J$  = 11.6 Hz, 1 H), 4.42 (d,  $J$  = 11.6 Hz, 1 H), 3.96 (dd,  $J$  = 9.6, 4.8 Hz, 1 H), 3.81 (s, 3 H), 3.42 (dd,  $J$  = 9.6, 6.8 Hz, 1 H), 3.35 (dd,  $J$  = 9.8, 6.8 Hz, 1 H), 2.90–2.76 (m, 5 H), 2.14–2.05 (m, 1 H), 1.96–1.81 (m, 2 H), 1.80–1.73 (m, 1 H), 1.70 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 144.5, 130.4, 129.1, 113.7, 113.1, 72.5, 72.2, 55.3, 45.0, 43.5, 35.8, 30.4, 29.9, 26.2, 19.8; HRMS (ESI–TOF) calcd for C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup> 361.1272, found 361.1270.

**Dithiane 39.** To a solution of dithiane **38** (183 mg, 0.541 mmol) in THF (5.1 mL) and HMPA (0.5 mL) was added *t*-BuLi (1.77 M in pentane, 0.31 mL, 0.541 mmol) at –78 °C. The mixture was stirred at the same temperature for 10 min. To the mixture was added alkyl iodide **30** (113

mg, 0.188 mmol) in THF (0.9 mL + 0.5 mL + 0.5 mL) at  $-78\text{ }^{\circ}\text{C}$ . The mixture was warmed up to room temperature for 1 h. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 20:1, 10:1) gave dithiane **39** (70.6 mg, 46% from alkyl iodide **30**) and dithiane **38** (123 mg). For **39**: colorless oil;  $R_f = 0.67$  (hexane/EtOAc = 2:1);  $[\alpha]_{\text{D}}^{23} +13.1$  ( $c$  0.20,  $\text{CHCl}_3$ ); IR (neat) 2950, 2927, 2855, 1646, 1613  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.5$  Hz, 2 H), 6.86 (d,  $J = 8.5$  Hz, 2 H), 4.89 (brs, 1 H), 4.85 (brs, 1 H), 4.66 (d,  $J = 6.8$  Hz, 1 H), 4.63 (d,  $J = 6.8$  Hz, 1 H), 4.47 (d,  $J = 11.6$  Hz, 1 H), 4.44 (d,  $J = 11.6$  Hz, 1 H), 4.17–4.13 (m, 1 H), 4.02–3.96 (m, 1 H), 3.87–3.83 (m, 1 H), 3.80 (s, 3 H), 3.66–3.60 (m, 2 H), 3.44–3.35 (m, 2 H), 3.36 (s, 3 H), 2.89–2.71 (m, 5 H), 2.32 (dd,  $J = 14.8, 2.8$  Hz, 1 H), 2.21–2.14 (m, 2 H), 2.07–1.60 (m, 9 H), 1.77 (s, 3 H), 1.29 (s, 3 H), 0.89 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 147.4, 130.8, 129.0, 113.6, 112.2, 96.1, 82.9, 81.9, 78.8, 77.2, 72.2, 67.1, 59.6, 55.5, 55.3, 50.3, 44.4, 43.8, 42.8, 41.6, 39.8, 29.8, 26.7, 26.1, 26.0, 26.0, 26.0, 25.0, 21.0, 18.3, 18.1,  $-4.0$ ,  $-4.1$ ,  $-5.2$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{76}\text{O}_7\text{S}_2\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  835.4469, found 835.4473.

**Alcohol 40.** To a solution of bis-TBS ether **39** (61.3 mg, 75.4  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (1.1 mL) and MeOH (0.4 mL) was added CSA (3.5 mg, 15.1  $\mu\text{mol}$ ) at  $0\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 1 h. The reaction was quenched with  $\text{Et}_3\text{N}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1, 3:1) gave alcohol **40** (22.4 mg) and bis-TBS ether **39** (25.7 mg).

To a solution of bis-TBS ether **39** recovered above (25.7 mg) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) and MeOH (0.2 mL) was added CSA (1.5 mg, 6.32  $\mu\text{mol}$ ) at  $0\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 30 min. The reaction was quenched with  $\text{Et}_3\text{N}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1, 3:1) gave alcohol **40** (9.6 mg, totally 32.0 mg, 61% in two cycles) and bis-TBS ether **39** (10.8 mg). For **40**: colorless oil;  $R_f = 0.31$  (hexane/EtOAc = 2:1);  $[\alpha]_{\text{D}}^{24} +26.2$  ( $c$  1.04,  $\text{CHCl}_3$ ); IR (neat) 3466, 2930, 2856, 1646, 1613  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.8$  Hz, 2 H), 6.86 (d,  $J = 8.8$  Hz, 2 H), 4.88 (brs, 1 H), 4.86 (brs, 1 H), 4.66 (d,  $J = 6.4$  Hz, 1 H), 4.63 (d,  $J = 6.4$  Hz, 1 H), 4.45 (s, 2 H), 4.18–4.09 (m, 2 H), 3.86–3.77 (m, 2 H), 3.80 (s, 3 H), 3.72–3.66 (m, 1 H), 3.40–3.35 (m, 2 H), 3.37 (s, 3 H), 2.87–2.78 (m, 3 H), 2.71 (t,  $J = 5.7$  Hz, 2 H), 2.35 (dd,  $J = 15.0, 2.3$  Hz, 1 H), 2.20–2.14 (m, 1 H), 2.08–1.70 (m, 10 H), 1.77 (s, 3 H), 1.31 (s, 3 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.07 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 147.3, 130.6, 129.1, 113.6, 112.2, 96.1, 82.3, 81.3, 79.4, 73.3, 72.3, 69.0, 60.0, 55.6, 55.3, 53.8, 49.6, 45.5, 44.0, 42.9, 39.9, 39.3, 26.7, 26.0, 25.9, 25.6, 24.9, 21.2, 18.0,  $-4.3$ ,  $-4.3$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{36}\text{H}_{62}\text{O}_7\text{S}_2\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  721.3604,

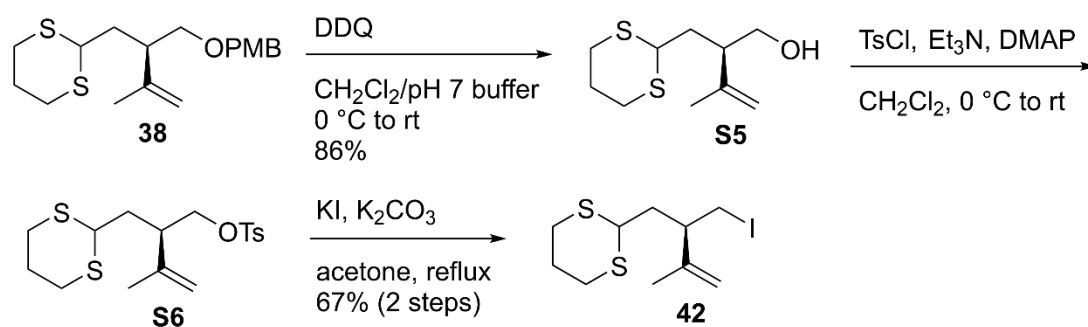
found 721.3602.

**Alkene 41.** To a solution of alcohol **40** (9.9 mg, 14.2  $\mu\text{mol}$ ) in THF (0.4 mL) were added 2- $\text{NO}_2\text{C}_6\text{H}_4\text{SeCN}$  (25.7 mg, 0.113 mmol) and *n*- $\text{Bu}_3\text{P}$  (31  $\mu\text{L}$ , 0.113 mmol) at room temperature. The mixture was stirred at the same temperature for 10 min. Concentration and short column chromatography (hexane/EtOAc = 7:1) gave the corresponding selenide (11.5 mg), which was used for the next step without further purification.

To a solution of the selenide obtained above (11.5 mg) in THF (0.7 mL) were added  $\text{NaHCO}_3$  (6.6 mg, 78.0  $\mu\text{mol}$ ) and 30% aqueous  $\text{H}_2\text{O}_2$  (3.2  $\mu\text{L}$ , 31.2  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . The mixture was stirred at 40  $^\circ\text{C}$  for 2 h. The mixture was diluted with EtOAc, washed with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and short column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  = 30:1) gave the corresponding alkene (8.7 mg), which was used for the next step without further purification.

To a mixture of  $\text{P}_2\text{I}_4$  (78.3 mg, 0.138 mmol) and  $\text{Et}_3\text{N}$  (87  $\mu\text{L}$ , 0.625 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.7 mL) was added the monosulfoxide obtained above (8.7 mg) in  $\text{CH}_2\text{Cl}_2$  (0.4 mL + 0.3 mL + 0.2 mL) 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  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1) gave alkene **41** (4.0 mg, 41% in three steps): colorless oil;  $R_f$  = 0.40 (hexane/EtOAc = 4:1);  $[\alpha]_D^{20}$  +27.2 (*c* 0.17,  $\text{CHCl}_3$ ); IR (neat) 2954, 2928, 2854, 1646, 1613  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J$  = 8.8 Hz, 2 H), 6.85 (d,  $J$  = 8.8 Hz, 2 H), 5.84 (ddd,  $J$  = 17.2, 10.4, 6.8 Hz, 1 H), 5.11 (d,  $J$  = 17.2 Hz, 1 H), 4.99 (d,  $J$  = 10.4 Hz, 1 H), 4.90 (brs, 1 H), 4.86 (brs, 1 H), 4.66 (d,  $J$  = 6.8 Hz, 1 H), 4.63 (d,  $J$  = 6.8 Hz, 1 H), 4.47 (d,  $J$  = 11.6 Hz, 1 H), 4.43 (d,  $J$  = 11.6 Hz, 1 H), 4.31–4.22 (m, 1 H), 4.16–4.12 (m, 1 H), 3.86–3.77 (m, 1 H), 3.80 (s, 3 H), 3.44–3.34 (m, 2 H), 3.36 (s, 3 H), 2.88–2.71 (m, 5 H), 2.33 (dd,  $J$  = 14.9, 2.4 Hz, 1 H), 2.27 (dd,  $J$  = 13.2, 7.6 Hz, 1 H), 2.17 (dd,  $J$  = 14.9, 6.8 Hz, 1 H), 2.05–1.83 (m, 4 H), 1.77–1.61 (m, 3 H), 1.77 (s, 3 H), 1.33 (s, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.03 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 147.5, 142.5, 130.8, 129.0, 113.6, 113.4, 112.2, 96.1, 83.0, 81.8, 78.5, 73.3, 72.2, 71.9, 55.5, 55.3, 53.7, 51.2, 44.2, 43.6, 42.8, 39.7, 29.8, 26.7, 26.3, 26.0, 25.0, 21.0, 18.2, –3.6, –4.5; HRMS (ESI–TOF) calcd for  $\text{C}_{36}\text{H}_{60}\text{O}_6\text{S}_2\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  703.3499, found 703.3499.

**Synthesis of 42.** Oxidative deprotection of PMB ether **38** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave alcohol **S5** in 86% yield (Scheme S2). Tosylation of **S5** and subsequent nucleophilic iodination using  $\text{KI}/\text{K}_2\text{CO}_3$  afforded alkyl iodide **42** in 67% yield in two steps.

**Scheme S2.** Synthesis of alkyl iodide **42**.

**Alcohol S5.** To a solution of PMB ether **38** (110 mg, 0.326 mmol) in  $\text{CH}_2\text{Cl}_2$  (6.0 mL) and phosphate pH standard solution (0.6 mL) was added DDQ (114 mg, 0.489 mmol) at  $0\text{ }^\circ\text{C}$ . The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous  $\text{NaHCO}_3$ . The mixture was diluted with EtOAc, washed with saturated aqueous  $\text{NaHCO}_3$  three times,  $\text{H}_2\text{O}$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 5:1) gave alcohol **S5** (61.1 mg, 86%): colorless oil;  $R_f = 0.21$  (hexane/EtOAc = 4:1);  $[\alpha]_{\text{D}}^{31} -9.5$  ( $c$  1.00,  $\text{CHCl}_3$ ); IR (neat) 3401, 2931, 2900, 1645  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.01 (t,  $J = 1.2$  Hz, 1 H), 4.90 (t,  $J = 1.2$  Hz, 1 H), 3.98 (t,  $J = 7.2$  Hz, 1 H), 3.58–3.52 (m, 2 H), 2.89 (ddd,  $J = 13.8, 11.4, 2.4$  Hz, 1 H), 2.84–2.80 (m, 3 H), 2.71–2.66 (m, 1 H), 2.14–2.09 (m, 1 H), 1.91–1.81 (m, 3 H), 1.73 (s, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 114.8, 63.8, 46.2, 44.8, 35.1, 30.4, 30.0, 26.0, 19.3; HRMS (ESI-TOF) calcd for  $\text{C}_{10}\text{H}_{18}\text{OS}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  241.0697, found 241.0690.

**Alkyl Iodide 42.** To a solution of alcohol **S5** (17.8 mg, 81.5  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) were added  $\text{Et}_3\text{N}$  (55  $\mu\text{L}$ , 0.391 mmol), DMAP (3.0 mg, 24.5  $\mu\text{mol}$ ), and  $\text{TsCl}$  (51.3 mg, 0.269 mmol) at  $0\text{ }^\circ\text{C}$ . The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous  $\text{NaHCO}_3$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and short column chromatography (hexane/EtOAc = 20:1, 10:1) gave tosylate **S6** (24.6 mg), which was used for the next step without further purification.

To a solution of tosylate **S6** obtained above (24.6 mg) in acetone (2.2 mL) were added  $\text{K}_2\text{CO}_3$  (54.7 mg, 0.396 mmol) and  $\text{KI}$  (87.6 mg, 0.528 mmol) at room temperature. The mixture was stirred at reflux for 18 h. The reaction was quenched with  $\text{H}_2\text{O}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 80:1) gave alkyl iodide **42** (17.8 mg, 67% in two steps): yellow oil;  $R_f = 0.51$  (hexane/EtOAc = 10:1);  $[\alpha]_{\text{D}}^{22} -143$  ( $c$  0.40,  $\text{CHCl}_3$ ); IR (neat) 2922, 2850, 1644  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.85 (brs, 1 H), 4.84 (brs, 1 H), 4.54 (dd,  $J = 6.0, 1.8$  Hz, 1 H), 3.29 (t,  $J = 6.6$  Hz, 2 H), 3.19–3.13 (m, 1 H), 3.08 (ddd,  $J = 10.2, 7.2, 1.2$  Hz, 1 H), 2.79–2.76 (m, 1 H), 2.73–2.70 (m, 2 H), 2.26–2.23 (m, 1 H), 2.21–2.16 (m, 1 H), 2.14–2.07 (m,

2 H), 1.79 (s, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 111.0, 52.0, 48.2, 42.5, 35.9, 33.6, 32.6, 21.4, 5.1; HRMS (ESI-TOF) calcd for  $\text{C}_{10}\text{H}_{17}\text{IS}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  350.9714, found 350.9713.

**Allylic Alcohol 48.** To a suspension of NaH (60%, 640 mg, 16.0 mmol) in THF (50 mL) was added  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et}$  (3.2 mL, 16.0 mmol) at room temperature. The mixture was stirred at the same temperature for 30 min. To the mixture was added ketone **47** (4.00 g, 9.03 mmol) in THF (20 mL + 10 mL + 10 mL) at room temperature. The mixture was stirred at the same temperature for 30 min. The reaction was quenched with  $\text{H}_2\text{O}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and short column chromatography (hexane/EtOAc = 8:1) gave the corresponding  $\alpha,\beta$ -unsaturated ester (5.70 g) as a mixture of geometric isomers, which was used for the next step without further purification.

To a solution of the  $\alpha,\beta$ -unsaturated ester obtained above (5.70 g) in  $\text{CH}_2\text{Cl}_2$  (90 mL) was added DIBAL-H (1.03 M in hexane, 22 mL, 22.6 mmol) at  $-78^\circ\text{C}$ . The mixture was stirred at the same temperature for 10 min. The reaction was quenched with saturated aqueous sodium potassium tartrate. The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 6:1) gave allylic alcohol **48** (4.13 g, 97% in two steps) as a mixture of geometric isomers: colorless oil;  $R_f$  = 0.29, 0.29 (hexane/EtOAc = 7:1); IR (neat) 3349, 2939, 2893, 2857  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68–7.66 (m, 4 H), 7.46–7.36 (m, 6 H), 5.89–5.87 (m, 0.6 H), 5.77–5.74 (m, 0.4 H), 4.23–4.18 (m, 5 H), 4.01 (d,  $J$  = 6.7 Hz, 1 H), 1.07 (s, 5.4 H), 1.04 (s, 3.6 H), 0.90 (s, 3.6 H), 0.85 (s, 5.4 H), 0.06 (s, 2.4 H), 0.03 (s, 3.6 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.4, 135.6, 135.5, 133.5, 133.2, 129.8, 129.7, 127.7, 127.7, 125.4, 124.9, 65.4, 64.4, 60.0, 59.5, 58.7, 58.6, 26.8, 26.7, 25.9, 25.8, 19.3, 19.1, 18.4, 18.2, -5.4, -5.5; HRMS (ESI-TOF) calcd for  $\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  493.2570, found 493.2572.

**Allylic Bromide 49.** To a mixture of allylic alcohol **48** (1.53 g, 3.25 mmol) and  $\text{Ph}_3\text{P}$  (1.15 g, 4.55 mmol) in  $\text{CH}_2\text{Cl}_2$  (33 mL) was added  $\text{CBr}_4$  (1.29 g, 3.90 mmol) at  $0^\circ\text{C}$ . The mixture was stirred at the same temperature for 10 min. The mixture was filtered through short column chromatography (EtOAc). Concentration and column chromatography (hexane/EtOAc = 10:1) gave allylic bromide **49** (1.86 g, quant) as a mixture of geometric isomers: colorless oil;  $R_f$  = 0.31, 0.31 (hexane/EtOAc = 30:1); IR (neat) 3071, 2929, 2857  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68–7.66 (m, 4 H), 7.46–7.36 (m, 6 H), 5.99–5.96 (m, 0.6 H), 5.86–5.83 (m, 0.4 H), 4.27–4.23 (m, 4 H), 4.13 (d,  $J$  = 8.8 Hz, 1 H), 3.87 (d,  $J$  = 8.8 Hz, 1 H), 1.07 (s, 5.4 H), 1.04 (s, 3.6 H), 0.91 (s, 3.6 H), 0.82 (s, 5.4 H), 0.07 (s, 2.4 H), 0.01 (s, 3.6 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 142.9, 135.6, 135.5, 133.4, 133.1, 129.8, 129.7, 127.8, 127.7, 121.0, 120.9, 64.8, 64.0, 59.4, 58.8, 27.5, 27.4, 26.8, 26.7, 25.9, 25.8, 19.3, 19.1, 18.4, 18.2, -5.4, -5.5; HRMS (ESI-TOF) calcd for  $\text{C}_{27}\text{H}_{41}^{79}\text{BrO}_2\text{Si}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  555.1726, found 555.1722.



**Imide 51.** To a mixture of allylic bromide **49** (3.06 g, 5.74 mmol) and imide **50** (744 mg, 2.87 mmol) in THF (29 mL) was added NaHMDS (1.0 M in THF, 3.5 mL, 3.50 mmol) at  $-78\text{ }^{\circ}\text{C}$ . The mixture was warmed up to  $0\text{ }^{\circ}\text{C}$  and stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1) gave imide **51** (1.60 g, 78% from imide **50**) as a mixture of geometric isomers and allylic bromide **49** (1.39 g). For **51**: yellow oil;  $R_f = 0.23, 0.20$  (hexane/EtOAc = 7:1); IR (neat) 3070, 2929, 2893, 2857, 1784, 1699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71–7.63 (m, 4 H), 7.43–7.29 (m, 8 H), 7.27–7.24 (m, 1 H), 7.19–7.15 (m, 2 H), 5.64 (t,  $J = 7.4$  Hz, 0.7 H), 5.50 (t,  $J = 7.4$  Hz, 0.3 H), 4.93 (s, 0.7 H), 4.91 (t,  $J = 1.4$  Hz, 0.7 H), 4.85 (t,  $J = 1.4$  Hz, 0.3 H), 4.83 (s, 0.3 H), 4.65–4.58 (m, 1 H), 4.52 (dd,  $J = 8.2, 6.4$  Hz, 0.7 H), 4.39 (dd,  $J = 8.2, 6.4$  Hz, 0.3 H), 4.34–4.21 (m, 4 H), 4.15–4.09 (m, 2 H), 3.28–3.24 (m, 1 H), 2.73–2.66 (m, 1 H), 2.60 (dd,  $J = 13.2, 10.0$  Hz, 0.7 H), 2.53–2.45 (m, 1 H), 2.26–2.21 (m, 0.3 H), 1.84 (s, 2.1 H), 1.72 (s, 0.9 H), 1.03 (s, 9 H), 0.89 (s, 2.7 H), 0.82 (s, 6.3 H), 0.04 (s, 1.8 H), 0.01 (s, 4.2 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 172.9, 153.0, 152.9, 142.7, 139.3, 139.2, 135.6, 135.6, 135.5, 135.5, 135.4, 133.8, 129.5, 129.4, 129.4, 128.9, 127.7, 127.6, 127.6, 127.2, 127.2, 122.4, 122.3, 114.1, 113.9, 65.8, 65.7, 65.1, 64.4, 59.8, 59.0, 55.7, 55.6, 50.3, 50.2, 38.0, 28.7, 26.9, 26.8, 26.8, 25.9, 25.8, 21.2, 21.1, 19.3, 18.2,  $-5.3, -5.4$ ; HRMS (ESI-TOF) calcd for  $\text{C}_{42}\text{H}_{57}\text{NO}_5\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  734.3673, found 734.3676.

**Allylic Alcohol 52.** To a solution of bis-silyl ether **51** (5.10 g, 7.16 mmol) in  $\text{CH}_2\text{Cl}_2$  (35 mL) and MeOH (35 mL) was added CSA (166 mg, 0.716 mmol) at  $0\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 1 h. The reaction was quenched with  $\text{Et}_3\text{N}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 2:1) gave allylic alcohol **52** (1.64 g) as a mixture of geometric isomers and bis-silyl ether **51** (2.13 g).

To a solution of bis-silyl ether **51** recovered above (2.13 g) in  $\text{CH}_2\text{Cl}_2$  (17 mL) and MeOH (17 mL) was added CSA (81.0 mg, 0.350 mmol) at  $0\text{ }^{\circ}\text{C}$ . The mixture was stirred at the same temperature for 1 h. The reaction was quenched with  $\text{Et}_3\text{N}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 2:1) gave allylic alcohol **52** (1.49 g, totally 3.13 g, 73% in two cycles) as a mixture of geometric isomers and bis-silyl ether **51** (507 mg). For **52**: colorless oil;  $R_f = 0.21, 0.21$  (hexane/EtOAc = 3:1); IR (neat) 3470, 3051, 2929, 2856, 1781, 1698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73–7.64 (m, 3 H), 7.44–7.39 (m, 3 H), 7.37–7.34 (m, 3 H), 7.31–7.23 (m, 4 H), 7.18–7.14 (m, 2 H), 5.53 (t,  $J = 7.3$  Hz, 0.8 H), 5.47 (t,  $J = 7.3$  Hz, 0.2 H), 4.90 (t,  $J = 1.5$  Hz, 0.8 H), 4.88 (s, 0.8 H), 4.84 (t,  $J = 1.5$  Hz, 0.2 H), 4.80 (s, 0.2 H), 4.64–4.58 (m, 1 H), 4.50 (dd,  $J = 9.1, 5.3$  Hz, 0.8 H), 4.42 (dd,  $J = 9.1, 5.3$  Hz, 0.2 H), 4.38–4.35 (m, 1

H), 4.25 (d,  $J = 12.6$  Hz, 1 H), 4.22 (d,  $J = 12.6$  Hz, 1 H), 4.17–4.11 (m, 3 H), 3.25–3.19 (m, 1 H), 2.85–2.79 (m, 0.8 H), 2.73 (dd,  $J = 13.8, 9.7$  Hz, 0.2 H), 2.66 (dd,  $J = 13.8, 9.7$  Hz, 0.8 H), 2.57 (brs, 1 H), 2.43–2.39 (m, 1 H), 1.85 (s, 2.4 H), 1.70 (s, 0.6 H), 1.05 (s, 1.8 H), 1.04 (s, 7.2 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 142.7, 139.4, 135.6, 135.5, 135.5, 135.1, 133.3, 129.7, 129.4, 128.9, 127.8, 127.7, 127.3, 125.4, 113.8, 67.3, 65.9, 59.1, 55.6, 50.4, 38.0, 29.0, 26.8, 26.8, 21.4, 21.1, 19.2; HRMS (ESI–TOF) calcd for  $\text{C}_{36}\text{H}_{43}\text{NO}_5\text{SiNa}$  [ $\text{M} + \text{Na}$ ] $^+$  620.2808, found 620.2804.

**Diene 54.** To a mixture of allylic alcohol **52** (1.14 g, 1.92 mmol),  $\text{Ph}_3\text{P}$  (604 mg, 2.30 mmol), and *N*-isopropylidene-*N'*-2-nitrobenzenesulfonyl hydrazine (**53**, 593 mg, 2.30 mmol) in THF (64 mL) was added DEAD (2.2 M in toluene, 1.1 mL, 2.42 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. To the mixture were added  $\text{Ph}_3\text{P}$  (302 mg, 1.15 mmol), *N*-isopropylidene-*N'*-2-nitrobenzenesulfonyl hydrazine (**53**, 297 mg, 1.15 mmol), and DEAD (2.2 M in toluene, 0.6 mL, 1.32 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. To the mixture was added a premixed solution of  $\text{CF}_3\text{CH}_2\text{OH}$  (16 mL) and  $\text{H}_2\text{O}$  (16 mL) at room temperature. The mixture was stirred at room temperature for 19 h. The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 7:1) gave diene **54** (826 mg, 74%): yellow oil;  $R_f = 0.38$  (hexane/EtOAc = 4:1);  $[\alpha]_D^{19} +47.6$  ( $c$  1.34,  $\text{CHCl}_3$ ); IR (neat) 3070, 2967, 2930, 2846, 1783, 1697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70–7.65 (m, 4 H), 7.43–7.36 (m, 6 H), 7.33–7.30 (m, 2 H), 7.27–7.24 (m, 1 H), 7.22–7.20 (m, 2 H), 5.20 (d,  $J = 2.0$  Hz, 1 H), 4.91 (s, 1 H), 4.87 (s, 2 H), 4.65–4.61 (m, 1 H), 4.42–4.39 (m, 1 H), 4.15–4.11 (m, 3 H), 3.33 (dd,  $J = 13.2, 3.5$  Hz, 1 H), 2.70 (dd,  $J = 13.2, 3.5$  Hz, 1 H), 2.05–1.99 (m, 3 H), 1.78 (s, 3 H), 1.07–1.04 (m, 2 H), 1.05 (s, 9 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 147.4, 142.8, 135.5, 135.5, 133.6, 129.6, 129.4, 128.9, 127.7, 127.3, 114.0, 109.2, 66.3, 65.8, 55.7, 50.0, 38.1, 30.8, 28.7, 26.8, 20.9, 19.4; HRMS (ESI–TOF) calcd for  $\text{C}_{36}\text{H}_{43}\text{NO}_4\text{SiNa}$  [ $\text{M} + \text{Na}$ ] $^+$  604.2859, found 604.2860.

**Alcohol 55.** To a solution of imide **54** (2.65 g, 4.55 mmol) in  $\text{Et}_2\text{O}$  (46 mL) and EtOH (0.8 mL) was added  $\text{LiBH}_4$  (296 mg, 13.6 mmol) at 0 °C. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 2:1) gave alcohol **55** (1.49 g, 80%): yellow oil;  $R_f = 0.20$  (hexane/EtOAc = 7:1);  $[\alpha]_D^{20} -2.3$  ( $c$  0.50,  $\text{CHCl}_3$ ); IR (neat) 3365, 3071, 2929, 2856, 1646  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69–7.65 (m, 4 H), 7.44–7.36 (m, 6 H), 5.17 (d,  $J = 1.8$  Hz, 1 H), 4.94–4.93 (m, 1 H), 4.86–4.85 (m, 1 H), 4.80–4.79 (m, 1 H), 4.09 (s, 2 H), 3.50–3.44 (m, 2 H), 2.26–2.21 (m, 1 H), 2.00 (ddd,  $J = 15.6, 9.6, 5.4$  Hz, 1 H), 1.91 (ddd,  $J = 15.6, 9.6, 6.6$  Hz, 1 H), 1.64 (s, 3 H), 1.49–1.39 (m, 2 H), 1.06 (s, 9 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )

$\delta$  147.9, 144.6, 135.5, 133.6, 129.6, 127.6, 114.2, 108.7, 66.3, 63.9, 49.6, 30.2, 27.1, 26.8, 19.3, 18.6; HRMS (ESI-TOF) calcd for  $C_{26}H_{36}O_2SiNa$   $[M + Na]^+$  431.2382, found 431.2377.

**Alkyl Iodide 56.** To a mixture of alcohol **55** (32.1 mg, 78.5  $\mu$ mol),  $Ph_3P$  (61.8 mg, 0.236 mmol), and imidazole (21.4 mg, 0.314 mmol) in benzene (1.0 mL) was added  $I_2$  (59.8 mg, 0.236 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous  $Na_2S_2O_3$ . The mixture was diluted with EtOAc, washed with  $H_2O$  and brine, and then dried over  $Na_2SO_4$ . Concentration and column chromatography (hexane/EtOAc = 20:1) gave alkyl iodide **56** (38.7 mg, 95%): colorless oil;  $R_f$  = 0.26 (hexane/EtOAc = 50:1);  $[\alpha]_D^{22} +3.5$  ( $c$  1.11,  $CHCl_3$ ); IR (neat) 3071, 3042, 2930, 2857, 1647  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.69–7.67 (m, 1 H), 7.44–7.37 (m, 6 H), 5.17 (d,  $J$  = 1.7 Hz, 1 H), 4.90–4.89 (m, 1 H), 4.87 (d,  $J$  = 1.7 Hz, 1 H), 4.73 (t,  $J$  = 0.6 Hz, 1 H), 4.09 (s, 2 H), 3.18 (dd,  $J$  = 9.6, 6.0 Hz, 1 H), 3.13 (dd,  $J$  = 9.6, 7.8 Hz, 1 H), 2.31–2.26 (m, 1 H), 2.02–1.97 (m, 1H), 1.92–1.87 (m, 1 H), 1.68–1.63 (m, 1 H), 1.61 (s, 3 H), 1.50–1.43 (m, 1 H), 1.06 (s, 9 H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  147.5, 144.7, 135.5, 133.6, 129.6, 127.7, 113.8, 109.0, 66.3, 49.0, 30.8, 30.5, 26.8, 19.3, 18.3, 11.2; HRMS (ESI-TOF) calcd for  $C_{26}H_{35}IOSiNa$   $[M + Na]^+$  541.1400, found 541.1400.

**Alcohol 57.** To a solution of  $BH_3 \cdot SME_2$  (1.5 mL, 15.7 mmol) in THF (20 mL) was added cyclohexene (3.5 mL, 34.0 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. To the mixture was added alkene **29** (1.19 g, 2.43 mmol) in THF (5.0 mL + 2.5 mL + 2.5 mL) at 0 °C. The mixture was stirred at room temperature for 2 h. To the mixture were added 3 M aqueous NaOH (12.0 mL, 36.0 mmol) and 30% aqueous  $H_2O_2$  (4.0 mL, 39.0 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. The mixture was diluted with EtOAc, washed with saturated aqueous  $Na_2S_2O_3$ ,  $H_2O$ , and brine, and then dried over  $Na_2SO_4$ . Concentration and column chromatography (hexane/EtOAc = 4:1) gave alcohol **57** (1.14 g, 93%): colorless oil;  $R_f$  = 0.19 (hexane/EtOAc = 3:1);  $[\alpha]_D^{20} +10.4$  ( $c$  1.22,  $CHCl_3$ ); IR (neat) 3455, 2958, 2929, 2857  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  4.64 (d,  $J$  = 6.8 Hz, 1 H), 4.62 (d,  $J$  = 6.8 Hz, 1 H), 4.03–3.98 (m, 2 H), 3.93–3.90 (m, 1 H), 3.77 (t,  $J$  = 5.9 Hz, 2 H), 3.67–3.60 (m, 2 H), 3.35 (s, 3 H), 2.26 (dd,  $J$  = 13.5, 7.9 Hz, 1 H), 1.93–1.88 (m, 1 H), 1.79–1.66 (m, 6 H), 1.32 (s, 3 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  96.1, 82.6, 82.3, 81.8, 66.9, 61.4, 59.4, 55.5, 49.7, 44.7, 41.5, 36.0, 25.9, 25.9, 25.5, 18.2, 18.0, -4.1, -4.3, -5.4; HRMS (ESI-TOF) calcd for  $C_{25}H_{54}O_6Si_2Na$   $[M + Na]^+$  529.3357, found 529.3354.

**Aldehyde 58.** To a solution of alcohol **57** (12.3 mg, 24.3  $\mu$ mol) in  $CH_2Cl_2$  (0.6 mL) were added  $PhI(OAc)_2$  (9.3 mg, 28.9  $\mu$ mol) and TEMPO (0.8 mg, 5.12  $\mu$ mol) at 0 °C. The mixture was stirred at room temperature for 5 h. The reaction was quenched with saturated aqueous  $Na_2S_2O_3$ .

The mixture was diluted with EtOAc, washed with saturated aqueous NaHCO<sub>3</sub>, H<sub>2</sub>O, and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 4:1) gave aldehyde **58** (13.8 mg, quant): colorless oil;  $R_f$  = 0.31 (hexane/EtOAc = 4:1);  $[\alpha]_D^{21}$  +13.9 ( $c$  1.08, CHCl<sub>3</sub>); IR (neat) 2958, 2929, 2893, 2857, 1729 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (t,  $J$  = 2.4 Hz, 1 H), 4.63 (d,  $J$  = 6.7 Hz, 1 H), 4.62 (d,  $J$  = 6.7 Hz, 1 H), 4.29 (dt,  $J$  = 7.8, 4.8 Hz, 1 H), 4.02–3.98 (m, 1 H), 3.92 (dt,  $J$  = 7.8, 4.8 Hz, 1 H), 3.67–3.60 (m, 2 H), 3.35 (s, 3 H), 2.68 (ddd,  $J$  = 7.0, 5.0, 2.4 Hz, 1 H), 2.59 (ddd,  $J$  = 7.0, 5.0, 2.4 Hz, 1 H), 2.27 (dd,  $J$  = 13.2, 7.6 Hz, 1 H), 1.81 (dd,  $J$  = 13.2, 4.8 Hz, 1 H), 1.76–1.72 (m, 2 H), 1.69–1.64 (m, 2 H), 1.33 (s, 3 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  201.0, 96.2, 82.1, 66.9, 59.5, 55.5, 49.7, 47.8, 44.6, 41.6, 25.9, 25.9, 25.6, 18.0, -4.1, -4.3, -5.4; HRMS (ESI-TOF) calcd for C<sub>26</sub>H<sub>56</sub>O<sub>7</sub>Si<sub>2</sub>Na [M + MeOH + Na]<sup>+</sup> 559.3462, found 559.3467.

**Alcohol 59.** To a solution of alkyl iodide **56** (938 mg, 1.80 mmol) in Et<sub>2</sub>O (10 mL) was added *t*-BuLi (1.77 M in pentane, 2.0 mL, 3.54 mmol) at -78 °C. The mixture was stirred at the same temperature for 1 h. To the mixture was added aldehyde **58** (454 mg, 0.899 mmol) in Et<sub>2</sub>O (4.0 mL + 2.0 mL + 2.0 mL) at -78 °C. The mixture was warmed up to 0 °C and stirred at the same temperature for 1 h. The reaction was quenched with saturated aqueous NH<sub>4</sub>Cl. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 8:1) gave alcohol **59** (835 mg, quant from aldehyde **58**) as a diastereomeric mixture: colorless oil;  $R_f$  = 0.27, 0.23 (hexane/EtOAc = 7:1); IR (neat) 3508, 3071, 2967, 2930, 2856, 1645 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.68–7.65 (m, 4 H), 7.43–7.36 (m, 6 H), 5.15 (s, 1 H), 4.85 (s, 1 H), 4.78–4.77 (m, 0.5 H), 4.74 (d,  $J$  = 2.3 Hz, 0.5 H), 4.73–4.72 (m, 0.5 H), 4.66 (d,  $J$  = 2.3 Hz, 0.5 H), 4.64–4.60 (m, 2 H), 4.08 (s, 2 H), 4.05–3.90 (m, 2.5 H), 3.85–3.82 (m, 0.5 H), 3.77–3.71 (m, 1 H), 3.67–3.58 (m, 2 H), 3.35 (s, 1.5 H), 3.34 (s, 1.5 H), 2.38–2.33 (m, 0.5 H), 2.27–2.22 (m, 1 H), 2.19–2.13 (m, 0.5 H), 1.96–1.61 (m, 9 H), 1.60 (s, 1.5 H), 1.60 (s, 1.5 H), 1.52–1.35 (m, 4 H), 1.31 (s, 1.5 H), 1.31 (s, 1.5 H), 1.06 (s, 9 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 1.5 H), 0.07 (s, 1.5 H), 0.05 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.4, 148.4, 146.6, 135.5, 133.7, 133.7, 129.6, 129.6, 127.6, 127.5, 112.8, 111.9, 108.2, 108.1, 96.2, 96.1, 83.0, 82.9, 82.2, 82.1, 82.1, 79.9, 69.6, 67.0, 66.9, 66.8, 66.5, 59.4, 59.3, 55.5, 55.5, 49.8, 49.6, 44.9, 44.4, 43.7, 43.6, 41.5, 41.4, 41.1, 41.0, 40.9, 40.6, 31.9, 31.0, 30.5, 30.3, 26.8, 25.9, 25.9, 25.5, 25.4, 19.3, 18.2, 18.0, 17.8, 17.7, -4.1, -4.3, -5.3, -5.4; HRMS (ESI-TOF) calcd for C<sub>51</sub>H<sub>88</sub>O<sub>7</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup> 919.5736, found 919.5738.

**MOM Ether S7.** To a solution of alcohol **59** (310 mg, 0.345 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) were added *i*-Pr<sub>2</sub>NEt (0.71 mL, 4.14 mmol), MOMCl (0.16 mL, 2.07 mmol), and TBAI (51.0 mg, 0.138 mmol) at room temperature. The mixture was stirred at reflux for 17 h. The reaction was

quenched with saturated aqueous NaHCO<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 10:1) gave MOM ether **S7** (321 mg, 99%) as a diastereomeric mixture: colorless oil; *R*<sub>f</sub> = 0.28, 0.28 (hexane/EtOAc = 7:1); IR (neat) 3060, 2930, 2893, 1645 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.69–7.65 (m, 4 H), 7.43–7.37 (m, 6 H), 5.16 (d, *J* = 1.7 Hz, 1 H), 4.85 (s, 1 H), 4.77–4.76 (m, 0.6 H), 4.74–4.73 (m, 0.4 H), 4.71 (d, *J* = 2.3 Hz, 0.6 H), 4.69–4.59 (m, 4 H), 4.67 (d, *J* = 2.3 Hz, 0.4 H), 4.08 (s, 2 H), 4.03–3.95 (m, 1.4 H), 3.88–3.84 (m, 1 H), 3.82–3.79 (m, 0.6 H), 3.68–3.60 (m, 2 H), 3.59–3.53 (m, 1 H), 3.37 (s, 2.4 H), 3.34 (s, 3.6 H), 2.33–2.28 (m, 0.6 H), 2.20–2.11 (m, 1.4 H), 1.95–1.63 (m, 9 H), 1.62 (s, 1.2 H), 1.59 (s, 1.8 H), 1.54–1.40 (m, 4 H), 1.29 (s, 1.2 H), 1.28 (s, 1.8 H), 1.06 (s, 9 H), 0.88 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 1.2 H), 0.07 (s, 1.8 H), 0.06 (s, 1.2 H), 0.06 (s, 1.8 H), 0.03 (s, 2.4 H), 0.03 (s, 3.6 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 148.4, 148.3, 146.7, 146.7, 135.5, 133.7, 133.7, 129.6, 129.6, 127.6, 112.9, 112.4, 108.1, 108.0, 96.7, 96.0, 95.9, 95.9, 82.8, 82.6, 81.6, 81.4, 78.8, 78.7, 74.9, 73.9, 67.0, 66.8, 66.5, 59.5, 59.5, 55.6, 55.5, 55.5, 55.4, 50.1, 50.1, 44.8, 43.8, 43.5, 41.5, 41.5, 41.1, 39.8, 39.2, 38.5, 31.9, 31.3, 30.5, 30.3, 26.8, 25.9, 25.9, 25.7, 25.5, 19.3, 18.2, 18.0, 17.6, 17.5, -4.2, -4.3, -5.3, -5.4; HRMS (ESI-TOF) calcd for C<sub>53</sub>H<sub>92</sub>O<sub>8</sub>Si<sub>3</sub>Na [M + Na]<sup>+</sup> 963.5998, found 963.5994.

**Alcohol 60.** To a solution of tris-silyl ether **S7** (319 mg, 0.339 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) and MeOH (1.0 mL) was added CSA (16.0 mg, 68.0 μmol) at 0 °C. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with Et<sub>3</sub>N. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 3:1) gave alcohol **60** (108 mg) as a diastereomeric mixture and tris-silyl ether **S7** (146 mg).

To a solution of tris-silyl ether **S7** recovered above (146 mg) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) and MeOH (0.5 mL) was added CSA (7.2 mg, 31.0 μmol) at 0 °C. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with Et<sub>3</sub>N. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 3:1) gave alcohol **60** (38.7 mg) as a diastereomeric mixture and tris-silyl ether **S7** (110 mg).

To a solution of tris-silyl ether **S7** recovered above (110 mg) in CH<sub>2</sub>Cl<sub>2</sub> (0.9 mL) and MeOH (0.3 mL) was added CSA (5.0 mg, 23.0 μmol) at 0 °C. The mixture was stirred at the same temperature for 1 h. The reaction was quenched with Et<sub>3</sub>N. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and column chromatography (hexane/EtOAc = 3:1) gave alcohol **60** (49.4 mg, totally 196 mg, 70% in three cycles) as a diastereomeric mixture and tris-silyl ether **S7** (86.5 mg). For **60**: colorless oil; *R*<sub>f</sub> = 0.24, 0.23 (hexane/EtOAc = 3:1); IR (neat) 3467, 3072, 2931, 2893, 2857, 1645 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.68–7.65 (m, 4 H), 7.43–7.36 (m, 6 H), 5.16 (d, *J* = 1.7 Hz, 1 H), 4.85 (s,

1 H), 4.79–4.78 (m, 0.6 H), 4.74–4.73 (m, 0.4 H), 4.71 (d,  $J = 1.7$  Hz, 0.6 H), 4.69–4.58 (m, 4 H), 4.66 (d,  $J = 1.7$  Hz, 0.4 H), 4.16–4.10 (m, 1 H), 4.08 (s, 2 H), 3.96–3.89 (m, 1 H), 3.85–3.78 (m, 2 H), 3.71–3.70 (m, 1 H), 3.59–3.55 (m, 1 H), 3.37 (s, 2.4 H), 3.34 (s, 3.6 H), 2.76 (brs, 0.6 H), 2.68 (brs, 0.4 H), 2.30–2.26 (m, 0.4 H), 2.16–2.10 (m, 0.6 H), 2.06–1.64 (m, 10 H), 1.60 (s, 1.8 H), 1.56 (s, 1.2 H), 1.51–1.39 (m, 4 H), 1.31 (s, 1.8 H), 1.30 (s, 1.2 H), 1.06 (s, 5.4 H), 1.06 (s, 3.6 H), 0.89 (s, 5.4 H), 0.88 (s, 3.6 H), 0.10 (s, 1.2 H), 0.09 (s, 1.8 H), 0.07 (s, 1.2 H), 0.07 (s, 1.8 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 146.8, 146.6, 135.5, 133.7, 133.6, 129.6, 129.6, 127.6, 112.9, 112.2, 108.1, 96.6, 96.0, 95.9, 95.6, 82.3, 82.1, 81.1, 81.0, 79.7, 79.4, 74.5, 73.8, 69.0, 68.8, 66.5, 66.4, 59.8, 59.7, 55.7, 55.5, 55.4, 49.2, 49.0, 45.9, 45.7, 43.8, 43.5, 41.2, 39.9, 39.2, 39.2, 38.8, 38.5, 31.8, 31.1, 30.4, 30.3, 26.8, 25.8, 25.8, 25.2, 24.9, 19.3, 17.9, 17.9, 17.7, 17.6, –4.5, –4.5, –4.6; HRMS (ESI–TOF) calcd for  $\text{C}_{47}\text{H}_{78}\text{O}_8\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  849.5133, found 849.5133.

**Triene 61.** To a solution of alcohol **60** (26.0 mg, 31.0  $\mu\text{mol}$ ) in THF (1.0 mL) were added 2- $\text{NO}_2\text{C}_6\text{H}_4\text{SeCN}$  (56.0 mg, 0.248 mmol) and *n*- $\text{Bu}_3\text{P}$  (76  $\mu\text{L}$ , 0.310 mmol) at room temperature. The mixture was stirred at the same temperature for 5 min. The mixture was filtered through short column chromatography (hexane/EtOAc = 4:1). Concentration gave the corresponding selenide (110 mg), which was used for the next step without further purification.

To a solution of the selenide obtained above (110 mg) in THF (1.0 mL) were added  $\text{NaHCO}_3$  (52.0 mg, 0.620 mmol) and 30% aqueous  $\text{H}_2\text{O}_2$  (25  $\mu\text{L}$ , 0.248 mmol) at 0 °C. The mixture was stirred at 40 °C for 1 h. The mixture was diluted with EtOAc, washed with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 10:1) gave triene **61** (21.1 mg, 84% in two steps) as a diastereomeric mixture: brown oil;  $R_f$  = 0.26, 0.26 (hexane/EtOAc = 7:1); IR (neat) 3051, 2931, 2884, 1645  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69–7.65 (m, 4 H), 7.43–7.37 (m, 6 H), 5.87–5.81 (m, 1 H), 5.16 (d,  $J = 1.7$  Hz, 1 H), 5.10 (d,  $J = 18.0$  Hz, 1 H), 4.98 (d,  $J = 10.2$  Hz, 1 H), 4.85 (s, 1 H), 4.78–4.77 (m, 0.6 H), 4.74–4.73 (m, 0.4 H), 4.71 (d,  $J = 1.7$  Hz, 0.6 H), 4.69–4.58 (m, 4 H), 4.67 (d,  $J = 1.7$  Hz, 0.4 H), 4.29–4.25 (m, 1 H), 4.08 (s, 2 H), 3.97–3.94 (m, 0.6 H), 3.88–3.83 (m, 1 H), 3.82–3.78 (m, 0.4 H), 3.60–3.54 (m, 1 H), 3.37 (s, 2.4 H), 3.34 (s, 3.6 H), 2.32–2.28 (m, 0.6 H), 2.26–2.22 (m, 1 H), 2.17–2.13 (m, 0.4 H), 1.98–1.62 (m, 8 H), 1.59 (s, 1.2 H), 1.56 (s, 1.8 H), 1.54–1.40 (m, 3 H), 1.33 (s, 1.2 H), 1.32 (s, 1.8 H), 1.06 (s, 9 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.03 (s, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 148.3, 146.8, 146.7, 142.6, 135.5, 133.7, 133.7, 129.6, 129.6, 127.6, 113.4, 113.4, 112.8, 112.3, 108.1, 108.0, 96.7, 96.0, 95.9, 95.8, 82.9, 82.6, 81.5, 81.3, 78.5, 78.5, 74.9, 73.9, 71.7, 66.4, 55.6, 55.4, 51.0, 44.7, 44.6, 43.8, 43.5, 41.0, 39.8, 39.0, 38.4, 31.8, 31.3, 30.5, 30.3, 26.8, 25.9, 19.3, 19.3, 18.1, 17.6, 17.5, –3.8, –3.8, –4.6, –4.7; HRMS (ESI–TOF) calcd for  $\text{C}_{47}\text{H}_{76}\text{O}_7\text{Si}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  831.5027, found 831.5031.

**Lactone 63.** To a solution of TBDPS ether **61** (17.6 mg, 21.7  $\mu\text{mol}$ ) in THF (1.0 mL) was added TBAF (1.0 M in THF, 87  $\mu\text{L}$ , 87.0  $\mu\text{mol}$ ) at room temperature. The mixture was stirred at the same temperature for 22 h. The mixture was filtered through short column chromatography (EtOAc). Concentration gave the corresponding alcohol (17.8 mg), which was used for the next step without further purification.

To a solution of the alcohol obtained above (17.8 mg) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) were added  $\text{PhI}(\text{OAc})_2$  (8.4 mg, 26.0  $\mu\text{mol}$ ) and TEMPO (0.8 mg, 5.12  $\mu\text{mol}$ ) at 0  $^\circ\text{C}$ . The mixture was stirred at room temperature for 9 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 saturated aqueous  $\text{NaHCO}_3$ ,  $\text{H}_2\text{O}$ , and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration gave the corresponding aldehyde (28.9 mg), which was used for the next step without further purification.

To a mixture of the aldehyde obtained above (28.9 mg) and  $\text{NaH}_2\text{PO}_4$  (19.0 mg, 0.156 mmol) in 2-methyl-2-butene (0.5 mL), *t*-BuOH (0.5 mL), and  $\text{H}_2\text{O}$  (0.5 mL) was added  $\text{NaClO}_2$  (79%, 19.0 mg, 0.163 mmol) at 0  $^\circ\text{C}$ . The mixture was stirred at room temperature for 2 h. The mixture was diluted with EtOAc and washed with  $\text{H}_2\text{O}$  and brine. The aqueous phase was extracted with EtOAc twice and the combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ . Concentration gave the corresponding carboxylic acid (24.3 mg), which was used for the next step without further purification.

To a solution of the carboxylic acid obtained above (24.3 mg) in  $\text{CH}_2\text{Cl}_2$  (10 mL) were added MNBA (27.0 mg, 78.0  $\mu\text{mol}$ ) and DMAP (19.0 mg, 0.156 mmol) at room temperature. The mixture was stirred at the same temperature for 8 h. The reaction was quenched with saturated aqueous  $\text{NaHCO}_3$ . The mixture was diluted with EtOAc, washed with  $\text{H}_2\text{O}$  and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . Concentration and column chromatography (hexane/EtOAc = 5:1) gave lactone **63** (5.7 mg, 58% in four steps) as a diastereomeric mixture: colorless oil;  $R_f$  = 0.24, 0.24 (hexane/EtOAc = 4:1); IR (neat) 3071, 2930, 2874, 2822, 1714, 1644, 1629  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  6.16 (d,  $J$  = 1.4 Hz, 0.4 H), 6.14 (d,  $J$  = 1.4 Hz, 0.6 H), 5.84–5.76 (m, 1 H), 5.60–5.57 (m, 0.6 H), 5.50–5.47 (m, 0.4 H), 5.40 (s, 0.6 H), 5.36 (s, 0.4 H), 5.20–5.15 (m, 1 H), 5.11–5.07 (m, 1 H), 4.77–4.69 (m, 2 H), 4.63–4.57 (m, 4 H), 4.02 (dd,  $J$  = 9.4, 7.3 Hz, 0.4 H), 3.93–3.85 (m, 1.2 H), 3.78–3.74 (m, 1 H), 3.59–3.55 (m, 0.4 H), 3.37 (s, 1.8 H), 3.36 (s, 1.8 H), 3.35 (s, 1.2 H), 3.33 (s, 1.2 H), 2.55–2.52 (m, 0.4 H), 2.47–2.39 (m, 1 H), 2.24–2.10 (m, 3 H), 2.05–1.98 (m, 0.6 H), 1.87–1.60 (m, 4 H), 1.65 (s, 1.8 H), 1.63 (s, 1.2 H), 1.53–1.46 (m, 2 H), 1.43–1.33 (m, 2 H), 1.35 (s, 1.2 H), 1.32 (s, 1.8 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 167.2, 147.3, 146.4, 140.3, 139.8, 137.5, 137.5, 127.4, 127.1, 115.0, 114.8, 112.3, 111.5, 96.4, 96.4, 95.3, 94.8, 82.5, 82.4, 81.0, 80.5, 78.1, 76.0, 73.7, 73.6, 71.2, 71.0, 55.5, 55.5, 55.3, 55.2, 44.4, 44.0, 42.3, 42.1, 41.0, 40.6, 37.5, 36.9, 36.5, 34.0, 29.6, 29.5, 29.3, 28.7, 28.3, 25.9, 18.7, 17.7; HRMS (ESI–TOF) calcd for  $\text{C}_{25}\text{H}_{40}\text{O}_7\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  475.2672, found 475.2671.

**Diol 64.** To a solution of bis-MOM ether **63** (11.0 mg, 24.3  $\mu\text{mol}$ ) in  $\text{Me}_2\text{S}$  (3.0 mL) was added

BF<sub>3</sub>·OEt<sub>2</sub> (15 μL, 0.122 mmol) at –30 °C. The mixture was stirred at the same temperature for 1 h. The mixture was filtered through short column chromatography (EtOAc/MeOH = 1:1). Concentration gave a mixture of diol **64**, bis-MOM ether **63**, and the alcohol in which one MOM group was removed (16.1 mg). The mixture was used for the next step without further purification.

To the mixture obtained above (16.1 mg) in Me<sub>2</sub>S (3.0 mL) was added BF<sub>3</sub>·OEt<sub>2</sub> (15 μL, 0.122 mmol) at –30 °C. The mixture was stirred at the same temperature for 1 h. The mixture was filtered through short column chromatography (EtOAc/MeOH = 1:1). Concentration gave a mixture of diol **64** and the alcohol in which one MOM group was removed (17.6 mg). The mixture was used for the next step without further purification.

To the mixture obtained above (17.6 mg) in Me<sub>2</sub>S (1.5 mL) was added BF<sub>3</sub>·OEt<sub>2</sub> (6.0 μL, 48.8 μmol) at –30 °C. The mixture was stirred at the same temperature for 1 h. The mixture was filtered through short column chromatography (EtOAc/MeOH = 1:1). Concentration and column chromatography (hexane/EtOAc = 1:1, EtOAc) gave diol **64** (4.5 mg, 51% in three cycles) as a diastereomeric mixture: colorless oil; *R*<sub>f</sub> = 0.44, 0.44 (EtOAc); IR (neat) 3457, 2958, 2921, 2846, 1696, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.18 (d, *J* = 1.8 Hz, 0.6 H), 6.17 (d, *J* = 1.8 Hz, 0.4 H), 5.84–5.76 (m, 1 H), 5.58–5.55 (m, 0.4 H), 5.52–5.49 (m, 0.6 H), 5.41 (s, 1 H), 5.20–5.15 (m, 2 H), 4.78 (dd, *J* = 2.4, 1.8 Hz, 0.4 H), 4.74 (d, *J* = 2.4 Hz, 0.4 H), 4.71 (dd, *J* = 2.4, 1.8 Hz, 0.6 H), 4.61 (d, *J* = 2.4 Hz, 0.6 H), 4.01–3.90 (m, 2 H), 3.85–3.82 (m, 0.4 H), 3.80–3.77 (m, 0.6 H), 2.52 (dt, *J* = 14.4, 4.8 Hz, 0.6 H), 2.47 (dt, *J* = 14.4, 4.8 Hz, 0.4 H), 2.40 (dd, *J* = 13.2, 8.4 Hz, 0.4 H), 2.29 (dd, *J* = 13.2, 8.4 Hz, 0.6 H), 2.22–2.14 (m, 2 H), 2.02–1.97 (m, 1 H), 1.93–1.53 (m, 6 H), 1.66 (s, 1.2 H), 1.65 (s, 1.8 H), 1.47–1.38 (m, 2 H), 1.37 (s, 1.8 H), 1.35 (s, 1.2 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.3, 165.5, 147.2, 140.1, 137.4, 137.4, 127.4, 127.3, 115.1, 115.0, 111.8, 80.8, 80.4, 79.6, 77.7, 76.5, 71.4, 71.1, 68.4, 44.6, 44.3, 44.2, 40.9, 40.7, 39.4, 38.4, 36.1, 29.5, 29.5, 29.4, 28.9, 26.1, 18.4, 18.2; HRMS (ESI–TOF) calcd for C<sub>21</sub>H<sub>32</sub>O<sub>5</sub>Na [M + Na]<sup>+</sup> 387.2147, found 387.2144.

**Scabrolide F (7)**. To a solution of diol **64** (2.1 mg, 5.76 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) was added Dess–Martin periodinane (15.0 mg, 35.4 μmol) at 0 °C. The mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration and short column chromatography (hexane/EtOAc = 1:1) gave the corresponding diketone (2.2 mg), which was used for the next step without further purification.

To a solution of the triene obtained above (2.2 mg) in toluene (1.0 mL) was added the second-generation Hoveyda–Grubbs catalyst (**65**, 0.8 mg, 1.28 μmol) at room temperature. The mixture was stirred at 80 °C for 2 h. The mixture was filtered through short column chromatography (EtOAc). Concentration and column chromatography (hexane/EtOAc = 2:1) gave scabrolide F (**7**) (2.0 mg, quant in two steps): white solid; *R*<sub>f</sub> = 0.33 (hexane/EtOAc = 1:1); [α]<sub>D</sub><sup>25</sup> –5.1 (*c*



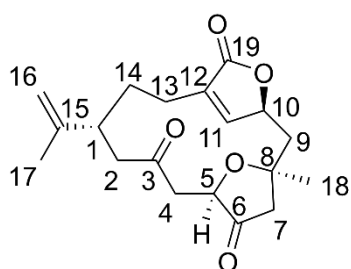
0.075, CHCl<sub>3</sub>); IR (neat) 2921, 2851, 1746, 1708, 1645 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR in Table S1; HRMS (ESI-TOF) calcd for C<sub>19</sub>H<sub>24</sub>O<sub>5</sub>Na [M + Na]<sup>+</sup> 355.1521, found 355.1521.

**Table S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data and chemical shift differences of natural<sup>[a]</sup> and synthetic scabrolide F ( $\text{CDCl}_3$ ).<sup>[b]</sup>

position	$^1\text{H}$ NMR			$^{13}\text{C}$ NMR		
	natural <sup>[c]</sup>	synthetic <sup>[d]</sup>	$\Delta(\delta_{\text{N}}-\delta_{\text{S}})^{[e]}$	natural <sup>[c]</sup>	synthetic <sup>[d]</sup>	$\Delta(\delta_{\text{N}}-\delta_{\text{S}})^{[e]}$
1	2.23 (dddd, $J = 10.5, 10.5, 2.5, 2.5$ Hz) <sup>[f]</sup>	2.23 (m)	0	41.2	41.2	0
2	2.47 (dd, $J = 12.0, 2.5$ Hz) 2.32 (dd, $J = 12.0, 10.5$ Hz)	2.47 (dd, $J = 11.7, 2.6$ Hz) 2.32 (m)	0 0	48.8	48.7	+0.1
3				206.7	206.6	+0.1
4	2.75 (dd, $J = 17.5, 10.5$ Hz) 2.66 (dd, $J = 17.5, 2.5$ Hz)	2.75 (dd, $J = 17.4, 10.3$ Hz) 2.67 (dd, $J = 17.4, 2.4$ Hz)	0 -0.01	44.2	44.1	+0.1
5	4.61 (dd, $J = 10.5, 2.5$ Hz)	4.62 (dd, $J = 10.3, 2.4$ Hz)	-0.01	76.0	76.0	0
6				214.5	214.5	0
7	2.60 (d, $J = 19.0$ Hz) 2.50 (d, $J = 19.0$ Hz)	2.60 (d, $J = 18.6$ Hz) 2.51 (d, $J = 18.6$ Hz)	0 -0.01	49.8	49.8	0
8				78.6	78.6	0
9	2.59 (dd, $J = 13.5, 5.5$ Hz) 1.51 (m)	2.59 (dd, $J = 13.2, 5.4$ Hz) 1.51 (m)	0	48.8	48.7	+0.1
10	5.13 (br dd, $J = 5.0, 2.5$ Hz)	5.13 (m)	0	78.0	78.0	0

11	7.57 (s)	7.57 (s)	0	151.7	151.7	0
12				131.4	131.4	0
13	2.35 (ddd, <i>J</i> = 17.0, 5.5, 2.5 Hz)	2.34 (m)	+0.01	20.4	20.4	0
	2.19 (m)	2.19 (m)	0			
14	1.75 (m)	1.77 (m)	-0.02	28.7	28.7	0
	1.65 (m)	1.65 (m)	0			
15				145.2	145.1	+0.1
16	4.83 (s)	4.83 (s)	0	113.1	113.1	0
	4.72 (s)	4.72 (s)	0			
17	1.65 (s)	1.65 (s)	0	18.3	18.3	0
18	1.52 (s)	1.52 (s)	0	25.9	25.9	0
19				173.5	173.5	0

<sup>[a]</sup>Data reported in reference 2. <sup>[b]</sup>The carbon numbering is as follows. <sup>[c]</sup>The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the natural product were recorded at 300 MHz and 75 MHz, respectively. <sup>[d]</sup>The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the synthetic product were recorded at 600 MHz and 150 MHz, respectively. <sup>[e]</sup> $\delta_N$  and  $\delta_S$  are chemical shifts of the natural product and the synthetic product, respectively. <sup>[f]</sup>The chemical shift of H-1 of the natural product was incorrectly reported as 2.33 ppm in the isolation paper (reference 2). This assignment has been revised by the private communication with Professor Jyh-Horng Sheu at National Sun Yat-sen University and Professor Atallah F. Ahmed at King Saud University.



**Antifouling Activity and Toxicity.** Adult barnacles of *Amphibalanus amphitrite* attached to stones were collected in Kobe, Japan during 2022–2023 and maintained in aquaria. Nauplii released from adults were cultured in filtered sea water (FSW) containing penicillin/streptomycin (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and fed with *Chaetoceros calcitrans* at 25 °C under a 12h:12h light:dark cycle. Larvae reached the cypris stage after 5–6 days. Cyprids were collected, rinsed with FSW, and stored in the dark at 5 °C for 2–3 days until used. The effects of the compounds on the barnacle cyprids were evaluated using 24-well polystyrene plates (Corning Inc., NY, USA). Each compound was dissolved in

MeOH, and the solution was diluted with the same solvent to concentrations of 0.01, 0.03, 0.1, 0.3, 1.0, and 5.0  $\mu\text{g}/\mu\text{L}$ . The 10  $\mu\text{L}$  aliquots of the solutions were added to the wells of the polystyrene plates and air-dried. Each well was charged with approximately ten cypris larvae and 1.0 mL FSW. The plates were kept at 25 °C in the dark for 96 h. The number of larvae that settled (including metamorphosed larvae), died, and did not settle was counted under a microscope. Each concentration level was tested in three wells and the experiment was performed three times with different batches of larvae. The assay was conducted using  $\text{CuSO}_4$  (0.01, 0.03, 0.1, 0.3, 1.0, 3.0, and 10  $\mu\text{g}$ ) as a positive control. An assay without any compound was performed as a negative control. The settlement inhibition was calculated on the basis of the negative control settlement. The antifouling activity ( $\text{EC}_{50}$ ) and toxicity ( $\text{LC}_{50}$ ) were calculated by probit analysis, respectively.

## References

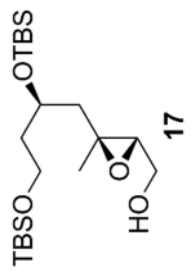
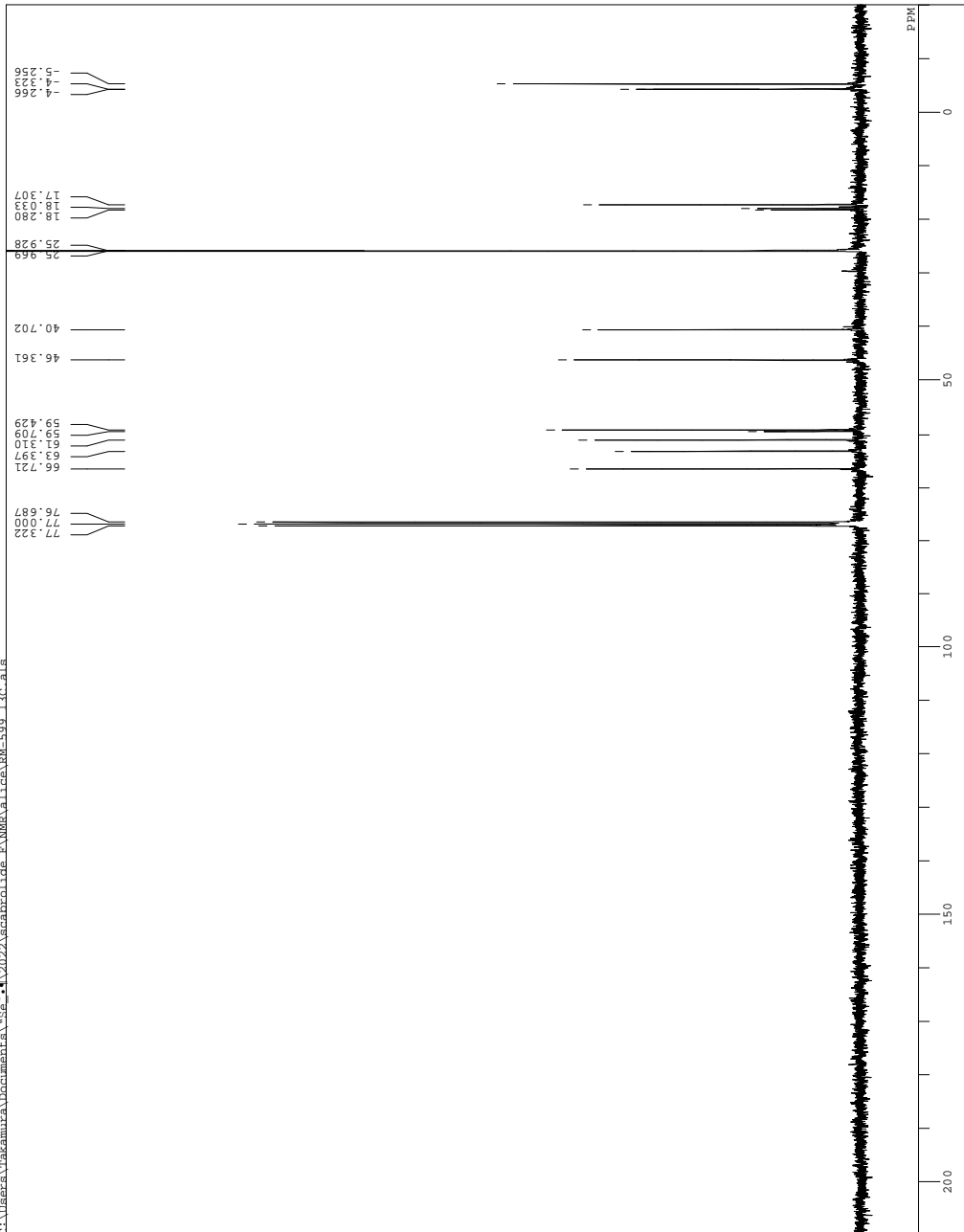
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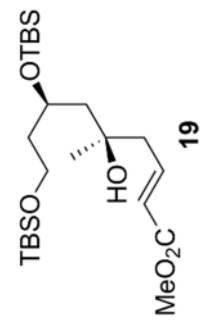
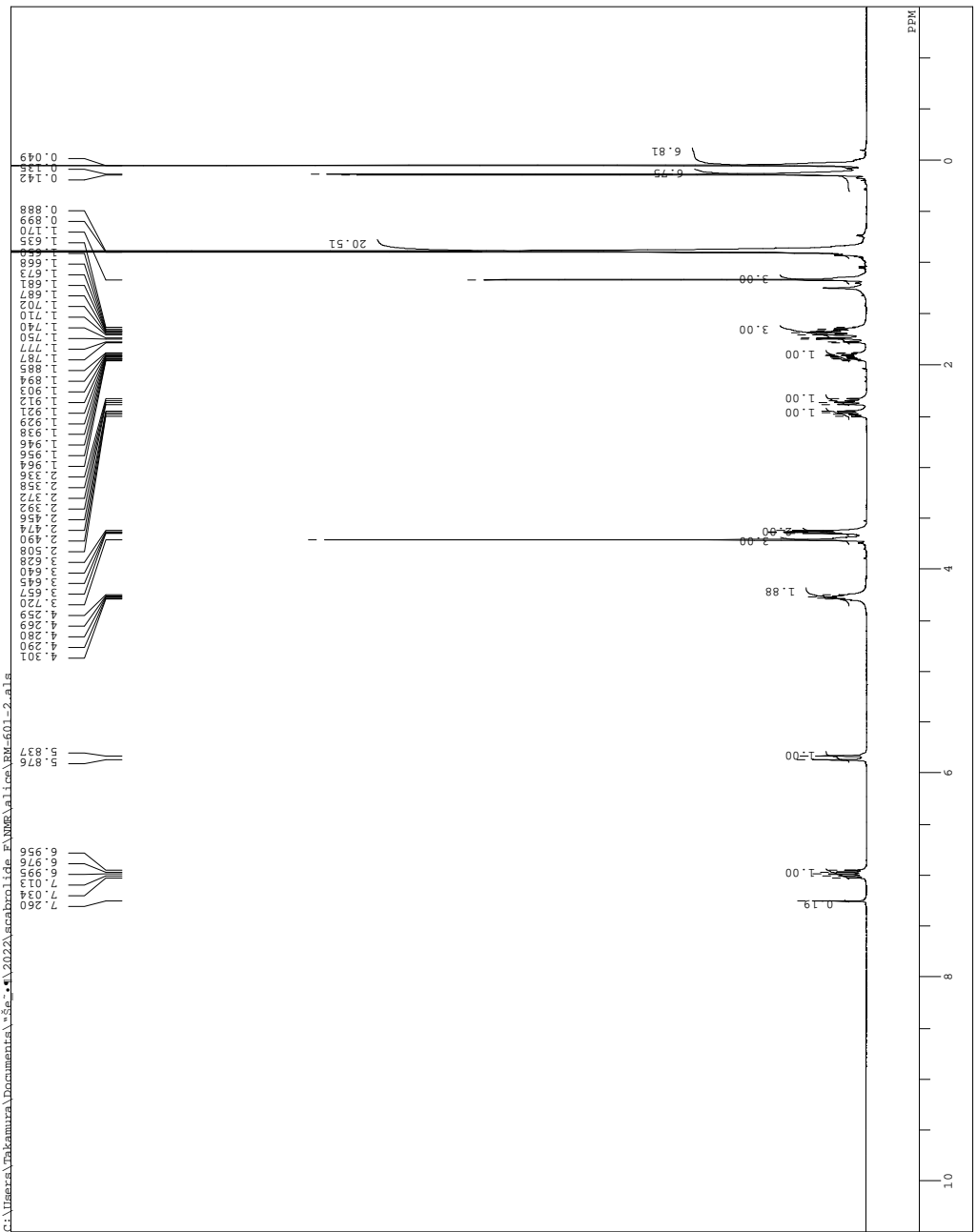






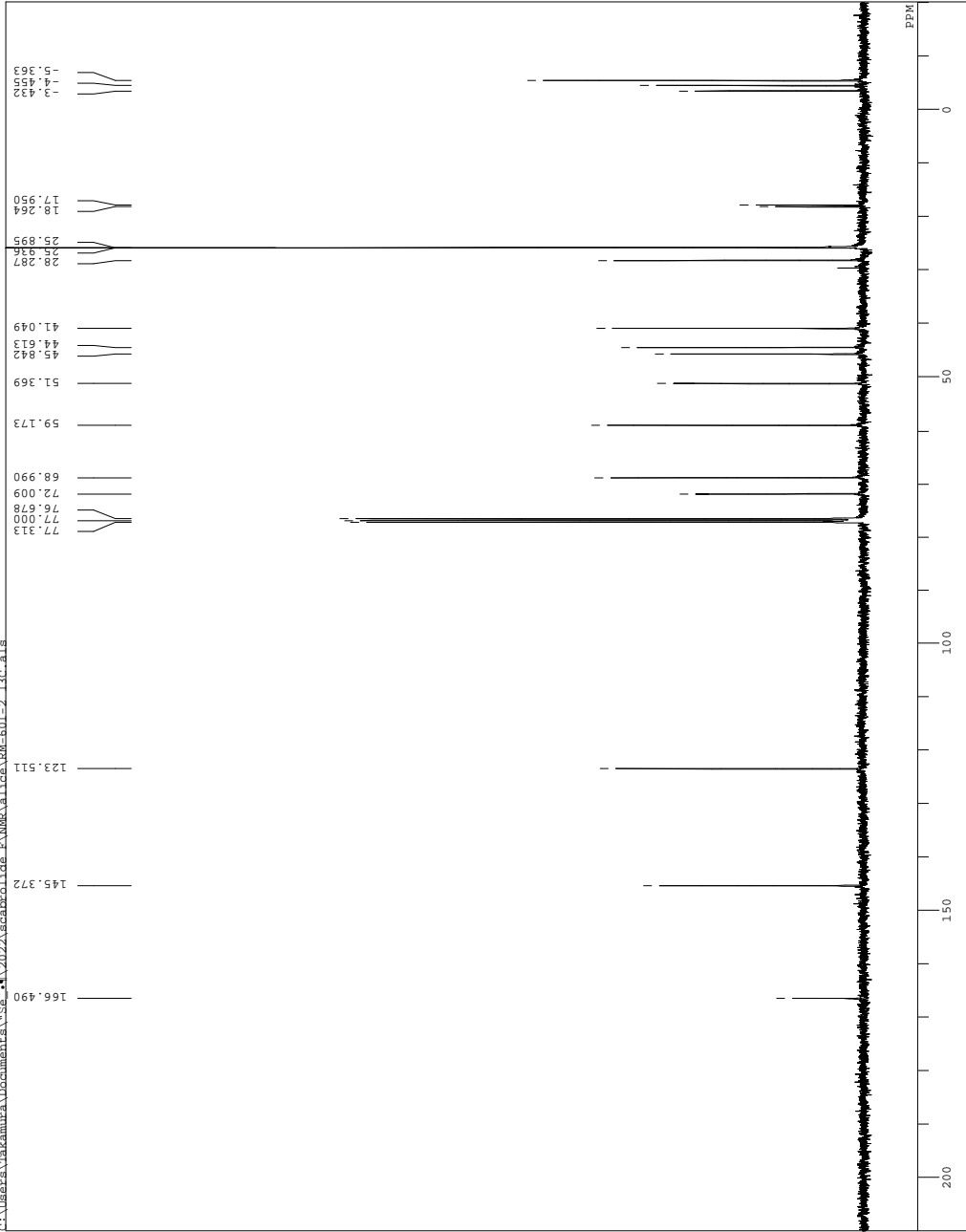


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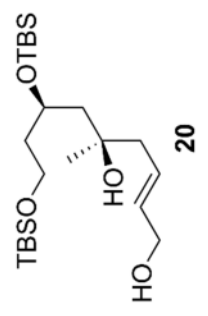
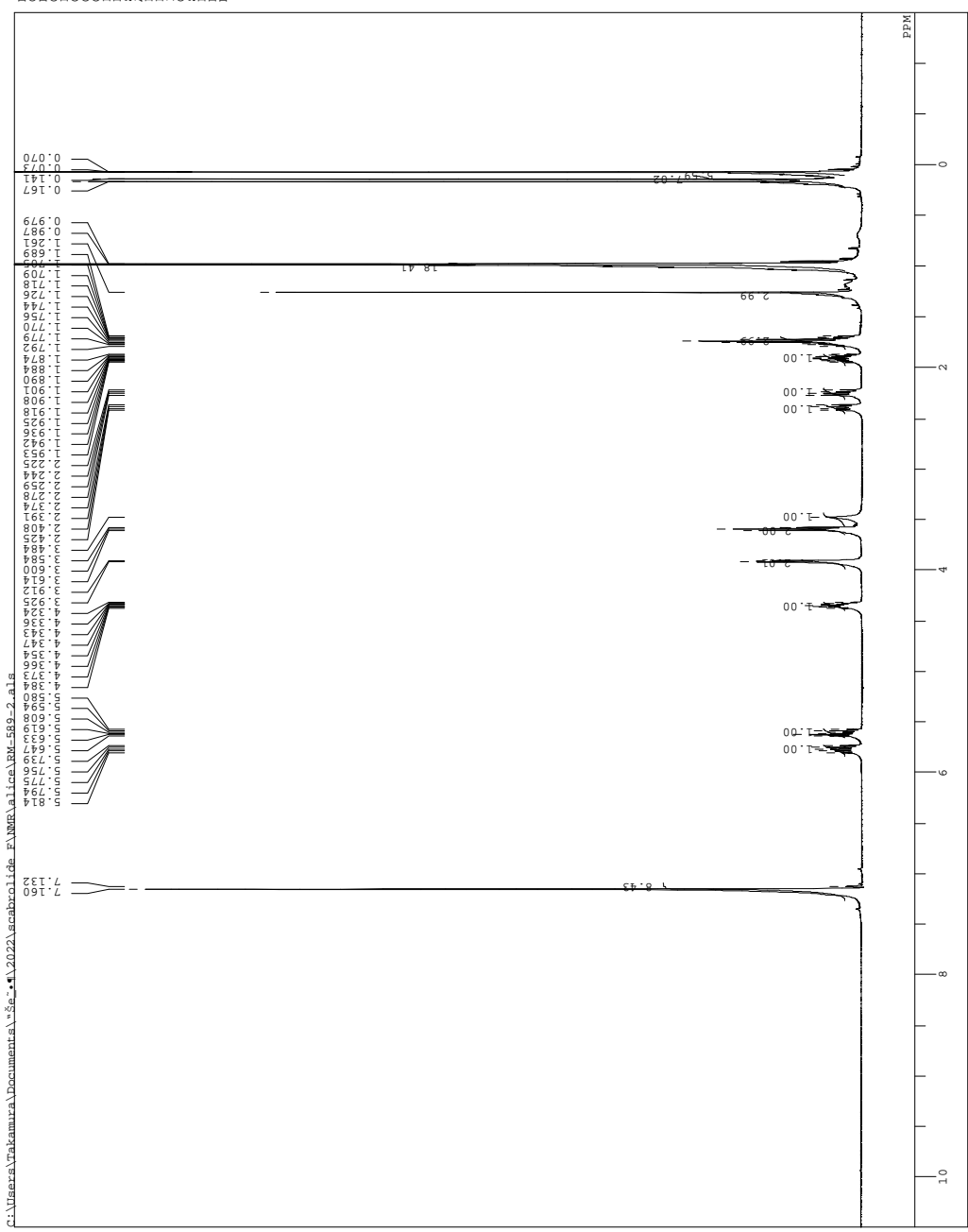


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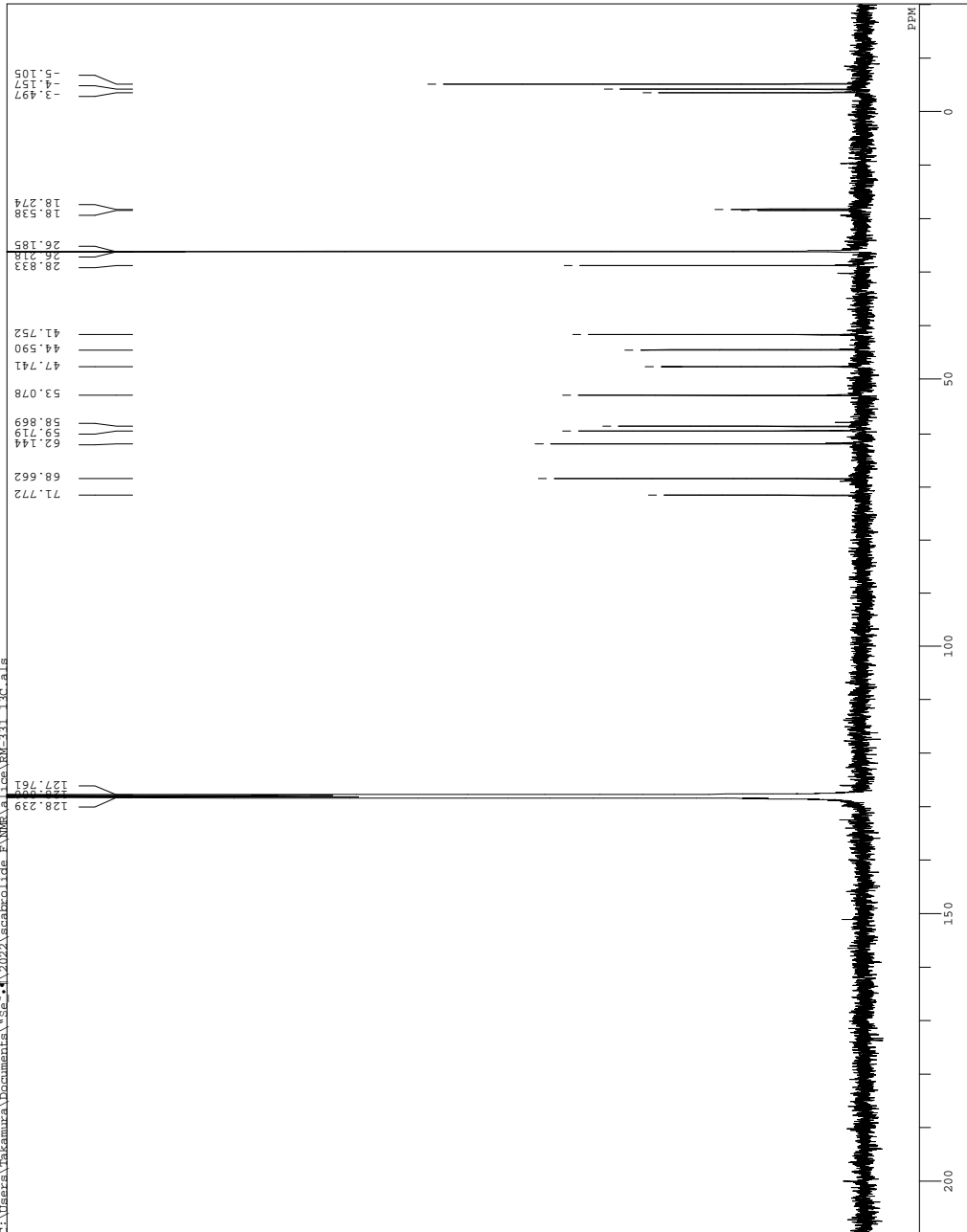




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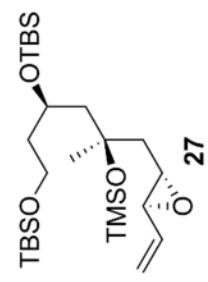
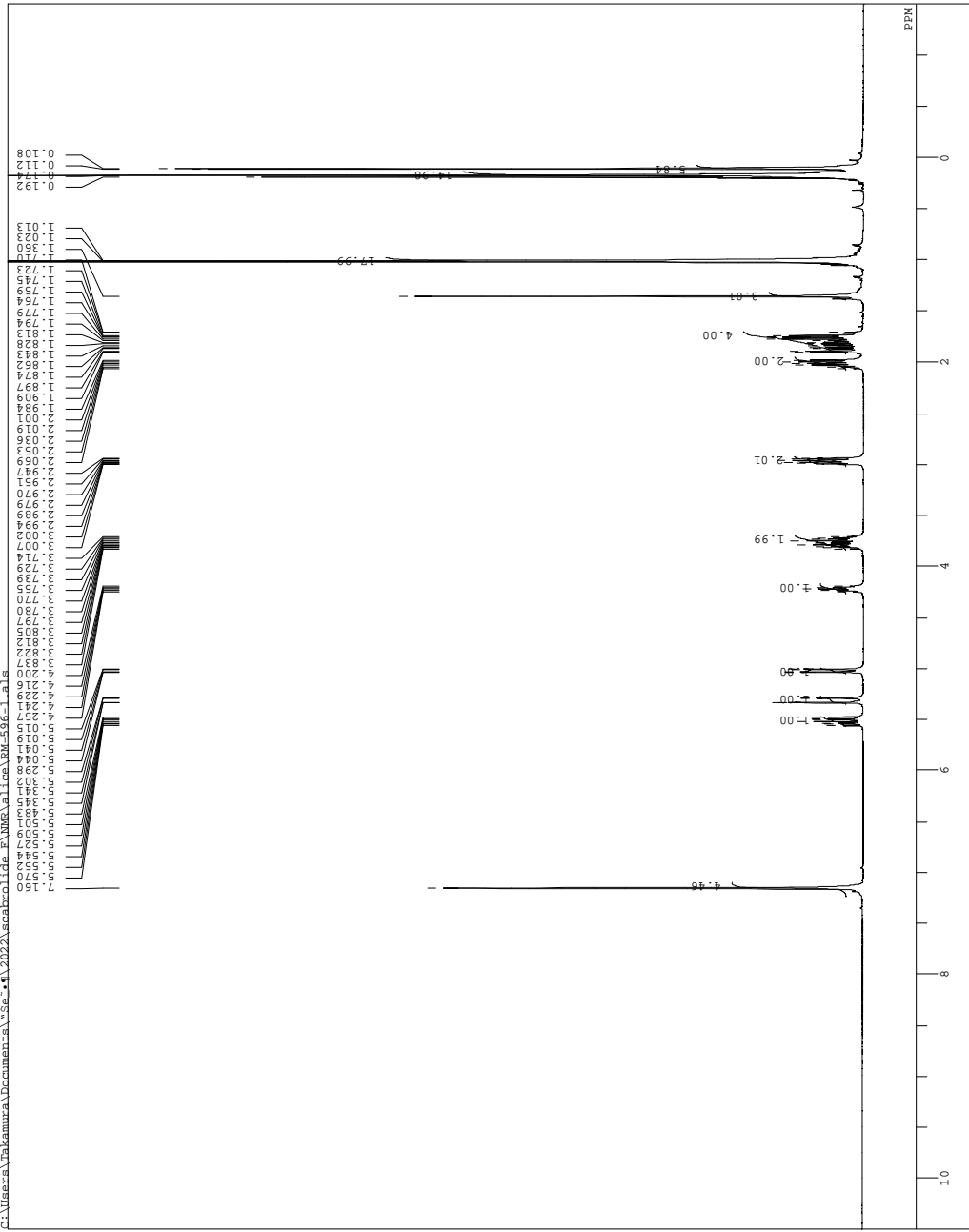
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PF1E RM-311 13c.als  
DATE\_ 20221231  
DATIM Thu Dec 19 10:38:50 2013  
OBNUC 13C  
EXMDC BCM  
EXMDD BCM  
OBESSI 100.40 MHz  
OBESSI 125.00 KHz  
OBEPIN 10500.00 Hz  
OBEPIN 10500.00 Hz  
FREQU 27134790 Hz  
SCANS 720  
PCQTM 1.7200 sec  
PCQTM 1.6780 usec  
PWL  
IRNMC 1H 27.1 c  
IRNMC 13C 101.25 c  
SLVNT C6D6  
EXREF 128.00 ppm  
EXREF 2.09 Hz  
RGAIN



C:\Users\Tshikamura\Documents\Se\_4\2022\scabroliide\_F\NMR\valice\RM-596-1\_als

FILE RM-596-1\_als  
 COMMENT RM-596-1  
 DATE Tue Jan 07 19:17:45 2014  
 EXMOD NMR  
 OBPRQ 399.65 MHz  
 OBPRM 101541.00 Hz  
 POINT 32768  
 PRMU 7993.60 Hz  
 ACQTM 4.0993 sec  
 PD 2.9010 sec  
 FM 6.40 usec  
 TRMJC 1H  
 CTMPC 23.1 c  
 SLANT C6D6  
 SF 101.625 MHz  
 RGAIN 1.11

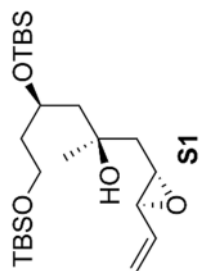
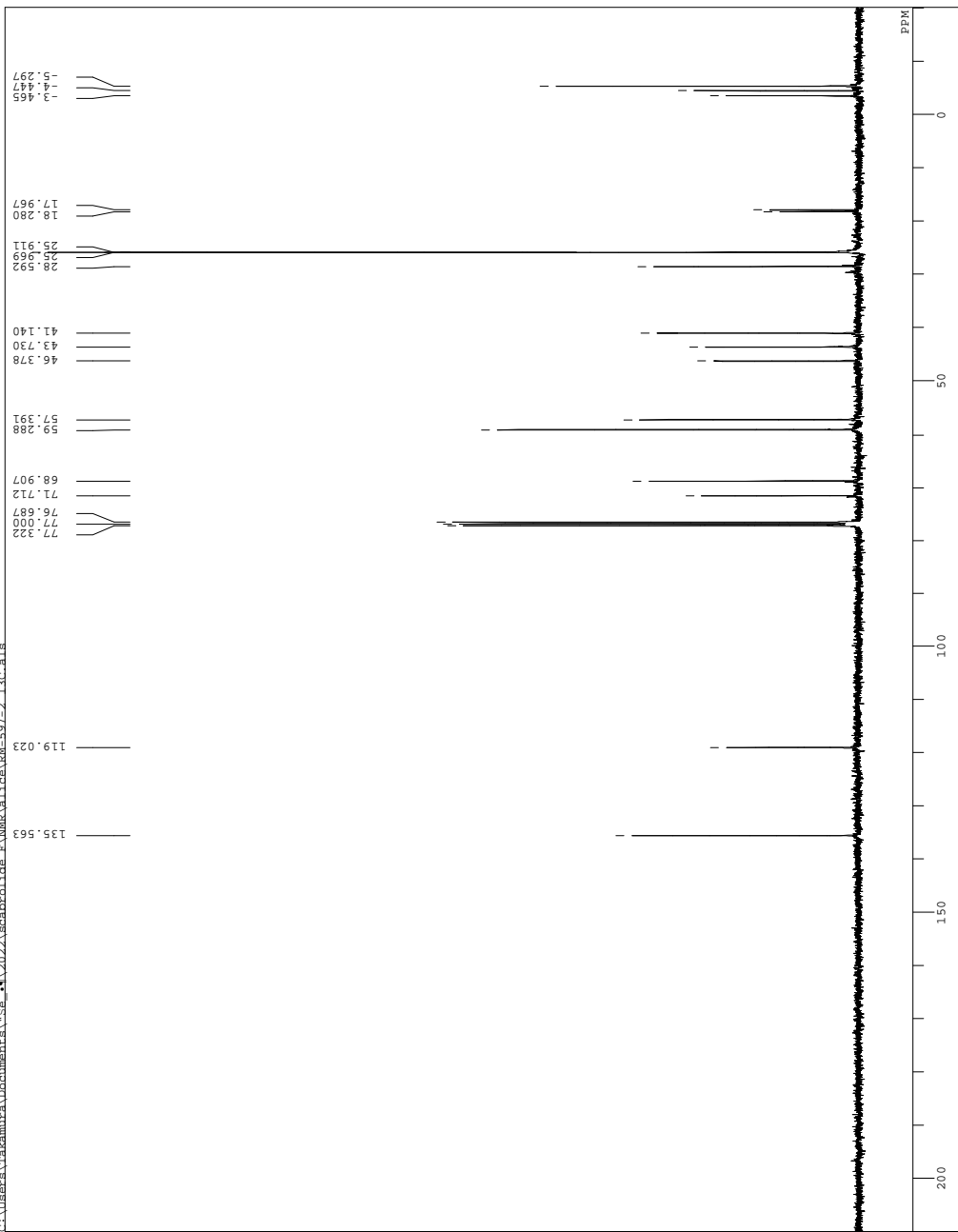






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DPF1E RM-597-2\_13c.a1s  
COMPT RM-597-2\_13c.a1s  
DATEM Wed Jan 08 21:26:31 2014  
P1 00  
EXMOD BCN  
OBFRQ 100.40 MHz  
OBSEF 1025.00 Hz  
OBSEF 3768.00 Hz  
POINT 27173.90 Hz  
FREQU 1.2059 sec  
ACQTM 1.7940 sec  
PD 6.50 usec  
INSTR 1H  
PRGNAME 27.2 c  
SOLVENT CDCL3 77.00 PPM  
P1 2.00 Hz  
RGAIN 24





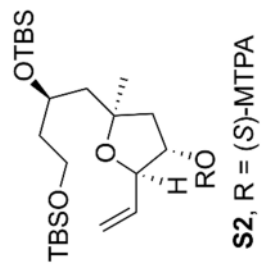
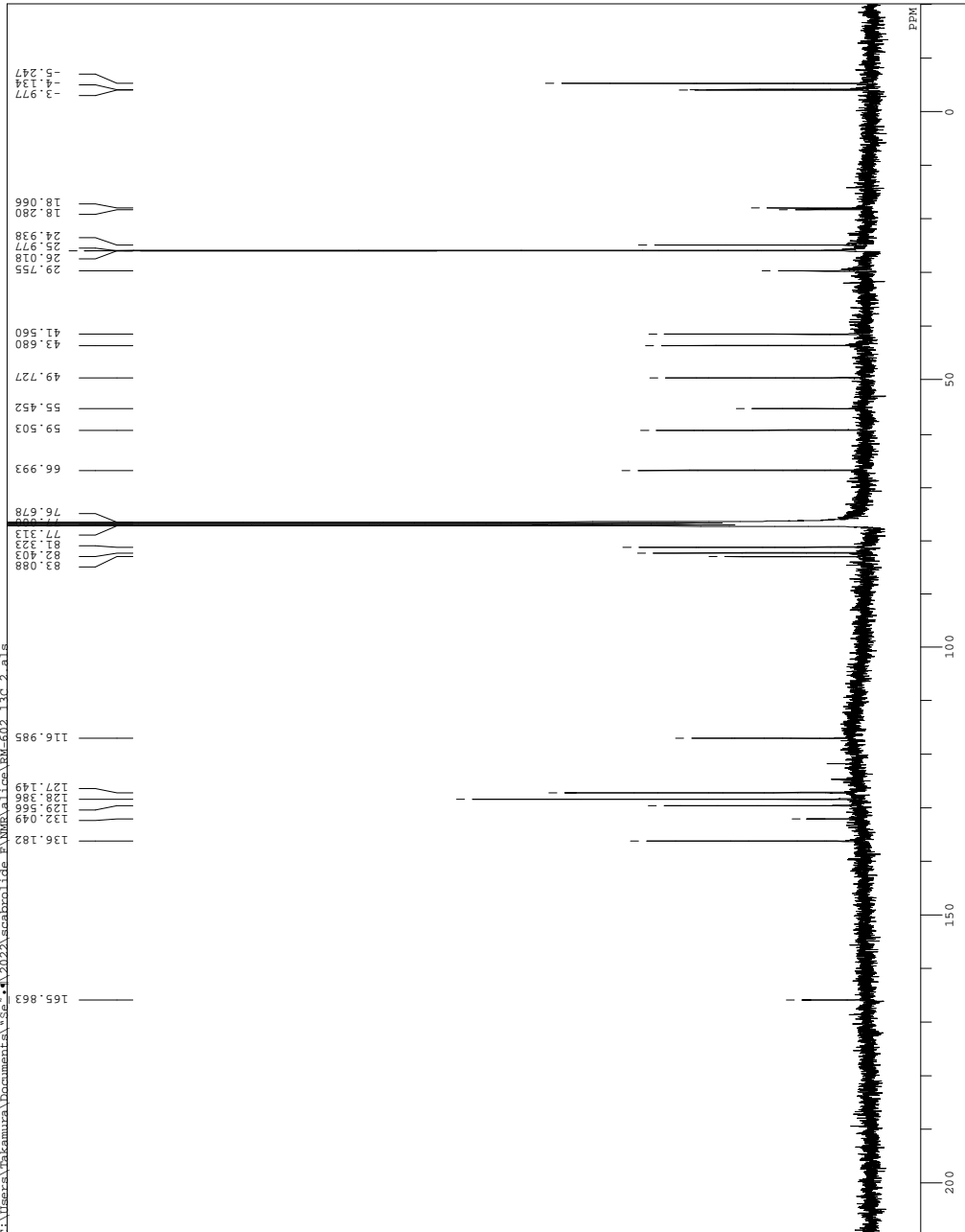






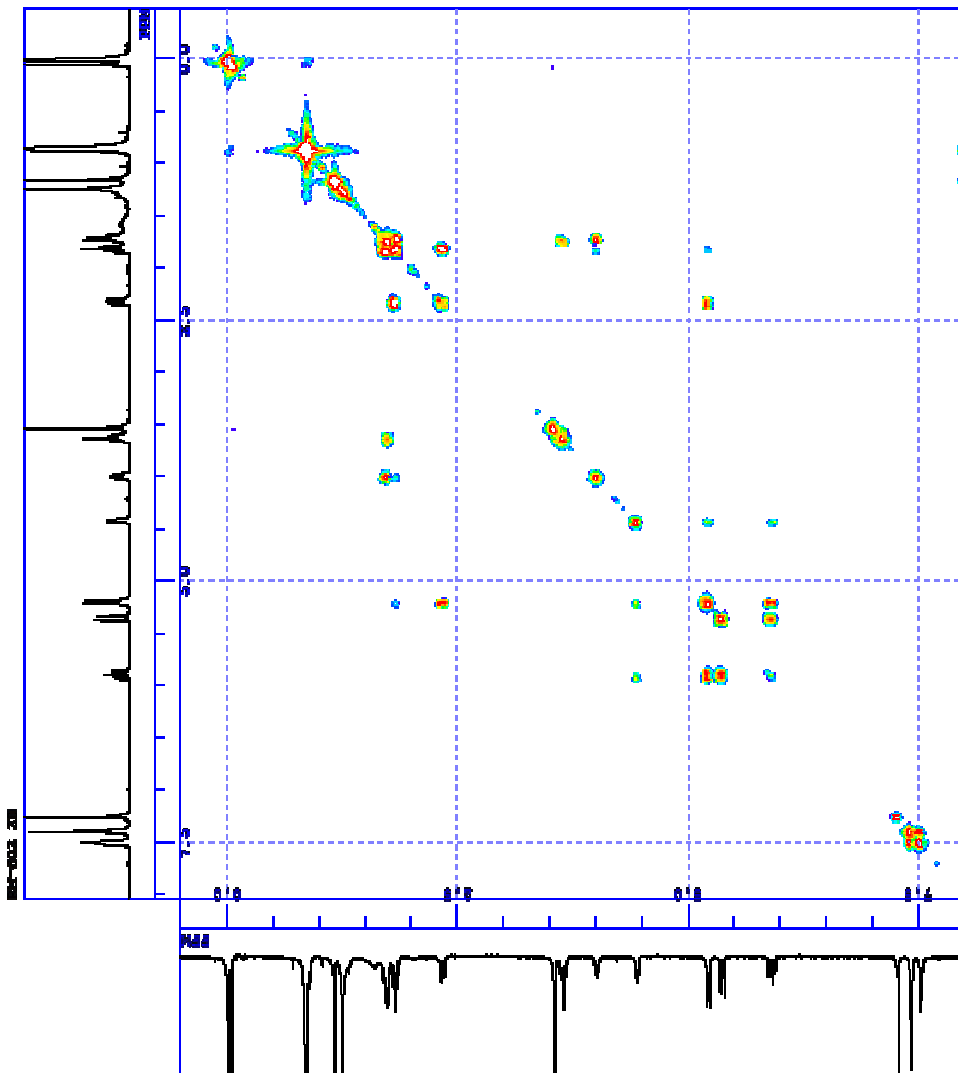
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DFILE RM-602\_13C\_2.als  
 COMMT RM-602  
 DATE\_ TIME 13 Jan 30 09:06:16 2014  
 INSTR 13C  
 EXMID BCM  
 EXMOD BCM  
 ORFNO 100.40 MHz  
 ORFID 10500.00 Hz  
 ORFIR 327.68 Hz  
 POINT 2711056 Hz  
 SCANS 111056 Hz  
 ACQTM 1.2059 sec  
 PUL 1.7900 sec  
 PD1 6.00 usec  
 IRENUC 1H 26.6 c  
 CTXMP CDCL3 77.00 PPM  
 EXREF BF 2.00 Hz  
 RGAIN 23



<sup>1</sup>H-<sup>1</sup>H COSY (400 MHz, CDCl<sub>3</sub>)

C:\Users\msh\Documents\NMR\NMR-002 20.1.13



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MS-002 20

Wed Jul 29 22:45:44 2013

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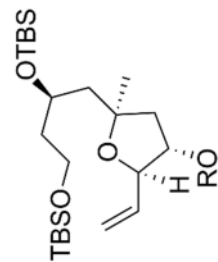
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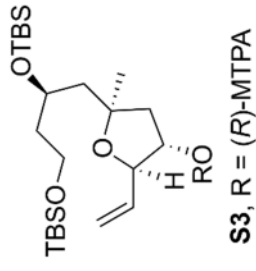
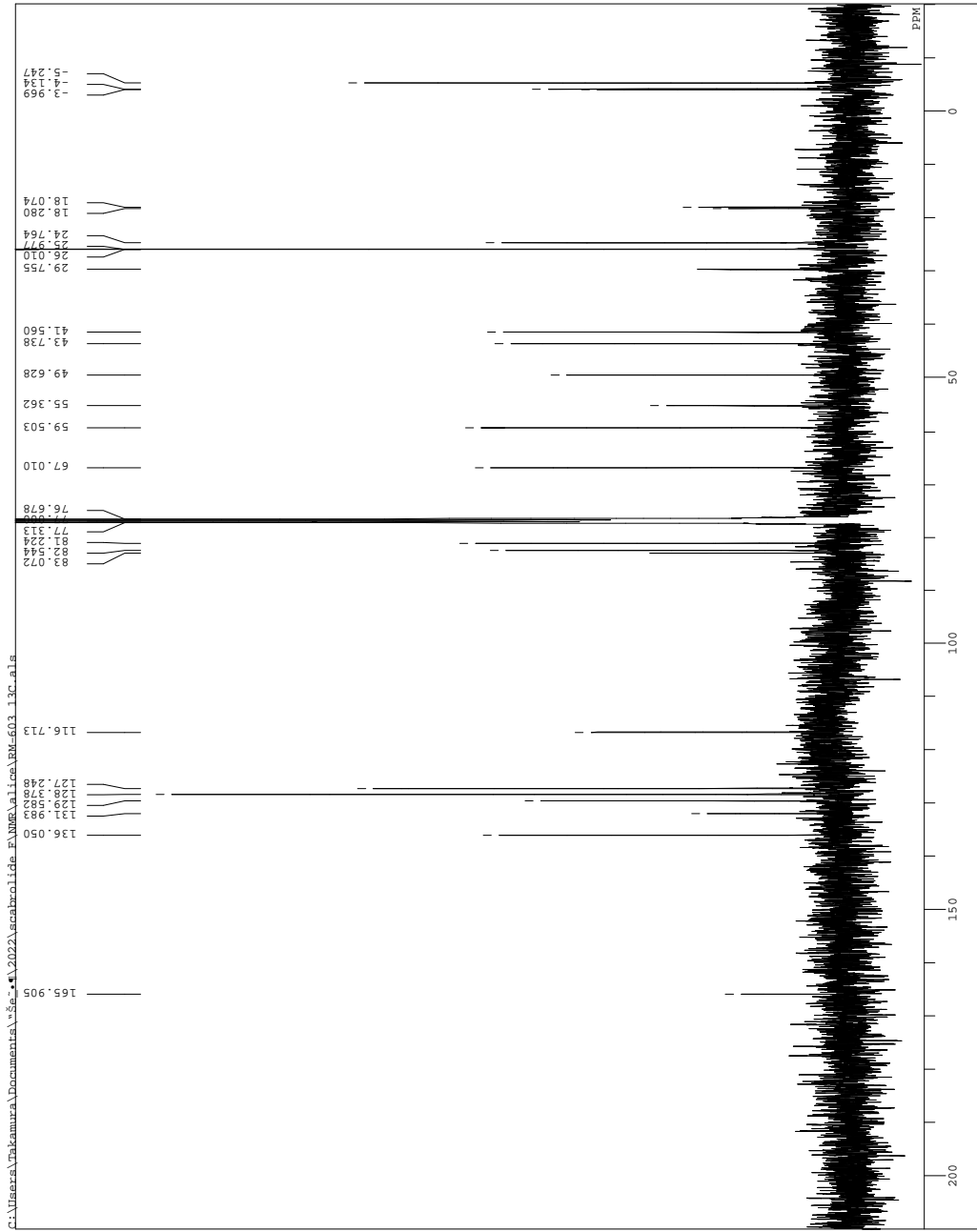
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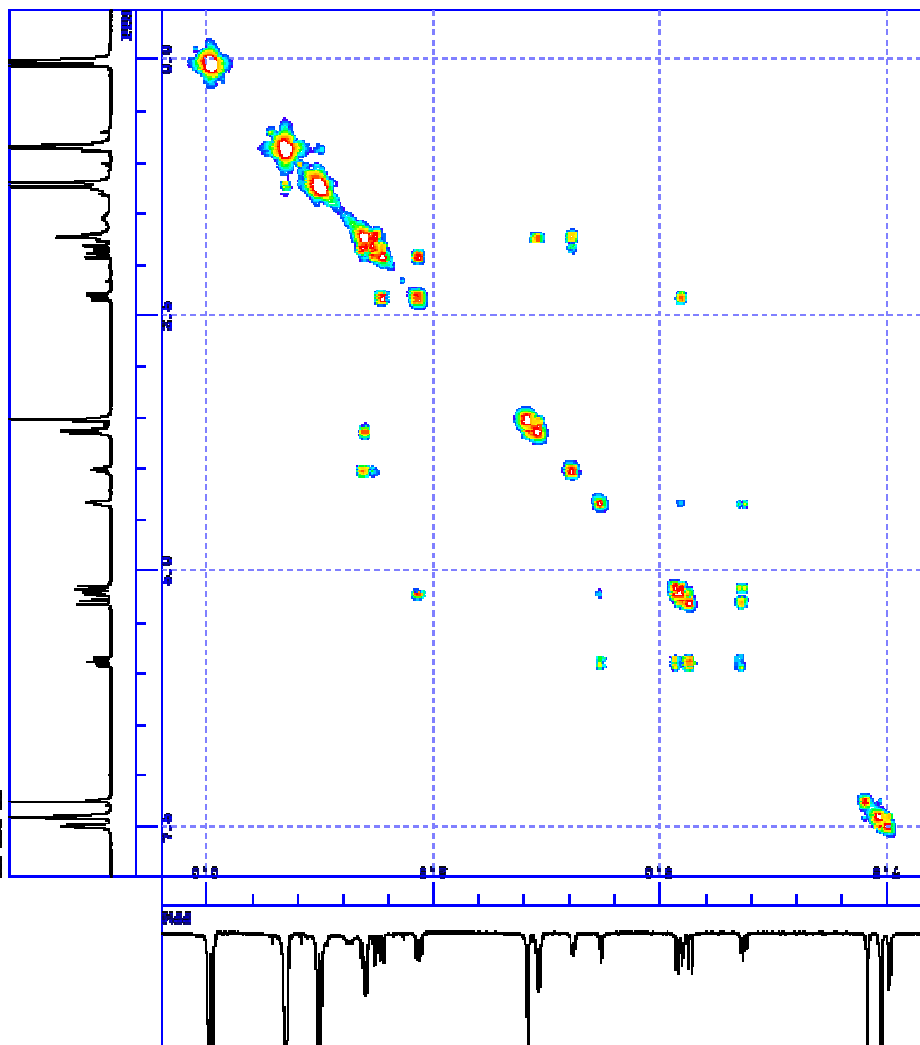


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 COMMIT RM-603  
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 EXPROD BOM  
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 OBSRQ 105300.00 Hz  
 OBSRQ 10532768 Hz  
 POINT 27173.90 Hz  
 PRGDU 1.2659 sec  
 ACQTM 6.80 usec  
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 TRMJC 1H  
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 SLVNT CDCL3 77.00 ppm  
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 RGAIN 2.3

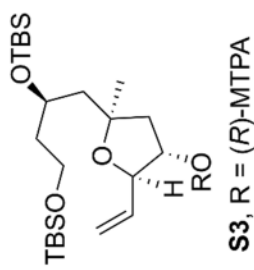


<sup>1</sup>H-<sup>1</sup>H COSY (400 MHz, CDCl<sub>3</sub>)

C:\ProgramData\NMR\NMR\data\FFLF<sup>2</sup>\NMR-608 20 2..als  
 NMR-608 20



NAME	VALUE
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PROBHD2	5MM QNP 1H
PROBHD3	5MM QNP 1H
PROBHD4	5MM QNP 1H
PROBHD5	5MM QNP 1H
PROBHD6	5MM QNP 1H
PROBHD7	5MM QNP 1H
PROBHD8	5MM QNP 1H
PROBHD9	5MM QNP 1H
PROBHD10	5MM QNP 1H
PROBHD11	5MM QNP 1H
PROBHD12	5MM QNP 1H
PROBHD13	5MM QNP 1H
PROBHD14	5MM QNP 1H
PROBHD15	5MM QNP 1H
PROBHD16	5MM QNP 1H
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PROBHD18	5MM QNP 1H
PROBHD19	5MM QNP 1H
PROBHD20	5MM QNP 1H
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PROBHD23	5MM QNP 1H
PROBHD24	5MM QNP 1H
PROBHD25	5MM QNP 1H
PROBHD26	5MM QNP 1H
PROBHD27	5MM QNP 1H
PROBHD28	5MM QNP 1H
PROBHD29	5MM QNP 1H
PROBHD30	5MM QNP 1H
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PROBHD32	5MM QNP 1H
PROBHD33	5MM QNP 1H
PROBHD34	5MM QNP 1H
PROBHD35	5MM QNP 1H
PROBHD36	5MM QNP 1H
PROBHD37	5MM QNP 1H
PROBHD38	5MM QNP 1H
PROBHD39	5MM QNP 1H
PROBHD40	5MM QNP 1H
PROBHD41	5MM QNP 1H
PROBHD42	5MM QNP 1H
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PROBHD95	5MM QNP 1H
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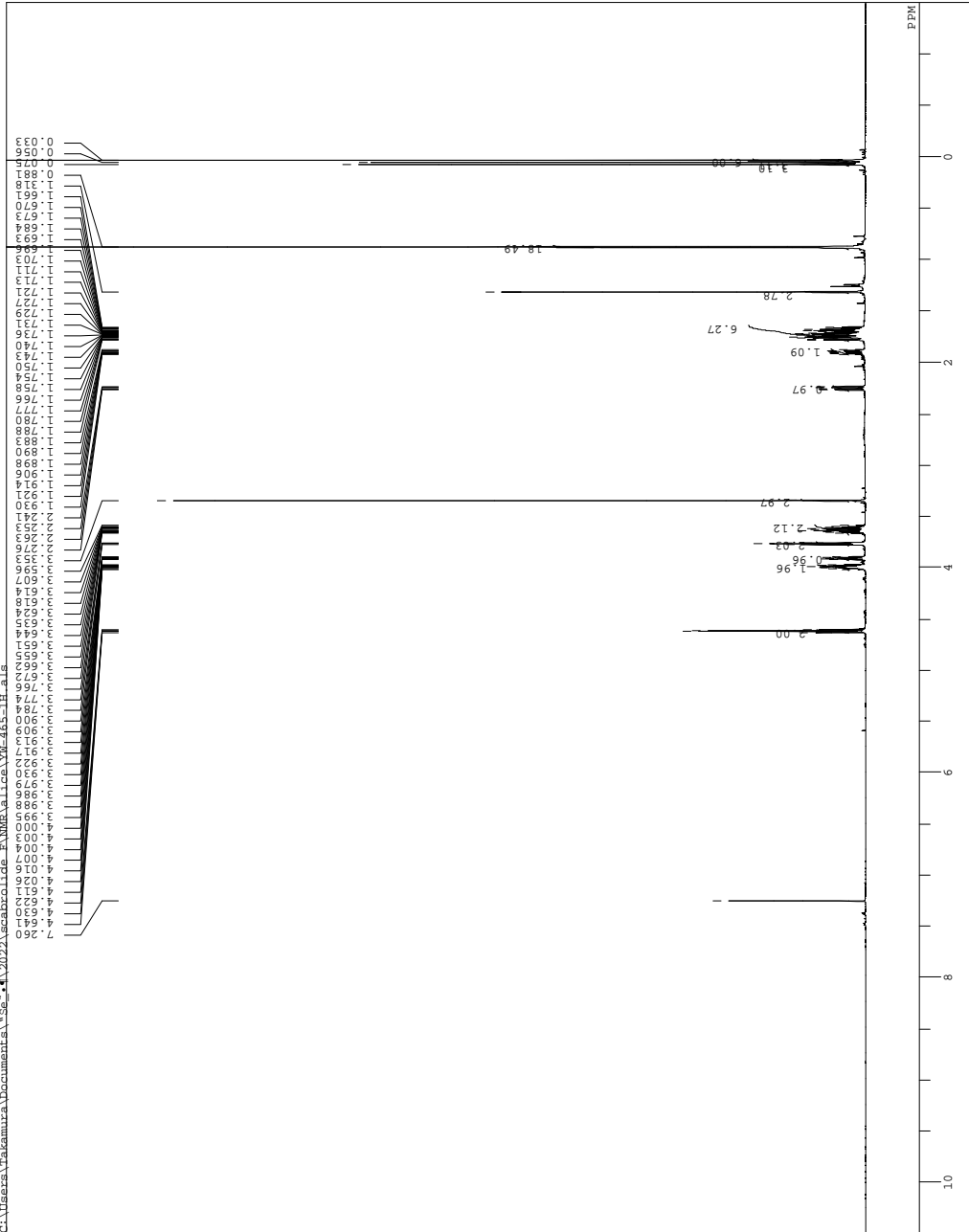








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 OBF2 0.60 Hz  
 OBFIN 32768 Hz  
 POINT 9e15.32  
 SCANS 32  
 ACQTM 3.4079 sec  
 P1 1.570 sec  
 P2 5.470 sec  
 IRNUC cdcl3 20.0 c  
 CTMP 7.26 ppm  
 EXREF 0.12 Hz  
 BFA 0.20  
 RGAIN

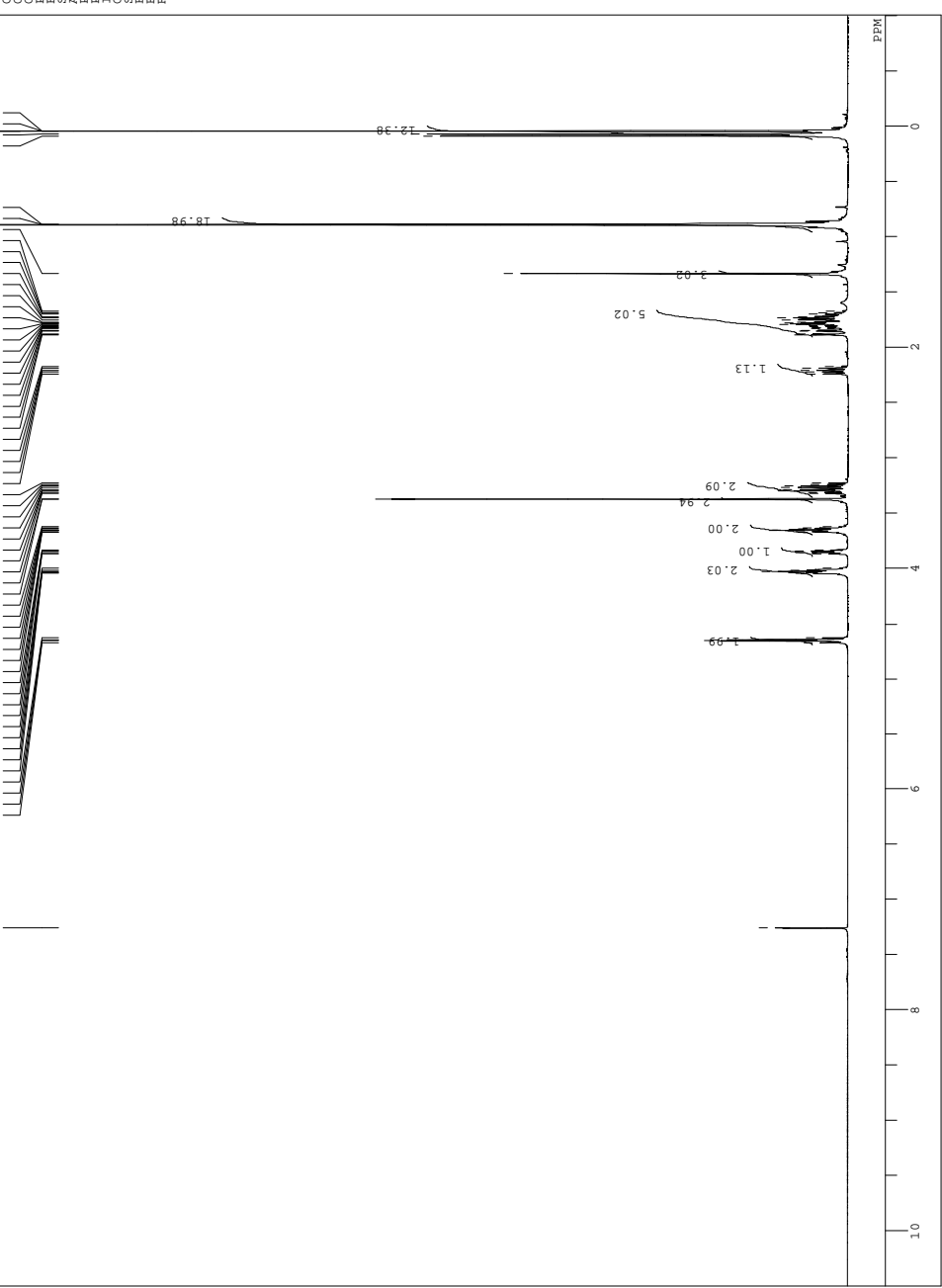




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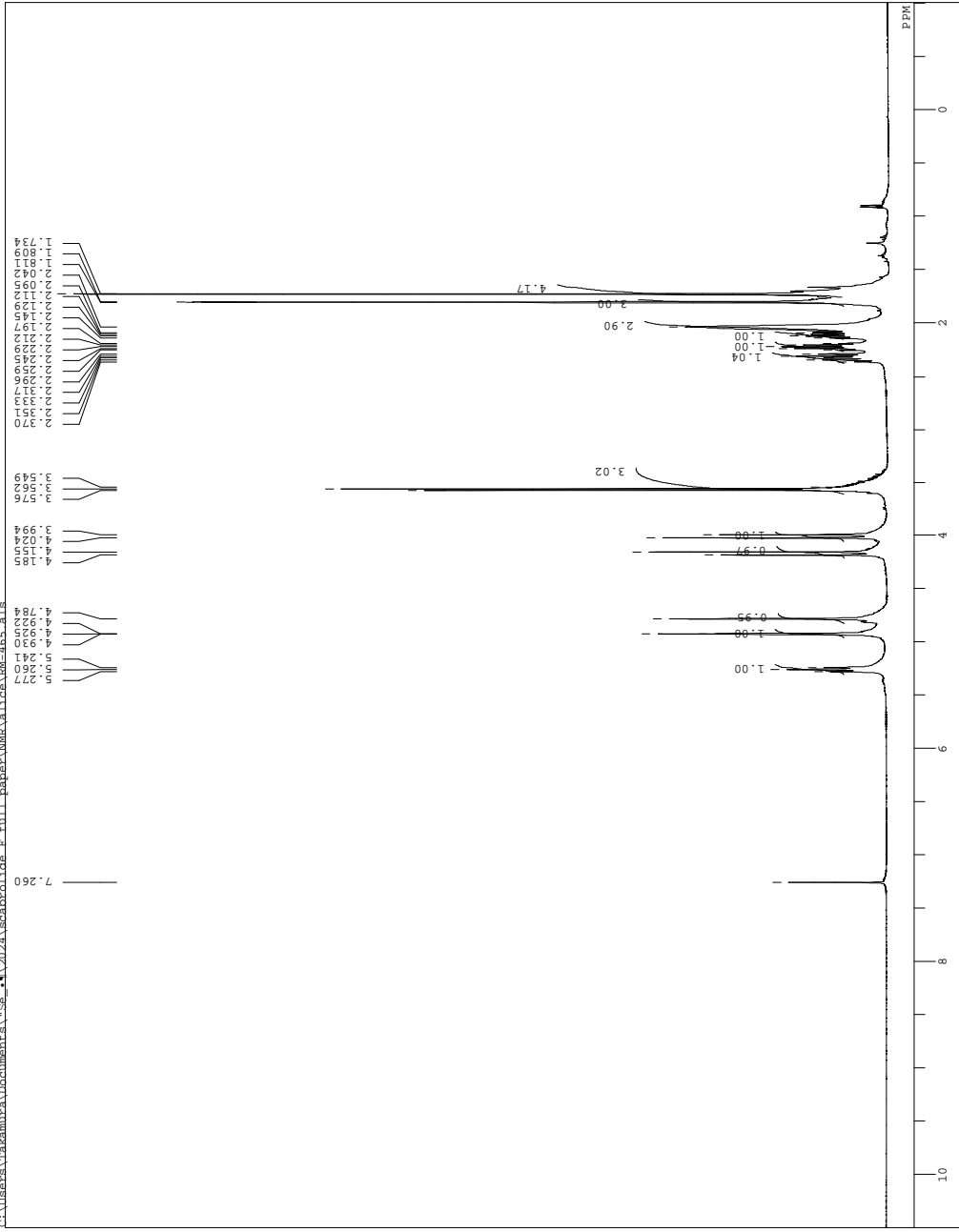
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OBFTN   10300.00 Hz
POINT   32768
SFOU    7993.60 Hz
AQTM    4.0993 sec
PD      2.9010 usec
PC      6.40 usec
IRNUC  1H
CTEMP   23.5 c
SOLVENT CDCL3
NS      7.26 PPM
DS      0.112 Hz
SF      0.112 Hz
RGAIN   1.12
  
```



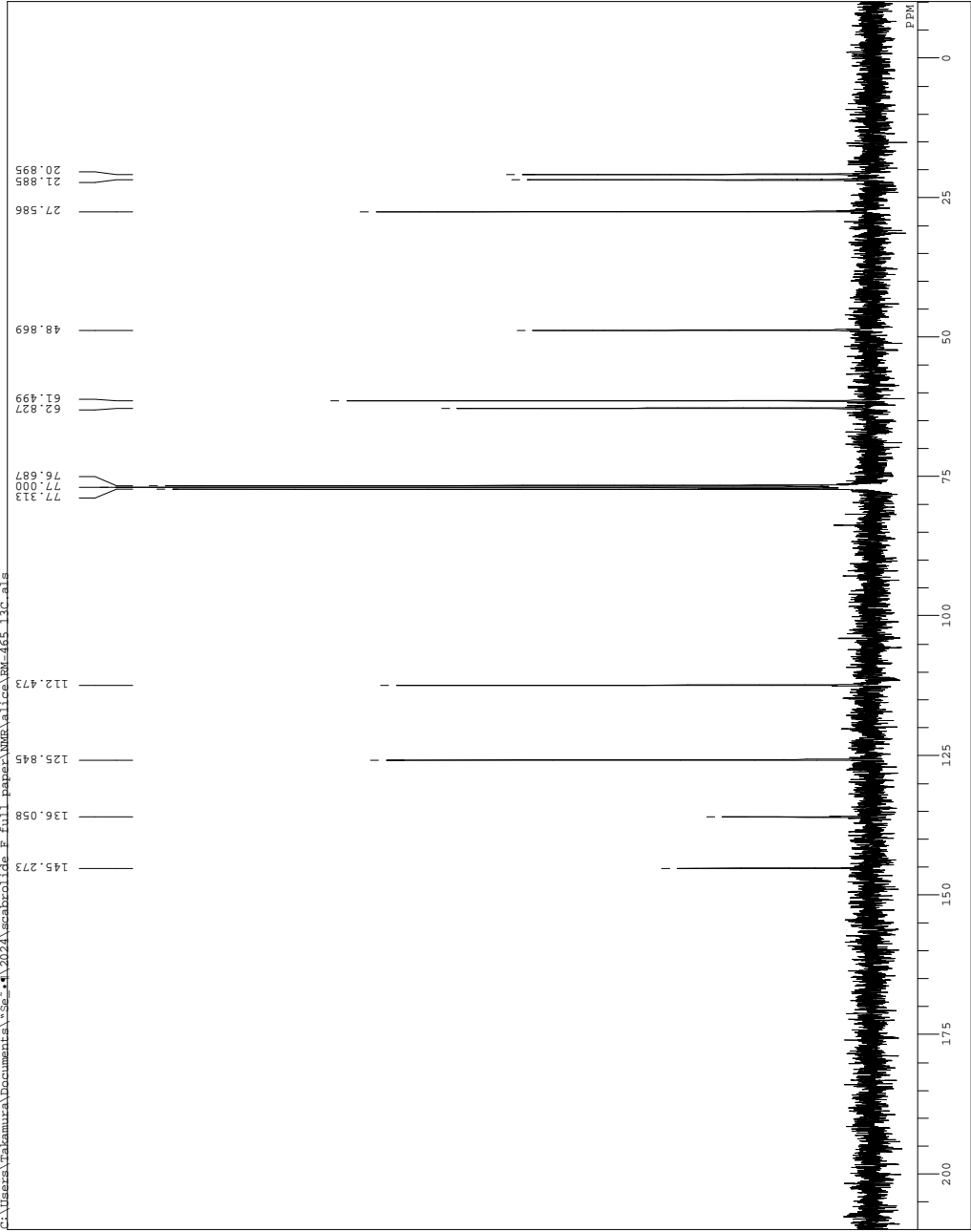
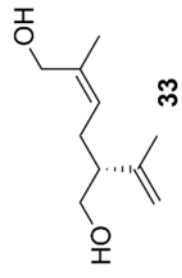


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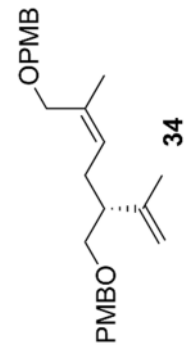
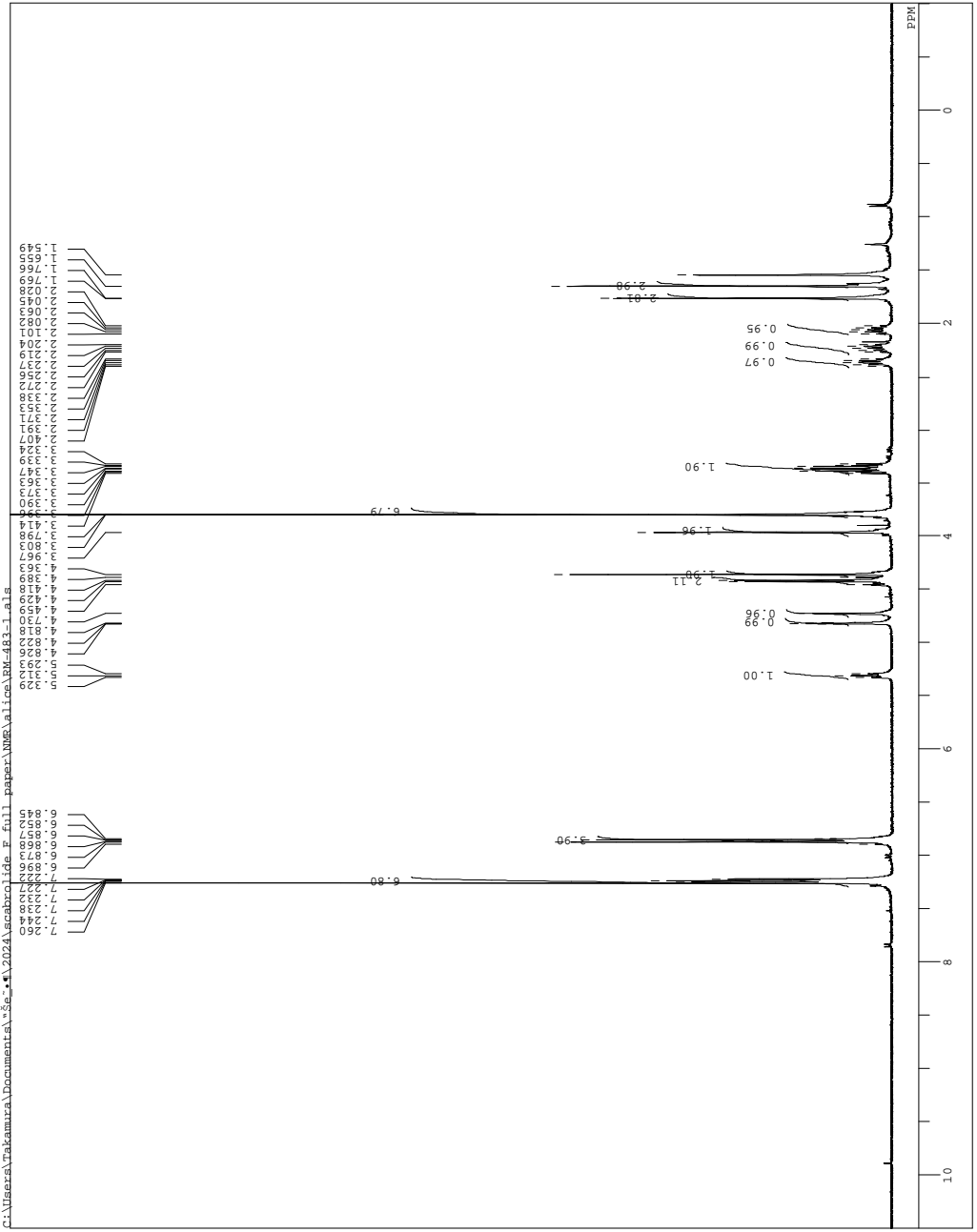
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 POINT 327.68 Hz  
 FREQ 7993.60 Hz  
 ACQ 4.0993 sec  
 PD 2.9010 sec  
 PRG 6.40 usec  
 PULSE 1H  
 FWHM 27.9 c  
 CTMP CDCL3 7.26 ppm  
 SLOPE  
 REF 0.12 Hz  
 RGAIN 0.12



C:\Users\takamura\Documents\5e\_4\2024\acsbrolide\_F\_full\_paper\NMR\valid\RM-465\_13C\_als  
 DFILE RM-465\_13C\_als  
 COMMT RM-465  
 CONV 13C  
 DATE\_13C Dec 02 19:07:13 2013  
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 OBRIN 10500.00 Hz  
 POINT 32768  
 SCMS 2717200 Hz  
 ACQTM 1.2059 sec  
 PD 1.7940 sec  
 P1 6.60 usec  
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 CTMP CDCL3 28.7 C  
 EXREF 77.00 PPM  
 EXREF 2.00 Hz  
 BFA  
 KGAIN 2.23

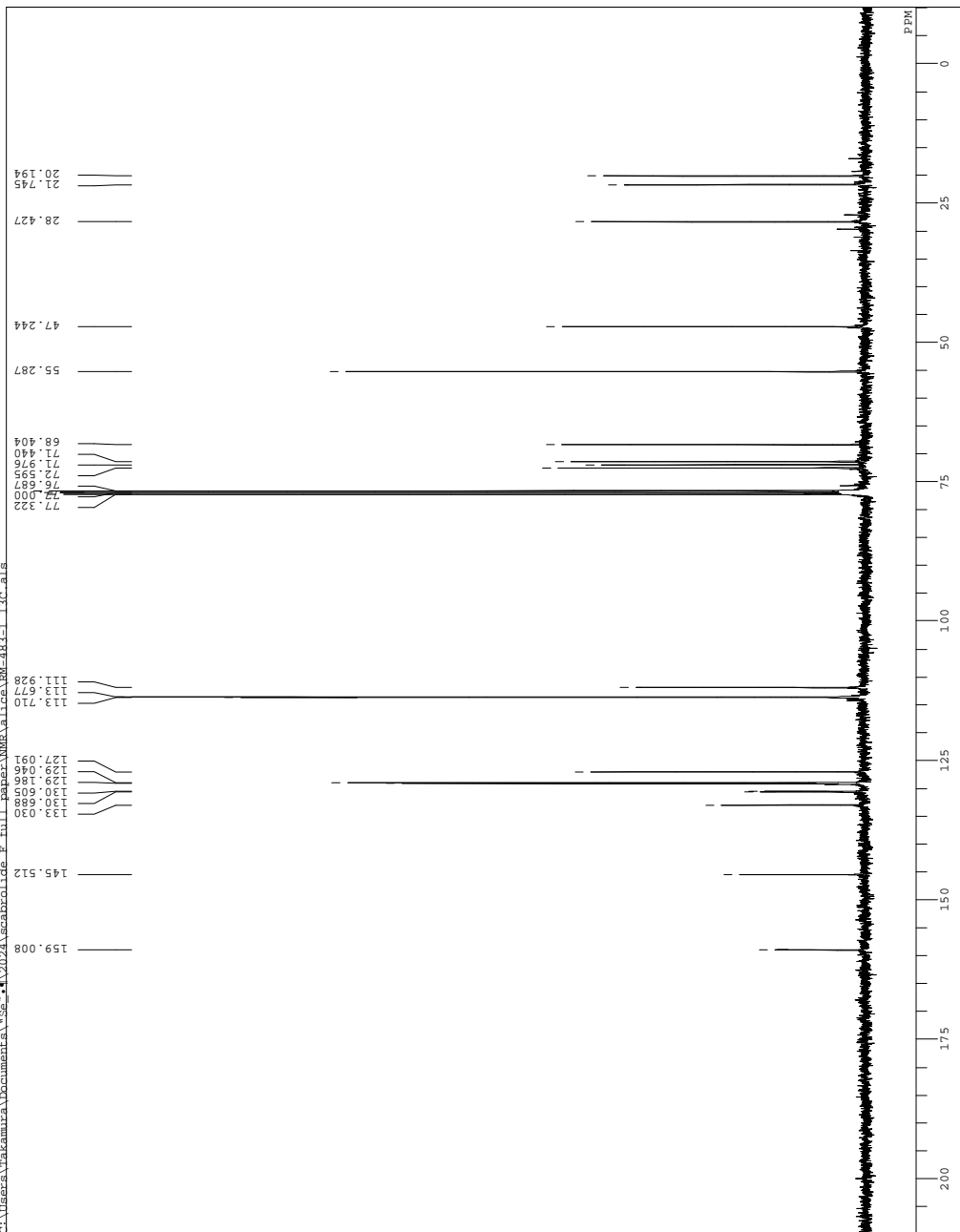


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 DATIM Wed Dec 04 15:26:39 2013  
 DELOC 1H  
 M NS  
 OBFRQ 399.65 MHz  
 OBSST 124.00 KHz  
 PULPROG zgpg30  
 PZ 100  
 FREQ 7993.60 Hz  
 ACQNS 4.0993 sec  
 PD 2.9010 sec  
 PD 6.40 usec  
 PWD 1H  
 CTMP 25.0 c  
 SLVNT CDCL3  
 REFP 7.26 ppm  
 REF 0.15 ppm  
 RGAIN 0.20



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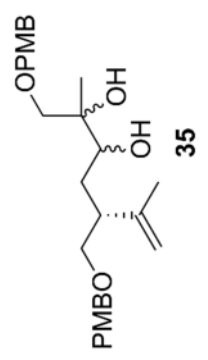
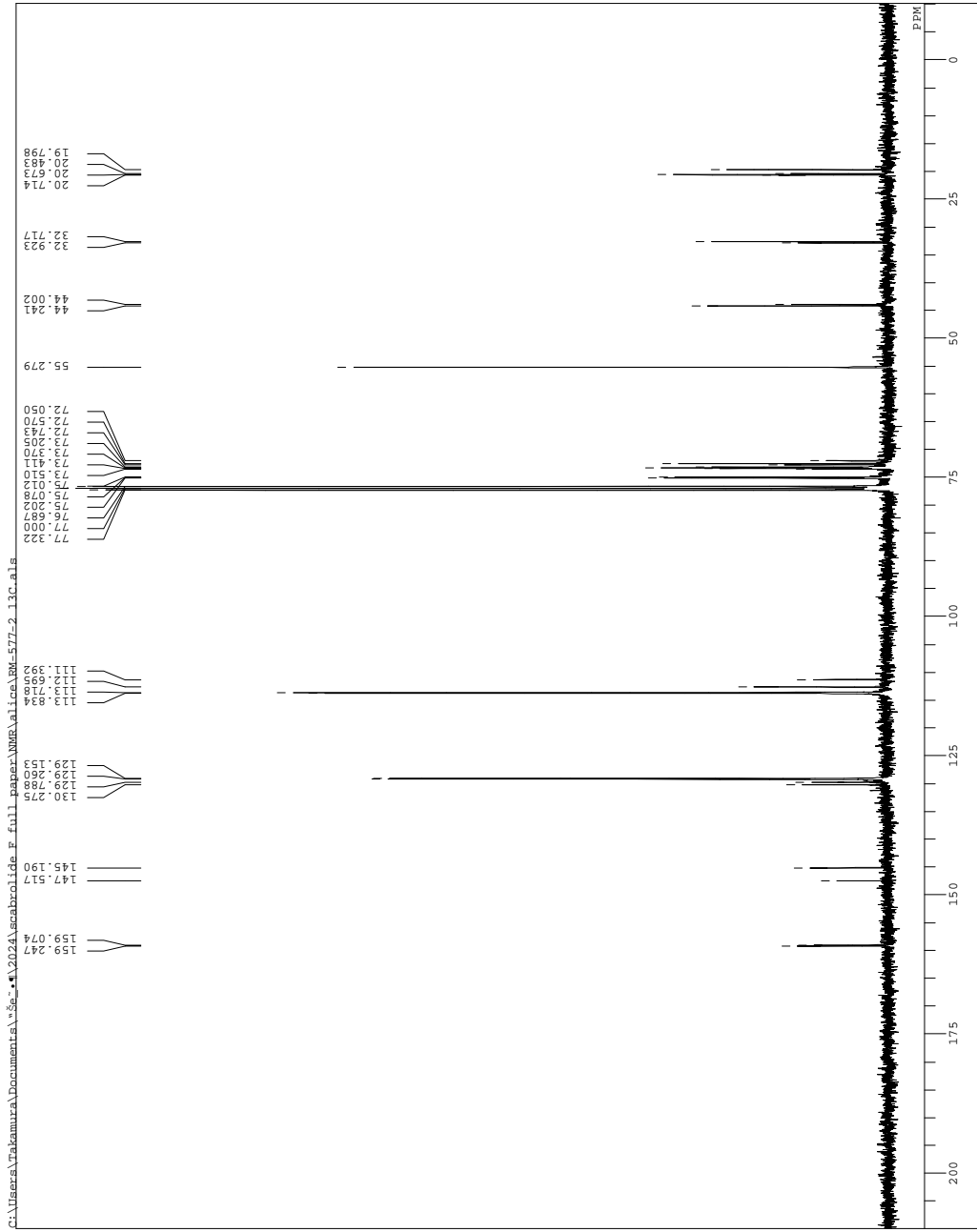
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OBFTN 10540.00 Hz  
POINT 32768 Hz  
FREQ 271714.4 Hz  
SFO 271714.4 Hz  
ACQTM 1.2059 sec  
PL 1.7940 sec  
PULPROG zgpg30  
PRGNAME 13C-1H  
INSTRUM spect  
C13PRGNAME zgpg30  
C13PULPROG zgpg30  
C13PC13 28.7 c  
C13PC13 CDCL3  
C13PC13 77.00 ppm  
SFO 100.40 MHz  
BF 2.00 Hz  
RGAIN 23







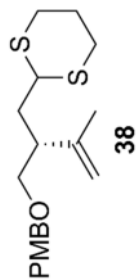
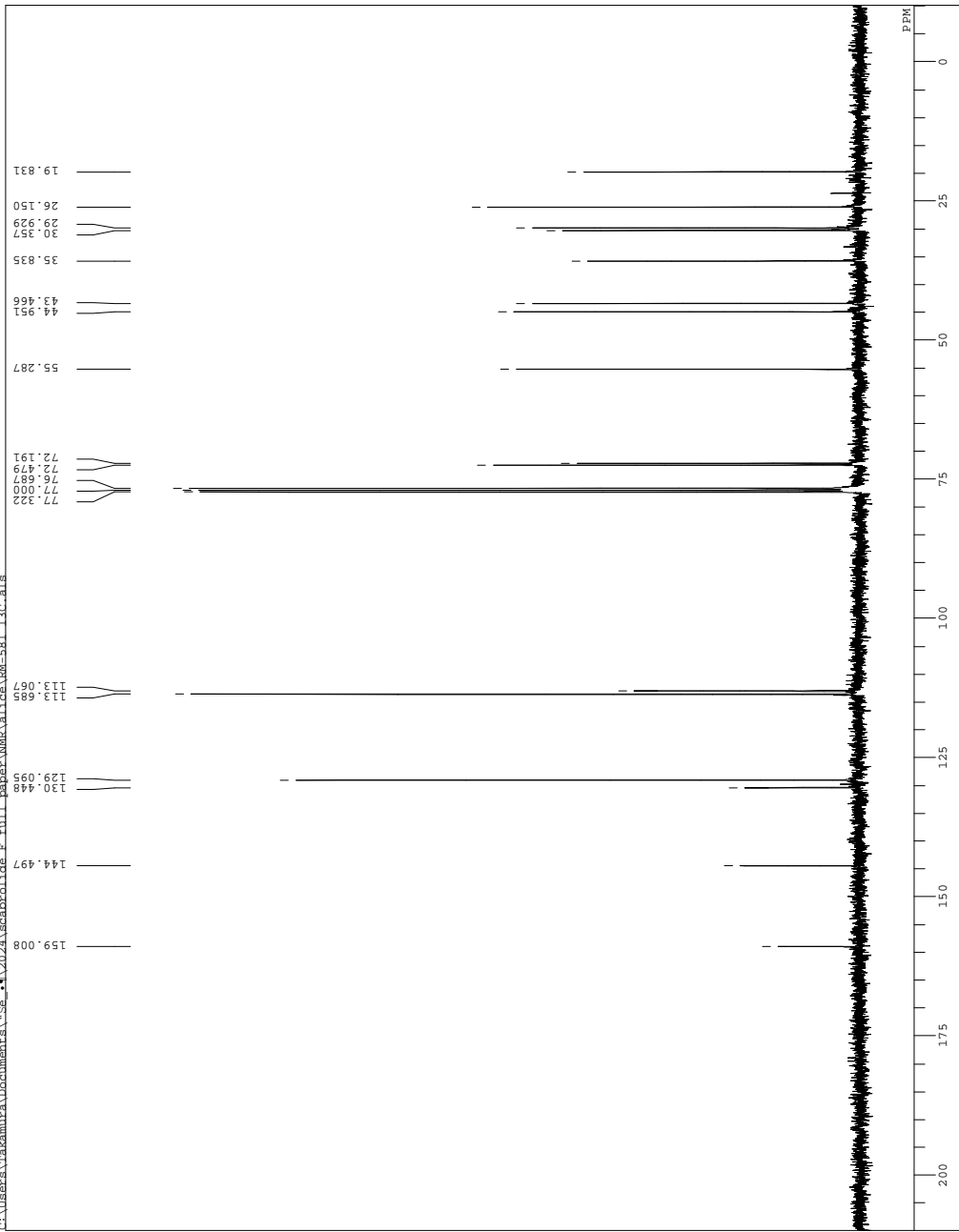
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 PULPROG zgpg30  
 POINT1 332768 Hz  
 FREQ0 2717190 Hz  
 ACOU1 1.2655 sec  
 PD 1.7940 sec  
 INJ1 6.80 usec  
 INJ2 1H  
 TEMPC 28.9 c  
 CTEMP CDCL3  
 SILV1 BF  
 SUFF BF  
 RGAIN 2.00 Hz  
 23





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DRIF RM-581\_13C\_als  
COM1 RM-581  
DATE Thu Dec 12 18:35:11 2013  
TIME 18:35:11  
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PROCNO 1  
PROCPS 1  
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ORFREQ 100.40 MHz  
OBSFREQ 100.40 MHz  
NUC1 13C  
NUC2 13C  
PULPROG zgpg30  
FREQ 27173.90 Hz  
AQ 0.05  
RG 1.2055 sec  
PD 1.7940 sec  
TE 300.2 K  
WALTZ16 1H  
WALTZ16 6.80 usec  
C13 28.8 c  
SOLVENT CDCl3  
SOLVENT 77.00 ppm  
NS 2048  
DS 4  
BF 2.00 Hz  
RGAIN 23





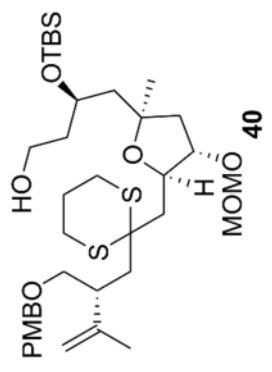
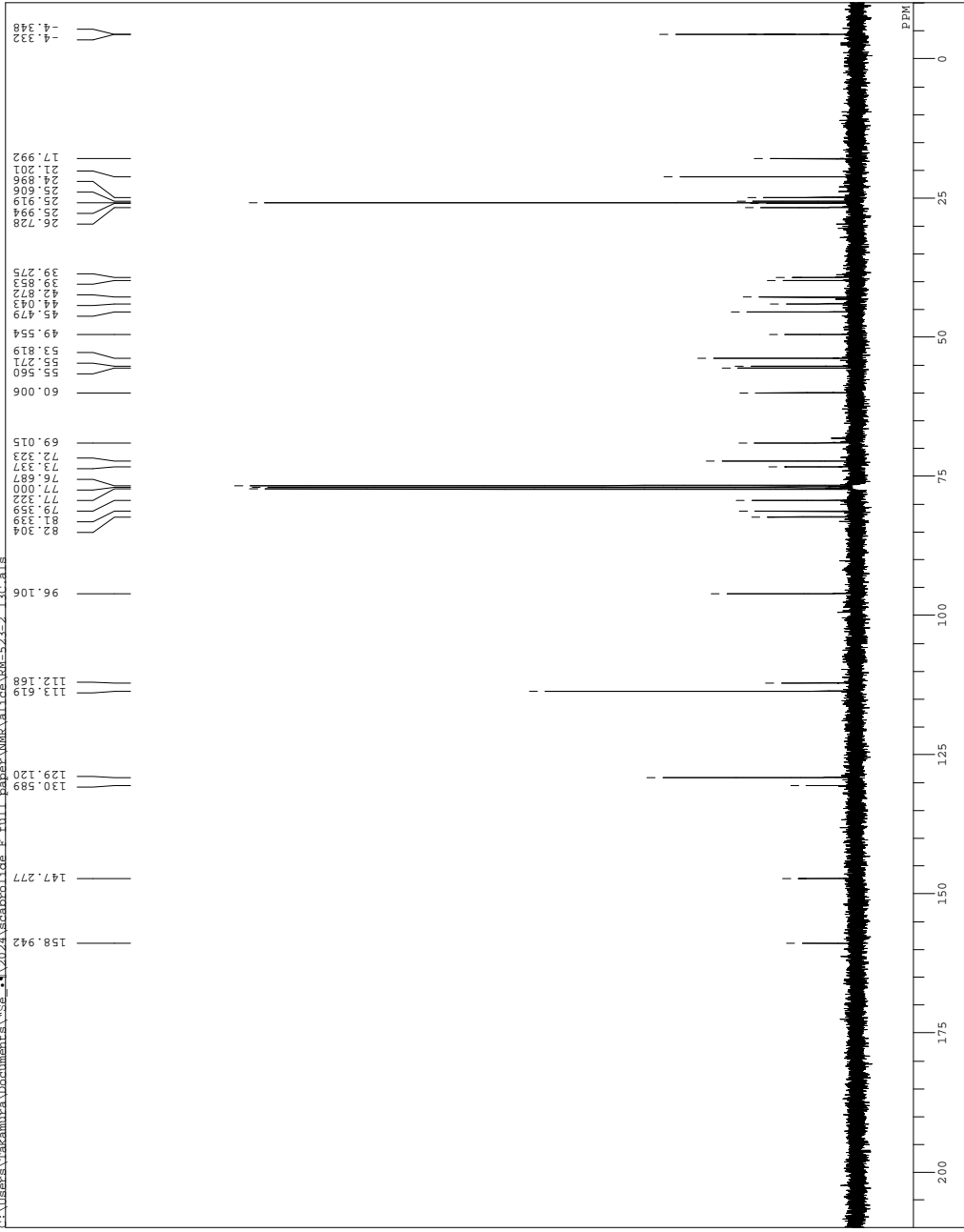




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F2F1R RM-523-2_13C-als
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DATIM Sat Feb 08 11:19:17 2014
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DETC  13C
PULPROG zgpg30
OBPFRQ 100.40 MHz
OBSECT 10125.00 KHz
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
FREQ 27173.30 Hz
SFO 100.625 MHz
AQ 0.099 sec
RG 1.7940 sec
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RGAIN 0.23
  
```



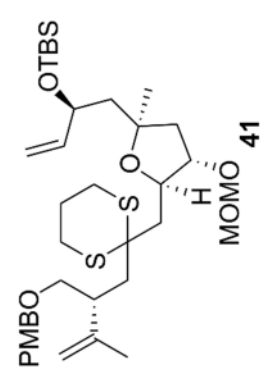
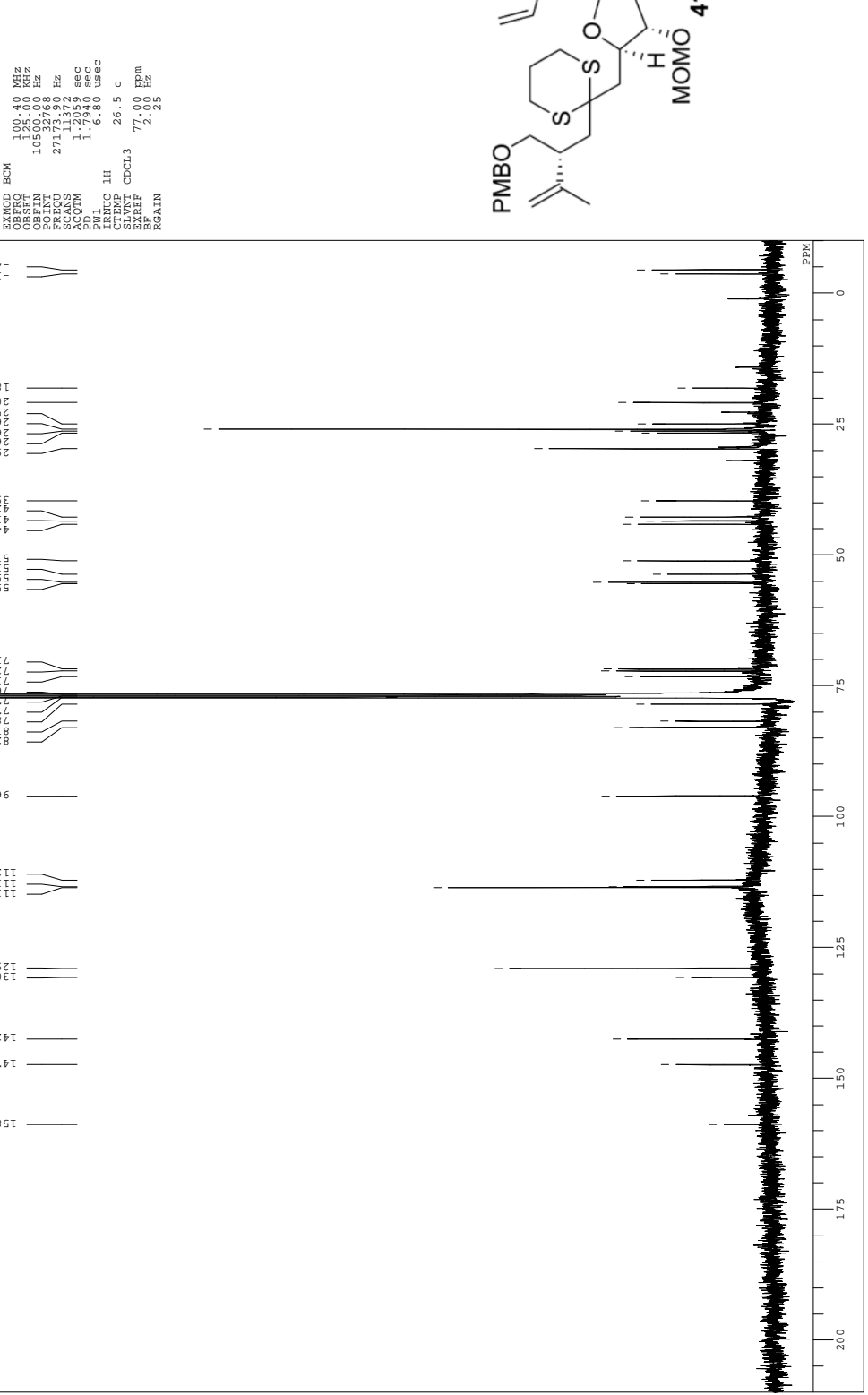




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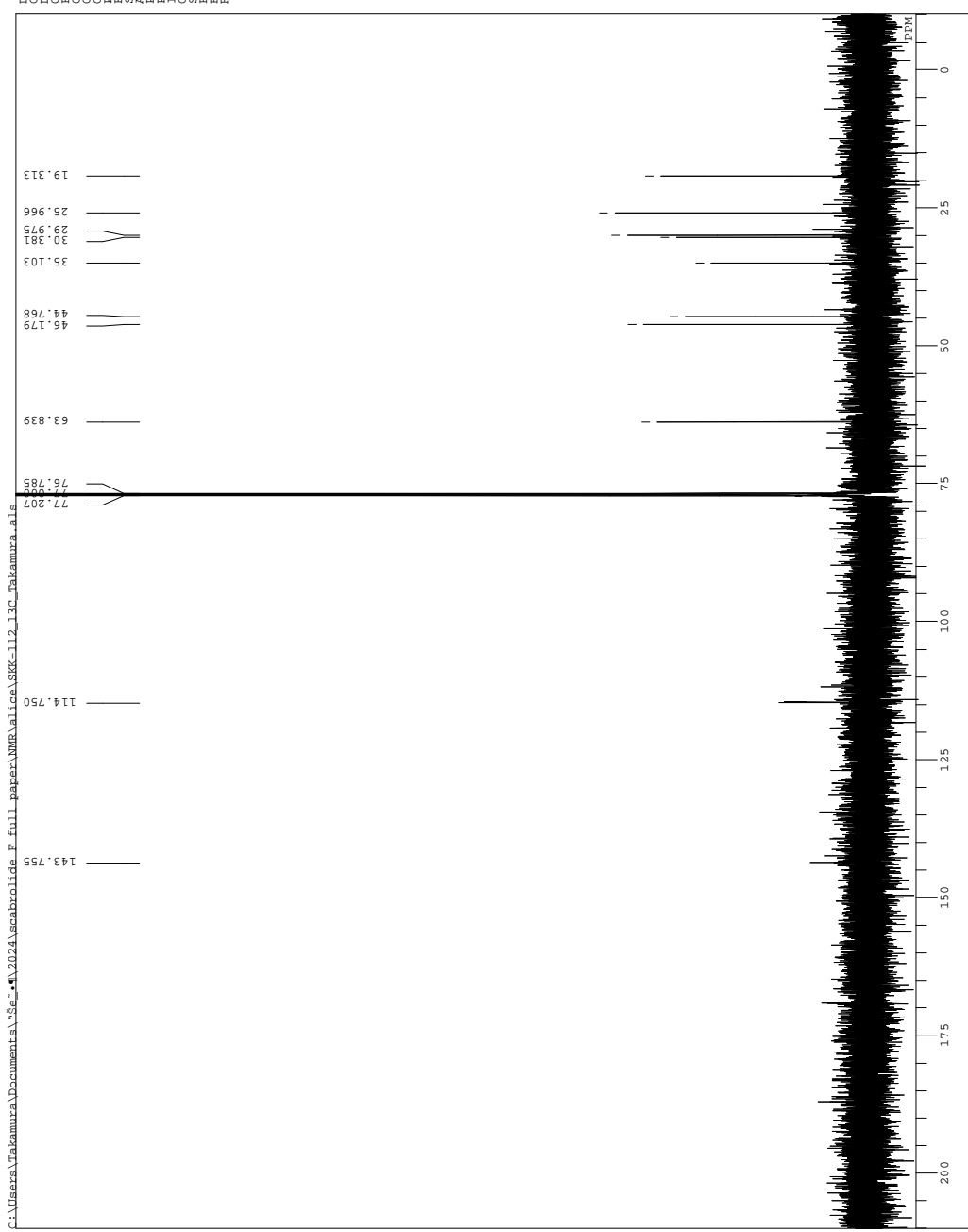
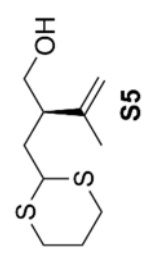
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ORPRO 13C
ORFRO BCR
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OBSF1 125.00 MHz
OBSF2 105.32768 Hz
PULPR 12.000000
PULPT 27173.90 Hz
SCANS 1.7652
PD2RN 1.7940 sec
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PMTIC 1H
CTEMP 26.5 c
SLVNT CDCL3
SREF 77.00 PPM
RGAIN 2.25
  
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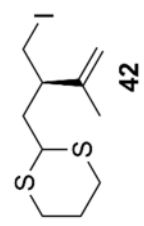
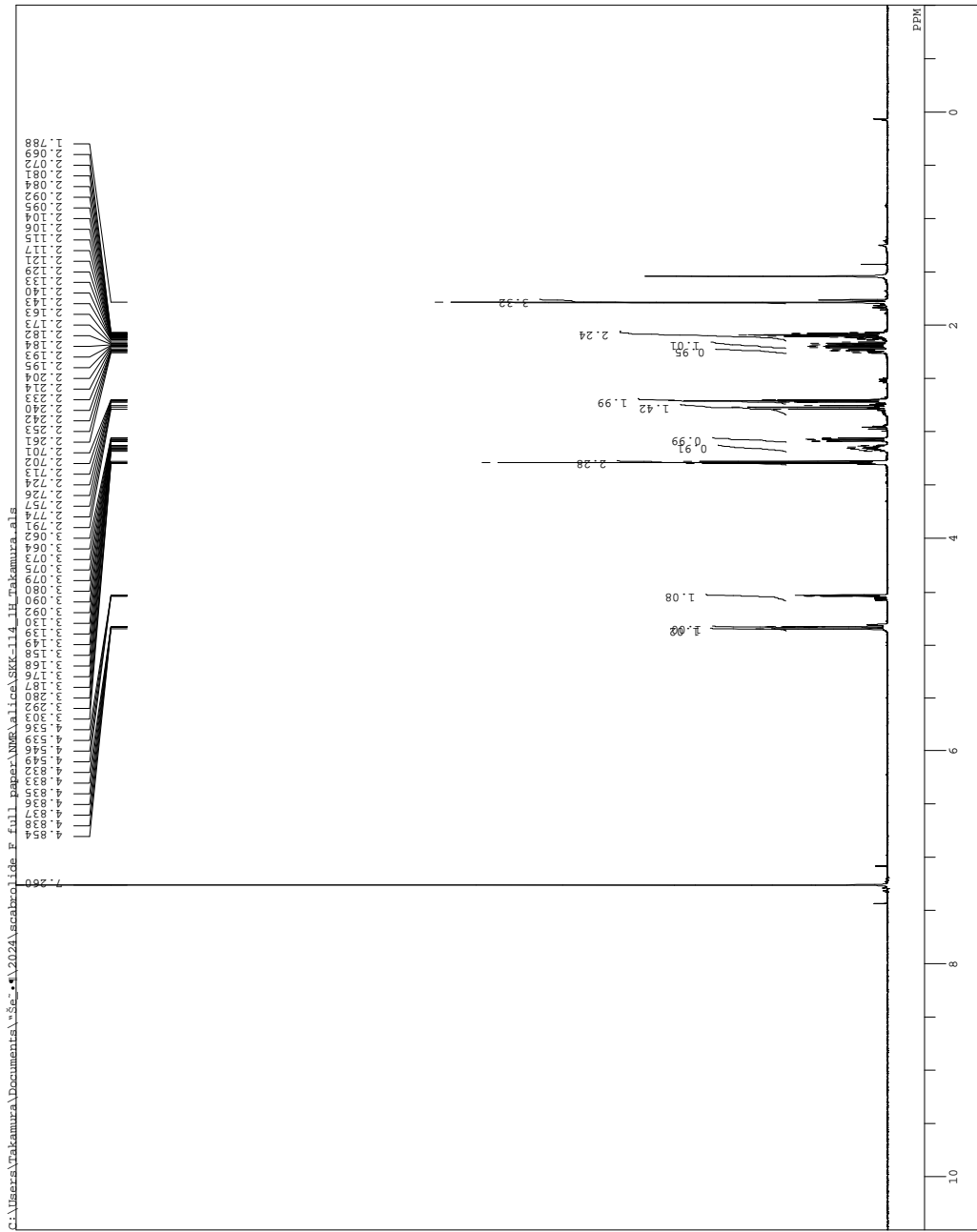




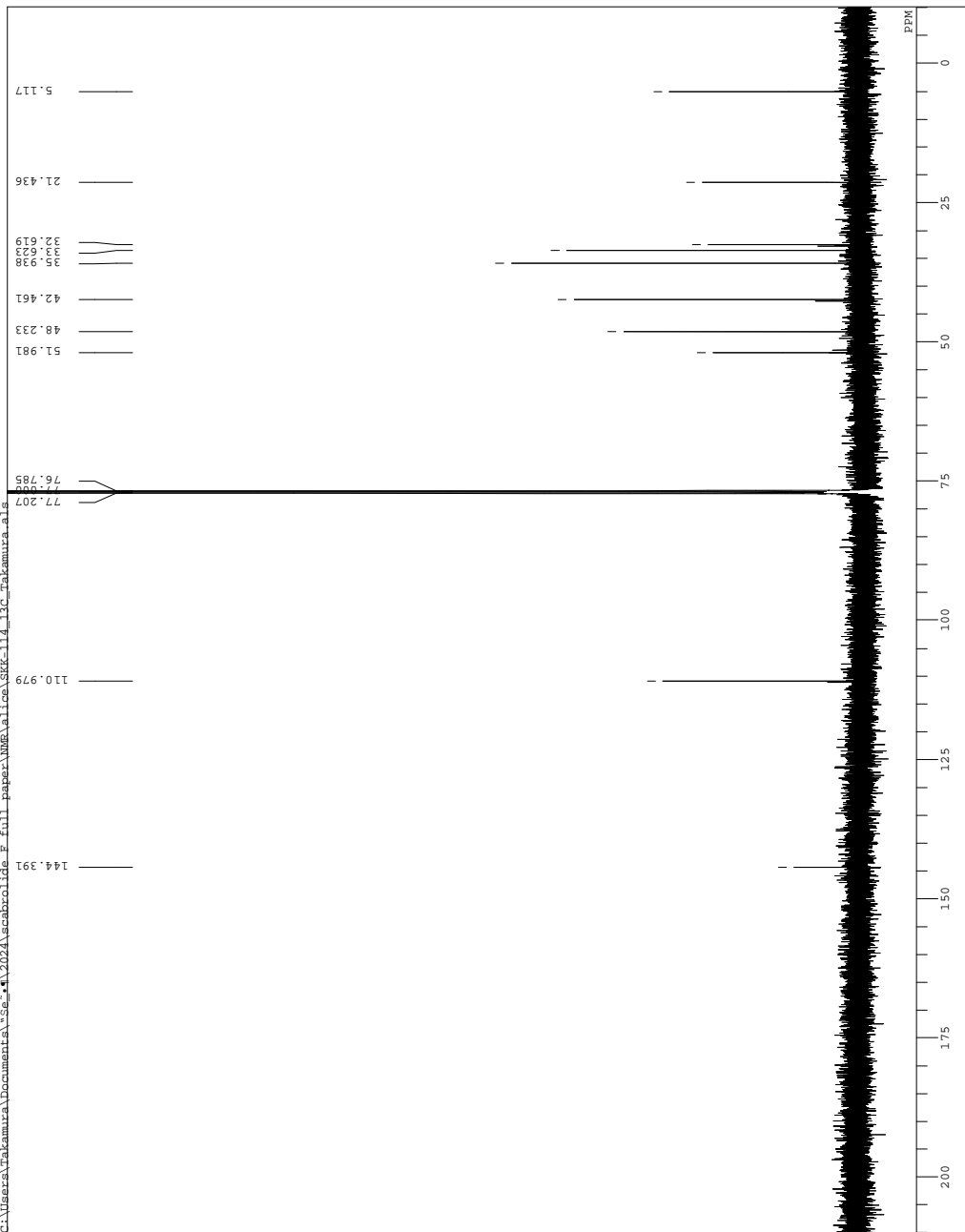
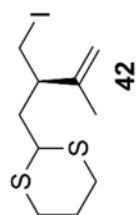
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 OBSPT 6.72 kHz  
 POINT 37878 Hz  
 FREQU 37878.79 Hz  
 ACQTM 0.8651 sec  
 PD 2.1349 sec  
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 SLOWP 0.12 Hz  
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 RGAIN 60



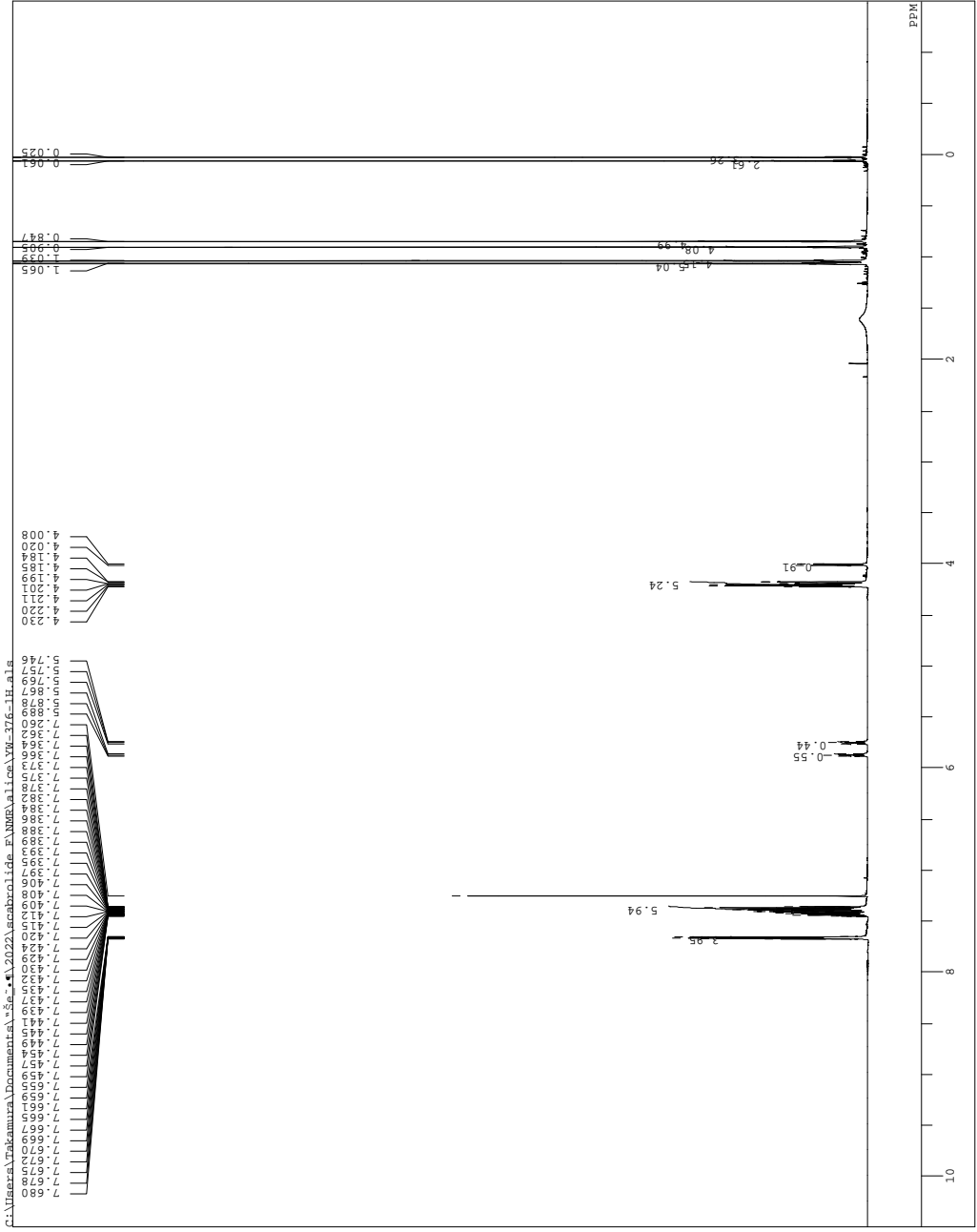
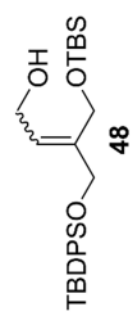
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 OBSF1 0.60 Hz  
 FREQU 9635.98 Hz  
 SCANS 32  
 ACQTM 3.4979 sec  
 PW1 1.5765 usec  
 IRNUC  
 CLINT 55.0 c  
 SLVNT cdcl3  
 EXREF 7.26 ppm  
 RGAIN 0.12 Hz



C:\Users\takamura\Documents\Se\*\2024\scabrolicide\_F\_full\_paper\NMR\alice\SKK-114\_13C\_takamura.sls  
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 OBFM 8.70 Hz  
 POINT 378768 Hz  
 SCANS 64  
 ACQTM 0.8651 sec  
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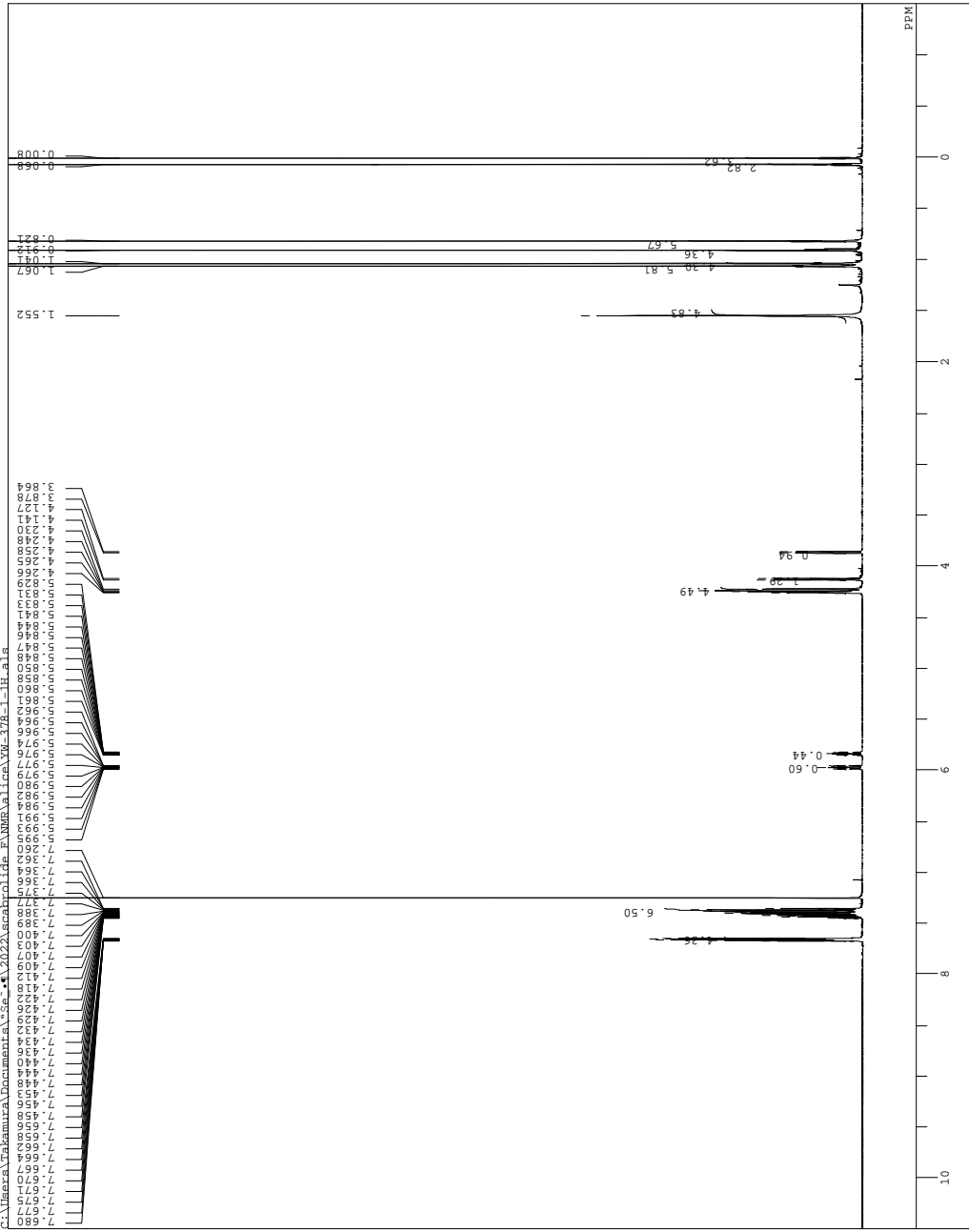
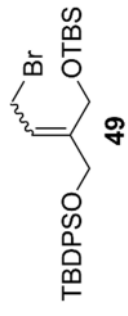
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 TIME 20211102 11:10:46  
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 PROC 0  
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 OBNUC H1 5.06 KHz  
 OBSER 307.68 Hz  
 OBSET 307.68 Hz  
 FREQ1 9615.38 Hz  
 SCANS 3.4032 sec  
 PD GM 1.5921 sec  
 PULP 1.5.40 usec  
 PULPROG zgpg30  
 CTMPC 10.0 c  
 CTMPC2  
 SLVNT cdcl3 7.26 ppm  
 EXREF 0.40 Hz  
 RGAIN







C:\Users\Takamura\Documents\Se\_4\2022\acabroliide\_F\NMR\data\VM-378-1-1H\_41a  
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 F1 - 0.06 MHz  
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 FREQ 9615.38 MHz  
 ACQTIME 3.4079 sec  
 PD 1.5221 sec  
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 SF 48  
 RGAIN









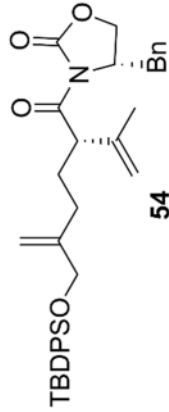
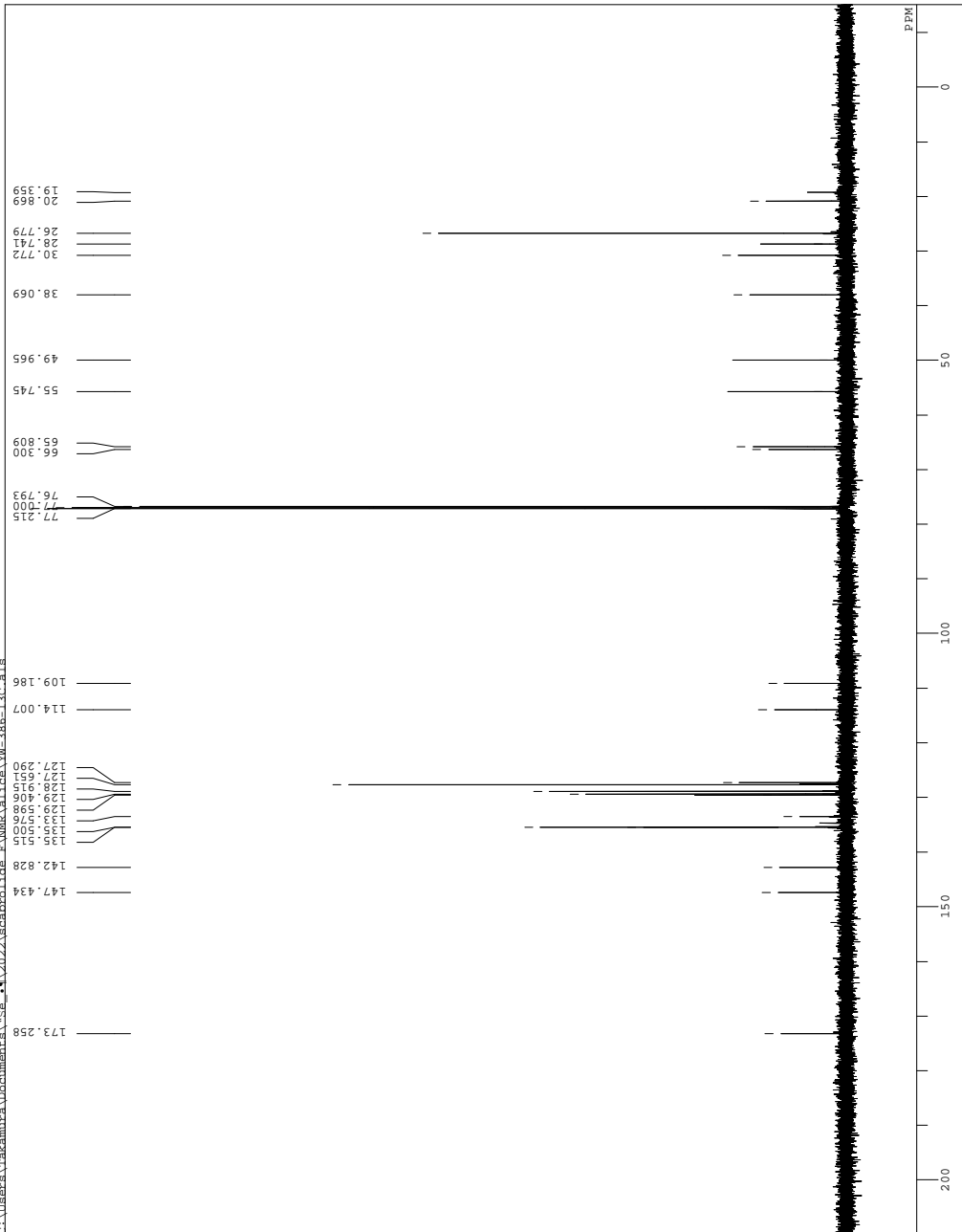




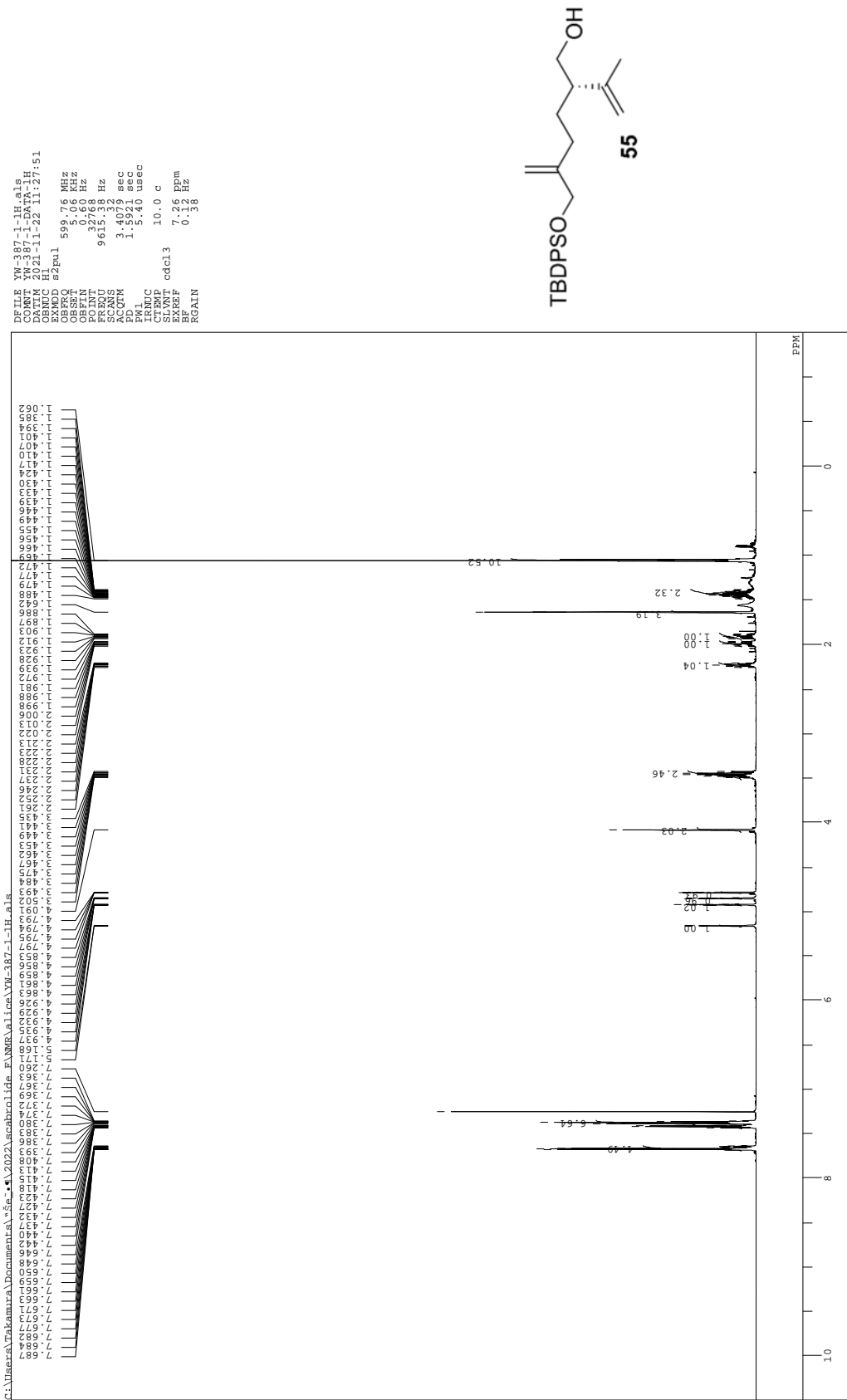


C:\Users\takamura\Documents\5a-4\2022\scabrolide\_FNAME\alice\W-386-13C.a1s

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 OBFT 6.76 Hz  
 POINT 32768 Hz  
 FREQ 37878.79 Hz  
 ACQTM 0.8651 sec  
 PD 2.1349 sec  
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 CTEMP edcl3 77.00 Kpm  
 SLVNT BF 0.12 Hz  
 RGAIN 60







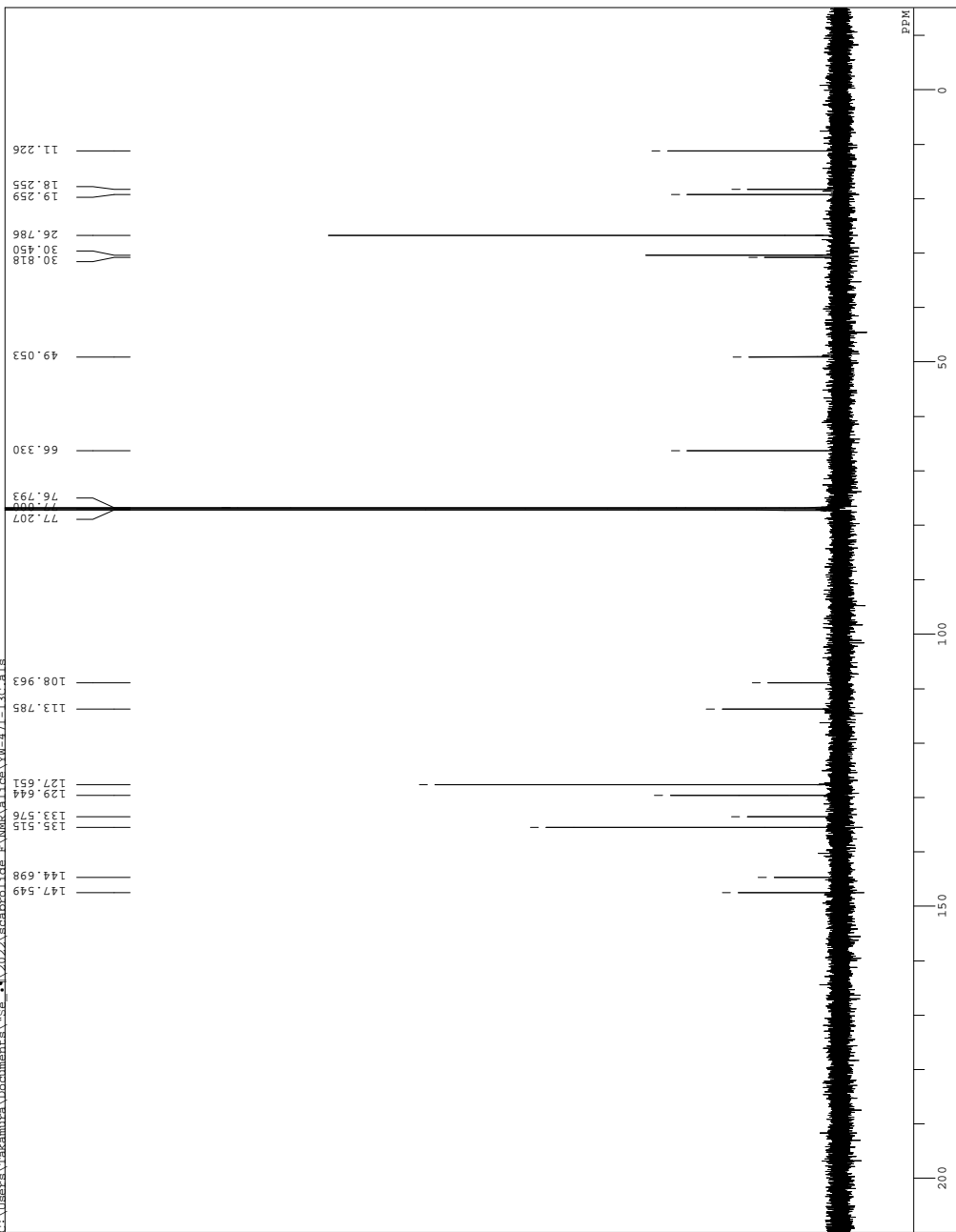




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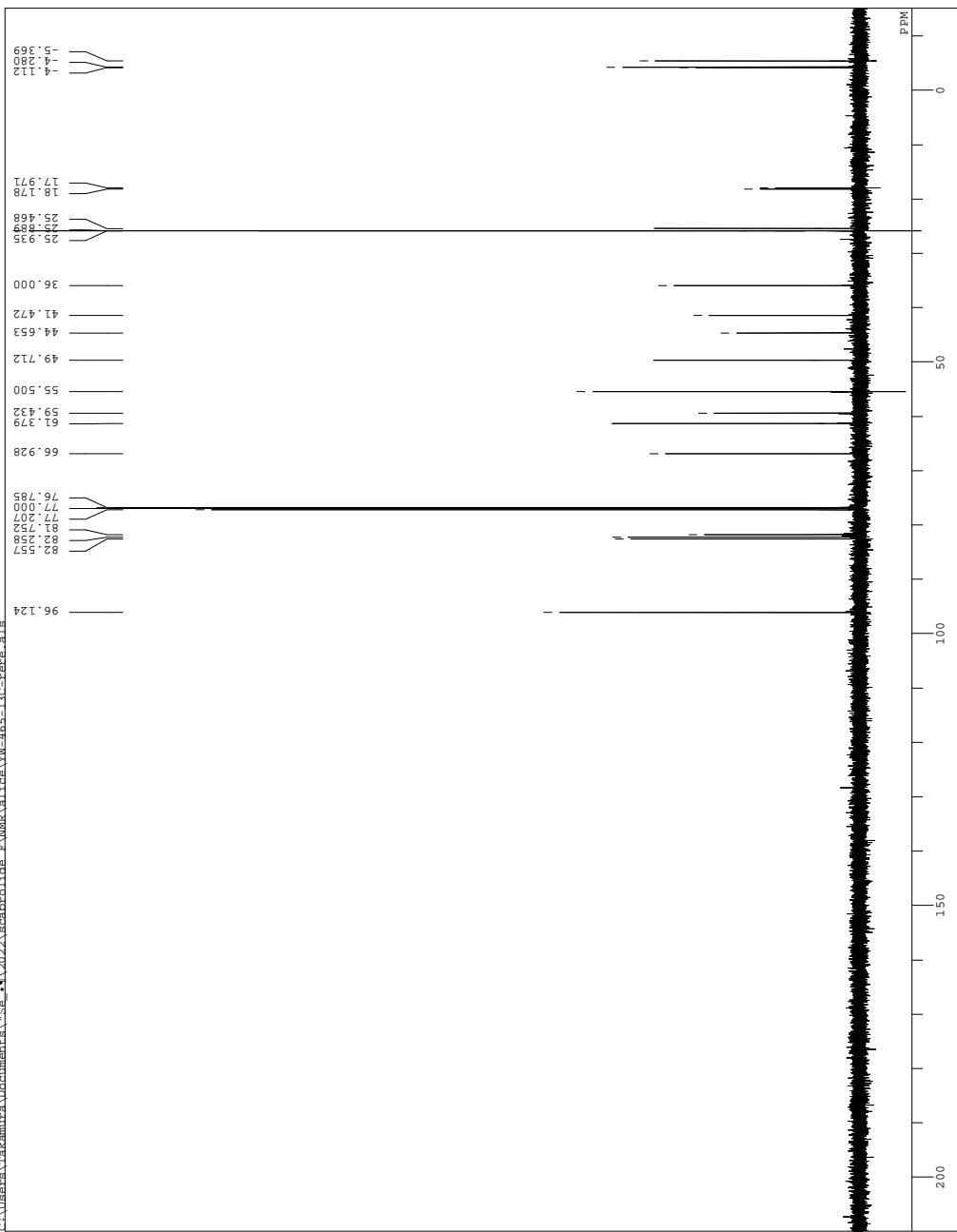
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F2      150.82 MHz
NUC1    13C
PROBHD  5 mm QNP 1H/13
P1       12.00 usec
PL1     0.00 dB
SFO     37878.79 Hz
AQ       0.8651 sec
RG       2.1349 sec
DELTA   6.05 usec
TEMP    10.0 c
PROCPRG cdc13
SOLVENT cdcl3
NS       77.00 ppm
DS       4
AQ       0.12 Hz
RGAIN    60
  
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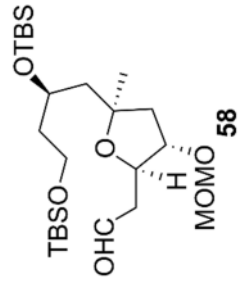
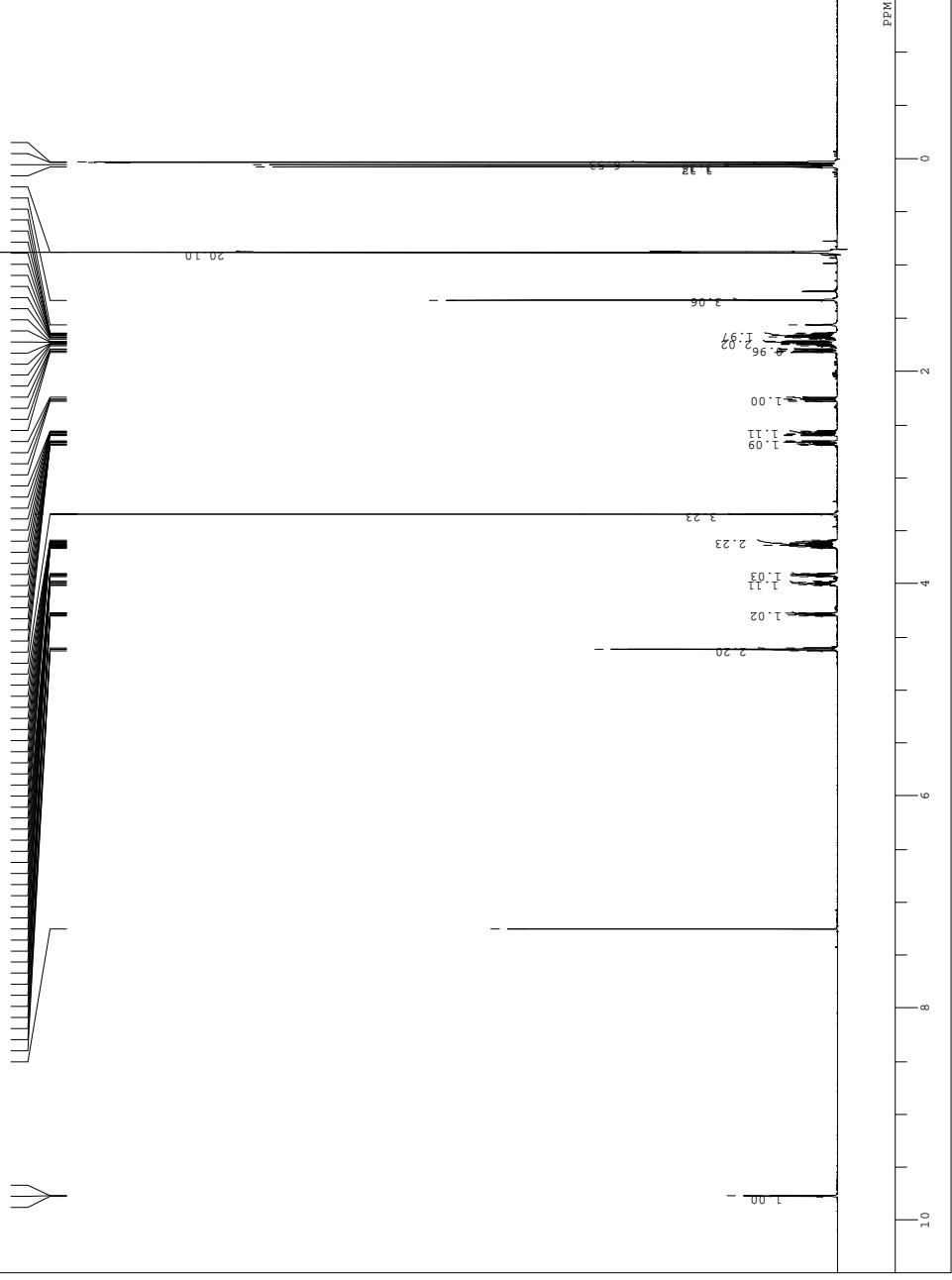
DETL: YW-465-13C-rere\_als  
COMT: YW-465-DATA-13C-rere  
DATIM: 2021-11-12 10:03:57  
EXMOD: S2pul  
OBSFQ: 150.82 MHz  
OBSFN: 6.72 KHz  
POINT: 32768  
FREQU: 37878.79 Hz  
ACQTM: 0.8651 sec  
PD: 2.1349 sec  
PRNUC: 6.05 usec  
CTEMP: 20.0 c  
SLOWP: cdc13 77.00 ppm  
RGAIN: 0.12 Hz  
RGAIN: 60



C:\Users\takamura\Documents\5e-4\2022\acbrn\1da\_1\NMR\data\vw-468-1h\_als

```

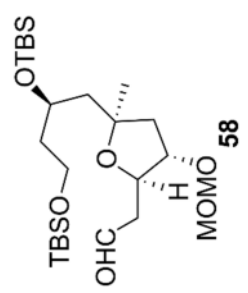
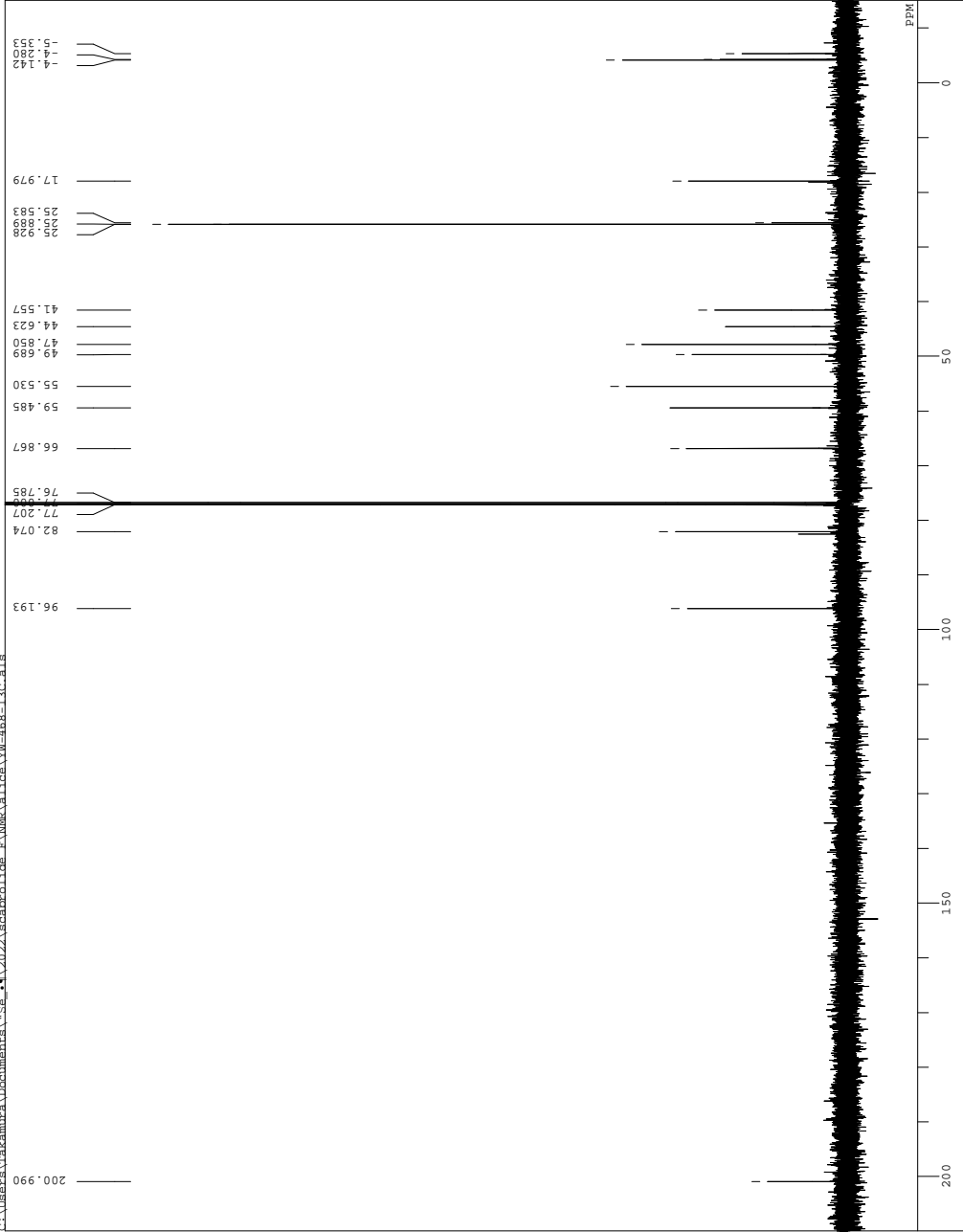
DFILE  VW-468-1h_als
COMNT  VW-468-DATA-1H
DATE_  2021-11-16 14:10:19
EXNO   1
EXMOD  #2pul
OBFRQ  599.76 MHz
OBSOL  0.160 Hz
OBSWA  32768 Hz
POINT  9615.3 Hz
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
AQCTM  3.4079 sec
PD      1.5921 sec
PC      5.40 usec
PRNUC  1
CTEMP  20.0 c
SOLVENT cdcl3
NS      7.26 Ppm
DS      0.112 Hz
SF      600.132 MHz
RGAIN   3.8
  
```



C:\Users\takamura\Documents\Se\_\*\2022\scabronide\_F\NMR\data\vw-468-13c.a1s

```

DETELE VW-468-13c.a1s
COMMT VW-468-DATA-13c
DATIM 2021-11-16 14:11:45
FNAME vw-468-13c
EXMOD s2pul
OBFRQ 150.82 MHz
OBSF1 8.72 kHz
OBSF2 8.72 kHz
POINT 32768
PRSQD 37878.79 Hz
AQ 0.8651 sec
ACQTM 2.1349 sec
PD 6.05 USEC
IRNUC
CTEMP 20.0 c
SLOTT cdc13
SOLNT
RFPRF 77.00 PPM
RGAIN 0.12 Hz
RGAIN 60
  
```



















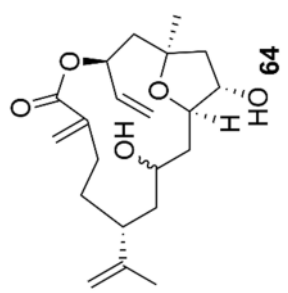
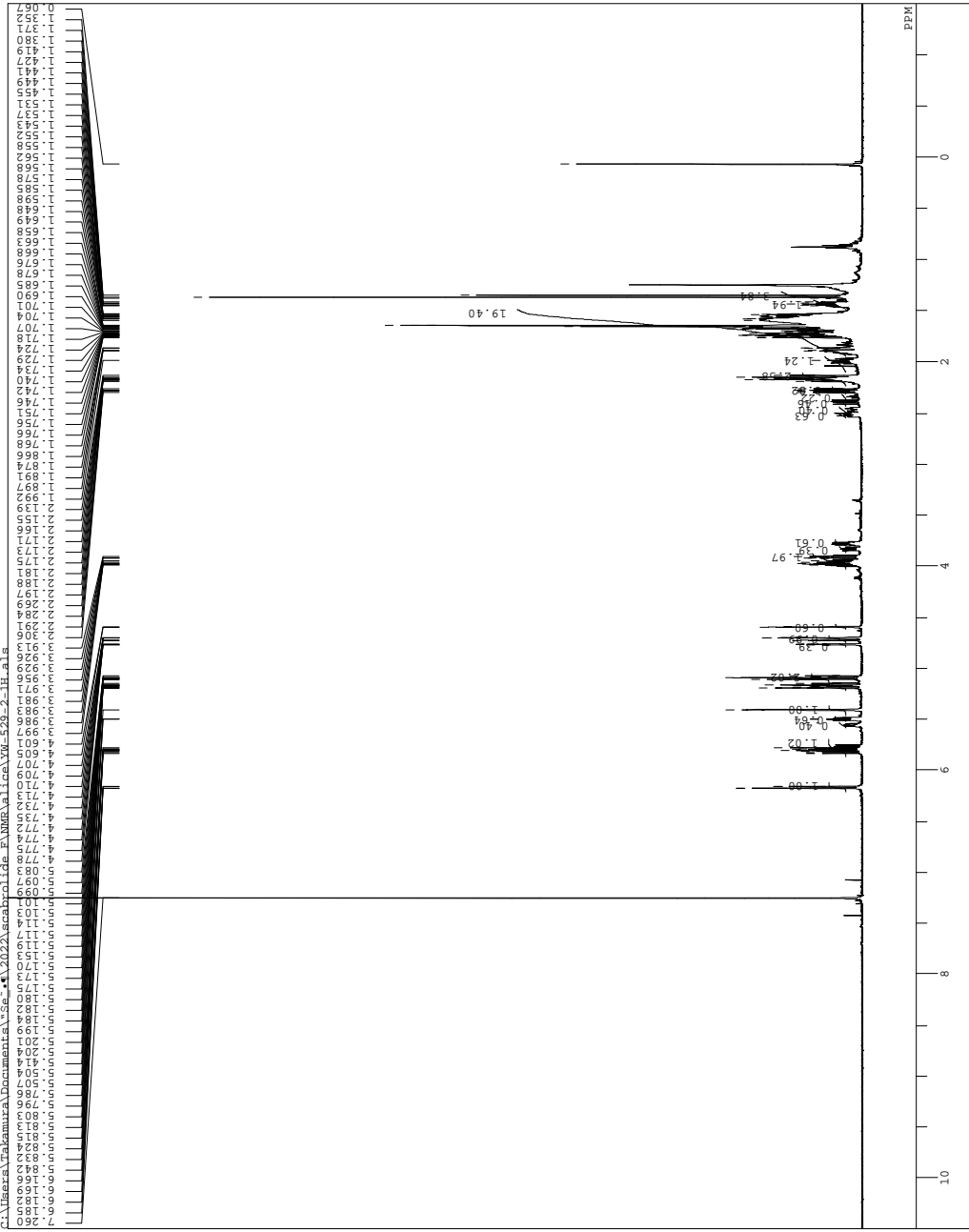






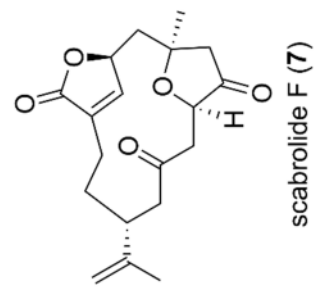
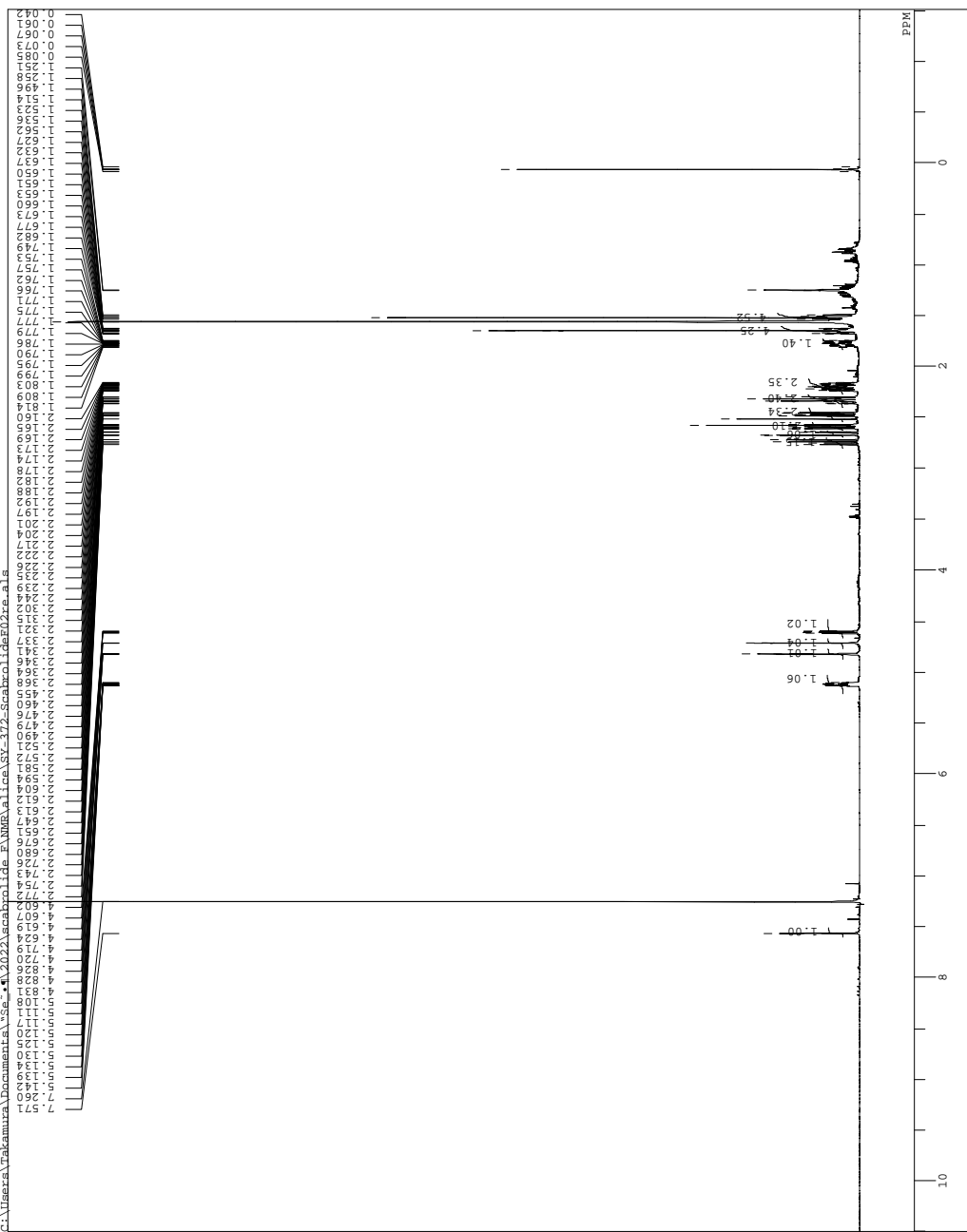


C:\Users\takamura\Documents\Se\_4\2022\scabroliide\_F\NMR\data\VM-529-2-1H\_als  
 FILE VM-529-2-1H\_als  
 COM1 VM-529-2  
 DATE 2022-03-15 16:06:52  
 EXMO 82pul  
 OBFRQ 599.76 MHz  
 OBREV 0.06 Hz  
 POINT 32768  
 FREQU 9615.38 Hz  
 ACQTM 3.4079 sec  
 PD 1.5921 sec  
 IM 5.40 usec  
 TRNUC 10.0 c  
 CTMP cgc13  
 SLVT  
 SREF 7.26 ppm  
 SF 0.12 Hz  
 RGAIN 50

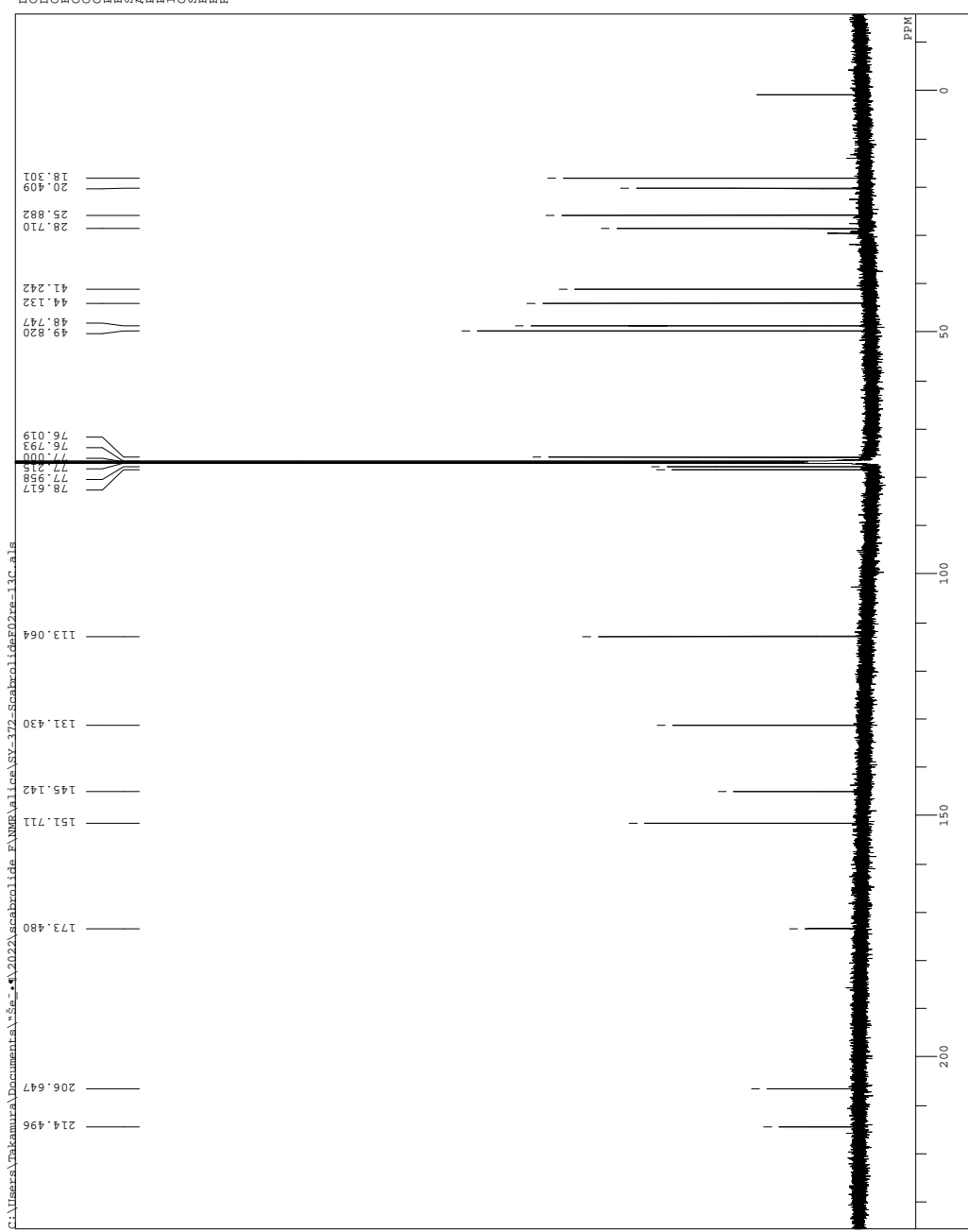
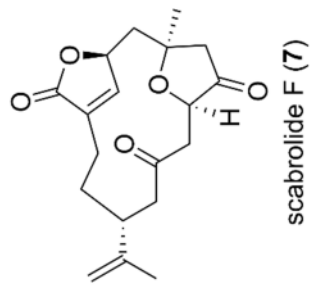




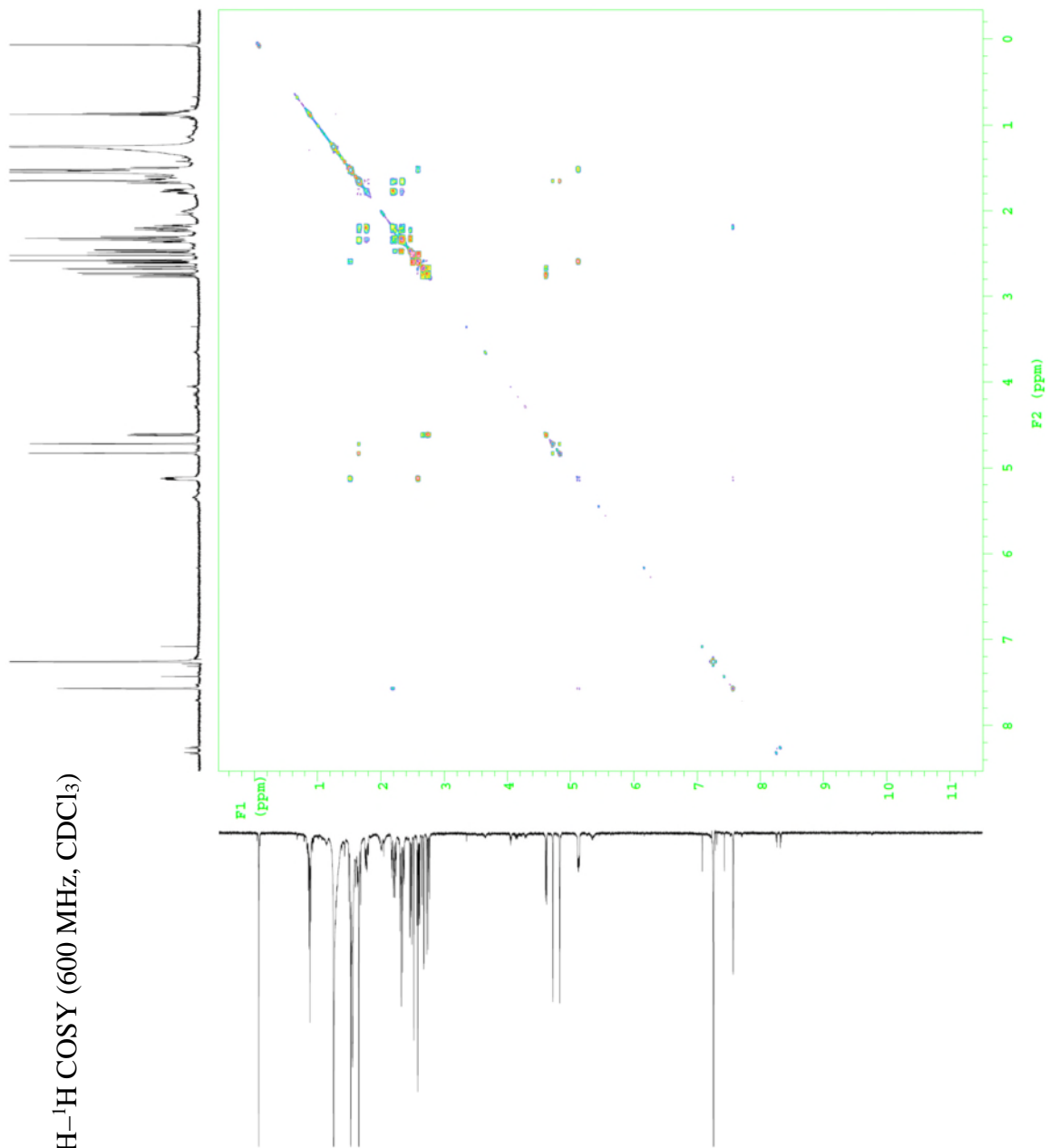
C:\Users\Ynkamura\Documents\se\_4\2022\scabrolide\_FMMG\alice\SY-372-Scabrolide\_F02ze.a1  
 FILE SY-372-ScabrolideF02ze.a1  
 COM1 2022-10-08 12:05:03  
 DATE 2022-10-08 12:05:03  
 TIME 12:05:03  
 EXPT 1  
 F2 599.76 MHz  
 F1 0.00 MHz  
 OBSN 0  
 POINT 32768  
 FREQ 9615.38 Hz  
 ACQ 3.4079 sec  
 P.D. 1.5921 sec  
 SFO 5.40 usec  
 T1 21.0 c  
 T1RMLC cdcl3  
 CTEMP 7.26 PPM  
 SLOWT 0.12 Hz  
 SLOWP 50  
 RGAIN 50



DFILE SV-372-ScabrolideF02re-13  
 DATE 2022-10-08 12:25:34  
 DAUM 53  
 EXMOD 52pul  
 OBSFQ 150.42 MHz  
 OBSFI 6.76 Hz  
 POINT 327768 Hz  
 FREQU 37878.79 Hz  
 ACQTM 0.8651 sec  
 PD 2.1349 sec  
 ITRNUC 6.05 usec  
 CTMP 21.0 c  
 SLVNT cdcl3 77.00 PPM  
 REF BF 0.12 Hz  
 RGAIN 60



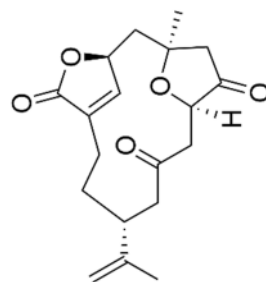
<sup>1</sup>H-<sup>1</sup>H COSY (600 MHz, CDCl<sub>3</sub>)



```

YH-512-7e
exp3 gcosy

SAMPLE          FLAGS
date   Mar 22 2022   hs          mn
solvent cdc13        sepul      y
sample  6120         hsg1v1
ACQUISITION
aw      9615.4      temp    not used
at      0.280      gain
cp      4000       F2 PROCESSING 0
ss      32        sb      -0.075
d1      1.000     sbw     not used
ht      16        fn      4096
2D ACQUISITION F1 PROCESSING
sw1     9615.4     sb1     -0.053
n1      512       sbw1    not used
d2      0        procl   lp
PREPARATION    n      fn1     DISPLAY
satmode
wet       n      sp      -203.2
TRANSMITTER   n      wp      5319.4
tn        n1     sp1     -334.4
sfrq     599.765   wp1     7239.7
cof      599.7    ril     5562.2
tpr      58       fp     4354.3
pw       10.800   fill    3571.3
GRABBLE 5102     F1P1    4354.3
GRB      0.001000  wc      351.9
EDratio  1.000    sc      9.8
grstab  0.000500  wc2     208.9
DECOUPLER     c13   vs      255
dm        mmn   th      6
ai      cdc   av
  
```



scabrolide F (7)

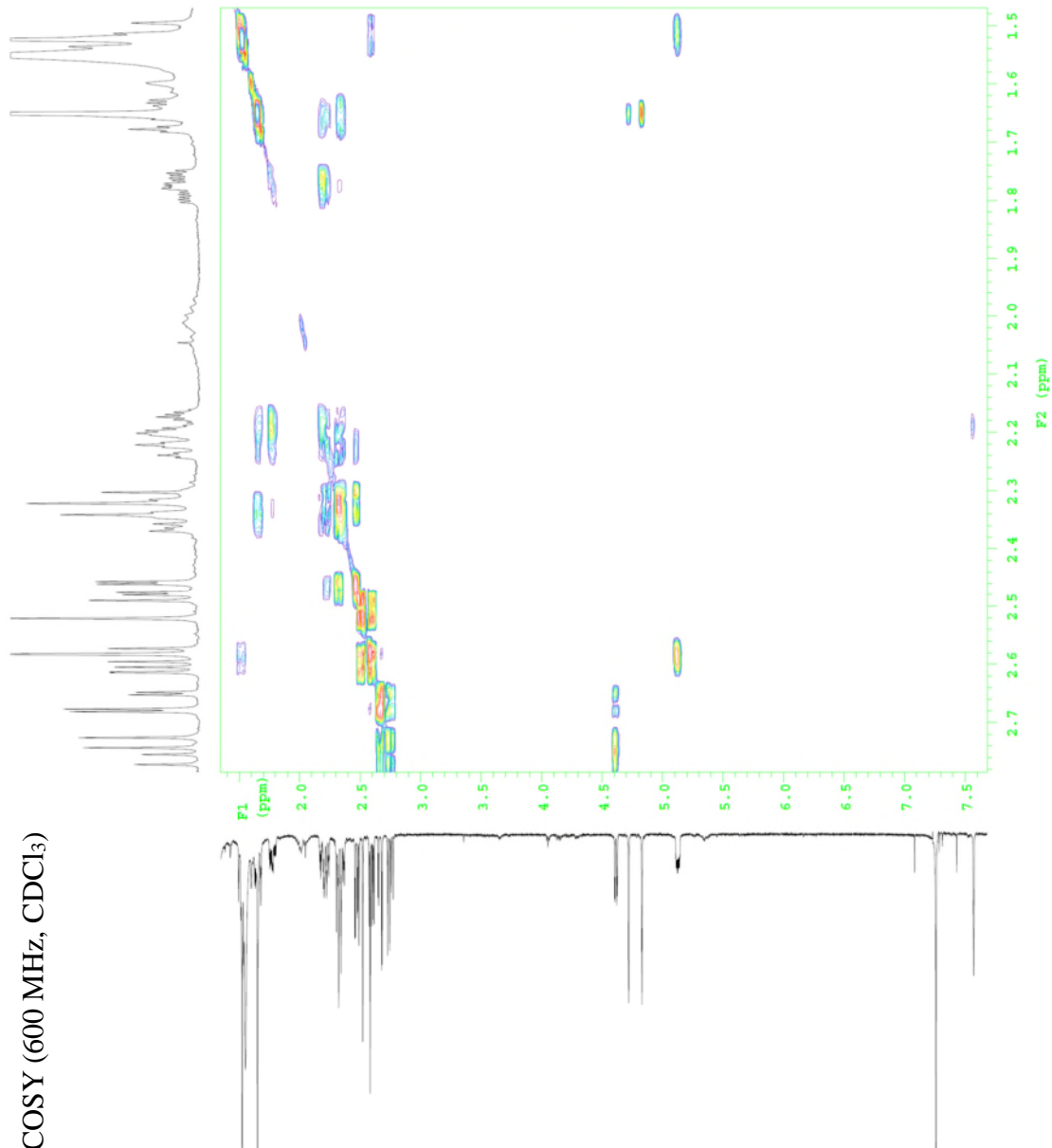
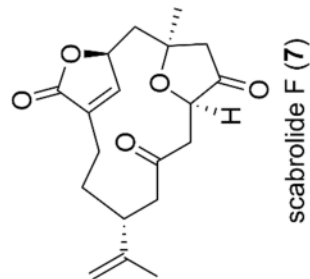
$^1\text{H}$ - $^1\text{H}$  COSY (600 MHz,  $\text{CDCl}_3$ )

YH-512-7e

exp2 gCOSY

```

SAMPLE          FLAGS
date   Mar 22 2022   hr   mn
solvent  cdcl3  expul   y
sample   6120
ACQUISITION
sv      9615.4  temp  not used
at      0.150  gain   54
np      2884  ppin   0
zb      4000  F2 PROCESSING
ss      32   ab     -0.075
dl      1.000  abs   not used
nt      16   fn     4096
2D ACQUISITION  F1 PROCESSING
sw1     9615.4  ab1   -0.053
rl      512  abal  not used
ds      0     pfool
PRESENTATION  n  CH1  DISPLAY
satmode
wet      n  sp     881.5
            TRSMITTER  n  sp     788.8
tn      808.5
afreq   599.765  wpl   3798.3
tof     599.7  rfl   5582.1
tpw     58  rfp   4354.3
pw      10.800  rfil  5589.3
pw  GRANULETE  rfp1  4354.3
sw1v12  0.001800  wv   FLOT  351.9
dB      0.001800  wc
EDratio 1.000  ac   9.8
gntab   0.000500  wv2  208.9
DECOUPLER  C13  va   255
dm      mm  th   6
            at  cdc  av
    
```





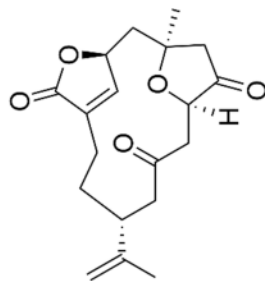
$^1\text{H}$ - $^1\text{H}$  COSY (600 MHz,  $\text{CDCl}_3$ )

YM-512-r4

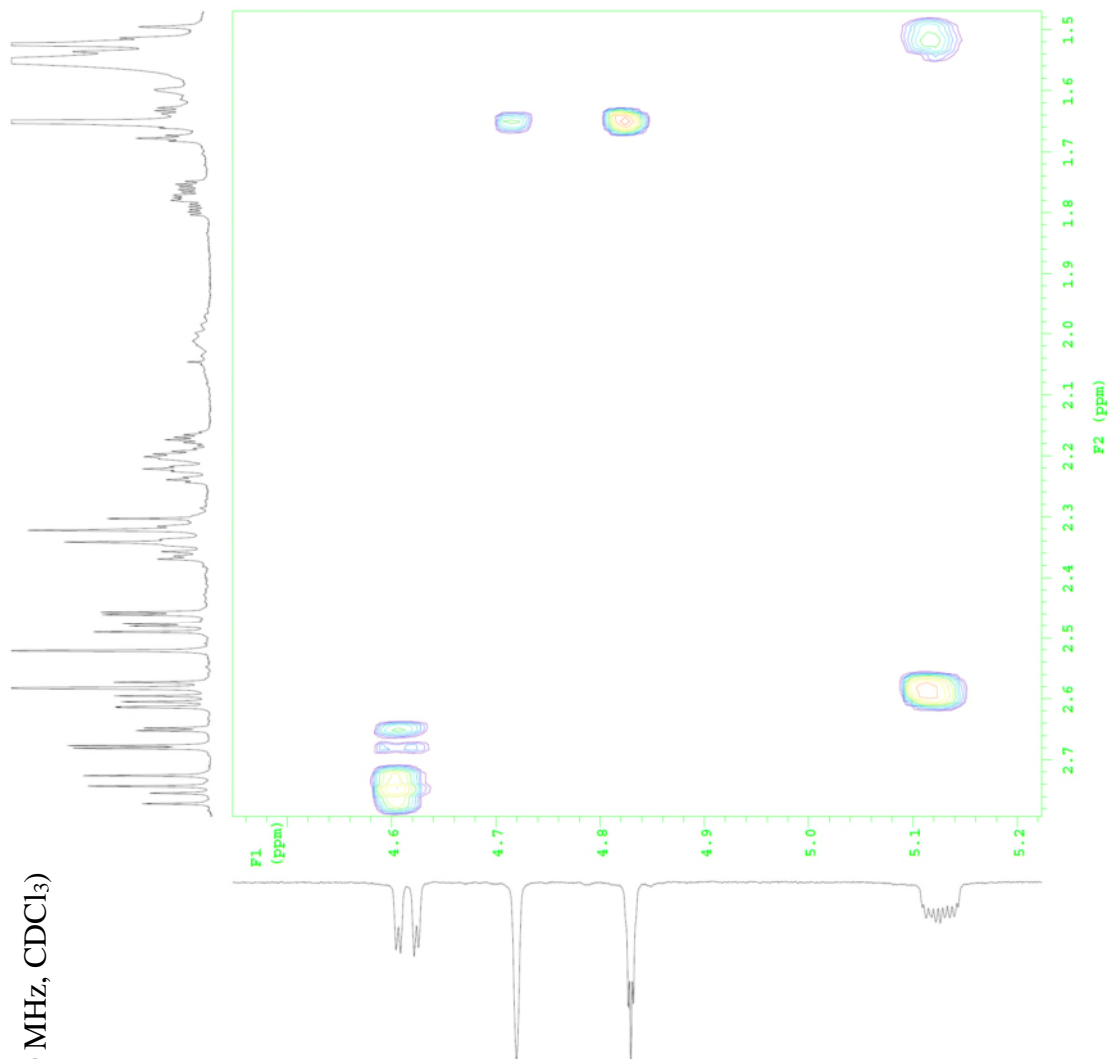
exp2 gcosy

```

SAMPLE          FLAGS
date   Mar 22 2022   hs
solvent cdc13       spul
sample  cdcl3       y
ACQUISITION      SPECIAL
ac      9615.4      temp not used
ns      0.150      gain  54
ds      2884      ph1d  5
eb      4000      F2 PROCESSING  0
as      32      ab -0.075
dl      1.000      abs not used
nt      16      fn  4096
2D ACQUISITION  F1 PROCESSING
sw1     9615.4      sb1 -0.053
nl      512      sbal not used
ds      0      procl  lp
DESATURATION    fnl  4096
asmode          n      DISPLAY  881.5
wt      TRANSMITTER  n      gp      793.5
tn      598.765      wp1  2667.7
afreq   598.765      wp1  464.8
tof     598.7      ffl  5562.1
tpwf   10.800      ffp  4354.3
pw     10.800      ffl1  5569.3
          GRADIENTS  ffl1  4354.3
          F1G1     5102      F1G2  351.8
          F1G3     1000      F1G4  9.8
          F1G5     0.000000      F1G6  208.9
          F1G7     0.000500      F1G8  208.9
          DECOUPLER  c13 vs  255
          dm      mm  th  6
          ai  cdc  av
    
```



scabrolide F (7)

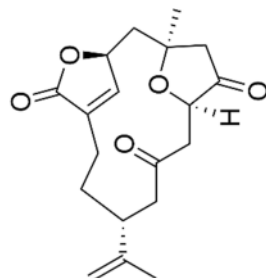


<sup>1</sup>H-<sup>1</sup>H COSY (600 MHz, CDCl<sub>3</sub>)

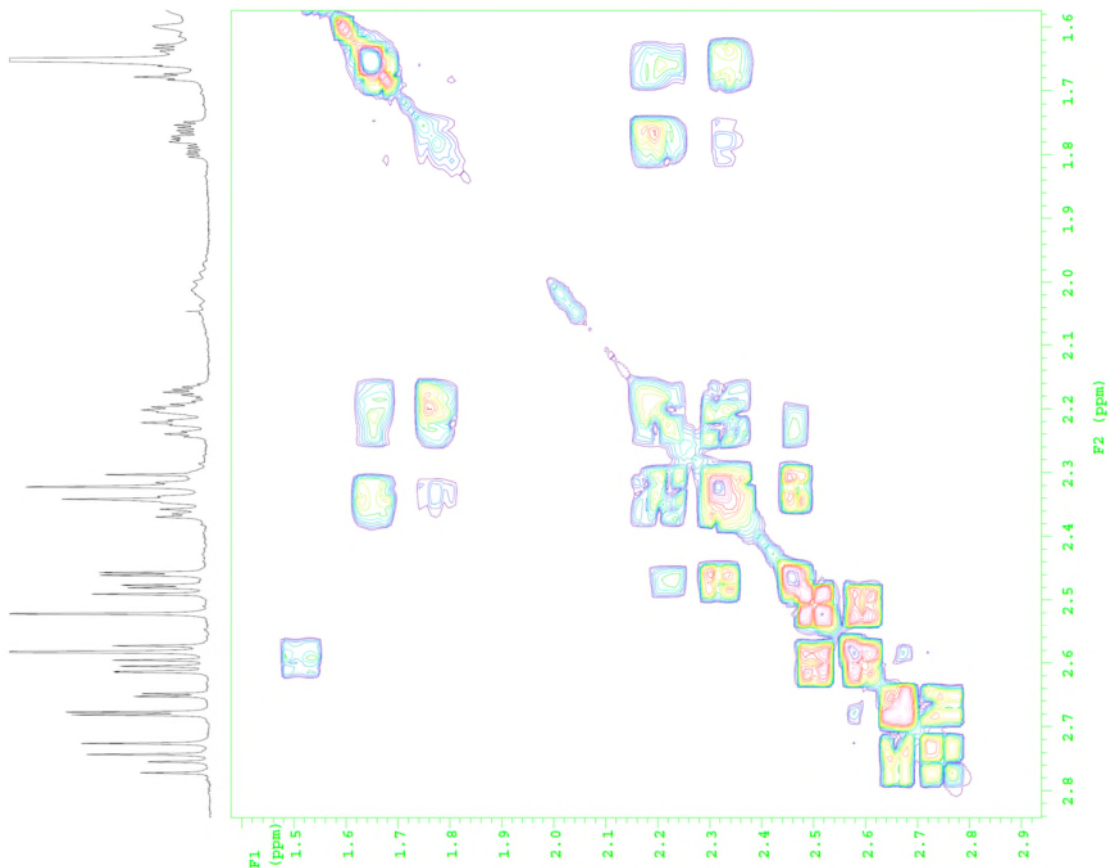
TM-532-re  
exp2\_gcosy

```

SAMPLE          FLAGS
date Mar 22 2022 hs
solvent cdcl3   y
sample          6120
ACQUISITION    SPECIAL
sw 9615.4 temp not used
at 0.150 gain 54
sp 4884 spin 0
ds 4096 F2 PROCESSING 0
hl 32 sh -0.075
dl 1.000 shs not used
nt 16 fn not used 4096
2D ACQUISITION F1 PROCESSING
sw1 9615.4 ab1 -0.053
nl 512 abal not used
d2 0 proc1 1p
PREPARATION    fn1 DISPLAY 4096
acqmode n
wet TRANSMITTER n sp DISPLAY 944.0
                    wf 944.0
                    tn 827.7
                    sfrq 599.765 wf1 934.3
                    tof 599.7 rf1 5560.6
                    tpwr 58 rfp 4354.3
                    pw 10.800 rfill 5568.9
                    pw GRADIENTS rfp1 4354.3
                    g1v1e 5102 PLOT
                    sFE 0.001000 wc 351.9
                    Edratio 1.000 sc 9.8
                    grab 0.000500 wcz 208.9
                    dn DECOUPLER c13 wcz 255
                    dm hnn th 6
                    dm ai cdc av
    
```



scabrolide F (7)

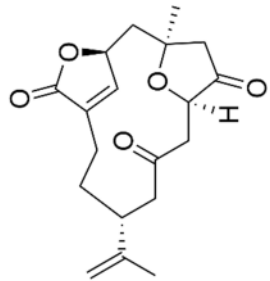
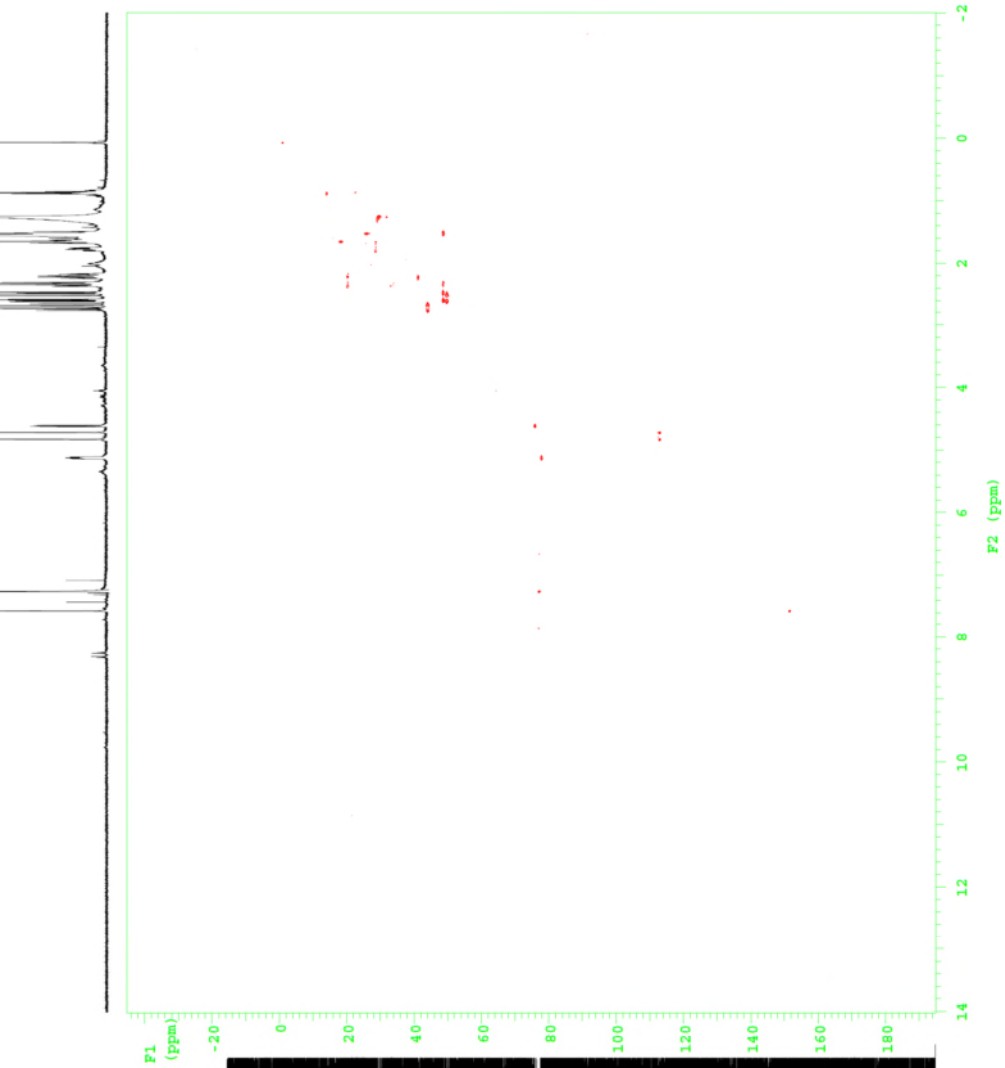


# HMQC (600 MHz, CDCl<sub>3</sub>)

exp3 ghmqc

```

SAMPLE          FLAGS
date   Mar 24 2022   hs
solvent cdcl3       spsol
sample          y
ACQUISITION beglvl  6120
sw          5615.4   SPECIAL
ac          0.150    temp   not used
cp          4800     gain   24
ds          4800     sftm   24
ss          32       GRADIENTS 0
d1          1.000    solvle  5102
nt          32       GIE      0.002000
2D ACQUISITION Etratio 3.978
sw1         36199.1  gstab  0.000500
nl          512     F2 PROCESSING
phase arrayed gf
PERSATURATION gfs not used
satnoise   n   in   F1 PROCESSING 4096
wrt         TRANSMITTER n   gfs 0.018
td          599.765  procl  1p
tof         599.7   fn1    4096
tpwr        10.800  sp     -1202.3
Fw          9610.7
dn          C13  sp1   -6804.8
dcf         -2982.0  sp1   36181.4
dm          mpy  f1l   5561.2
dm         wave M40  mpy  f1l   18434.8
dbr         35088   f1l   18434.8
dpr         45     ffp1  11612.4
pocvl      62     PLOT  351.9
pwx        11.800  wc     9.8
j1kh       146.0  wc2   208.5
multiflg   y     ac2    0
mult       2     vs     37
          th     cdc  ph
          al     cdc  ph
  
```



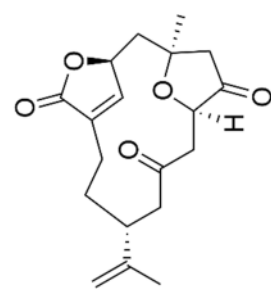
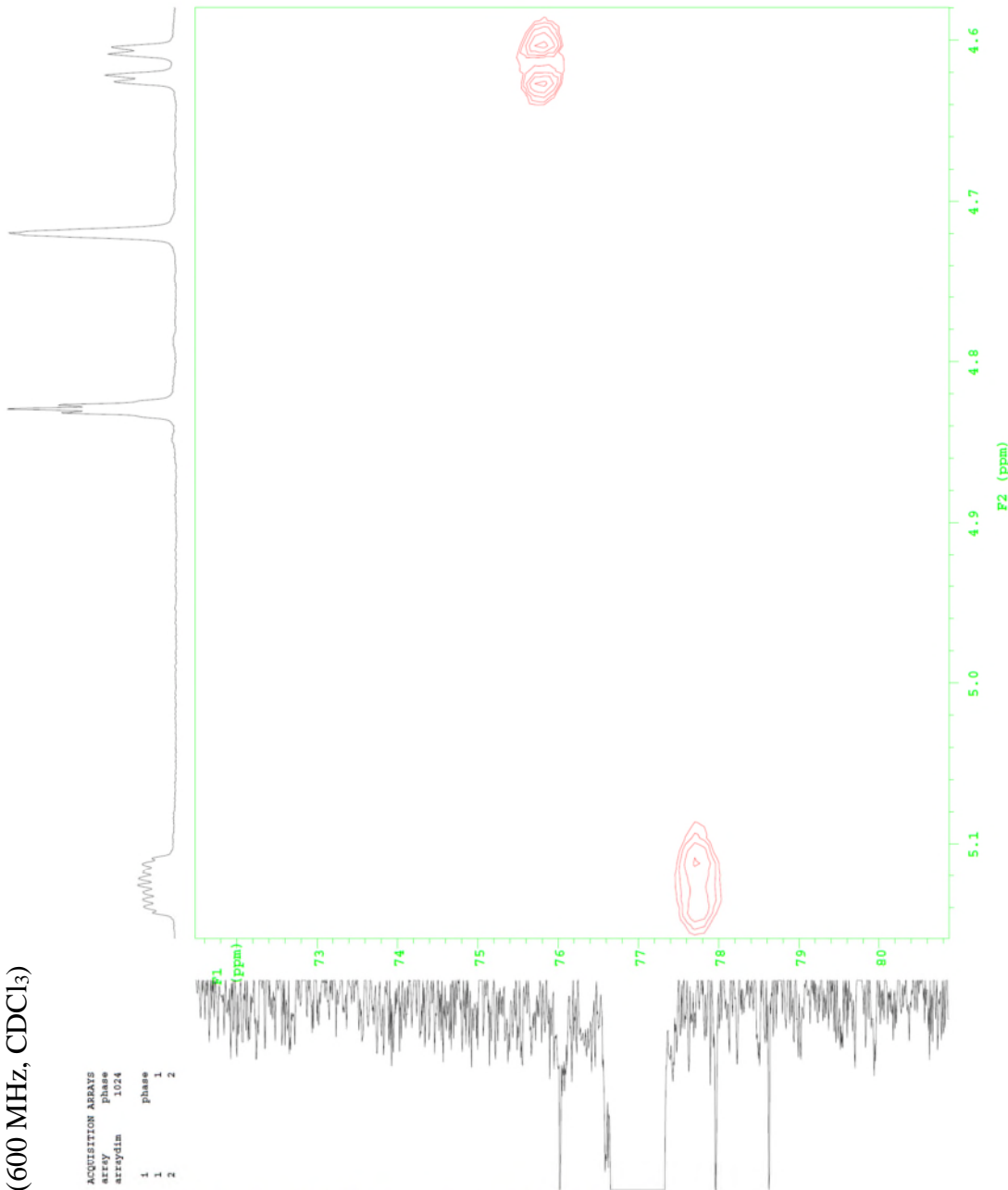
scabrolide F (7)

# HMQC (600 MHz, CDCl<sub>3</sub>)

exp3 ghmqc

```

SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Mar 24 2022   hs          array
solvent  cdcl3          segul          phase
sample   y          arraydim  1024
ACQUISITION  begiv1          1          phase
sw       9615.4          SPECIAL  6120          1
ac       0.150          temp    not used          2
dd       4800          spm     20
dd       4000          spm     20
ss       32          GRADIENTS  0
d1       1.000          g1/v1/e  5102
nt       32          GE      0.002000
2D ACQUISITION  Etratio  3.978
sw1      36199.1          gatab  0.000500
n1       512          F2 PROCESSING
phase    arrayed  gf          0.069
PRESATURATION  n          in          4096
satmode  n          in          4096
wet       TRANSMITTER  n          F1 PROCESSING  2016
tn        10.000          sp          2746.7
af1q      599.765          procl  lp
tof       599.7          fml     DISPLAY  4096
tpwr      58
pw       10.800          sp          2746.7
DECOUPLER  wp          347.4
dn        C13          sp1          10781.1
dof       -2982.0          wp1          1414.0
dm        nutt          r11          5560.8
decouple  W40          channel  r1p          4354.3
dnt       35000          r11          18495.9
pqc1/v1   48          r1p1          11812.4
pqc2/v1   62          r1p1          351.9
pqc       11.800          ac          9.8
j1kh      146.0          wc2          208.9
nullflg   y          sc2          0
mult      2          vs          422
mult      th          cdc          ph          3
  
```



scabrolide F (7)



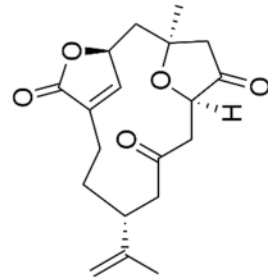
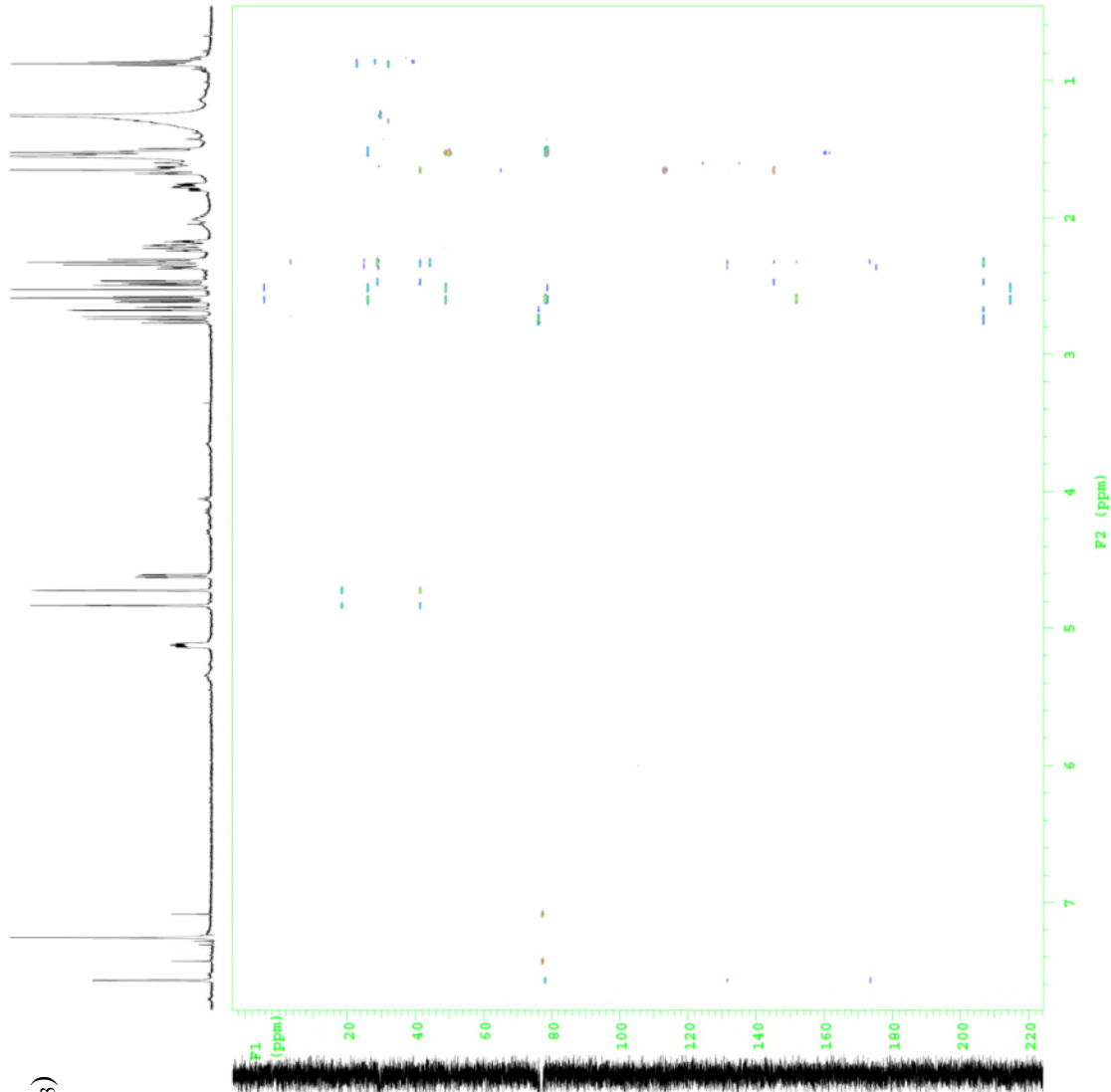
# HMBC (600 MHz, CDCl<sub>3</sub>)

YH-512-re

exp3 gHMBC

```

SAMPLE          FLAGS          ACQUISITION ARRAYS
date   Mar 22 2022   hs          nm          phase
solvent cdcl3      spul          y          array
sample  36199.1     y          arraydim 1024
acq      9615.4     1          1          phase
ns       0.150     temp not used  2
at       2884     gain          3
zb       4000     spin          2
ss       32       GRADIENTS  0
nt       1.000     gvlvl          0
nt       64       gvl          0.001000
2D ACQUISITION  gvlvl          1500
sw1      36199.1   gvl          0.001000
nl       512     gscab          0.000500
phase   arrayed   f2 PROCESSING
PREPARATION    sb          not used
saltmode       n          not used
wet           n          4096
TRANSMITTER    n          F1 PROCESSING
tn          H1       gvl          0.013
sfrq       599.765   gfm          not used
tof        599.7   pfm          lp
tpwf       58       fml          4096
pw         10.800   DISPLAY  274.5
db         C13      sp          4394.5
dc         1542.3   sp1         -3863.3
de         1542.3   sp2         3863.3
decouple   W40_chanm  rfl          3209.1
dsf        35088   rfp          0
dprf       45       rfl1         2264.5
pwxlv1     62       rfp1          0
pwx        11.800   PLOT
           HMCB
j1xh      146.0   ac          9.8
j1xh      8.0    wv2         208.9
j1xh      0      wv2          0
j1xh      285    wv          285
tn         cdcl3  ay          3
  
```



scabrolide F (7)

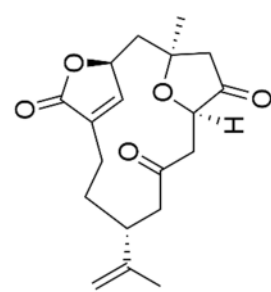
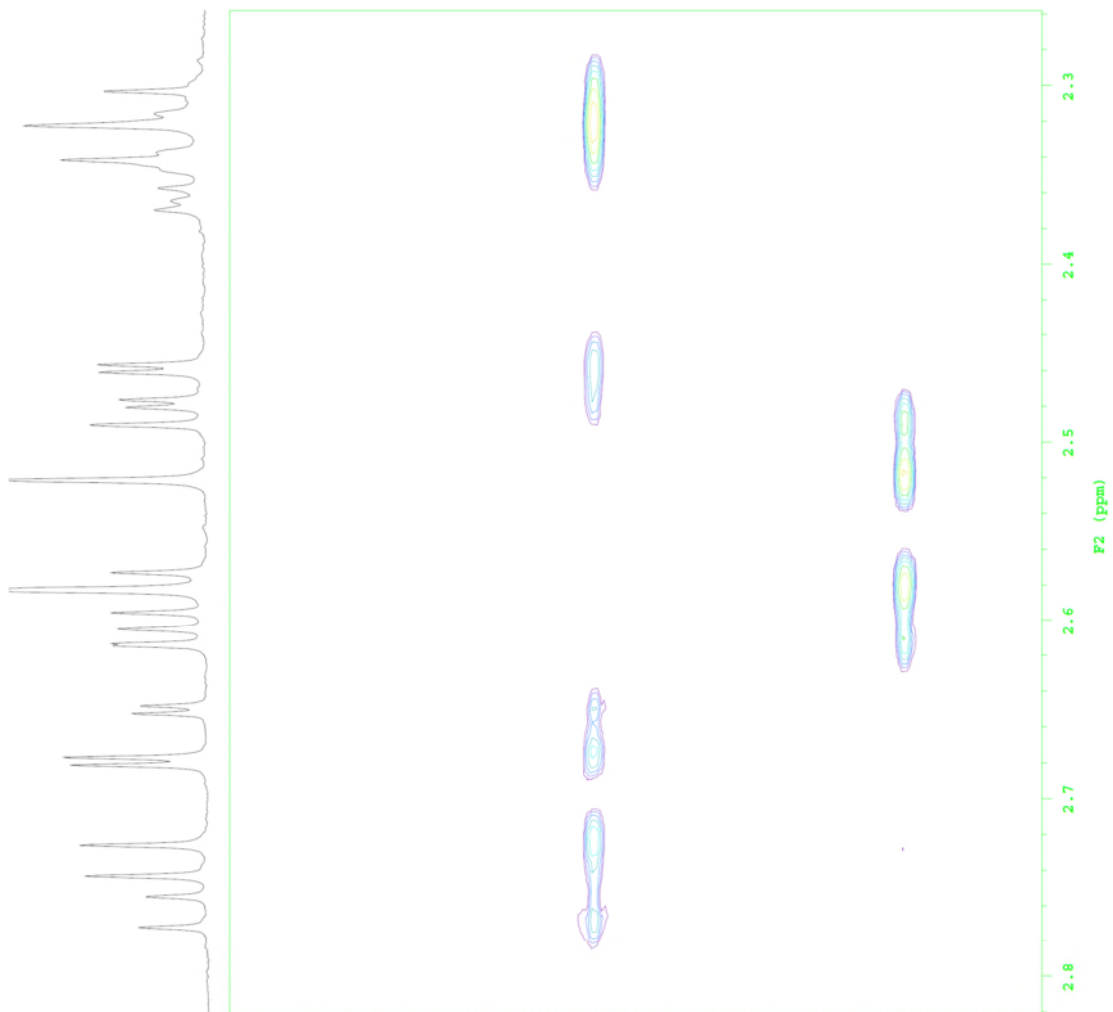
# HMBC (600 MHz, CDCl<sub>3</sub>)

TM-512-1e

exp3 ghmrc

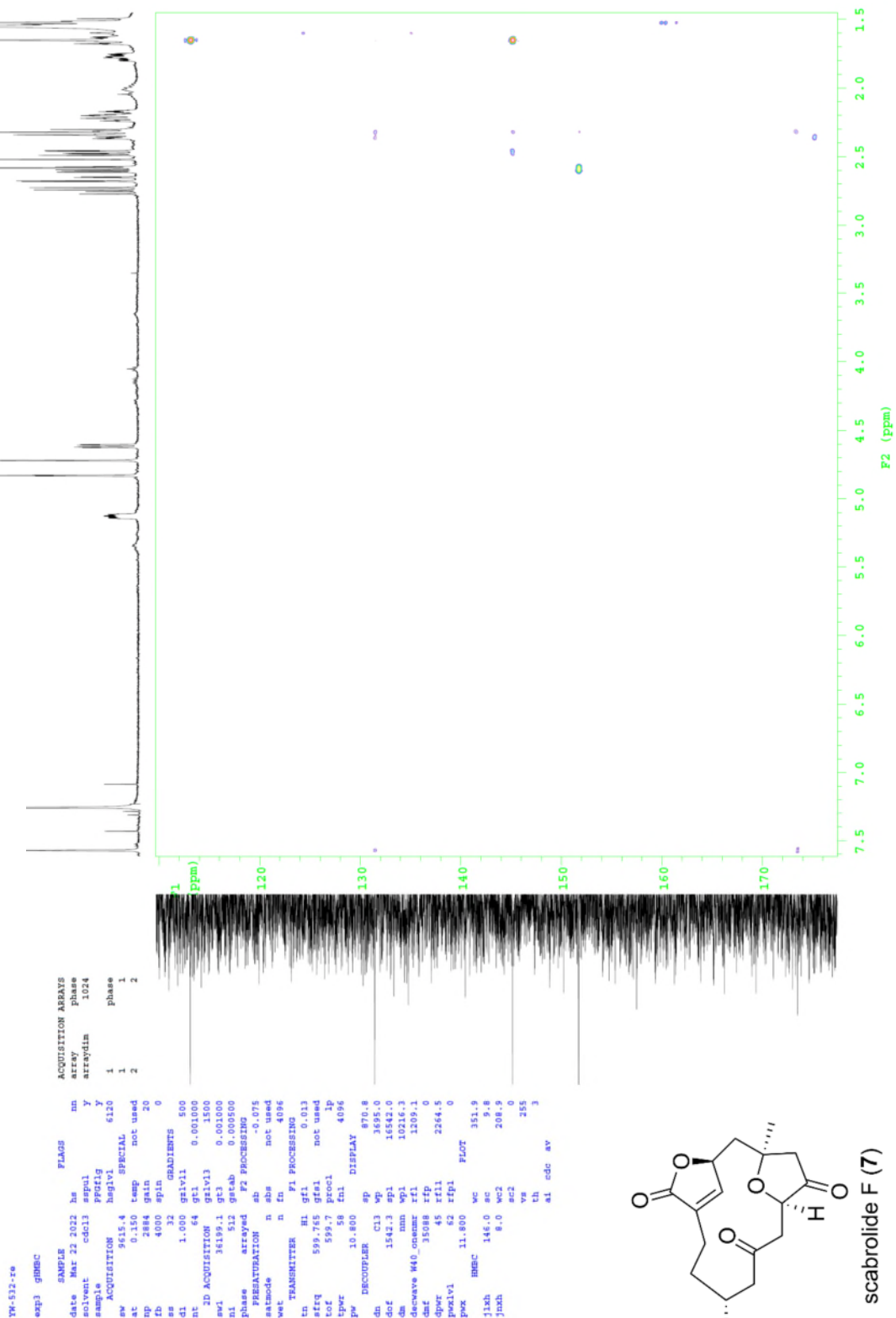
```

SAMPLE          FLAG      tm          ACQUISITION ARRAYS
date Mar 22 2022 hs          array      phase
solvent cdcl3  sepul      y          arraydim  1024
sample 7       PROCS   y
acq  9615.4  Mag-13  6120  1      Phase
sw  0.150  temp  SPECIAL  2
at  2884  gain  not used  1
np  4000  spin  0
ss  32    GRADIENTS  0
d1  1.000  gvlvl1  500
nt  64    gtl      0.001000
2D ACQUISITION  gvlvl3  1500
sw1  36199.1  gtl3  0.001000
hl  512  grab  0.000500
Phase arrayed  F2 PROCESSING
PRESATURATION  sh  -0.075
satmode  n  abs  not used
wet  n  fn  not used
4096
TRANSMITTER  n  fn  not used
4096
tn  H1  gfl  0.013
sfrq  599.765  gfl  not used
tof  599.7  ptocl  1p
tpwr  58  fnl  4096
pw  10.800  DISPLAY
4096
dm  DECOUPLER  cl3  1864.3
dmc  1864.3  pfl  33780.0
dmc  1542.3  pfl  33780.0
dm  nnn  wpl  3093.2
decouwa  M0  conmmr  rfl  1209.1
dmf  35098  rfp  0
qpr  45  rfl1  2164.5
pmlvl1  52  rfp1  0
pwk  11.800  PLOT  0
HMC  wc  351.9
j1kh  146.0  ac  9.8
jmh  8.0  w2  208.9
w2  285
w1  285
th  3
tl  cdc  av
    
```



scabrolide F (7)

# HMBC (600 MHz, CDCl<sub>3</sub>)





# HMBC (600 MHz, CDCl<sub>3</sub>)

YW-512-rs  
exp3\_gRMB

date	Mar 22 2022	hr	10	min	1024
solvent	cdcl3	spul	y	array	phase
sample	PF071g	haglvi	6130	1	phase
acq	901.4	temp	not used	2	
sw	4.154	temp	not used	2	
sp	2884	gain	20		
zb	4000	spin	0		
ss	32	GRADIENTS	500		
d1	1.000	gslv11	0.001000		
nt	64	gt1	0.001000		
2D ACQUISITION	gslv13	1500			
sw1	36199.1	gt3	0.001000		
n1	512	gstab	0.000500		
Phase	arrayed	F2 PROCESSING			
PREHEATING	ab	-0.075			
astmode	n	not used			
wt	0.096	not used			
wt	0.096	not used			
wt	0.096	not used			
TRANSMITTER	hl	gt1	0.013		
sfreq	599.765	gfs1	not used		
tof	599.7	procl	lp		
tpwr	58	fn1	4096		
pw	10.800	DISPLAY			
DECOUPLER	pf	659.5			
dn	cl3	wp	1070.5		
dof	1542.3	sp1	1783.1		
dm	mm	wp1	12850.0		
decouple	M40	cp1	12850.0		
decouple	F1	cp1	12850.0		
decouple	F2	cp1	12850.0		
decouple	F3	cp1	12850.0		
decouple	F4	cp1	12850.0		
decouple	F5	cp1	12850.0		
decouple	F6	cp1	12850.0		
decouple	F7	cp1	12850.0		
decouple	F8	cp1	12850.0		
decouple	F9	cp1	12850.0		
decouple	F10	cp1	12850.0		
decouple	F11	cp1	12850.0		
decouple	F12	cp1	12850.0		
decouple	F13	cp1	12850.0		
decouple	F14	cp1	12850.0		
decouple	F15	cp1	12850.0		
decouple	F16	cp1	12850.0		
decouple	F17	cp1	12850.0		
decouple	F18	cp1	12850.0		
decouple	F19	cp1	12850.0		
decouple	F20	cp1	12850.0		
decouple	F21	cp1	12850.0		
decouple	F22	cp1	12850.0		
decouple	F23	cp1	12850.0		
decouple	F24	cp1	12850.0		
decouple	F25	cp1	12850.0		
decouple	F26	cp1	12850.0		
decouple	F27	cp1	12850.0		
decouple	F28	cp1	12850.0		
decouple	F29	cp1	12850.0		
decouple	F30	cp1	12850.0		
decouple	F31	cp1	12850.0		
decouple	F32	cp1	12850.0		
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decouple	F34	cp1	12850.0		
decouple	F35	cp1	12850.0		
decouple	F36	cp1	12850.0		
decouple	F37	cp1	12850.0		
decouple	F38	cp1	12850.0		
decouple	F39	cp1	12850.0		
decouple	F40	cp1	12850.0		
decouple	F41	cp1	12850.0		
decouple	F42	cp1	12850.0		
decouple	F43	cp1	12850.0		
decouple	F44	cp1	12850.0		
decouple	F45	cp1	12850.0		
decouple	F46	cp1	12850.0		
decouple	F47	cp1	12850.0		
decouple	F48	cp1	12850.0		
decouple	F49	cp1	12850.0		
decouple	F50	cp1	12850.0		
decouple	F51	cp1	12850.0		
decouple	F52	cp1	12850.0		
decouple	F53	cp1	12850.0		
decouple	F54	cp1	12850.0		
decouple	F55	cp1	12850.0		
decouple	F56	cp1	12850.0		
decouple	F57	cp1	12850.0		
decouple	F58	cp1	12850.0		
decouple	F59	cp1	12850.0		
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decouple	F61	cp1	12850.0		
decouple	F62	cp1	12850.0		
decouple	F63	cp1	12850.0		
decouple	F64	cp1	12850.0		
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decouple	F66	cp1	12850.0		
decouple	F67	cp1	12850.0		
decouple	F68	cp1	12850.0		
decouple	F69	cp1	12850.0		
decouple	F70	cp1	12850.0		
decouple	F71	cp1	12850.0		
decouple	F72	cp1	12850.0		
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decouple	F79	cp1	12850.0		
decouple	F80	cp1	12850.0		
decouple	F81	cp1	12850.0		
decouple	F82	cp1	12850.0		
decouple	F83	cp1	12850.0		
decouple	F84	cp1	12850.0		
decouple	F85	cp1	12850.0		
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decouple	F94	cp1	12850.0		
decouple	F95	cp1	12850.0		
decouple	F96	cp1	12850.0		
decouple	F97	cp1	12850.0		
decouple	F98	cp1	12850.0		
decouple	F99	cp1	12850.0		
decouple	F100	cp1	12850.0		

