

Supporting Information for

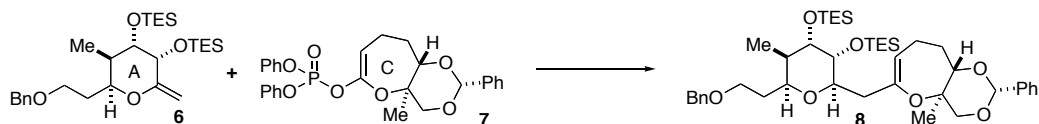
Total Synthesis of (–)-Brevisin: A Concise Synthesis of a New Marine Polycyclic Ether

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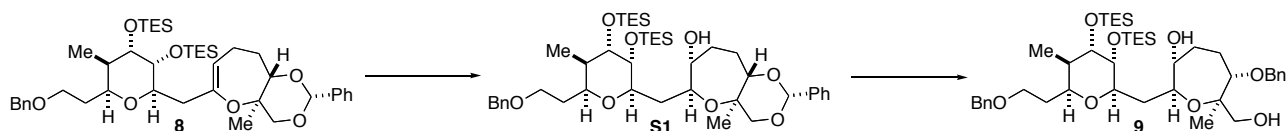
General methods: All moisture and/or air sensitive reactions were carried out in oven-dried (>100 °C) glassware under argon atmosphere unless otherwise noted. Anhydrous dichloromethane (CH₂Cl₂), diethyl ether (Et₂O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Inc. Other solvents and reagents were purchased at highest commercial grade and used as supplied, unless otherwise noted. Some reactions were firstly run on small scales and perfectly purified for the characterization, and then run on larger scales without perfect purification. Analytical thin-layer chromatography (TLC) was performed on E. Merck silica gel 60 F₂₅₄ plates (0.25 mm thickness). Column chromatography was performed using Kanto Chemical silica gel 60N (40–100 mesh, spherical, neutral). Flash column chromatography was performed using Fuji Silysia silica gel BW-300 (200–400 mesh). Optical rotations were recorded on a JASCO DIP-350 digital polarimeter. IR spectra were recorded on a JASCO FT/IR-420 instrument. ¹H and ¹³C spectra were recorded on a JEOL ECA-500 and ECX-400 spectrometer and calibrated with residual undeuterated solvent as an internal reference [¹H NMR, CHCl₃ (7.24), C₆HD₅ (7.15), CHD₂OD (3.31), C₅HD₄N (7.58); ¹³C NMR, CDCl₃ (77.0), C₆D₆ (128.0), CD₃OD (49.0), C₅D₅N (135.5)]. Chemical shifts are reported in δ (ppm). Coupling constants are reported in Hz (hertz). The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700P mass spectrometer under fast atom bombardment (FAB) conditions using *m*-nitrobenzylalcohol (NBA) as a matrix and a JEOL JMS-T100TD mass spectrometer under direct analysis in real time (DART) conditions.

enol **8**



Exocyclic enol ether **6** (1.68 g, 3.31 mmol) in THF (20 mL) at 0 °C was treated with 9-BBN-H (0.5 M in THF, 13.2 mL, 6.62 mmol) and stirred for 2 h. To the solution were added 3 M aqueous Cs₂CO₃ (5.5 mL), the ketene acetal phosphate **7** (1.35 g, 2.73 mmol) in DMF (15 mL + 9.0 mL rinse) and PdCl₂(dppf)·CH₂Cl₂ (165 mg, 0.202 mmol). The resultant solution was stirred at 50 °C for 1 h, brine was added. The aqueous phase was extracted twice with Et₂O. The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st: 15% ethyl acetate/hexane, containing 0.5% of Et₃N, 2nd: 2% acetone/hexane, containing 0.5% of Et₃N) to afford the enol ether **8** (1.76 g, 86%) as a colorless oil: [α]_D²⁸ 73.4 (*c* 0.0273, C₆H₆); IR (film) 2952, 2875, 2360, 1750, 1698, 1540, 1454, 1105, 1017, 734, 696, 670 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 7.59 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.19–7.17 (m, 2H), 7.11 (dd, *J* = 7.6, 7.6 Hz, 2H), 5.38 (s, 1H), 5.09 (dd, *J* = 8.8, 2.9 Hz, 1H), 4.44 (d, *J* = 12.2 Hz, 1H), 4.40 (d, *J* = 12.2 Hz, 1H), 4.39–4.36 (m, 1H), 4.27 (dd, *J* = 10.1, 10.1 Hz, 1H), 4.02 (d, *J* = 10.5 Hz, 1H), 3.89 (dd, *J* = 2.9, 2.9 Hz, 1H), 3.72 (d, *J* = 10.5 Hz, 1H), 3.62–3.56 (m, 4H), 2.60 (d, *J* = 14.3 Hz, 1H), 2.13 (dd, *J* = 14.3, 10.5 Hz, 1H), 2.12–2.04 (m, 1H), 1.91–1.79 (m, 2H), 1.71–1.63 (m, 3H), 1.55 (s, 3H), 1.07 (q, *J* = 8.0 Hz, 9H), 1.01 (q, *J* = 8.0 Hz, 9H), 0.95 (d, *J* = 7.5 Hz, 3H), 0.73–0.59 (m, 12H); ¹³C NMR (100 MHz, C₆D₆) δ 152.7, 139.6, 139.0, 128.9, 128.5, 128.1, 127.9, 127.6, 127.5, 126.8, 109.2, 101.9, 85.6, 76.9, 76.5, 73.3, 72.9, 71.1, 70.6, 68.0, 42.2, 40.7, 33.1, 27.5, 22.3, 15.1, 11.3, 7.3, 7.2, 5.7, 5.5; HRMS (DART) calcd for C₄₃H₆₈O₇Si₂ [M+H]⁺ 753.4576, found 753.4578.

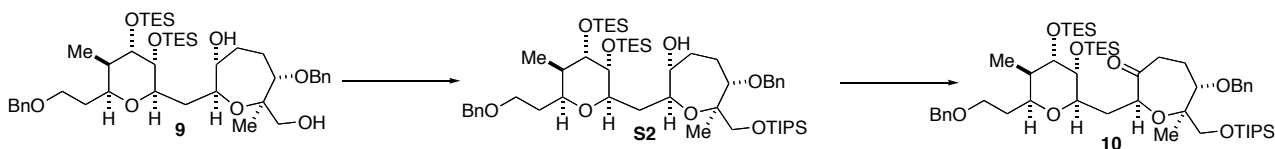
diol **9**



To a solution of the enol ether **8** (31.0 mg, 0.0412 mmol) in THF (1 mL) was added $\text{BH}_3 \cdot \text{SMe}_2$ (2.0 M in THF, 0.20 mL, 0.40 mmol) at 0 °C, and the resultant mixture was stirred at room temperature for 2 h. The reaction mixture was cooled to 0 °C and quenched with 3 M NaOH (0.2 mL), followed by 30% H_2O_2 (0.1 mL), and the mixture was stirred at room temperature for 2.5 h. The aqueous phase was extracted 4 times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (8–10% ethyl acetate/hexane) to afford the alcohol **S1** (24.6 mg, 77%) as a colorless oil: $[\alpha]_{\text{D}}^{28} -14.3$ (c 0.100, CHCl_3); IR (film) 3737, 2959, 2868, 2360, 1650, 1540, 1104, 1033, 737, 667 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.45–7.43 (m, 2H), 7.35–7.34 (m, 5H), 7.32–7.30 (m, 2H), 7.30–7.25 (m, 1H), 5.32 (s, 1H), 4.55 (d, $J = 12.2$ Hz, 1H), 4.48 (d, $J = 12.2$ Hz, 1H), 4.28 (ddd, $J = 8.8, 4.2, 2.5$ Hz, 1H), 4.07 (dd, $J = 9.6, 9.6$ Hz, 1H), 3.86 (d, $J = 2.9$ Hz, 1H), 3.76–3.71 (m, 1H), 3.61–3.54 (m, 3H), 3.51–3.47 (m, 2H), 3.40 (dd, $J = 9.2, 2.1$ Hz, 1H), 2.03 (dddd, $J = 13.9, 8.4, 8.4, 5.5$ Hz, 1H), 1.90 (dd, $J = 14.7, 5.0$ Hz, 1H), 1.87–1.78 (m, 2H), 1.76–1.70 (m, 3H), 1.69–1.58 (m, 2H), 1.36 (s, 3H), 0.97–0.93 (m, 18H), 0.90 (d, $J = 7.2$ Hz, 3H), 0.66–0.54 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 138.0, 128.9, 128.3, 128.2, 127.4, 127.3, 126.2, 101.6, 82.6, 75.5, 74.4, 72.8, 72.1, 71.5, 71.2, 70.9, 70.5, 69.8, 67.2, 41.6, 32.3, 29.3, 27.4, 25.1, 24.4, 22.6, 15.0, 10.9, 7.0, 6.9, 5.2, 5.1; HRMS (FAB) calcd for $\text{C}_{43}\text{H}_{70}\text{O}_8\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 793.4501, found 793.4514.

To a solution of alcohol **S1** (257 mg, 0.333 mmol) in CH_2Cl_2 (5 mL) was added DIBALH (1.02 M in hexane, 3.26 mL, 3.33 mmol) at 0 °C. After stirring at room temperature for 2.5 h, additional DIBALH (1.5 mL) was added. The resultant mixture was stirred for 3.5 h and quenched with saturated aqueous potassium sodium tartrate. The mixture was diluted with ethyl acetate and vigorously stirred for 2.5 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10–30% ethyl acetate/hexane) to afford the diol **9** (189 mg, 73%) as a colorless oil: $[\alpha]_{\text{D}}^{27} -61.9$ (c 0.319, CHCl_3); IR (film) 3747, 2952, 2876, 2360, 1540, 1455, 1103, 734, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33–7.32 (m, 8H), 7.29–7.25 (m, 2H), 4.57 (d, $J = 11.8$ Hz, 1H), 4.53 (d, $J = 11.8$ Hz, 1H), 4.46 (d, $J = 11.8$ Hz, 1H), 4.24 (d, $J = 11.8$ Hz, 1H), 4.24–4.21 (m, 1H), 3.99 (dd, $J = 9.7, 9.7$ Hz, 1H), 3.81 (ddd, $J = 9.2, 3.4, 3.4$ Hz, 1H), 3.74 (dd, $J = 2.5, 2.5$ Hz, 1H), 3.65 (d, $J = 3.0$ Hz, 1H), 3.53 (dd, $J = 6.3, 6.3$ Hz, 1H), 3.42 (dddd, $J = 8.8, 8.8, 8.8, 2.5$ Hz, 1H), 3.38 (dd, $J = 9.6, 2.5$ Hz, 1H), 3.34 (d, $J = 10.5$ Hz, 1H), 3.29 (d, $J = 6.8$ Hz, 1H), 3.14 (d, $J = 10.5$ Hz, 1H), 2.03 (brs, 1H), 1.98–1.92 (m, 1H), 1.86 (dd, $J = 14.7, 3.8$ Hz, 1H), 1.77–1.71 (m, 4H), 1.68–1.55 (m, 3H), 1.22 (s, 3H), 0.95 (q, $J = 8.0$ Hz, 18H), 0.90 (d, $J = 7.5$ Hz, 3H), 0.66–0.52 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.5, 128.3, 128.2, 127.5, 127.5, 127.4, 80.5, 80.0, 75.4, 73.8, 72.9, 72.0, 71.4, 71.3, 71.0, 69.7, 69.1, 67.3, 41.6, 34.4, 32.5, 27.4, 22.6, 16.7, 10.8, 7.0, 6.9, 5.2, 5.1; HRMS (FAB) calcd for $\text{C}_{43}\text{H}_{72}\text{O}_8\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 795.4658, found 795.4677.

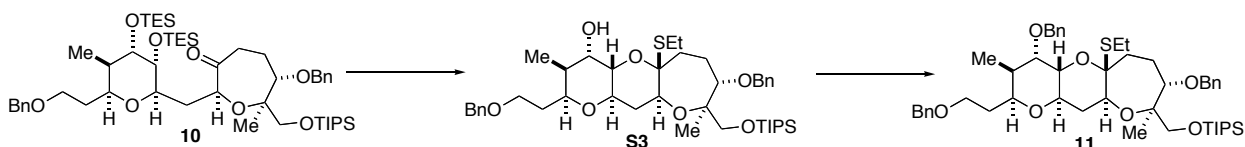
ketone **10**



To a solution of diol **9** (1.49 g, 1.93 mmol) in DMF (30 mL) was added TIPSCl (0.65 mL, 3.07 mmol) and imidazole (430 mg, 6.31 mmol) at room temperature. The resultant mixture was stirred at room temperature overnight, diluted with water, and extracted twice with ether. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5–15% ethyl acetate/hexane) to afford crude TIPS ether **S2**, which was used in the next reaction without further purification.

To a solution of **S2** in CH₂Cl₂ (15 mL) were added 4 Å molecular sieves (850 mg), NMO (640 mg, 5.46 mmol) and catalytic amount of TPAP (ca 80 mg) at room temperature. After stirring at room temperature for 13 h, additional TPAP (ca 160 mg) and NMO (670 mg) were added. The resultant mixture was stirred for 6 h, and then directly subjected to column chromatography on silica gel (10% ethyl acetate/hexane) to afford ketone **10** (1.67 g, 93% for 2 steps) as a colorless oil: [α]_D²⁷ -49.1 (*c* 0.402, CHCl₃); IR (film) 2952, 2875, 2360, 1716, 1540, 1456, 1106, 1004, 734, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.32–7.30 (m, 5H), 7.29–7.28 (m, 2H), 7.26–7.23 (m, 3H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.47 (s, 2H), 4.39 (d, *J* = 11.3 Hz, 1H), 4.32 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.00 (dd, *J* = 6.7, 6.7, 2.1 Hz, 1H), 3.83–3.79 (m, 2H), 3.71 (s, 1H), 3.65 (s, 2H), 3.52–3.49 (m, 2H), 3.41 (dd, *J* = 9.6, 1.2 Hz, 1H), 2.82 (ddd, *J* = 12.6, 9.6, 6.7 Hz, 1H), 2.19 (ddd, *J* = 11.7, 5.5, 5.5 Hz, 1H), 2.11–2.06 (m, 1H), 1.98 (ddd, *J* = 13.8, 9.2, 5.0 Hz, 1H), 1.56 (ddd, *J* = 13.4, 6.7, 6.7 Hz, 1H), 1.14 (s, 3H), 1.06–1.03 (m, 18H), 0.96–0.92 (m, 21H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.66–0.53 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 215.6, 138.6, 138.4, 128.2, 128.2, 127.6, 127.5, 127.4, 127.4, 81.1, 79.0, 76.2, 75.5, 73.0, 71.7, 71.3, 70.9, 70.6, 69.1, 68.0, 41.4, 36.4, 36.1, 32.2, 22.9, 18.0, 17.7, 12.3, 11.9, 11.0, 7.0, 5.2, 5.0; HRMS (FAB) calcd for C₅₂H₉₀O₈Si₃Na [M+Na]⁺ 949.5836, found 949.5864.

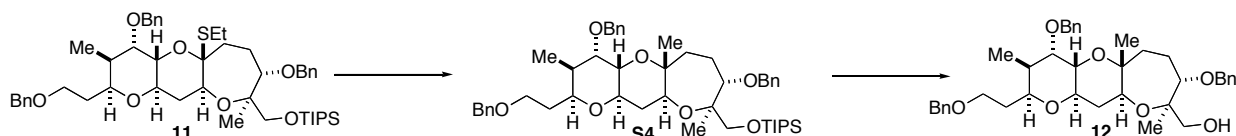
mixed thioacetal **11**



To a solution of the ketone **10** (31.0 mg, 0.0334 mmol) in THF (2 mL) were added EtSH (0.3 mL) and Zn(OTf)₂ (6.0 mg, 0.016 mmol). After stirring at room temperature for 2.5 h, additional three portions of Zn(OTf)₂ (9.2 mg, 9.0 mg, 9.5 mg) were added at 2 h, 6 h, 13 h intervals. The resultant mixture was quenched with Et₃N and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10–20% ethyl acetate/hexane) to afford the crude mixed thioacetal **S3**, which was used in the next reaction without further purification.

To a solution of **S3** in THF (2.5 mL) was added NaH (60% in oil, 25.0 mg, 0.625 mmol) at room temperature. After stirring at room temperature for 2 h, BnBr (0.10 mL, 0.842 mmol) and TBAI (44.0 mg, 0.119 mmol) were added. The reaction mixture was stirred for 15 h, and then quenched with saturated aqueous NH₄Cl. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5–15% ethyl acetate/hexane) to afford mixed thioacetal **11** (20.3 mg, 73% for 2 steps) as a colorless oil: $[\alpha]_D^{28} -34.6$ (*c* 0.282, CHCl₃); IR (film) 3747, 2939, 2865, 2360, 1650, 1540, 1455, 1108, 885, 808, 737, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.36–7.32 (m, 5H), 7.31–7.25 (m, 8H), 7.23–7.22 (m, 2H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.35 (d, *J* = 12.2 Hz, 1H), 4.01 (ddd, *J* = 9.2, 2.9, 2.9 Hz, 1H), 3.96 (ddd, *J* = 11.3, 5.4 Hz, 1H), 3.86 (d, *J* = 8.0 Hz, 1H), 3.84 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.65 (ddd, *J* = 10.5, 10.5, 5.0 Hz, 1H), 3.57–3.48 (m, 3H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.34 (d, *J* = 9.6 Hz, 1H), 2.38 (dq, *J* = 12.6, 7.6 Hz, 1H), 2.24 (dq, *J* = 12.6, 7.6 Hz, 1H), 2.12 (dddd, *J* = 12.2, 12.2, 4.2, 4.2 Hz, 1H), 2.03–1.91 (m, 2H), 1.88–1.75 (m, 3H), 1.57 (dddd, *J* = 14.3, 7.1, 7.1, 4.2 Hz, 1H), 1.27 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.09–0.96 (m, 21H), 0.94 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 138.7, 138.6, 128.2, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1, 93.9, 82.6, 78.9, 78.6, 72.9, 72.8, 72.6, 71.8, 71.4, 70.4, 70.1, 67.4, 38.8, 34.6, 32.5, 32.2, 21.3, 19.1, 18.9, 18.0, 14.9, 11.8, 11.4; HRMS (FAB) calcd for C₄₉H₇₂O₇SSiNa [M+Na]⁺ 855.4660, found 855.4670.

alcohol **12**

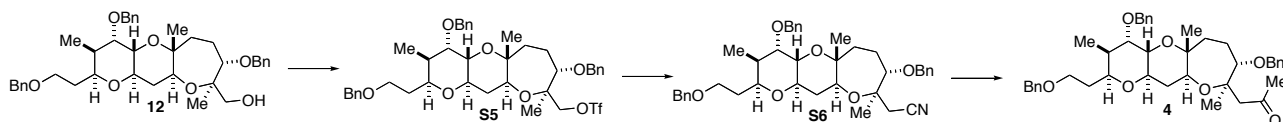


*m*CPBA (65%, 1.10 g, 4.14 mmol) in CH₂Cl₂ (20 mL) was washed twice with saturated aqueous NaHCO₃ and dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (8 mL), which was used in the next reaction.

To a solution of mixed thioacetal **11** (670 mg, 0.804 mmol) in CH₂Cl₂ (8 mL) at -78 °C was added the above *m*CPBA solution. The resultant solution was stirred at -78 °C for 1 h, three portions of Me₃Al (2 M in heptane, 1.6 mL, 3.2 mmol) were added at 50 min intervals while the reaction mixture was allowed to warm up to 0 °C. The reaction mixture was stirred at 0 °C for 30 min, and then quenched with MeOH and saturated aqueous potassium sodium tartrate. The mixture was diluted with ethyl acetate and vigorously stirred for 1 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10% ethyl acetate/hexane) to afford crude tricyclic ether **S4**, which was used in the next reaction without further purification.

To a solution of **S4** in THF (20 mL) was added TBAF (1.0 M in THF, 4.0 mL, 4.0 mmol) at room temperature. After stirring at room temperature for 30 min, the reaction was quenched with saturated aqueous NH₄Cl. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20–40% ethyl acetate/hexane) to afford alcohol **12** (440 mg, 87% for 2 steps) as a colorless oil: $[\alpha]_D^{27} -168$ (*c* 0.117, CHCl₃); IR (film) 3748, 2933, 2868, 2360, 1650, 1560, 1457, 1097, 1064, 737, 699, 667 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.35–7.25 (m, 15H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 4.58 (d, *J* = 12.6 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.00 (ddd, *J* = 9.2, 2.0, 2.0 Hz, 1H), 3.77 (dd, *J* = 11.8, 4.6 Hz, 1H), 3.61 (ddd, *J* = 11.8, 10.1, 4.2 Hz, 1H), 3.56 (dd, *J* = 2.5, 2.5 Hz, 1H), 3.54–3.45 (m, 2H), 3.42–3.40 (m, 2H), 3.36 (d, *J* = 10.9 Hz, 1H), 3.21 (dd, *J* = 10.5, 6.7 Hz, 1H), 2.01–1.90 (m, 3H), 1.86 (ddd, *J* = 11.7, 4.6, 4.6 Hz, 1H), 1.77 (dddd, *J* = 14.7, 9.6, 5.5, 5.5 Hz, 1H), 1.67 (dd, *J* = 13.4, 13.4 Hz, 1H), 1.57 (ddd, *J* = 11.3, 7.1, 3.8 Hz, 1H), 1.54–1.44 (m, 2H), 1.26 (s, 3H), 1.18 (s, 3H), 0.93 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.7, 138.5, 138.4, 128.4, 128.3, 128.1, 127.7, 127.5, 127.4, 127.4, 127.4, 127.1, 81.0, 80.2, 79.4, 77.2, 72.9, 71.9, 71.8, 71.3, 71.1, 70.2, 69.1, 67.4, 39.1, 34.9, 33.8, 32.5, 22.6, 17.3, 15.5, 11.6; HRMS (DART) calcd for C₃₉H₅₁O₇ [M+H]⁺ 631.3629, found 631.3618.

ketone **4**

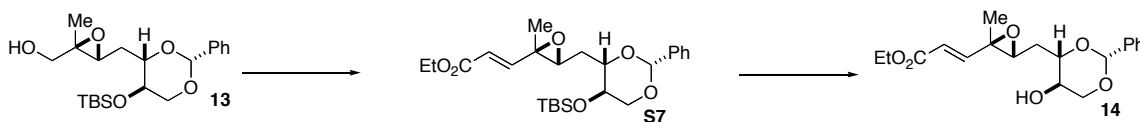


To a solution of alcohol **12** (30.3 mg, 0.0481 mmol) in CH_2Cl_2 (2 mL) at $-78\text{ }^\circ\text{C}$ were added 2,6-lutidine (0.10 mL, 0.86 mmol) and Tf_2O (0.050 mL, 0.30 mmol). The resultant solution was stirred for 15 min and quenched with Et_3N and saturated aqueous NaHCO_3 . The aqueous phase was extracted three times with EtOAc . The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to short column chromatography on silica gel (30% ethyl acetate/hexane) to afford crude triflate **S5**, which was used in the next reaction without further purification.

To a solution of **S5** in DMSO (1 mL) was added NaCN (19.2 mg, 0.392 mmol) at room temperature. After stirring at room temperature for 2.5 h, additional NaCN (19.0 mg, 0.387 mmol) was added. The resultant mixture was stirred at $80\text{ }^\circ\text{C}$ for 30 min, and then saturated aqueous NaHCO_3 was added. The aqueous phase was extracted three times with EtOAc . The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to short column chromatography on silica gel (30% ethyl acetate/hexane) to afford crude nitrile **S6**, which was used in the next reaction without further purification.

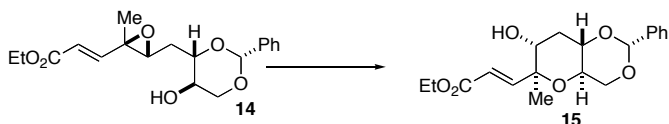
To a solution of **S6** in ether (3.5 mL) was added MeLi (1.07 M in ether, 0.5 mL, 0.54 mmol) at $-78\text{ }^\circ\text{C}$. After stirring at the same temperature for 20 min, the reaction mixture was allowed to warm to $0\text{ }^\circ\text{C}$. After stirring for 75 min, the reaction was quenched with saturated aqueous NH_4Cl . The aqueous phase was extracted three times with EtOAc . The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (30% ethyl acetate/hexane) to afford ketone **4** (21.6 mg, 68% for 3 steps) as a colorless oil: $[\alpha]_{\text{D}}^{28}$ 1.91 (c 0.0940, CHCl_3); IR (film) 3436, 2920, 2868, 2354, 1701, 1457, 1380, 1097, 1058, 737, 693 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33–7.25 (m, 11H), 7.23–7.18 (m, 4H), 4.82 (d, $J = 12.2$ Hz, 1H), 4.59 (d, $J = 5.5$ Hz, 1H), 4.56 (d, $J = 5.5$ Hz, 1H), 4.48 (d, $J = 12.2$ Hz, 1H), 4.44 (d, $J = 12.2$ Hz, 1H), 4.33 (d, $J = 12.2$ Hz, 1H), 3.99 (ddd, $J = 9.2, 2.9, 2.9$ Hz, 1H), 3.76 (dd, $J = 11.8, 4.6$ Hz, 1H), 3.62–3.49 (m, 5H), 3.40 (dd, $J = 10.1, 2.5$ Hz, 1H), 2.65 (d, $J = 13.0$ Hz, 1H), 2.18 (d, $J = 13.4$ Hz, 1H), 2.15 (s, 3H), 1.97–1.89 (m, 3H), 1.83 (ddd, $J = 11.3, 4.6, 4.6$ Hz, 1H), 1.75 (dddd, $J = 14.7, 9.6, 5.9, 5.9$ Hz, 1H), 1.67 (dd, $J = 14.7, 14.7$ Hz, 1H), 1.57–1.51 (m, 2H), 1.45 (ddd, $J = 12.2, 12.2, 12.2$ Hz, 1H), 1.31 (s, 3H), 1.21 (s, 3H), 0.92 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.0, 139.6, 138.5, 138.4, 128.3, 128.3, 128.1, 127.7, 127.4, 127.3, 127.1, 81.8, 80.3, 79.4, 77.2, 72.9, 72.8, 71.7, 71.4, 71.0, 70.2, 67.4, 53.7, 39.0, 34.8, 33.8, 32.5, 32.4, 29.7, 21.7, 19.5, 15.5, 11.6; HRMS (FAB) calcd for $\text{C}_{41}\text{H}_{52}\text{O}_7\text{Na}$ $[\text{M}+\text{Na}]^+$ 679.3605, found 679.3597.

hydroxy epoxide **14**



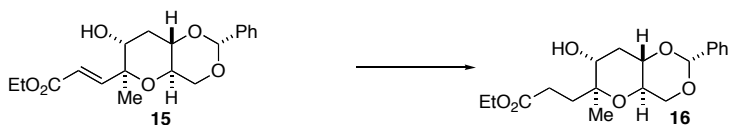
To a solution of alcohol **13** (1.66 g, 4.21 mmol) in CH_2Cl_2 (40 mL) at room temperature were added iodobenzene diacetate (1.89 g, 5.87 mmol) and TEMPO (210 mg, 1.34 mmol). After stirring for 3.5 h, $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ (2.05 g, 5.88 mmol) was added. The resultant mixture was stirred for 1.5 h and then saturated aqueous Na_2SO_3 was added to the solution. The aqueous phase was extracted three times with ether. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5% ethyl acetate/hexane) to afford the crude ester **S7**, which was used in the next reaction without further purification. To a solution of **S7** was added a stock solution of TBAF/AcOH [0.1 M solution prepared from TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol), AcOH (0.30 mL, 5.2 mmol), and THF (44.7 mL), 50.0 mL, 5.0 mmol] at room temperature. The reaction mixture was stirred at room temperature for 13 h, and then quenched with saturated aqueous NaHCO_3 . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (30–50% ethyl acetate/hexane) to afford hydroxy epoxide **14** (440 mg, 87% for 2 steps) as a colorless oil: $[\alpha]_{\text{D}}^{28} -30.3$ (c 0.276, CHCl_3); IR (film) 3748, 3445, 2971, 2856, 2360, 1716, 1650, 1540, 1456, 1308, 1076, 1027, 977, 756, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.46–7.43 (m, 2H), 7.37–7.32 (m, 3H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.01 (d, $J = 15.6$ Hz, 1H), 5.49 (s, 1H), 4.28 (dd, $J = 10.5, 5.0$ Hz, 1H), 4.17 (q, 7.1 Hz, 2H), 3.89–3.80 (m, 1H), 3.78–3.74 (m, 1H), 3.59 (dd, $J = 10.7, 10.7$ Hz, 1H), 3.23–3.20 (m, 1H), 2.43 (brs, 1H), 2.21–2.16 (m, 1H), 2.04–1.99 (m, 1H), 1.45 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 149.3, 137.5, 129.0, 128.3, 128.3, 126.1, 126.1, 121.9, 101.1, 79.7, 71.1, 64.7, 62.1, 60.6, 58.2, 30.8, 15.3, 14.2; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 349.1465, found 349.1450.

pyran **15**



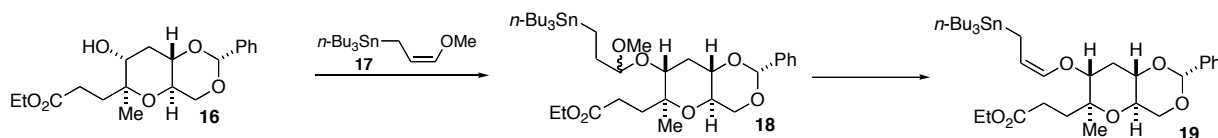
To a solution of the hydroxy epoxide **14** (3.52 g, 10.1 mmol) in CH₂Cl₂ (200 mL) at room temperature was added PPTS (3.51 g, 14.0 mmol). After stirring for 4 h, PPTS (1.54 g, 6.13 mmol) was added. The resultant mixture was stirred for 1 h, quenched with Et₃N and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20–40% ethyl acetate/hexane) to afford the pyran **15** (2.71 g, 77%) as a colorless amorphous solid: $[\alpha]_D^{18}$ 18.8 (*c* 0.927, CHCl₃); IR (film) 3748, 3463, 2982, 2360, 1715, 1653, 1456, 1369, 1305, 1187, 1092, 1019, 985, 754, 683 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.37 (m, 2H), 7.28–7.24 (m, 2H), 7.01 (d, *J* = 15.5 Hz, 1H), 5.97 (*J* = 16.0 Hz, 1H), 5.39 (s, 1H), 4.15 (dd, *J* = 9.7, 4.2 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.56 (dd, *J* = 9.9, 9.9 Hz, 1H), 3.50 (dd, *J* = 9.3, 9.3, 4.2 Hz, 1H), 3.36 (ddd, *J* = 12.0, 8.8, 4.2 Hz, 1H), 3.01 (brs, 1H), 2.10 (ddd, *J* = 11.8, 4.2, 4.2 Hz, 1H), 1.73 (ddd, *J* = 11.8, 11.6, 11.3 Hz, 1H), 1.25 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 150.1, 136.8, 128.7, 127.9, 127.9, 125.7, 125.7, 119.0, 101.3, 76.6, 76.4, 70.4, 69.3, 69.5, 60.2, 33.3, 14.6, 13.8; HRMS (DART) calcd for C₁₉H₂₅O₆ [M+H]⁺ 349.1651, found 349.1660.

ester **16**



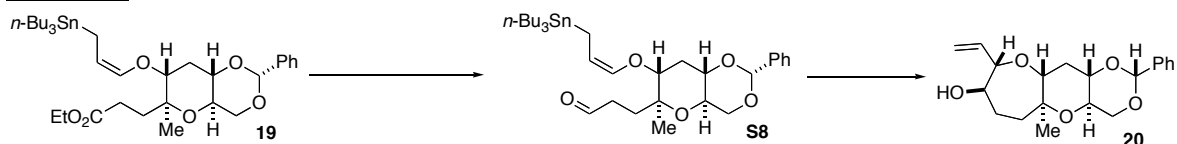
To a solution of the pyran **15** (1.25 g, 3.59 mmol) in EtOAc (25 mL) was added 5% Pd/C (125 mg). The reaction mixture was stirred at room temperature overnight under a hydrogen atmosphere. The mixture was filtered through a pad of Celite[®] and concentrated under reduced pressure to afford ester **16** (1.27 g, quant) as a colorless amorphous solid: $[\alpha]_D^{18}$ 23.1 (*c* 1.22, CHCl₃); IR (film) 3838, 3747, 3446, 2980, 2945, 2360, 1731, 1540, 1455, 1374, 1290, 1186, 1098, 1017, 754, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.37–7.35 (m, 1H), 7.26–7.21 (m, 4H), 5.38 (s, 1H), 4.08 (dd, *J* = 10.1, 4.2 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.49 (dd, *J* = 10.1, 10.1 Hz, 1H), 3.45–3.40 (m, 1H), 3.34 (ddd, *J* = 12.0, 8.6, 4.2 Hz, 1H), 2.70 (brs, 1H), 2.42–2.36 (m, 1H), 2.30–2.23 (m, 1H), 2.11 (ddd, *J* = 11.8, 4.2, 4.2 Hz, 1H), 1.89–1.78 (m, 2H), 1.72 (ddd, *J* = 11.8, 11.8, 11.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.0, 137.4, 129.0, 128.3, 128.3, 126.1, 126.1, 101.7, 77.7, 77.4, 69.9, 69.8, 66.2, 60.7, 33.7, 33.2, 27.6, 16.0, 14.1; HRMS (DART) calcd for C₁₉H₂₇O₆ [M+H]⁺ 351.1802, found 351.1808.

allylstannane **19**



To a solution of ester **16** (43.2 mg, 0.123 mmol) in CH₂Cl₂ (2 mL) were added allylstannane **17** (112 mg, 0.310 mmol) and CSA (5.4 mg, 0.0232 mmol) at room temperature. The resultant mixture was stirred for 12.5 h, quenched with Et₃N and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10% ethyl acetate/hexane, containing 0.5% of Et₃N) to afford mixed acetal **18** as a mixture of the diastereomers, which was used in the next reaction without further purification.

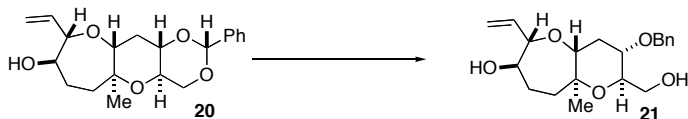
To a solution of **18** in CH₂Cl₂ (2 mL) were added HMDS (0.40 mL, 1.92 mmol) and TMSI (0.20 mL, 1.46 mmol) at 0 °C. The resultant mixture was stirred at 0 °C for 45 min, saturated aqueous NaHCO₃ was added. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (3–5% ethyl acetate/hexane, containing 0.5% of Et₃N) to afford allylstannane **19** (44.0 mg, 56% for 2 steps) as a colorless oil: [α]_D²⁸ 28.7 (*c* 0.0516, C₆H₆); IR (film) 3747, 2959, 2360, 1735, 1650, 1457, 1374, 1181, 1094, 1020, 750, 693 cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 7.75–7.73 (m, 1H), 7.30–7.27 (m, 2H), 7.22–7.20 (m, 1H), 5.77 (d, *J* = 6.3 Hz, 1H), 5.45 (s, 1H), 4.78–4.72 (m, 1H), 4.20 (ddd, *J* = 7.6, 1.7, 1.7 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.61–3.48 (m, 2H), 3.42 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.12 (ddd, *J* = 12.1, 8.5, 4.2 Hz, 1H), 2.58–2.45 (m, 2H), 2.33–2.28 (m, 2H), 2.14–2.09 (m, 1H), 1.95–1.87 (m, 2H), 1.73–1.65 (m, 6H), 1.51–1.44 (m, 6H), 1.23 (s, 3H), 1.08–0.99 (m, 19H); ¹³C NMR (100 MHz, C₆D₆) δ 173.0, 140.4, 138.6, 128.9, 128.8, 126.7, 126.7, 107.6, 101.7, 80.7, 77.3, 76.5, 70.0, 66.6, 60.1, 35.5, 32.0, 29.7, 29.6, 29.5, 28.4, 28.0, 27.8, 27.5, 16.1, 14.3, 14.0, 14.0, 14.0, 9.7, 9.7, 9.7, 6.5; HRMS (DART) calcd for C₃₄H₅₇O₆Sn [M+H]⁺ 681.3172, found 681.3171.

alcohol 20

To a solution of allylstannane **19** (44.0 mg, 0.0647 mmol) in CH_2Cl_2 (3 mL) was added DIBALH (1.0 M in hexane, 0.24 mL, 0.24 mmol) at -78°C . After stirring at the same temperature for 5 min, the resultant mixture was quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted with EtOAc and vigorously stirred for 1 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to afford crude aldehyde **S8**, which was used in the next reaction without purification.

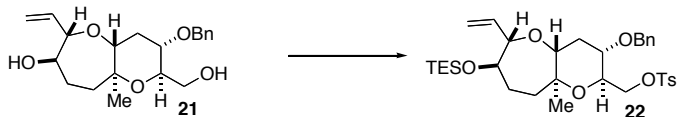
To a solution aldehyde **S8** in CH_2Cl_2 (3 mL) was added $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.010 mL, 0.079 mmol) at -78°C . After stirring at the same temperature for 5 min, the resultant mixture was quenched with saturated aqueous NaHCO_3 . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10% ethyl acetate/ CHCl_3) to afford alcohol **20** (20.2 mg, 90% for 2 steps) as a colorless amorphous solid: $[\alpha]_{\text{D}}^{25} -16.8$ (c 0.196, CHCl_3); IR (film) 3748, 3453, 3278, 2935, 2862, 2361, 1651, 1454, 1383, 1098, 1024, 946, 927, 754, 695 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48–7.46 (m, 2H), 7.36–7.31 (m, 3H), 5.75 (ddd, $J = 16.8, 11.3, 5.6$ Hz, 1H), 5.49 (s, 1H), 5.32 (dd, $J = 17.2, 1.3$ Hz, 1H), 5.14 (dd, $J = 10.5, 1.3$ Hz, 1H), 4.22 (dd, $J = 9.9, 4.0$ Hz, 1H), 4.15–4.13 (m, 1H), 3.92–3.90 (m, 1H), 3.81 (dd, $J = 12.0, 4.4$ Hz, 1H), 3.63 ($J = 9.9, 9.9$ Hz, 1H), 3.58 (ddd, $J = 9.7, 9.7, 4.6$ Hz, 1H), 3.47 (ddd, $J = 12.0, 8.6, 3.7$ Hz, 1H), 2.18 (ddd, $J = 11.8, 4.4, 4.4$ Hz, 1H), 1.97 (ddd, $J = 14.3, 10.4, 4.6$ Hz, 1H), 1.84–1.76 (m, 3H), 1.60–1.56 (m, 1H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 136.9, 129.0, 128.3, 128.3, 126.2, 126.2, 116.0, 101.6, 85.1, 78.2, 77.9, 76.5, 74.0, 70.1, 66.0, 34.4, 32.7, 25.5, 16.3; HRMS (DART) calcd for $\text{C}_{20}\text{H}_{27}\text{O}_5$ $[\text{M}+\text{H}]^+$ 347.1853, found 347.1867.

diol **21**



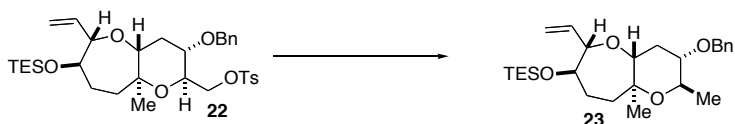
To a solution of alcohol **20** (205 mg, 0.592 mmol) in CH_2Cl_2 (6 mL) was added DIBALH (1.0 M in hexane, 3.0 mL, 3.0 mmol) at 0 °C. After stirring at room temperature for 22 h, the reaction was quenched with saturated aqueous potassium sodium tartrate. The mixture was diluted with ethyl acetate and vigorously stirred for 18 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (50% ethyl acetate/hexane) to afford the diol **21** (188 mg, 91%) as a colorless amorphous solid: $[\alpha]_{\text{D}}^{25}$ 58.4 (*c* 0.367, CHCl_3); IR (film) 3421, 2940, 2872, 2360, 1644, 1455, 1374, 1350, 1213, 1072, 1026, 923, 728, 699, 679 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29–7.19 (m, 5H), 5.70 (ddd, $J = 16.7, 11.0, 5.9$ Hz, 1H), 5.26 (dd, $J = 17.2, 1.3$ Hz, 1H), 5.09 (dd, $J = 10.5, 1.3$ Hz, 1H), 4.55 (d, $J = 11.8$ Hz, 1H), 4.37 (d, $J = 11.3$ Hz), 4.03–4.01 (m, 1H), 3.80 (brs, 1H), 3.71 (d, $J = 10.9$ Hz, 1H), 3.50 (br, 1H), 3.54 (dd, $J = 12.4, 4.4$ Hz, 1H), 3.45–3.42 (m, 1H), 3.33 (ddd, $J = 10.4, 10.4, 4.6$ Hz, 1H), 2.26 (ddd, $J = 12.2, 4.6, 4.6$ Hz, 1H), 2.21 (brs, 1H), 2.05 (brs, 1H), 1.90–1.84 (m, 1H), 1.74–1.69 (m, 2H), 1.59–1.48 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 137.1, 128.4, 128.4, 128.3, 127.7, 127.7, 116.0, 85.3, 76.7, 76.5, 73.9, 73.2, 72.4, 70.7, 62.9, 34.7, 32.5, 25.7, 16.0; HRMS (DART) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_5$ $[\text{M}+\text{H}]^+$ 349.2010, found 349.2009.

tosylate 22



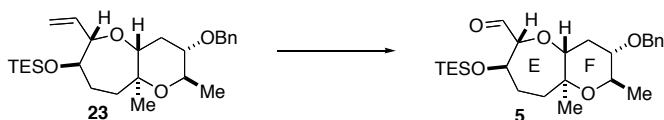
To a solution of diol **21** (101 mg, 0.290 mmol) in CH₂Cl₂ (6 mL) at 0 °C were added Et₃N (0.20 mL, 1.43 mmol), DMAP (4.5 mg, 0.037 mmol) and *p*-TsCl (65.0 mg, 0.341 mmol). After stirring at the same temperature for 14.5 h, *p*-TsCl (60.0 mg, 0.315 mmol) was added. The resultant mixture was stirred for 1.5 h and then TESOTf (0.10 mL, 0.44 mmol) was added. The resultant solution was stirred for 30 min and quenched with saturated aqueous NH₄Cl. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st and 2nd: 10% ethyl acetate/hexane) to afford tosylate **22** (136 mg, 76%) as a colorless oil: [α]_D²⁵ 38.6 (*c* 0.0230, CHCl₃); IR (film) 3447, 2920, 2360, 1650, 1540, 1093, 808, 748, 671 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.78–7.75 (m, 2H), 7.32–7.20 (m, 7H), 5.70 (ddd, *J* = 17.0, 10.7, 6.1 Hz, 1H), 5.24 (dd, *J* = 16.8, 1.3 Hz, 1H), 5.07 (dd, *J* = 11.6, 1.3 Hz, 1H), 4.54 (d, *J* = 11.3 Hz, 1H), 4.32 (d, *J* = 10.9 Hz), 4.21–4.14 (m, 2H), 4.08 (dd, *J* = 6.1, 1.3 Hz, 1H), 3.88 (d, *J* = 6.3 Hz, 1H), 3.65 (dd, *J* = 12.8, 4.6 Hz, 1H), 3.54 (dddd, *J* = 4.9, 4.9, 4.9, 2.1 Hz, 1H), 3.30–3.25 (m, 1H), 2.39 (s, 3H), 2.30–2.25 (m, 1H), 2.29 (ddd, *J* = 12.2, 4.8, 4.8 Hz, 1H), 1.88 (ddd, *J* = 12.8, 12.8, 3.8 Hz, 1H), 1.64–1.47 (m, 2H), 1.34 (ddd, *J* = 13.6, 5.3, 2.5 Hz, 1H), 1.12 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 137.8, 137.2, 133.2, 129.6, 129.6, 128.4, 128.1, 128.0, 128.0, 127.8, 127.8, 115.3, 85.9, 76.8, 74.9, 74.5, 72.7, 70.6, 70.5, 70.1, 34.0, 32.5, 25.3, 21.6, 15.3, 6.9, 4.8; HRMS (FAB) calcd for C₃₃H₄₈O₇SiSNa [M+Na]⁺ 639.2782, found 639.2784.

olefin **23**



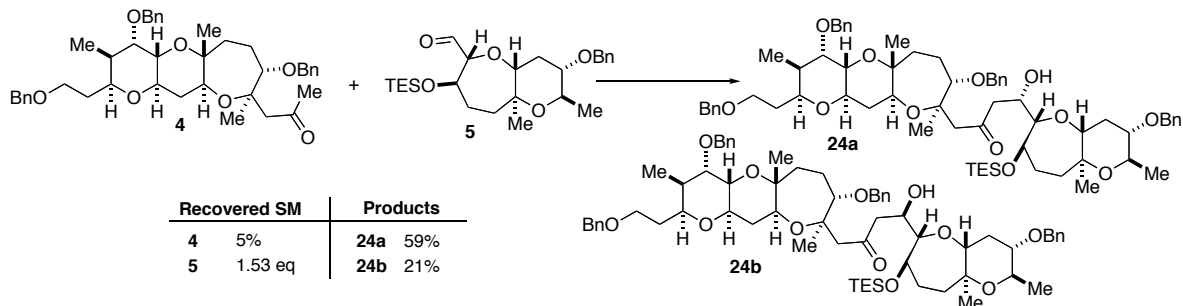
To a solution of tosylate **22** (136 mg, 0.221 mmol) in THF (5.5 mL) at 0 °C was added LiAlH₄ (101 mg, 2.66 mmol). The resultant mixture was gradually warmed to room temperature, stirred for 23 h, and then quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted with EtOAc and vigorously stirred for 3 h. The aqueous phase was extracted three times with ether. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5% ethyl acetate/hexane) to afford olefin **23** (59.3 mg, 60%) as a colorless oil: [α]_D²⁸ 23.8 (*c* 0.138, CHCl₃); IR (film) 3447, 2945, 2882, 2360, 1650, 1457, 1096, 739 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27–7.17 (m, 5H), 5.65 (ddd, *J* = 17.0, 10.7, 6.3 Hz, 1H), 5.20 (dd, *J* = 7.2, 1.3 Hz, 1H), 5.01 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 4.06–4.03 (m, 1H), 3.84–3.81 (m, 1H), 3.64 (dd, *J* = 12.2, 4.2 Hz, 1H), 3.48–3.42 (m, 1H), 2.94–2.89 (m, 1H), 2.20 (ddd, *J* = 12.2, 4.2, 4.2 Hz, 1H), 1.94–1.86 (m, 1H), 1.57–1.54 (m, 2H), 1.48–1.44 (m, 1H), 1.40–1.36 (m, 1H), 1.15 (d, *J* = 2.5 Hz, 3H), 1.14 (s, 3H), 0.89–0.85 (m, 9H), 0.53–0.48 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 137.4, 128.4, 128.4, 127.8, 127.8, 127.7, 115.2, 85.9, 79.1, 76.4, 75.6, 74.6, 70.8, 68.5, 34.5, 33.0, 25.4, 18.7, 15.7, 6.9, 4.8; HRMS (DART) calcd for C₂₆H₄₃O₄Si [M+H]⁺ 447.2925, found 447.2931.

aldehyde **5**



A solution of olefin **23** (58.0 mg, 0.130 mmol) in CH₂Cl₂ (30 mL) was cooled to -78 °C, and ozone was bubbled through the solution turned blue. Oxygen was bubbled through the solution turned colorless, and PPh₃ (88.8 mg, 0.339 mmol) was added. The mixture was warmed to room temperature, stirred for 1 h and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st: 10% ethyl acetate/hexane, 2nd: 8% ethyl acetate/hexane) to afford aldehyde **5** (53.8 mg, 92%) as a colorless oil: [α]_D²⁵ 36.7 (*c* 1.35, CHCl₃); IR (film) 2952, 2879, 1736, 1455, 1376, 1239, 1097, 1002, 812, 739, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.44 (s, 1H), 7.27–7.16 (m, 5H), 4.57–4.37 (m, 2H), 4.29 (d, *J* = 6.7 Hz, 1H), 3.94 (d, *J* = 1.7 Hz, 1H), 3.58 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.49–3.44 (m, 1H), 2.93 (ddd, *J* = 11.4, 8.9, 4.6 Hz, 1H), 2.25–2.21 (m, 1H), 1.93–1.84 (m, 1H), 1.70–1.64 (m, 1H), 1.57–1.50 (m, 1H), 1.42–1.38 (m, 1H), 1.36–1.30 (m, 1H), 1.15 (d, *J* = 2.5 Hz, 3H), 1.14 (s, 3H), 0.87–0.80 (m, 9H), 0.54–0.45 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 201.3, 138.2, 128.4, 128.4, 127.7, 127.7, 127.7, 90.3, 78.9, 77.1, 76.2, 71.2, 71.0, 68.5, 34.2, 32.7, 27.5, 18.6, 15.2, 6.8, 4.6; HRMS (DART) calcd for C₂₅H₄₁O₅Si [M+H]⁺ 449.2718, found 449.2714.

ketones **24a** and **24b**



To a solution of diisopropylamine (0.10 mL, 0.71 mmol) in THF (1 mL) was added *n*-BuLi (1.57 M in hexane, 0.30 mL, 0.46 mmol) at $-15\text{ }^{\circ}\text{C}$. After stirred at $0\text{ }^{\circ}\text{C}$ for 30 min, methyl ketone **4** (246 mg, 0.375 mmol) in THF (1.0 mL + 1.0 mL rinse) was added slowly to the above LDA solution at $0\text{ }^{\circ}\text{C}$. After stirring at $0\text{ }^{\circ}\text{C}$ for 1 h, aldehyde **5** (479 mg, 1.07 mmol) in THF (1.0 mL + 1.0 mL rinse) was added to the solution at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min, and then quenched with saturated aqueous NH_4Cl . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel three times (1st and 2nd: 20% ethyl acetate/hexane, 3rd: flash column chromatography 25% ethyl acetate/hexane) to afford ketone **24a** (245 mg, 59%), ketone **24b** (87.3 mg, 21%) and recovered ketone **4** (11.1 mg, 5 %) and recovered aldehyde **5** (258 mg, 0.576 mmol) as colorless oils.

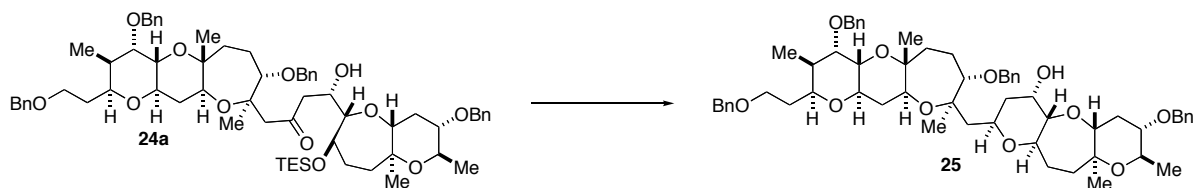
data for **24a**: $[\alpha]_{\text{D}}^{28}$ 2.33 (*c* 0.166, CHCl_3); IR (film) 3743, 3455, 2947, 2882, 2360, 1697, 1457, 1380, 1096, 1065, 735, 699, 676 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35–7.31 (m, 8H), 7.29–7.25 (m, 8H), 7.22–7.21 (m, 4H), 4.81 (d, $J = 12.2\text{ Hz}$, 1H), 4.63 (d, $J = 11.8\text{ Hz}$, 1H), 4.59 (d, $J = 11.8\text{ Hz}$, 1H), 4.57 (d, $J = 11.8\text{ Hz}$, 1H), 4.47 (d, $J = 11.8\text{ Hz}$, 1H), 4.44 (d, $J = 11.3\text{ Hz}$, 1H), 4.43 (d, $J = 12.2\text{ Hz}$, 1H), 4.34 (d, $J = 11.8\text{ Hz}$, 1H), 4.23 (d, $J = 6.3\text{ Hz}$, 1H), 3.98 (ddd, $J = 9.2, 2.9, 2.9\text{ Hz}$, 1H), 3.78 (dd, $J = 12.2, 4.6\text{ Hz}$, 1H), 3.68 (dddd, $J = 8.0, 8.0, 4.6, 2.9\text{ Hz}$, 1H), 3.61–3.55 (m, 3H), 3.53–3.48 (m, 4H), 3.42–3.38 (m, 2H), 2.98 (ddd, $J = 10.9, 9.6, 4.7\text{ Hz}$, 1H), 2.89 (d, $J = 5.0\text{ Hz}$, 1H), 2.80 (dd, $J = 17.6, 2.5\text{ Hz}$, 1H), 2.69 (d, $J = 13.0\text{ Hz}$, 1H), 2.65 (dd, $J = 17.6, 8.8\text{ Hz}$, 1H), 2.23 (d, $J = 13.4\text{ Hz}$, 1H), 2.20 (ddd, $J = 11.8, 4.6, 4.6\text{ Hz}$, 1H), 2.02–1.88 (m, 3H), 1.84 (ddd, $J = 11.3, 4.6, 4.6\text{ Hz}$, 1H), 1.77–1.66 (m, 3H), 1.57–1.53 (m, 3H), 1.50–1.40 (m, 3H), 1.34 (s, 3H), 1.22 (s, 3H), 1.21 (d, $J = 5.9\text{ Hz}$, 3H), 1.13 (s, 3H), 0.94 (t, $J = 8.0\text{ Hz}$, 9H), 0.90 (d, $J = 7.6\text{ Hz}$, 3H), 0.59 (q, $J = 8.0\text{ Hz}$, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 210.8, 139.6, 138.5, 138.3, 138.3, 128.4, 128.4, 128.3, 128.3, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1, 87.9, 81.7, 80.7, 79.3, 79.1, 77.2, 77.1, 76.6, 76.0, 72.9, 72.8, 71.8, 71.6, 71.6, 71.0, 71.0, 70.9, 70.2, 68.5, 67.4, 53.4, 48.1, 39.0, 34.8, 34.3, 33.8, 32.7, 32.5, 26.3, 21.7, 19.8, 18.7, 15.7, 15.5, 11.6, 6.9, 4.8; HRMS (FAB) calcd for $\text{C}_{66}\text{H}_{92}\text{O}_{12}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 1127.6250, found 1127.6234.

data for **24b**:

$[\alpha]_{\text{D}}^{28}$ 9.54 (*c* 0.0820, CHCl_3); IR (film) 3750, 3447, 2933, 2868, 2360, 1701, 1457, 1380, 1097, 1072, 737,

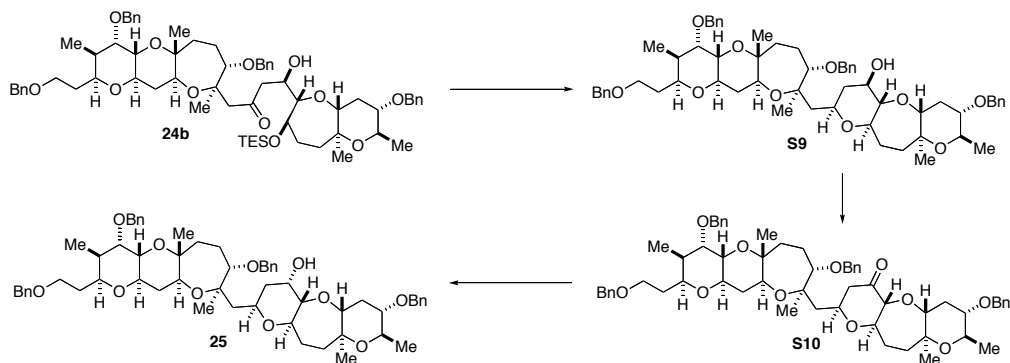
693, 671 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34–7.30 (m, 8H), 7.29–7.25 (m, 8H), 7.23–7.20 (m, 4H), 4.81 (d, $J = 12.2$ Hz, 1H), 4.62 (d, $J = 11.3$ Hz, 1H), 4.58 (d, $J = 11.8$ Hz, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.46 (d, $J = 12.2$ Hz, 1H), 4.44 (d, $J = 11.8$ Hz, 1H), 4.42 (d, $J = 12.2$ Hz, 1H), 4.34 (d, $J = 11.8$ Hz, 1H), 4.10 (dd, $J = 3.8, 2.1$ Hz, 1H), 3.99–3.95 (m, 2H), 3.77 (dd, $J = 12.2, 4.6$ Hz, 1H), 3.63–3.47 (m, 6H), 3.41 (dd, $J = 12.2, 4.6$ Hz, 1H), 3.38 (dd, $J = 10.1, 2.1$ Hz, 1H), 3.35 (dd, $J = 3.4, 2.1$ Hz, 1H), 3.00 (ddd, $J = 10.9, 9.6, 4.6$ Hz, 1H), 2.90 (d, $J = 4.6$ Hz, 1H), 2.76 (dd, $J = 16.8, 9.2$ Hz, 1H), 2.70 (d, $J = 13.4$ Hz, 1H), 2.55 (dd, $J = 16.4, 2.9$ Hz, 1H), 2.24 (d, $J = 13.8$ Hz, 1H), 2.18 (ddd, $J = 11.8, 4.6, 4.6$ Hz, 1H), 1.98–1.88 (m, 3H), 1.82 (ddd, $J = 11.3, 4.6, 4.6$ Hz, 1H), 1.76–1.65 (m, 4H), 1.55–1.51 (m, 3H), 1.48–1.40 (m, 2H), 1.32 (s, 3H), 1.22 (s, 3H), 1.21 (d, $J = 5.9$ Hz, 3H), 1.18 (s, 3H), 0.93 (t, $J = 8.0$ Hz, 9H), 0.88 (d, $J = 7.2$ Hz, 3H), 0.57 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.2, 139.6, 138.5, 138.3, 138.3, 128.4, 128.4, 128.3, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1, 88.4, 81.7, 80.6, 79.3, 79.2, 78.5, 77.2, 77.2, 76.0, 72.9, 72.8, 72.3, 71.8, 71.7, 71.5, 71.1, 71.0, 70.2, 68.5, 67.4, 53.8, 48.0, 39.0, 34.7, 33.9, 32.6, 32.5, 29.7, 28.4, 21.7, 19.6, 18.8, 15.7, 15.6, 11.6, 6.9, 4.8; HRMS (FAB) calcd for $\text{C}_{66}\text{H}_{92}\text{O}_{12}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 1127.6250, found 1127.6267.

alcohol **25**



To a solution of the ketone **24a** (74.0 mg, 0.0669 mmol) in CH_2Cl_2 (13 mL) and Et_3SiH (4 mL) at $-78\text{ }^\circ\text{C}$ was added dropwise TMSOTf (0.1 M in CH_2Cl_2 , 4.0 mL, 0.40 mmol). After stirring for 30 min, the reaction was quenched with saturated aqueous NH_4Cl . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (30–40% ethyl acetate/hexane) to afford alcohol **25** (63.7 mg, 98%) as a colorless oil: $[\alpha]_{\text{D}}^{28}$ 13.1 (c 0.106, CHCl_3); IR (film) 3743, 3447, 2933, 2868, 2360, 1650, 1560, 1453, 1381, 1082, 737, 699, 676 cm^{-1} ; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35–7.25 (m, 16H), 7.23–7.19 (m, 4H), 4.82 (d, $J=12.2$ Hz, 1H), 4.62 (d, $J=11.8$ Hz, 1H), 4.58 (d, $J=12.2$ Hz, 1H), 4.56 (d, $J=11.8$ Hz, 1H), 4.48 (d, $J=11.8$ Hz, 1H), 4.45 (d, $J=11.8$ Hz, 1H), 4.44 (d, $J=12.2$ Hz, 1H), 4.26 (d, $J=12.2$ Hz, 1H), 4.06 (ddd, $J=2.5, 2.5, 2.5$ Hz, 1H), 3.98 (ddd, $J=9.2, 2.9, 2.9$ Hz, 1H), 3.73 (dd, $J=11.8, 4.6$ Hz, 1H), 3.72–3.70 (m, 1H), 3.61–3.47 (m, 7H), 3.41–3.36 (m, 2H), 3.15 (dd, $J=9.6, 2.9$ Hz, 1H), 3.03 (ddd, $J=10.5, 10.5, 5.0$ Hz, 1H), 2.26 (ddd, $J=12.2, 4.6, 4.6$ Hz, 1H), 2.03 (s, 1H), 1.94–1.85 (m, 5H), 1.84–1.68 (m, 5H), 1.63–1.53 (m, 4H), 1.50–1.44 (m, 2H), 1.42–1.35 (m, 2H), 1.23 (s, 3H), 1.20–1.19 (m, 9H), 0.92 (d, $J=7.5$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.7, 138.8, 138.6, 138.1, 128.4, 128.3, 128.1, 127.8, 127.7, 127.4, 127.4, 127.3, 127.0, 81.4, 81.2, 80.3, 80.2, 79.4, 78.9, 77.5, 77.2, 76.5, 73.6, 72.9, 72.9, 71.7, 71.3, 71.3, 71.1, 71.0, 68.8, 68.1, 67.8, 67.5, 46.9, 39.1, 38.7, 38.5, 35.0, 34.1, 32.7, 32.5, 29.1, 21.8, 21.5, 18.7, 17.6, 15.6, 11.6; HRMS (FAB) calcd for $\text{C}_{60}\text{H}_{78}\text{O}_{11}\text{Na}$ $[\text{M}+\text{Na}]^+$ 997.5436, found 997.5430.

alcohol **25** (**24b** → **25**)

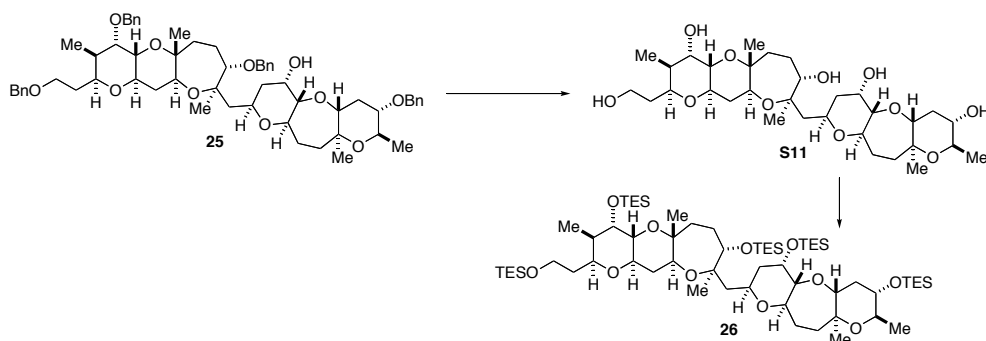


To a solution of the ketone **24b** (36.5 mg, 0.0330 mmol) in CH_2Cl_2 (6 mL) and Et_3SiH (2.0 mL) at $-78\text{ }^\circ\text{C}$ was added dropwise TMSOTf (0.1 M in CH_2Cl_2 , 2.0 mL, 0.20 mmol). After stirring for 20 min, the reaction was quenched with saturated aqueous NH_4Cl . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (30–60% ethyl acetate/hexane) to afford alcohol **S9** (28.2 mg, 88%) as a colorless oil: $[\alpha]_D^{28}$ 0.016 (*c* 0.550, CHCl_3); IR (film) 3729, 3434, 2933, 2868, 2360, 1650, 1560, 1454, 1380, 1084, 737, 693, 673 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35–7.24 (m, 16H), 7.23–7.19 (m, 4H), 4.82 (d, $J=12.2$ Hz, 1H), 4.63 (d, $J=11.3$ Hz, 1H), 4.58 (d, $J=11.8$ Hz, 1H), 4.57 (d, $J=12.2$ Hz, 1H), 4.48 (d, $J=12.2$ Hz, 1H), 4.45 (d, $J=11.8$ Hz, 1H), 4.44 (d, $J=12.2$ Hz, 1H), 4.25 (d, $J=12.2$ Hz, 1H), 3.99 (ddd, $J=9.6, 2.9, 2.9$ Hz, 1H), 3.72 (dd, $J=11.8, 4.6$ Hz, 1H), 3.59 (ddd, $J=11.3, 11.3, 4.6$ Hz, 1H), 3.56–3.47 (m, 6H), 3.41–3.39 (m, 2H), 3.29 (dd, $J=12.2, 3.8$ Hz, 1H), 3.04 (ddd, $J=10.5, 10.5, 5.0$ Hz, 1H), 3.02–2.96 (m, 2H), 2.56 (brs, 1H), 2.30 (ddd, $J=11.7, 4.2, 4.2$ Hz, 1H), 1.97 (ddd, $J=13.4, 4.2, 4.2$ Hz, 1H), 1.94–1.87 (m, 5H), 1.82 (ddd, $J=11.3, 5.0, 5.0$ Hz), 1.78–1.73 (m, 3H), 1.70–1.60 (m, 4H), 1.50–1.32 (m, 4H), 1.24–1.18 (m, 12H), 0.92 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.7, 138.6, 138.5, 138.1, 128.4, 128.3, 128.1, 127.8, 127.7, 127.4, 127.4, 127.0, 86.4, 81.4, 80.9, 80.0, 79.4, 79.0, 78.0, 77.4, 77.2, 76.4, 72.9, 72.8, 72.2, 71.7, 71.4, 71.2, 71.2, 71.1, 70.1, 68.8, 67.5, 47.3, 39.3, 39.1, 38.4, 35.0, 34.0, 32.5, 32.2, 28.8, 21.8, 21.5, 18.8, 17.0, 15.6, 11.6; HRMS (FAB) calcd for $\text{C}_{60}\text{H}_{78}\text{O}_{11}\text{Na}$ $[\text{M}+\text{Na}]^+$ 997.5436, found 997.5430.

To a solution of **S9** (36.0 mg, 0.0369 mmol) in CH_2Cl_2 (3 mL) were added 4 Å molecular sieves (40 mg), NMO (41.0 mg, 0.350 mmol) and catalytic amount of TPAP (ca 5 mg) at room temperature. After stirring at room temperature for 4 h, the reaction mixture was directly subjected to column chromatography on silica gel (40–80% ethyl acetate/hexane) to afford ketone **S10**, which was used in the next reaction without further purification.

To a solution of **S10** in THF (2 mL) was added L-Selectride (1.0 M in THF, 0.20 mL, 0.20 mmol) at $-78\text{ }^\circ\text{C}$. After stirring at the same temperature for 3.5 h, the reaction was quenched with saturated aqueous NH_4Cl . The aqueous phase was extracted three times with EtOAc. The combined organic fractions were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (30% ethyl acetate/hexane) to afford alcohol **25** (35.5 mg, 99% for 2 steps).

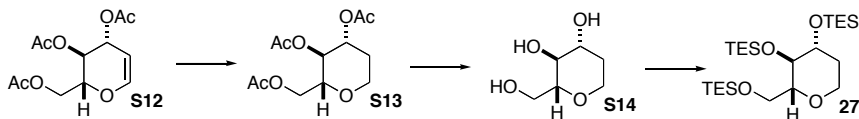
pentakis-TES ether **26**



To a solution of the alcohol **25** (9.7 mg, 0.010 mmol) in THF (2.0 mL) was added 10% Pd/C (11.5 mg). The reaction mixture was stirred at room temperature overnight under a hydrogen atmosphere. The mixture was directly subjected to column chromatography on silica gel (10–30% MeOH/CHCl₃) to afford crude pentaol **S11**, which was used in the next reaction without further purification.

To a solution of **S11** in CH₂Cl₂ (2 mL) at 0 °C were added 2,6-lutidine (0.033 mL, 0.285 mmol) and TESOTf (0.034 mL, 0.150 mmol). The resultant solution was stirred for 45 min and quenched with saturated aqueous NaHCO₃. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st: 5% ethyl acetate/hexane, 2nd: 2% ethyl acetate/hexane) to afford pentakis-TES ether **26** (882 mg, 84%) as a colorless oil: [α]_D²⁸ 8.89 (*c* 0.0970, CHCl₃); IR (film) 3743, 3438, 2945, 2868, 2360, 1650, 1560, 1451, 1386, 1084, 1014, 827, 744, 667 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 4.09 (d, *J* = 2.9 Hz, 1H), 4.05 (ddd, *J* = 9.6, 2.9, 2.9 Hz, 1H), 3.93 (d, *J* = 6.7 Hz, 1H), 3.85 (dd, *J* = 10.1, 8.8 Hz, 1H), 3.73 (dd, *J* = 2.5, 2.5 Hz, 1H), 3.68–3.66 (m, 2H), 3.63–3.59 (m, 2H), 3.47 (ddd, *J* = 11.7, 9.6, 4.6 Hz, 1H), 3.36 (dddd, *J* = 9.2, 5.9, 5.9, 5.9 Hz, 1H), 3.30 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.20–3.16 (m, 2H), 3.03 (dd, *J* = 9.6, 2.5 Hz, 1H), 1.99–1.94 (m, 2H), 1.92–1.83 (m, 2H), 1.78 (ddd, *J* = 11.7, 4.6, 4.6 Hz, 1H), 1.73–1.70 (m, 2H), 1.68–1.58 (m, 4H), 1.55–1.44 (m, 5H), 1.38 (d, *J* = 11.7 Hz, 1H), 1.34–1.29 (m, 2H), 1.17 (s, 3H), 1.13–1.11 (m, 9H), 0.96–0.89 (m, 47H), 0.62–0.50 (m, 30H); ¹³C NMR (100 MHz, CDCl₃) δ 82.5, 80.2, 79.7, 77.6, 77.2, 74.9, 73.8, 72.9, 72.8, 70.9, 70.4, 68.9, 68.6, 68.0, 59.8, 47.0, 42.0, 41.6, 38.7, 36.8, 35.4, 34.5, 34.2, 29.4, 26.3, 21.6, 18.6, 17.8, 15.8, 11.4, 7.0, 6.9, 6.8, 6.7, 5.0, 5.0, 4.8, 4.4; HRMS (FAB) calcd for C₆₂H₁₂₄O₁₁Si₅Na [M+Na]⁺ 1207.7882, found 1207.7870.

tris-TES ether 27

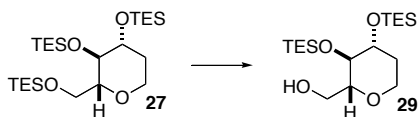


To a solution of tri-*O*-acetyl-D-glucal (**S12**) (820 mg, 3.01 mmol) in EtOAc (20 mL) was added 5% Pd/C (110 mg). The reaction mixture was stirred at room temperature for 6 h under a hydrogen atmosphere. The mixture was filtered through a pad of Celite[®] and concentrated under reduced pressure to afford **S13**, which was used in the next reaction without further purification.

To a solution of **S13** in MeOH (15 mL) was added K₂CO₃ (83.0 mg, 0.600 mmol) at room temperature. The mixture was stirred at room temperature overnight and then concentrated under reduced pressure to afford crude triol **S14**, which was used in the next reaction without purification.

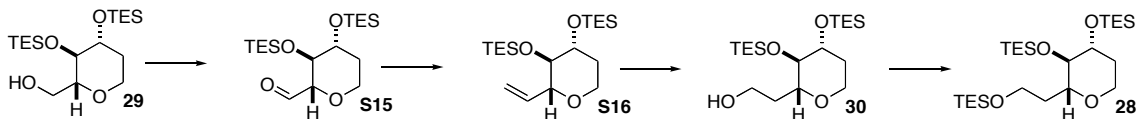
To a solution of **S14** in CH₂Cl₂ (60 mL) at 0 °C were added 2,6-lutidine (2.80 mL, 24.2 mmol) and TESOTf (2.70 mL, 12.0 mmol). The resultant solution was stirred for 20 min and quenched with saturated aqueous NaHCO₃. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st and 2nd: 3% ethyl acetate/hexane) to afford tris-TES ether **27** (780 mg, 53% for 3 steps) as a colorless oil: [α]_D²⁸ 8.64 (*c* 0.754, CHCl₃); IR (film) 2954, 2907, 2360, 1459, 1239, 1129, 1105, 1007, 981, 811, 739 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.86 (ddd, *J* = 12.0, 4.6, 2.1 Hz, 1H), 3.84 (dd, *J* = 10.9, 2.1 Hz, 1H), 3.68 (dd, *J* = 10.9, 6.3 Hz, 1H), 3.61–3.56 (m, 1H), 3.37–3.32 (m, 2H), 3.10 (ddd, 8.5, 6.2, 2.1 Hz, 1H), 1.88–1.84 (m, 1H), 1.62–1.55 (m, 1H), 0.96–0.92 (m, 27H), 0.65–0.56 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 81.9, 74.6, 73.2, 64.6, 63.2, 34.7, 7.0, 7.0, 6.8, 5.4, 5.2, 4.5; HRMS (FAB) calcd for C₂₄H₅₄O₄Si₃Na [M+Na]⁺ 513.3222, found 513.3212.

alcohol 29



To a solution of tris-TES ether **27** (780 mg, 1.59 mmol) in CH₂Cl₂ (16 mL) was added DIBALH (1.0 M in hexane, 8.0 mL, 8.0 mmol) at -40 °C. After stirring at the same temperature for 30 min, the resultant mixture was quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted with EtOAc and vigorously stirred for 8 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10–20% ethyl acetate/hexane) to afford alcohol **29** (586 mg, 98%) as a colorless oil: $[\alpha]_D^{28}$ 3.66 (*c* 0.777, CHCl₃); IR (film) 3469, 2954, 2877, 2360, 1459, 1415, 1380, 1239, 1127, 1103, 1007, 943, 808, 739, 679 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.88 (ddd, *J* = 11.7, 4.7, 2.1 Hz, 1H), 3.78 (d, *J* = 10.9 Hz, 1H), 3.65–3.58 (m, 2H), 3.40 (dt, *J* = 12.0, 2.1 Hz, 1H), 3.35 (t, 8.4 Hz, 1H), 3.14 (ddd, *J* = 8.8, 5.9, 2.9 Hz, 1H), 1.93 (br, 1H), 1.90–1.87 (m, 1H), 1.65–1.59 (m, 1H), 0.97–0.92 (m, 18H), 0.65–0.57 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 80.1, 74.5, 73.6, 65.1, 62.8, 34.9, 7.0, 6.9, 5.4, 5.1; HRMS (FAB) calcd for C₁₈H₄₀O₄Si₂Na [M+Na]⁺ 399.2357, found 399.2369.

tris-TES ether **28**



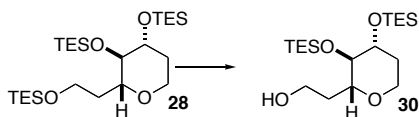
To a solution of alcohol **29** in CH₂Cl₂-DMSO (3:1, 8.0 mL) were added Et₃N (0.83 mL, 5.94 mmol) and SO₃·pyridine (601 mg, 3.78 mmol) at 0 °C. The resultant solution was stirred at room temperature for 1.5 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH₄Cl, dried over MgSO₄, filtered, and concentrated to afford crude aldehyde **S15**, which was used in the next reaction without further purification.

To a suspension of Ph₃P⁺CH₃Br⁻ (531 mg, 1.49 mmol) in THF (10.0 mL) at 0 °C was added NaHMDS (1.0 M in THF, 1.34 mL, 1.34 mmol) and the resultant solution was stirred at 0 °C for 50 min. To the solution was added dropwise a solution of **S15** in THF (2.0 mL + 2.0 mL rinse) at 0 °C. After stirring at 0 °C for 30 min, the reaction was quenched with acetone and saturated aqueous NH₄Cl. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (2% ethyl acetate/hexane) to afford olefin **S16** (178 mg, 64% for 2 steps) as a colorless oil.

To a solution of olefin **S16** (178 mg, 0.476 mmol) in THF (4.0 mL) was added 9-BBN-H (0.5 M in THF, 1.2 mL, 0.60 mmol) at 0 °C. After being stirred at 40 °C for 40 min, 3 M NaOH (2.0 mL) and 30% H₂O₂ (2.0 mL) were added at 0 °C. The resultant mixture was stirred at room temperature for 50 min, and then extracted twice with EtOAc. The combined organic fractions were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20% ethyl acetate/hexane) to afford alcohol **30**, which was used in the next reaction.

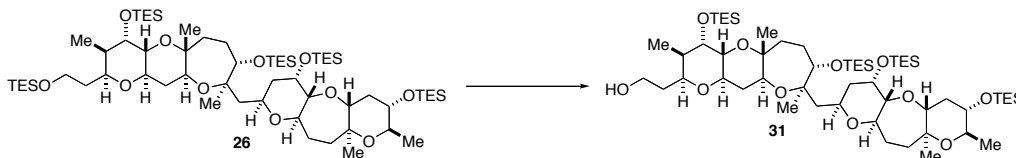
To a solution of alcohol **30** in CH₂Cl₂ (4.0 mL) at 0 °C were added 2,6-lutidine (0.073 mL, 0.632 mmol) and TESOTf (0.11 mL, 0.505 mmol). The resultant solution was stirred for 15 min and quenched with saturated aqueous NH₄Cl. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5% ethyl acetate/hexane) to afford tris-TES ether **28** (210 mg, 87% for 2 steps) as a colorless oil: [α]_D²⁸ 7.02 (*c* 0.246, CHCl₃); IR (film) 2954, 2877, 2360, 1458, 1412, 1380, 1239, 1127, 1103, 1007, 809, 739, 673 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.81 (ddd, *J* = 11.7, 4.7, 2.5 Hz, 1H), 3.73–3.64 (m, 2H), 3.56 (dd, *J* = 5.3, 5.3 Hz, 1H), 3.30 (ddd, *J* = 11.9, 1.7, 1.7 Hz, 1H), 3.16–3.10 (m, 2H), 2.06–2.01 (m, 1H), 1.89–1.86 (m, 1H), 1.63–1.50 (m, 2H), 0.96–0.90 (m, 27H), 0.65–0.55 (m, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 77.6, 77.5, 74.6, 64.7, 59.6, 35.4, 35.1, 7.1, 7.0, 6.8, 5.4, 5.3, 4.4; HRMS (FAB) calcd for C₂₅H₅₇O₄Si₃ [M+H]⁺ 505.3559, found 505.3559.

alcohol 30



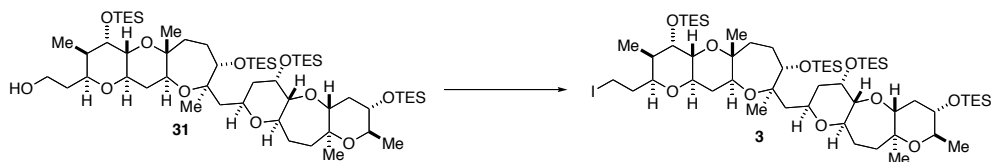
To a solution of tris-TES ether **28** (201 mg, 0.398 mmol) in CH_2Cl_2 (4.0 mL) was added DIBALH (1.0 M in hexane, 2.0 mL, 2.0 mmol) at $-40\text{ }^\circ\text{C}$. After stirring at the same temperature for 30 min, the resultant mixture was quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted with EtOAc and vigorously stirred for 4.5 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20% ethyl acetate/hexane) to afford alcohol **30** (149 mg, 96%) as a colorless oil: $[\alpha]_{\text{D}}^{28}$ 2.33 (c 0.543, CHCl_3); IR (film) 3430, 2954, 2877, 2360, 1459, 1415, 1379, 1239, 1127, 1094, 1052, 1007, 970, 924, 810, 738, 682 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.86 (ddd, $J = 11.7, 4.8, 1.7$ Hz, 1H), 3.79–3.73 (m, 2H), 3.56 (ddd, $J = 11.0, 7.5, 5.0$ Hz, 1H), 3.37 (ddd, $J = 12.2, 1.7, 1.7$ Hz, 1H), 3.25 (ddd, $J = 9.0, 2.1, 2.1$ Hz, 1H), 3.23–3.19 (m, 1H), 2.69 (br, 1H), 2.03–1.98 (m, 1H), 1.90–1.87 (m, 1H), 1.71–1.58 (m, 2H), 0.95 (t, $J = 7.6$ Hz, 9H), 0.94 (t, $J = 7.6$ Hz, 9H), 0.65–0.57 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.1, 77.2, 74.4, 65.3, 61.9, 35.0, 33.9, 7.0, 7.0, 5.4, 5.3; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{42}\text{O}_4\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 413.2514, found 413.2529.

alcohol **31**



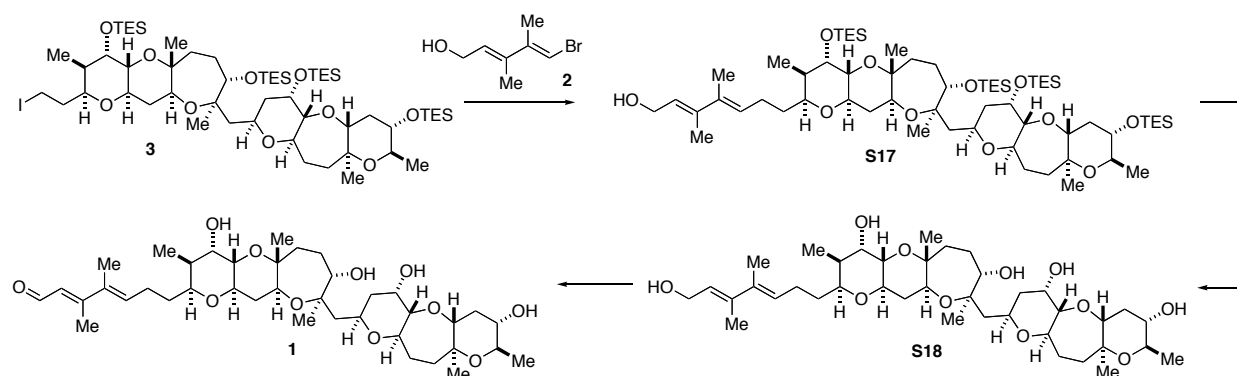
To a solution of pentakis-TES ether **26** (201 mg, 0.169 mmol) in CH_2Cl_2 (5.0 mL) was added DIBALH (1.0 M in hexane, 1.7 mL, 1.7 mmol) at $-40\text{ }^\circ\text{C}$. After stirring at the same temperature for 30 min, the mixture was gradually warmed up to $-20\text{ }^\circ\text{C}$ over 20 min and stirred at $-20\text{ }^\circ\text{C}$ for 1 h. Then the resultant mixture was quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted with EtOAc and vigorously stirred for 5 h. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20% ethyl acetate/hexane) to afford alcohol **31** (159 mg, 88%) as a colorless oil: $[\alpha]_{\text{D}}^{28}$ 6.57 (c 0.167, CHCl_3); IR (film) 3447, 2952, 2882, 2360, 1457, 1380, 1110, 1085, 1014, 827, 740, 667 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.12 (ddd, $J = 10.9, 2.1, 2.1$ Hz, 1H), 4.09 (ddd, $J = 2.5, 2.5, 2.5$ Hz, 1H), 3.94 (d, $J = 6.7$ Hz, 1H), 3.86 (dddd, $J = 10.5, 8.4, 2.1, 2.1$ Hz, 1H), 3.80 (ddd, $J = 10.5, 10.5, 2.9$ Hz, 1H), 3.75–3.71 (m, 2H), 3.63–3.59 (m, 2H), 3.56 (ddd, $J = 11.7, 9.6, 4.6$ Hz, 1H), 3.36 (dddd, $J = 9.2, 6.3, 6.3, 6.3$ Hz, 1H), 3.30 (dd, $J = 12.2, 4.2$ Hz, 1H), 3.21–3.15 (m, 2H), 3.03 (dd, $J = 9.6, 2.5$ Hz, 1H), 2.01–1.94 (m, 3H), 1.92–1.75 (m, 5H), 1.73–1.69 (m, 2H), 1.66–1.50 (m, 5H), 1.46–1.28 (m, 4H), 1.17 (s, 3H), 1.13–1.11 (m, 9H), 0.96–0.90 (m, 39H), 0.62–0.50 (m, 24H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.5, 80.3, 79.7, 77.5, 77.2, 75.7, 74.9, 73.8, 72.9, 72.6, 70.8, 70.7, 70.5, 68.6, 68.4, 67.9, 62.8, 47.1, 42.4, 41.6, 38.7, 36.8, 34.5, 34.2, 34.0, 29.4, 26.3, 21.8, 18.6, 17.8, 15.7, 11.7, 7.0, 7.0, 6.9, 6.8, 5.0, 5.0, 4.8; HRMS (FAB) calcd for $\text{C}_{56}\text{H}_{110}\text{O}_{11}\text{Si}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 1093.7017, found 1093.7002.

iodide **3**



To a solution of alcohol **31** (159 mg, 0.149 mmol) in benzene (6.0 mL) at room temperature were added imidazole (83.0 mg, 1.22 mmol), PPh₃ (145 mg, 0.553 mmol), and I₂ (240 mg, 0.946 mmol). After stirring at room temperature for 30 min, the reaction was quenched with saturated aqueous Na₂SO₃. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10% ethyl acetate/hexane) to afford iodide **3** (171 mg, 97%) as a colorless oil: $[\alpha]_D^{28}$ 14.8 (*c* 0.118, CHCl₃); IR (film) 3441, 2952, 2875, 2361, 1460, 1376, 1236, 1106, 1085, 1057, 997, 959, 831, 727 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 4.09 (ddd, *J* = 2.5, 2.5, 2.5 Hz, 1H), 3.96–3.93 (m, 2H), 3.85 (dddd, *J* = 10.9, 8.4, 2.1, 2.1 Hz, 1H), 3.73 (dd, *J* = 2.5, 2.5 Hz, 1H), 3.63–3.58 (m, 2H), 3.49 (ddd, *J* = 11.8, 9.6, 4.6 Hz, 1H), 3.36 (dddd, *J* = 8.8, 6.3, 6.3, 6.3 Hz, 1H), 3.30 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.22–3.15 (m, 3H), 3.03 (dd, *J* = 9.6, 2.1 Hz, 1H), 2.05–1.94 (m, 3H), 1.92–1.83 (m, 2H), 1.79 (ddd, *J* = 11.8, 4.6, 4.6 Hz, 1H), 1.76–1.68 (m, 3H), 1.55–1.44 (m, 3H), 1.17 (s, 3H), 1.13–1.12 (m, 9H), 0.96–0.89 (m, 39H), 0.62–0.50 (m, 24H); ¹³C NMR (100 MHz, CDCl₃) δ 82.5, 80.3, 79.7, 77.4, 77.2, 74.8, 74.2, 73.8, 72.9, 72.6, 70.8, 70.7, 70.5, 68.7, 68.6, 68.0, 47.1, 41.7, 41.6, 38.7, 36.8, 36.7, 34.5, 34.2, 29.4, 26.3, 21.7, 18.6, 17.8, 15.7, 11.5, 7.0, 6.9, 6.8, 5.0, 5.0, 4.8, 3.6; HRMS (FAB) calcd for C₅₆H₁₀₉IO₁₀Si₄Na [M+Na]⁺ 1203.6035, found 1203.6085.

brevisin (**1**)



To a solution of iodide **3** (159 mg, 0.134 mmol) in Et₂O (1.0 mL) at -78 °C were added *B*-MeO-9-BBN (1.0 M in hexane, 0.80 mL, 0.80 mmol), *t*-BuLi (1.58 M in heptane, 0.68 mL, 1.07 mmol). Then THF (1.5 mL) was added dropwise to the solution at the same temperature. After stirring at -78 °C for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 2.5 h. To the solution were added 3 M aqueous Cs₂CO₃ (0.90 mL), bromodienol **2** (99.0 mg, 0.518 mmol) in DMF (2.0 mL + 1.0 mL rinse) and PdCl₂(dppf)·CH₂Cl₂ (23.1 mg, 0.0283 mmol). After stirring at 50 °C for 8.5 h, brine was added to the solution. The aqueous phase was extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (15% ethyl acetate/hexane) to afford crude **S17**, which was used in the next reaction without further purification.

To a solution of **S17** in THF (3.5 mL) was added TBAF (1.0 M in THF, 1.6 mL, 1.6 mmol) at room temperature. After stirring at room temperature for 3 h, TBAF (1.0 M in THF, 1.6 mL, 1.6 mmol) was added. The reaction mixture was heated at reflux, stirred for 1 h, and then quenched with saturated aqueous NH₄Cl. The aqueous phase was extracted five times with EtOAc. The combined organic fractions were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (5–10% MeOH/CHCl₃) to afford crude **S18**, which was used in the next reaction without further purification.

To the solution of **S18** in CH₂Cl₂ (5 mL) was added MnO₂ (290 mg) at 0 °C. After stirring for 15 min, MnO₂ (310 mg) was added to the solution. The mixture was stirred at 0 °C for 1 h, MnO₂ (310 mg) was added. After stirring for 1 h, the reaction mixture was directly subjected to column chromatography on silica gel (3–5% MeOH/CHCl₃) to afford brevisin **1** (71.2 mg, 75% for 3 steps) as a colorless amorphous solid.

Data for synthetic 1:

$[\alpha]_D^{28} -25.6$ (c 0.0620, MeOH)

IR (film) 3442, 2933, 2360, 1647, 1458, 1420, 1380, 1123, 1084, 1046 cm^{-1}

^1H NMR (500 MHz, pyridine- d_5) δ 10.31 (d, $J = 8.0$ Hz, 1H), 6.68 (brs, 1H), 6.46 (brs, 1H), 6.18 (d, $J = 7.6$ Hz, 1H), 6.14 (dd, $J = 7.2, 7.2$ Hz, 1H), 6.09 (brs, 2H), 4.48–4.36 (m, 4H), 4.26 (brd, $J = 8.4$ Hz, 1H), 4.19 (brs, 1H), 4.12–4.02 (m, 2H), 3.78–3.67 (m, 3H), 3.66–3.56 (m, 1H), 3.34 (dd, $J = 9.7, 2.1$ Hz, 1H), 2.71 (dd, $J = 10.5, 10.5$ Hz, 1H), 2.46 (ddd, $J = 12.2, 4.2, 4.2$ Hz, 1H), 2.41–2.26 (m, 3H), 2.21–2.09 (m, 2H), 2.17 (s, 3H), 2.08–1.94 (m, 8H), 1.87 (ddd, $J = 14.3, 6.7, 6.7$ Hz, 1H), 1.82–1.72 (m, 3H), 1.73 (s, 3H), 1.71–1.65 (m, 1H), 1.67 (s, 3H), 1.54 (s, 3H), 1.50 (d, $J = 5.9$ Hz, 3H), 1.47–1.38 (m, 1H), 1.31 (s, 3H), 1.05 (d, $J = 7.2$ Hz, 3H)

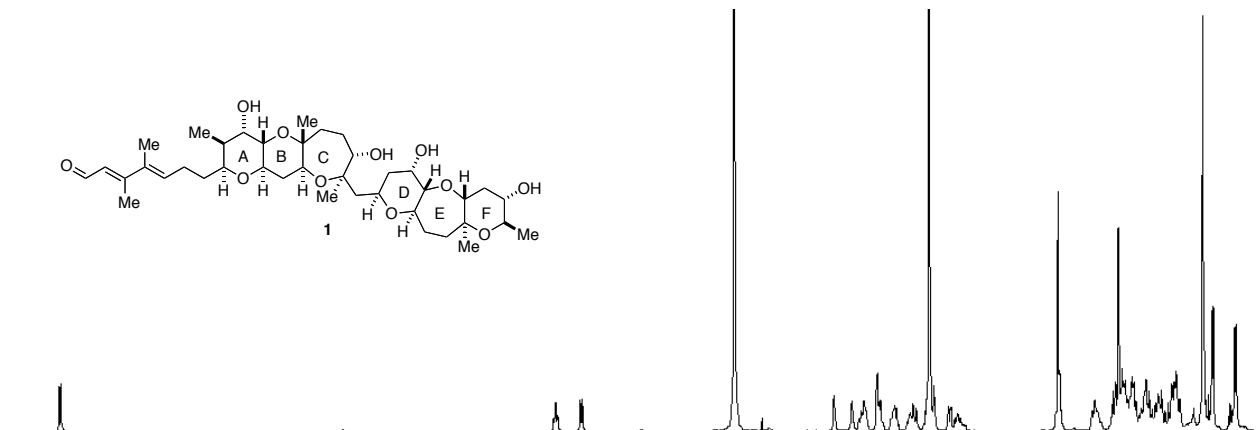
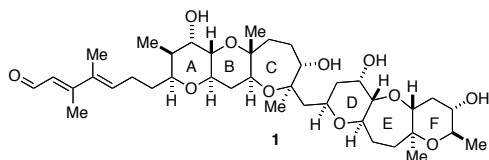
^{13}C NMR (100 MHz, pyridine- d_5) δ 191.9, 157.6, 125.8, 83.8, 81.1, 80.4, 78.6, 76.9, 74.7, 74.3, 73.2, 72.2, 71.9, 71.6, 70.4, 70.4, 68.8, 67.6, 47.8, 41.1, 40.9, 39.4, 37.4, 35.6, 32.1, 30.0, 26.7, 26.5, 21.9, 19.2, 18.3, 16.6, 14.1, 13.6, 11.6, some peaks were overlapped with the residual solvent peaks (C-4, C-5) or each other (C-12, C-14, C-32 at 71.6 ppm)^[ref 1a]

^1H NMR (500 MHz, CD_3OD) δ 10.06 (d, $J = 8.0$ Hz, 1H), 6.21 (dd, $J = 7.2, 7.2$ Hz, 1H), 6.01 (d, $J = 8.0$ Hz, 1H), 4.05 (brd, $J = 2.8$ Hz, 1H), 3.91 (dd, $J = 4.6, 4.6$ Hz, 1H), 3.86–3.77 (m, 2H), 3.73–3.65 (m, 2H), 3.61–3.54 (m, 1H), 3.47 (dd, $J = 11.8, 4.2$ Hz, 1H), 3.15 (dd, $J = 9.7, 3.0$ Hz, 1H), 3.09 (ddd, $J = 9.7, 9.7, 5.1$ Hz, 1H), 2.34–2.26 (m, 2H), 2.31 (s, 3H), 2.06–1.96 (m, 2H), 1.92–1.68 (m, 11H), 1.83 (s, 3H), 1.68–1.34 (m, 6H), 1.18 (brs, 3H), 1.11 (d, $J = 5.9$ Hz, 3H), 0.93 (d, $J = 7.6$ Hz, 3H)

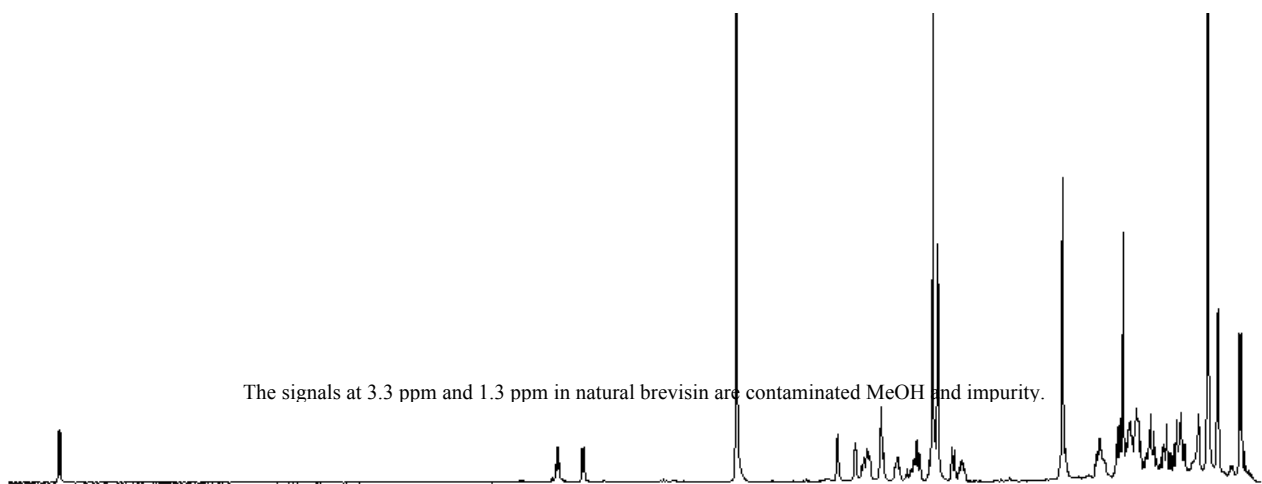
^{13}C NMR (100 MHz, CD_3OD) δ 194.3, 160.9, 137.2, 136.8, 126.2, 83.8, 81.6, 81.3, 79.3, 77.9, 75.5, 75.2, 74.5, 73.0, 72.9, 72.3, 72.1, 71.7, 70.4, 69.4, 68.8, 41.2, 41.1, 39.7, 37.0, 35.9, 35.4, 32.5, 30.3, 27.0, 26.9, 21.4, 18.8, 18.3, 16.6, 14.5, 13.9, 11.5, some peaks were overlapped with the residual solvent peaks (H-11, H-32, C-20)

HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{62}\text{O}_{11}\text{Na}$ $[\text{M}+\text{Na}]^+$ 729.4184, found 729.4192.

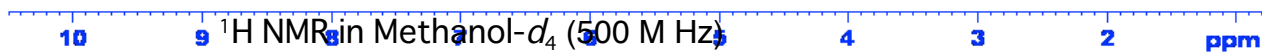
artificial



natural



The signals at 3.3 ppm and 1.3 ppm in natural brevisin are contaminated MeOH and impurity.





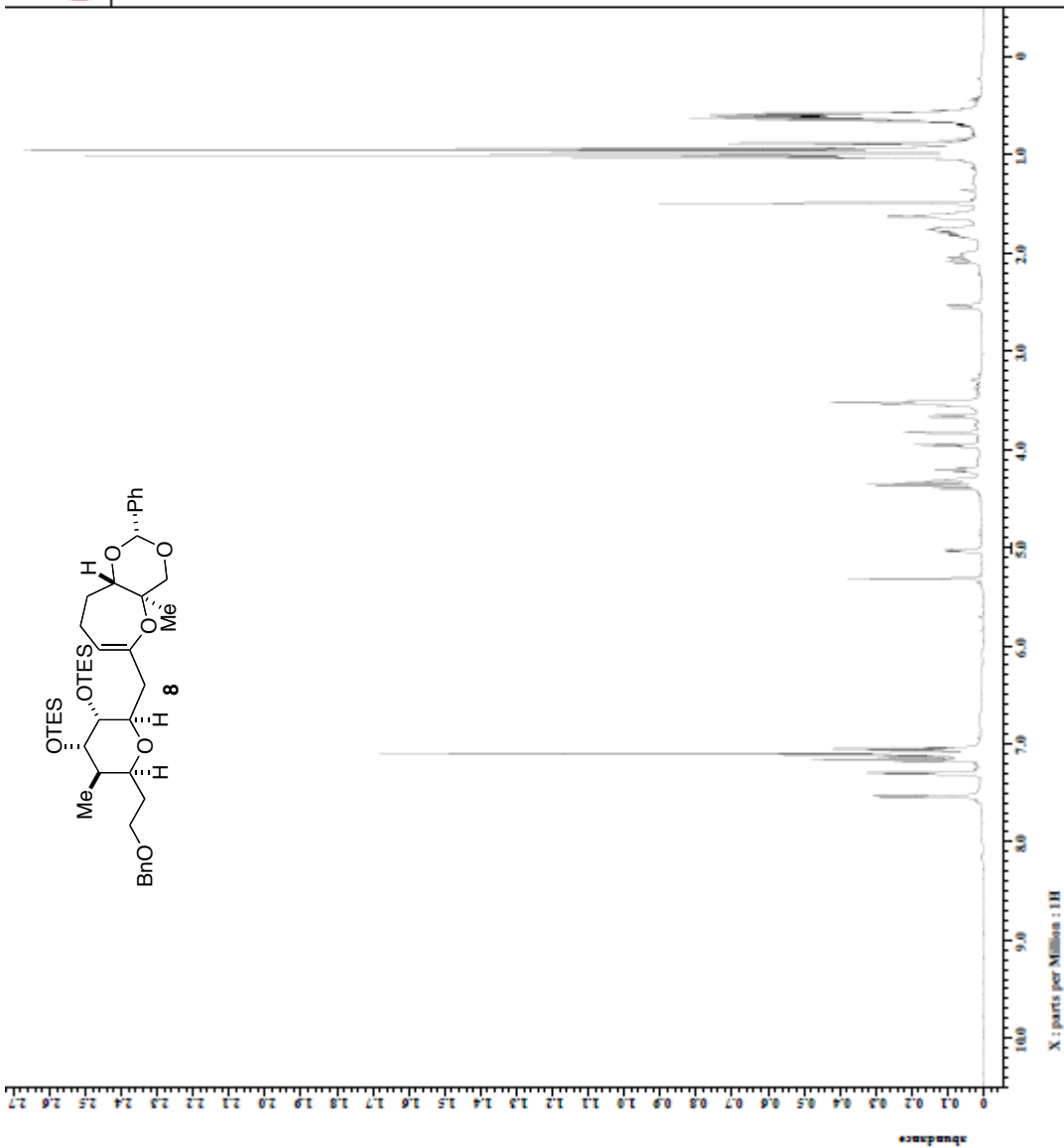
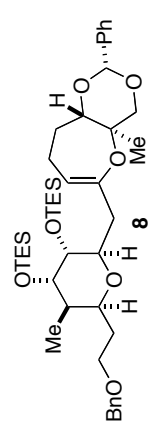
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Temp_set       = 23.3 [dC]
    
```





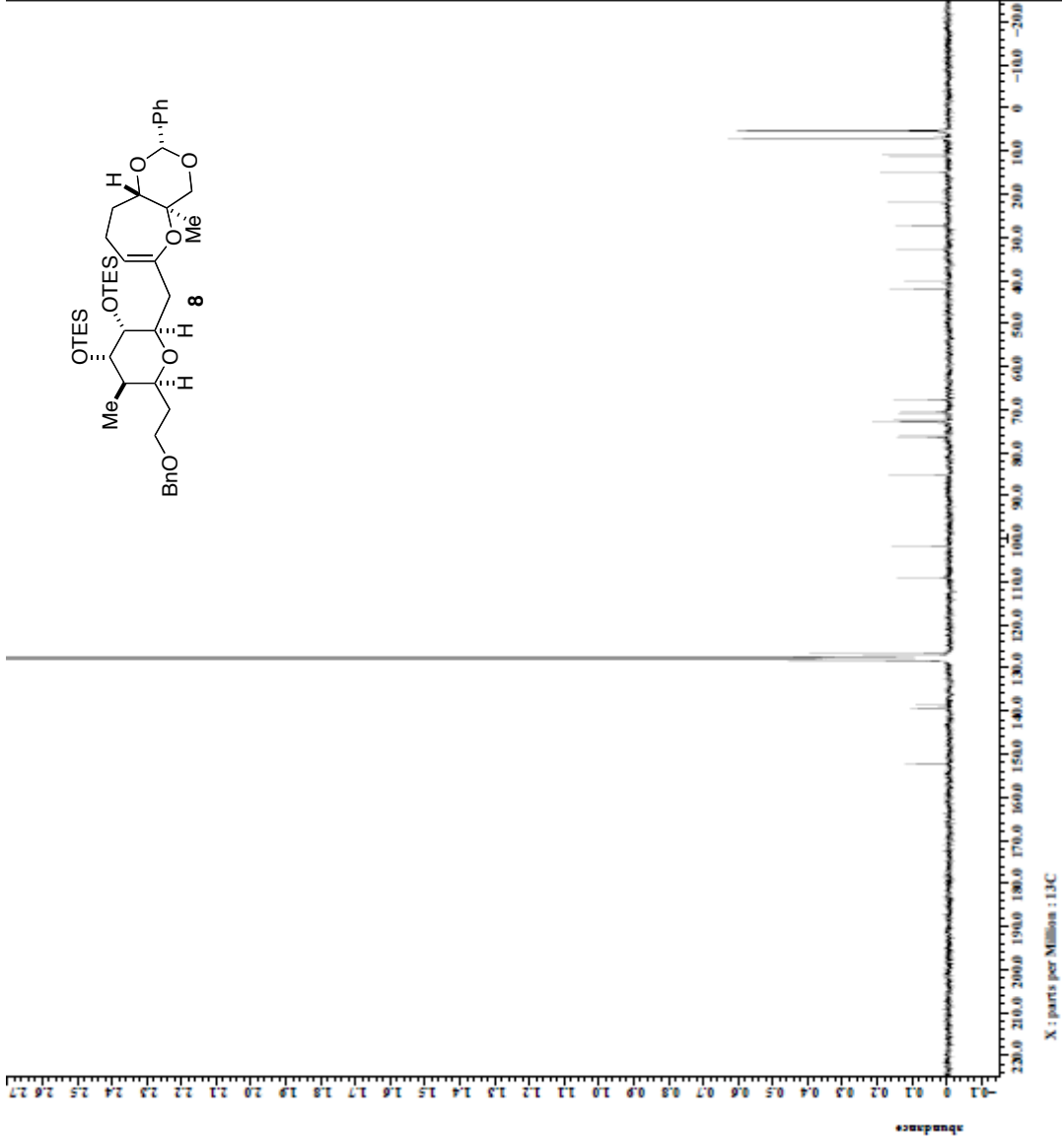
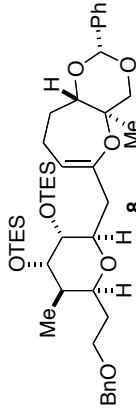
```

Filesnm  = 16-100722-13C-5.fid
Author    = delta
Experiment = single_pulse_dec
Repla_id  = sas
Solvent   = DMSO-d6
Creation_time = 22-Jul-2010 01:07:26
Revision_time = 3-Aug-2010 15:18:150
Current_time = 3-Aug-2010 15:19:115

Comment = single pulse decouple
Data format = 1D COMPLEX
Dir file   = 26214
Dir title  = 13C
Dir units  = [ppm]
Dimensions = KZ400
Spectrometer = DMZ700_NMR

Field_strength = 9.389766 [T] (400 [Mhz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 52830333 [Mhz]
F2_domain = 100 52830333 [Mhz]
F1_freq = 327.80 [MHz]
F2_freq = 327.80 [MHz]
F1_points = 4
F2_points = 4
F1_resolution = 0.95846665 [Hz]
F2_resolution = 31.40703518 [kHz]
F1_sweep = 18.79219938 [Mhz]
F2_sweep = 5 [Hz]
Irr_domain = 13C 52830333 [Mhz]
Irr_freq = 327.80 [MHz]
Irr_offset = 0 [Hz]
Clipped = FALSE
Mod_return = 1
Scan = 159
Total_scans = 159

X90_width = 16.8 [us]
X90_time = 1.04333312 [s]
X_pulse = 3.0 [dB]
X_min = 3.1 [dB]
X_max = 3.5 [us]
Irr_atn_dec = 20.276 [dB]
Irr_atn_noise = 20.276 [dB]
WALTZ = WALTZ
Sweeping = 1 [Hz]
Initial_gain = 1 [dB]
Roc_time = 2 [s]
Roc_gain = 2 [dB]
Socv_gain = 60
Relaxation_delay = 2 [s]
Repetition_time = 3.04333312 [s]
Temp_get = 22.0 [C]
    
```

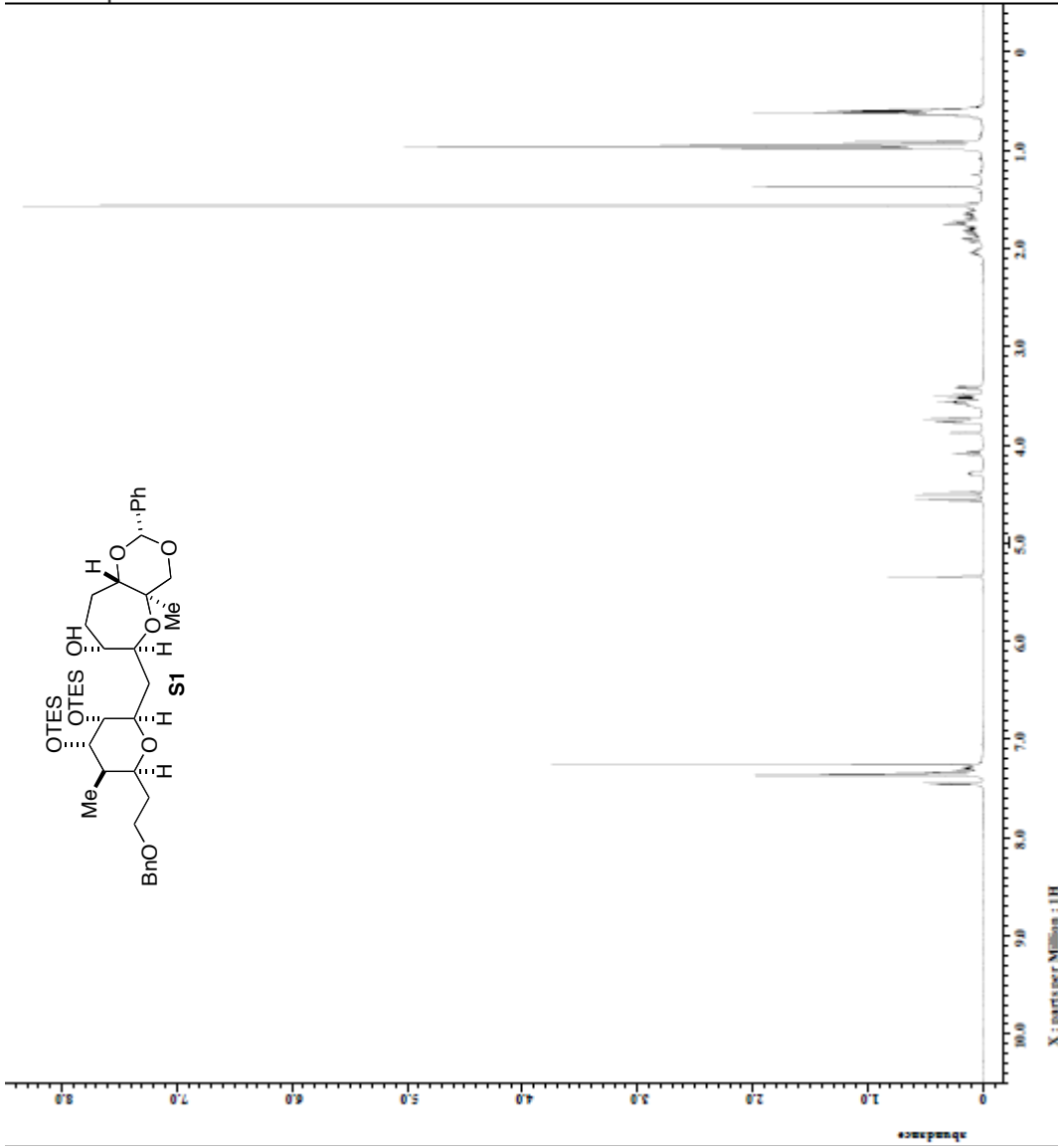
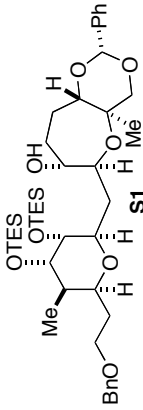




```

* WC-IT-01-090709-1H-9.
* delta
* single_pulse.ex2
* S#11157
* CMOHOFOM-D
* 9-JUL-2010 00:20:51
* 2-DMC-2010 15:49:31
* 2-DMC-2010 15:49:46
* single_pulse
* ID CMOHOFOM-D
* 13107
* 1H
* [ppm]
* ECA500
* DELTA2_DMR
Spectrometer
* DELTA2_DMR
* 11.7473579 [T] (500 [MHz])
* 2.30026752 [s]
* 500.15991521 [MHz]
* 5.0 [ppm]
* 16384
* 1
* 0.42012084 [Hz]
* 6.88225991 [kHz]
* 1H
* 500.15991521 [MHz]
* 5.0 [ppm]
* 1H
* 500.15991521 [MHz]
* 5.0 [ppm]
* PALSI
* 1
* 8
* 8
* 6 [use]
* 2.30026752 [s]
* 45 [deg]
* 3.2 [GHz]
* [use]
* Off
* Off
* PALSI
* Initial_wait
* 1 [s]
* Recv_gain
* 66
* Relaxation_delay
* 1.5 [s]
* Repetition_time
* 22.3 [dG]
* temp_set

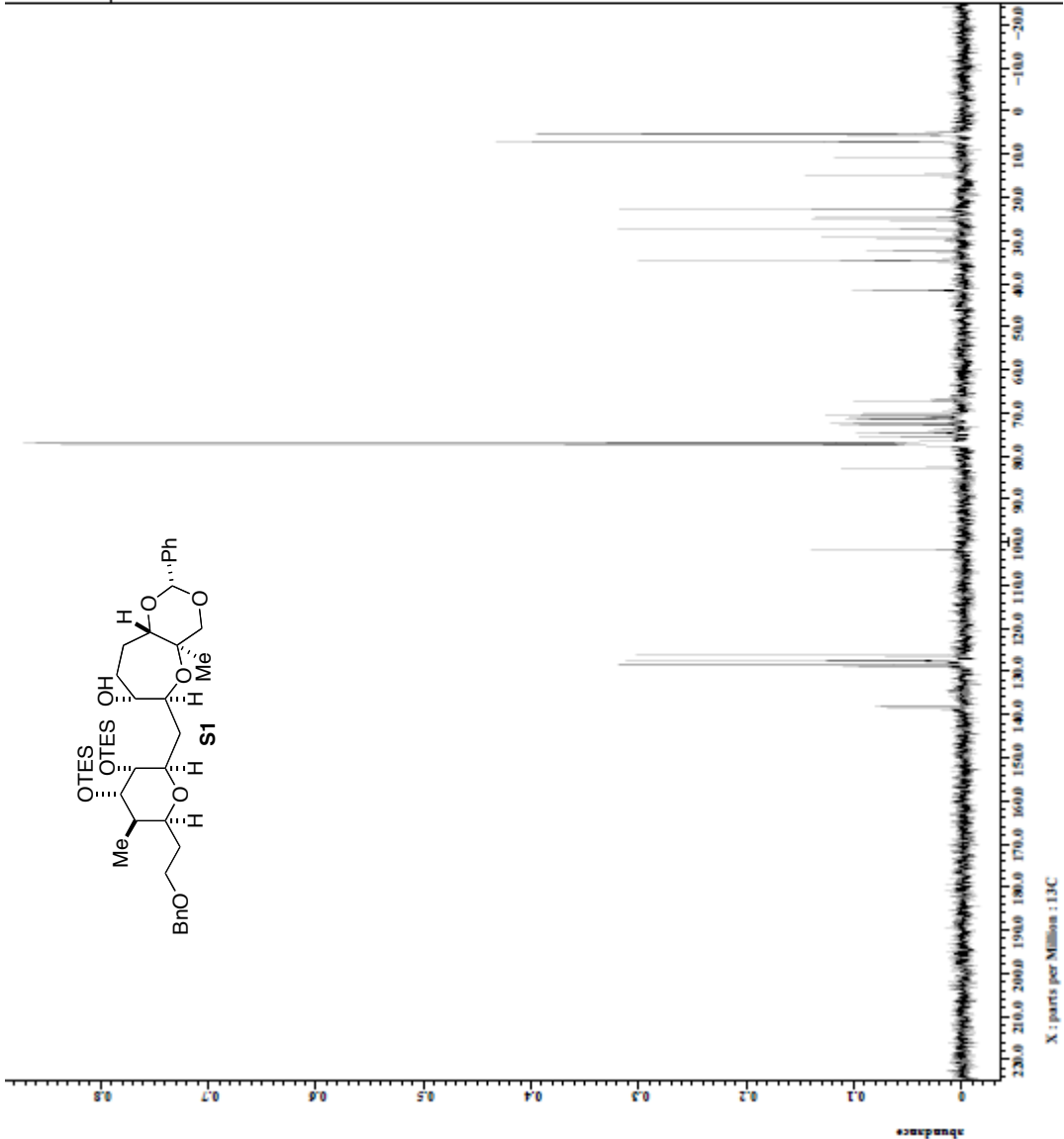
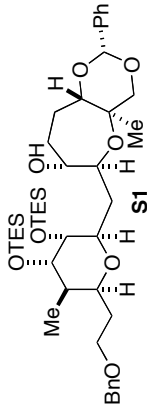
```





```

=====
Filename      = 81-100721-13C-5_1.je
Author        =
Experiment    =
Single_pulse_dec =
Sample_id     =
Solvent       = CHLOROFORM-D
Creation_time = 20-JUL-2010 22:54:10
Revision_time = 2-MAR-2010 16:03:01
Current_time  = 2-MAR-2010 16:03:15
=====
Comment       = single pulse decouple
Data Format    = 1D COMPLEX
Dir Size      = 26214
Dir Title     =
Dir Units     = [ppm]
Dimensions    = 627400
Spectrometer = DELTA2_NMR
Field Strength = 9.389766 [T] (400 [MHz])
Acq Duration  = 1.04333312 [s]
F1 Domain     = 13C
F2 Domain     = 100.62830333 [MHz]
F3 Domain     = 37.0 [ppm]
F4 Domain     = 4
F5 Domain     = 0.95846665 [Hz]
F6 Domain     = 31.40703518 [MHz]
F7 Domain     = 18.78219838 [MHz]
F8 Domain     = 5 [ppm]
F9 Domain     = 7800
Clipped       =
Mod Return    = 1
Scans         = 259
Total Scans   = 259
X10 Width     = 10.8 [us]
X10 Delay     = 0.04333312 [s]
X10 Delay     = 10 [dec]
X10 Delay     = 3 [dm]
X10 Delay     = 3.5 [us]
X10 Delay     = 20.276 [dB]
X10 Delay     = 20.276 [dB]
X10 Delay     = WAURE
X10 Delay     = 1 [s]
X10 Delay     = 1 [s]
X10 Delay     = 2 [s]
X10 Delay     = 60
X10 Delay     = 2 [s]
Relaxation Delay = 3.04333312 [s]
Repetition Time = 21.9 [sec]
Temp [jct]    =
    
```



X : parts per Million : 13C

diol 9



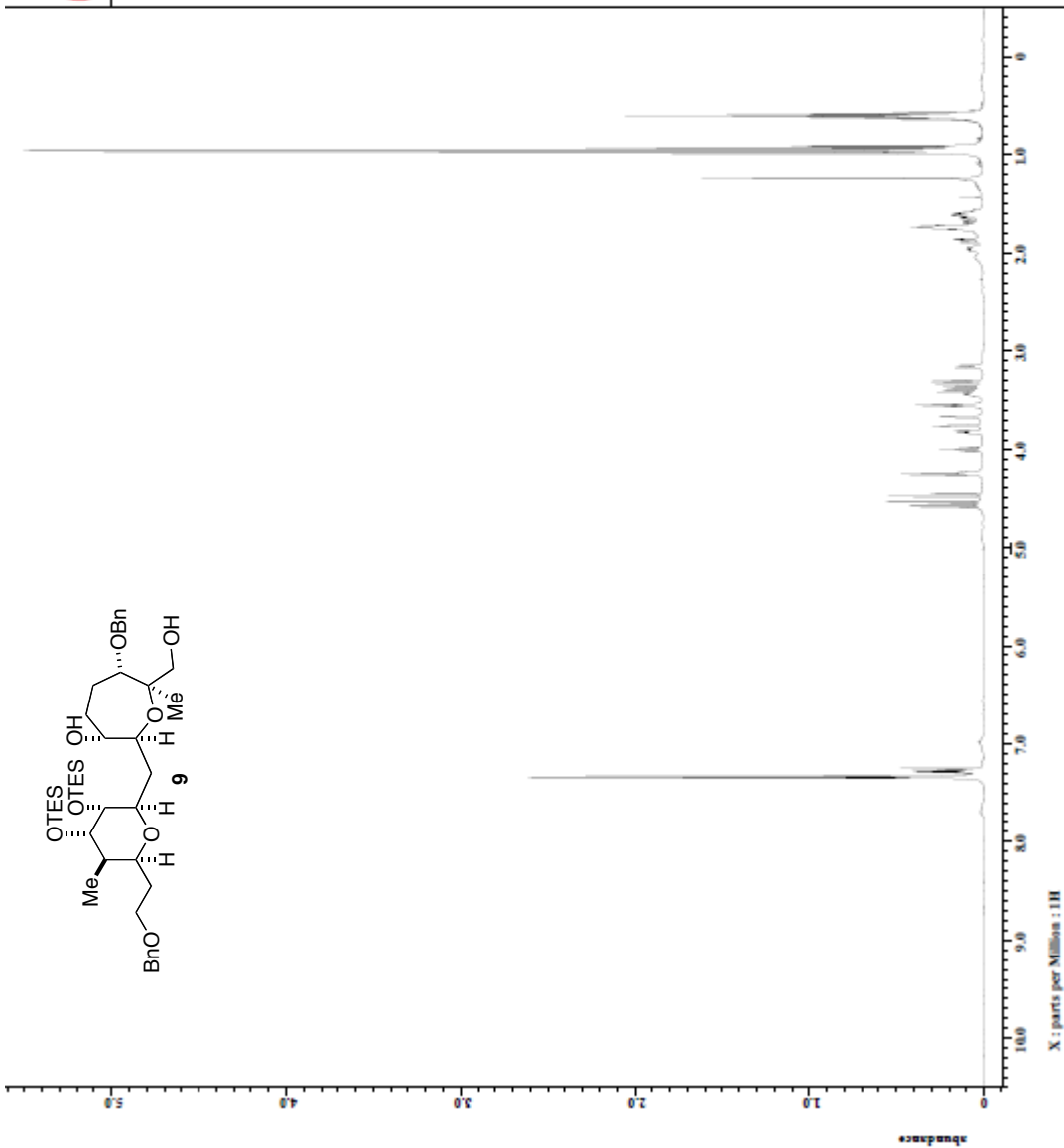
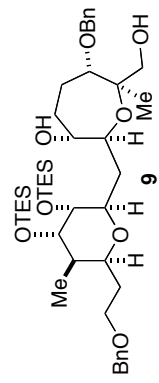
```

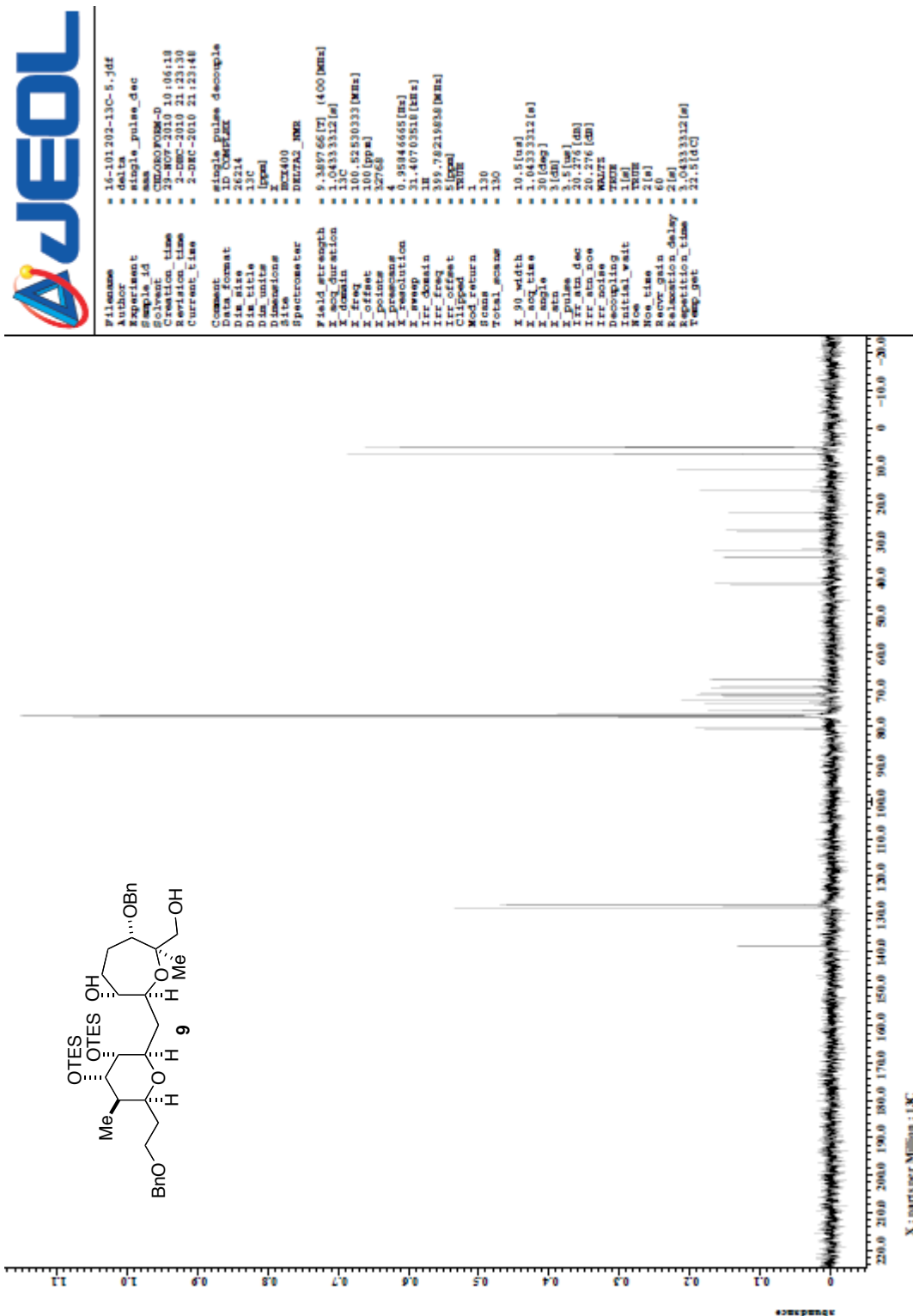
Filename      = 16-100720-1H-5.fde
Author        = delta
Experiment    = single_pulse.ac2
Sample_ID     = aas
Pulse_Prog   = CMLACPOPM-D
Creation_Time = 20-Jul-2010 22:08:16
Revision_Time = 2-DEC-2010 15:19:35
Current_Time  = 2-DEC-2010 15:19:35

Comment       = single_pulse
Data_Format   = 1D COMPLEX
Dir_Size      = 13107
Dir_Title     = 1H
Dim_Units     = [ppm]
Dimensions    = F2A500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain      = 1H
F2_domain      = 500.15691521 [MHz]
F1_offset      = 163 [ppm]
F2_offset      = 163 [ppm]
X_posits       = 1
X_prescans     = 1
X_resolution   = 0.42012084 [Hz]
X_sweep        = 6.68325951 [kHz]
IR_domain      = 1H
IR_offset      = 0.15091521 [MHz]
IR_resolution  = 5.0 [ppm]
T1_domain      = 1H
T1_offset      = 0 [ppm]
T1_freq        = 500.15691521 [MHz]
T1_offset      = 5.0 [ppm]
Clipped        = PARSE
Mod_return     = 1
Scans          = 8
Total_scans    = 8

X_90_width     = 6 [us]
X_acq_time     = 2.38026752 [s]
X_angle        = 45 [deg]
X_str          = 3.2 [dB]
X_pulse        = 3 [us]
X_prescans     = 1
X_mode         = Off
Dantec_present = Off
Initial_wait   = 1 [s]
Rever_gain     = 44
Relaxation_delay = 4 [s]
Repetition_time = 5.18026752 [s]
Temp_set       = 21.9 [C]
    
```





ketone 10



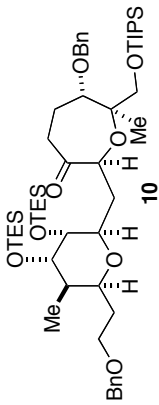
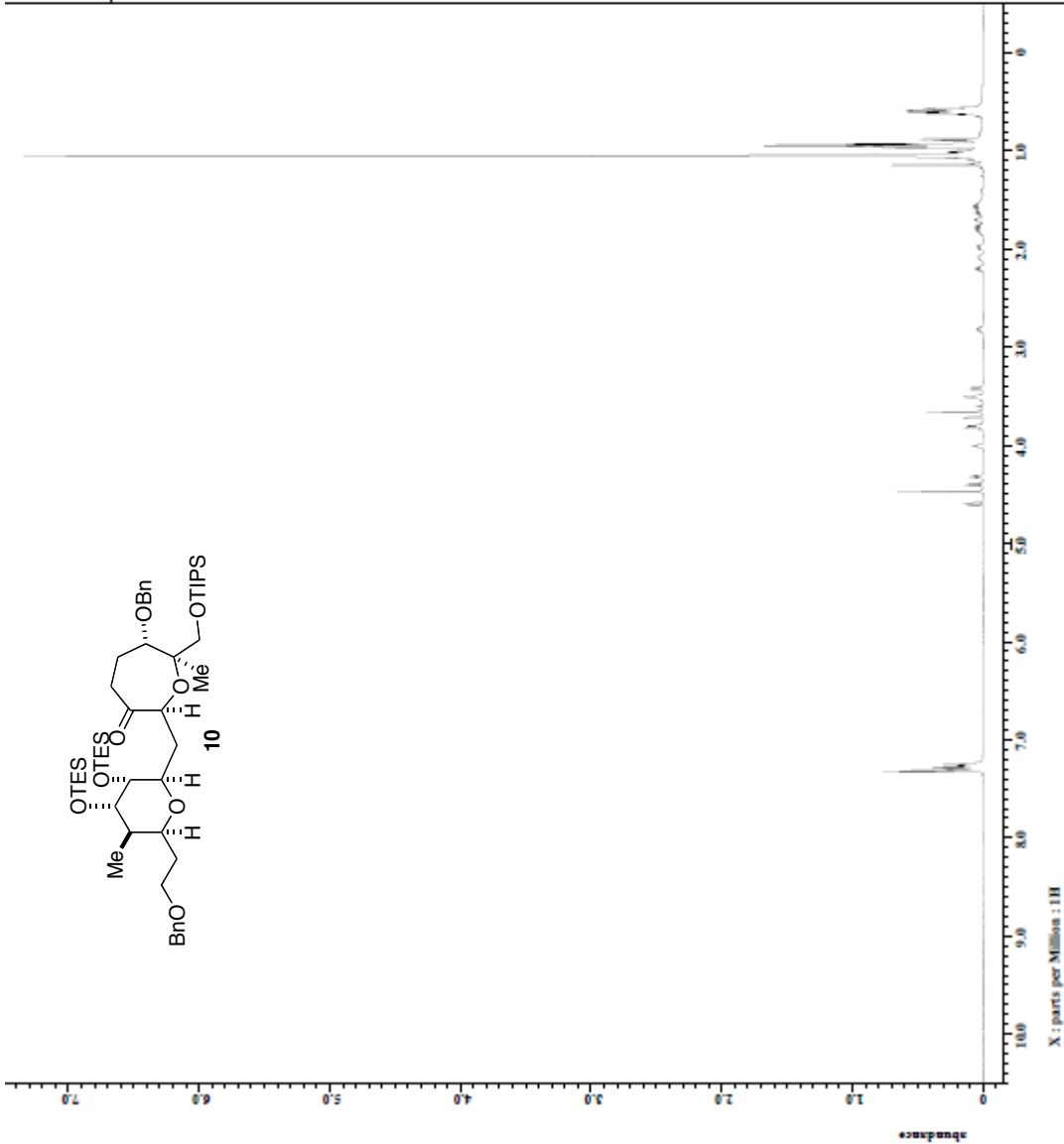
```

=====
File Name      = 17-100722-1R-0.fde
Author        = delta
Experiment    = single_pulse.ac2
Sample_ID     = sas
Solvent       = CHLOROFORM-D
Creation_Time = 22-JUL-2010 16:48:36
Revision_Time = 2-DEC-2010 15:40:04
Current_Time  = 2-DEC-2010 15:40:25

=====
Comment       = single_pulse
Data Format    = 1D COMPLEX
Dir Size     = 13107
Dir Title    = 1R
Dir Units    = [ppm]
Dimensions   = F2AS00
Spectrometer = DELTA2_NMR

=====
Field strength = 11.7473579 [T] (500 [MHz])
Acq duration   = 2.38026752 [s]
F2 domain      = 1R
F2 freq        = 500.15691521 [MHz]
F2 points      = 163 [ppm]
F2 resolution  = 1
F2 prescans    = 1
F2 resolution  = 0.42012084 [Hz]
F2 sweep       = 6.68325951 [kHz]
F2 domain      = 1R
F2 freq        = 50.15691521 [MHz]
F2 offset      = 5.0 [ppm]
F2 domain      = 1R
F2 freq        = 500.15691521 [MHz]
F2 offset      = 5.0 [ppm]
Mod return    = PARSE
Scans         = 1
Total scans   = 0

=====
F2 width       = 6 [us]
F2 acq time    = 2.38026752 [s]
F2 angle       = 45 [deg]
F2 str         = 3.2 [dB]
F2 pulse       = 3 [us]
F2 mode        = Off
F2 mode        = Off
Date Preset   = PARSE
Initial wait   = 1 [s]
Recvr gain    = 40
Relaxation delay = 4 [s]
Repetition time = 5.30026752 [s]
Temp [set]    = 23.3 [degC]
=====
  
```

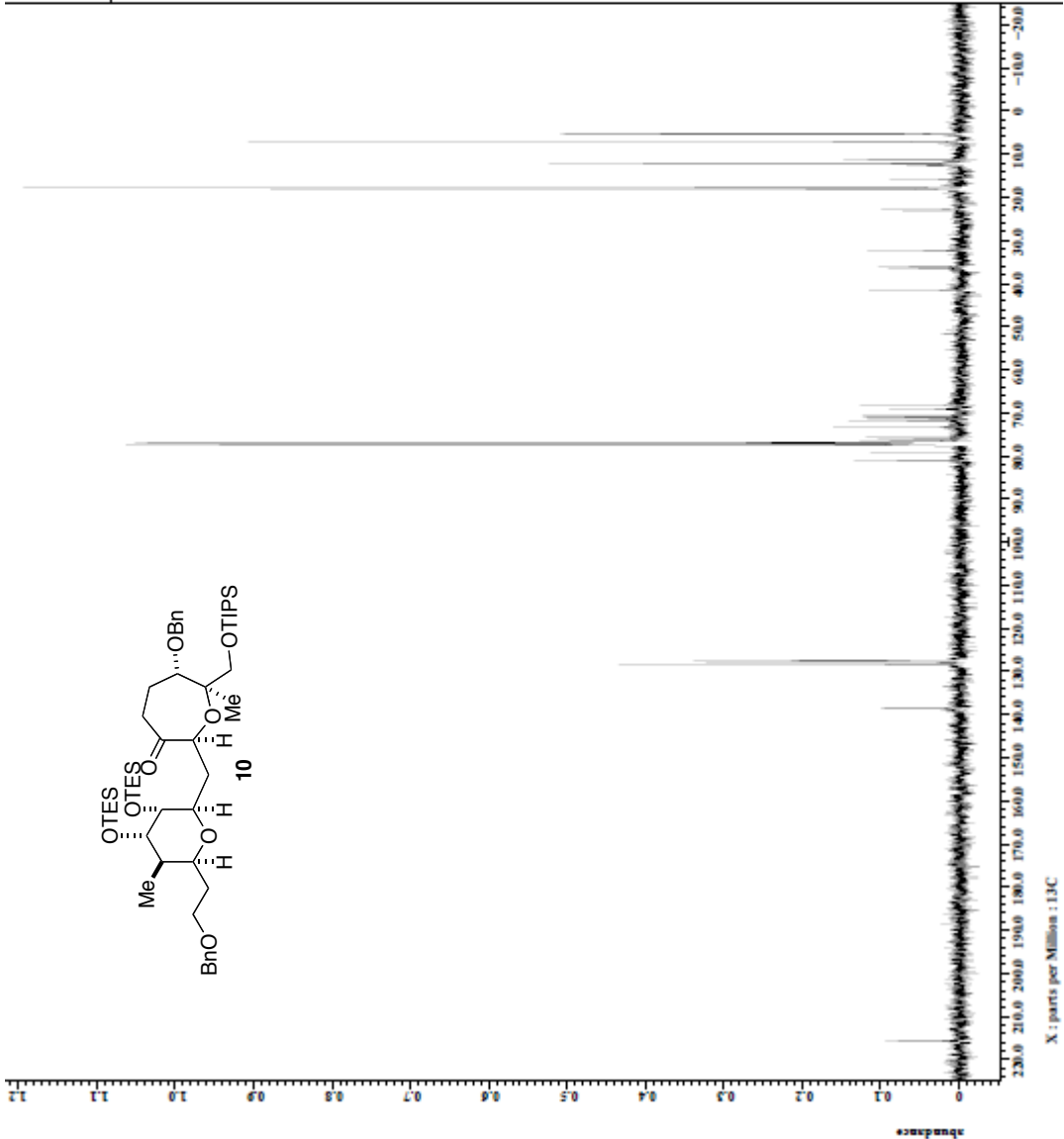
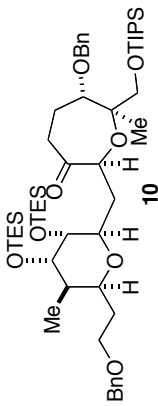


ketone 10



```

=====
Filenames  = 17-100722-13C-6-.jdr
Author     =
Experiment = single_pulse_dec
Sample_id  =
Solvent    = CHLOROFORM-D
Creation_time = 22-JUL-2010 01:50:41
Revision_time = 2-DEC-2010 15:55:24
Current_time = 2-DEC-2010 15:55:43
Comment    = single pulse decouple
Data Format = 1D COMPLEX
Dir_size   = 26214
Dir_title  = 13C
Dir_units  = [ppm]
Dimensions = 654x60
Spectrometer = JEOLJNM
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.0433312 [s]
F1_domain = 13C
F2_domain = 100.62830333 [MHz]
F1_offset = 327.0 [ppm]
F2_offset = 327.0 [ppm]
F1_posists = 4
F2_posists = 4
F1_prescans = 4
F2_prescans = 4
F1_resolution = 0.95846665 [Hz]
F2_resolution = 31.40703518 [MHz]
F1_sweep = 18.78219838 [MHz]
F2_sweep = 5 [ppm]
F1_clipset = Clipped
F2_clipset = Clipped
Mod_F return = 1
Scans = 195
Total_scans = 195
F0_width = 10.8 [us]
F0_acq_time = 0.0433312 [s]
F0_resolution = 3.0 [deg]
F0_sweep = 3 [dm]
F0_pulse = 3.5 [us]
F0_irr_atn_dec = 20.276 [dB]
F0_irr_atn_noise = 20.276 [dB]
F0_noise = WAURE
F0_sampling = 1 [Hz]
F0_initial_wait = 1 [s]
F0_restore = TRUE
F0_restore_time = 2 [s]
F0_restore_gain = 60
F0_relaxation_delay = 2 [s]
F0_repetition_time = 3.0433312 [s]
F0_temp_jpt = 31.9 [degC]
=====
  
```



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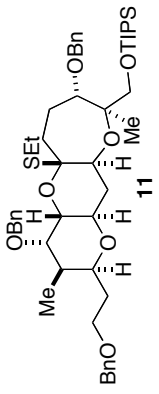
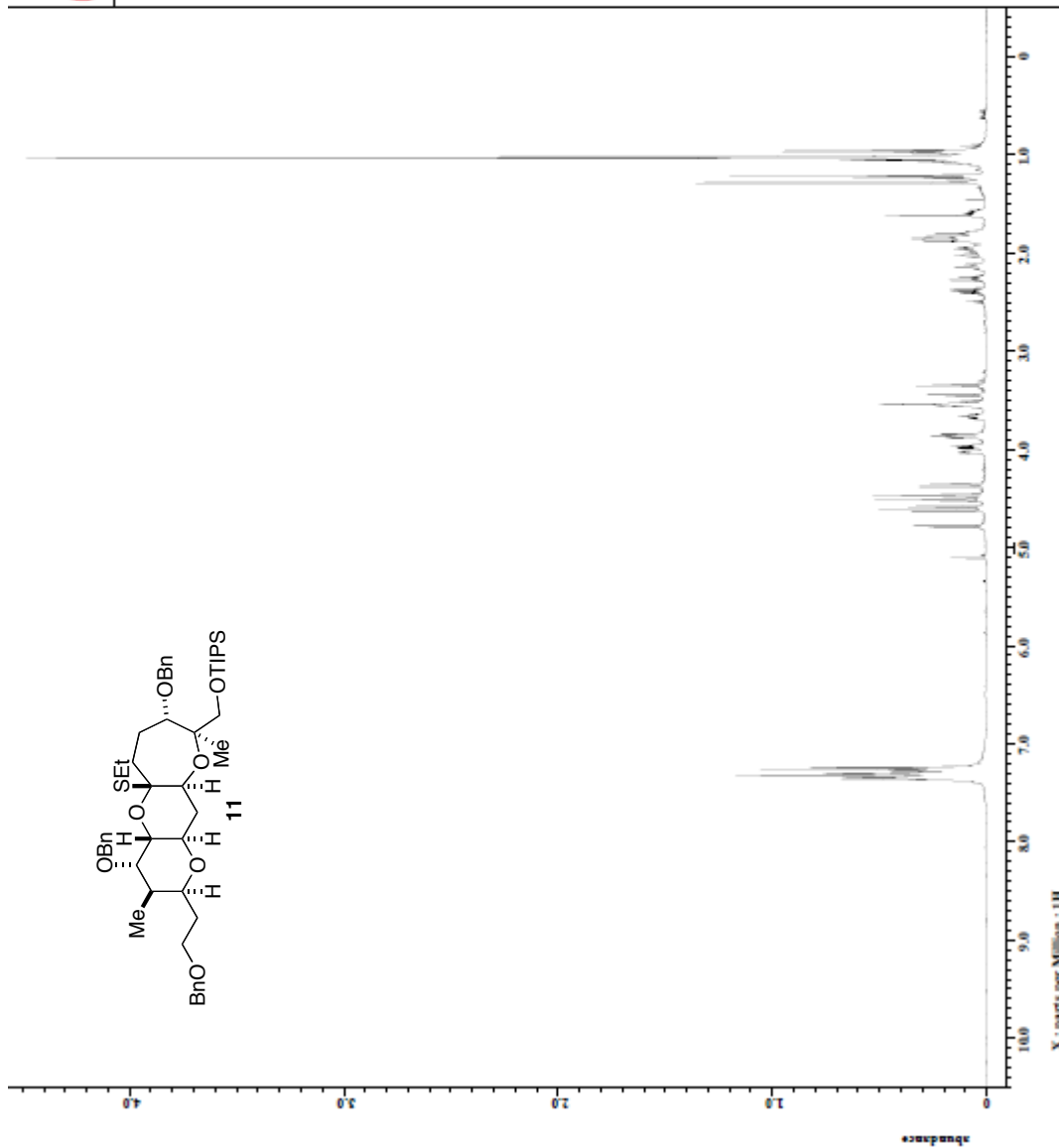


```
Filename  = 16-100722-IN-7.fde
Author    = delta
Experiment  = single_pulse.ac2
Sample_id  = sss
Solvent    = CHLOROFORM-D
Creation_time  = 22-JUL-2010 15:38:55
Revision_time  = 2-AUG-2010 15:40:30
Current_time  = 2-AUG-2010 15:40:30

Comment   = single_pulse
Data Format  = 1D COMPLETE
Dir_size   = 13107
Dir_title  = 1R
Dir_units  = [ppm]
Dimensions = F4500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
Acq_domain    = 1R
F1_freq       = 500.15591521 [MHz]
X_posits     = 163 [ppm]
X_prescans   = 1
X_resolution = 0.42012084 [Hz]
X_sweep      = 6.46932591 [kHz]
F2_domain    = 50.15591521 [MHz]
F2_freq      = 5.01 [ppm]
F2_domain    = 1R
F2_offset    = 500.15591521 [MHz]
F2_offset    = 5.01 [ppm]
Mod_return   = 1
Scaans      = 0
Total_scans = 0

X_90_width   = 6 [us]
X_acq_time   = 2.38026752 [s]
X_angle     = 45 [deg]
X_sfn       = 3.2 [dB]
X_pulse     = 3 [us]
X_offset    = 0 [ppm]
X_mode     = Off
Dantec_preset = FMR2H
Initial_wait = 1 [s]
Receiver_gain = 46
Relaxation_delay = 4 [s]
Repetition_time = 5.160008752 [s]
Temp_set    = 22.7 [OC]
```

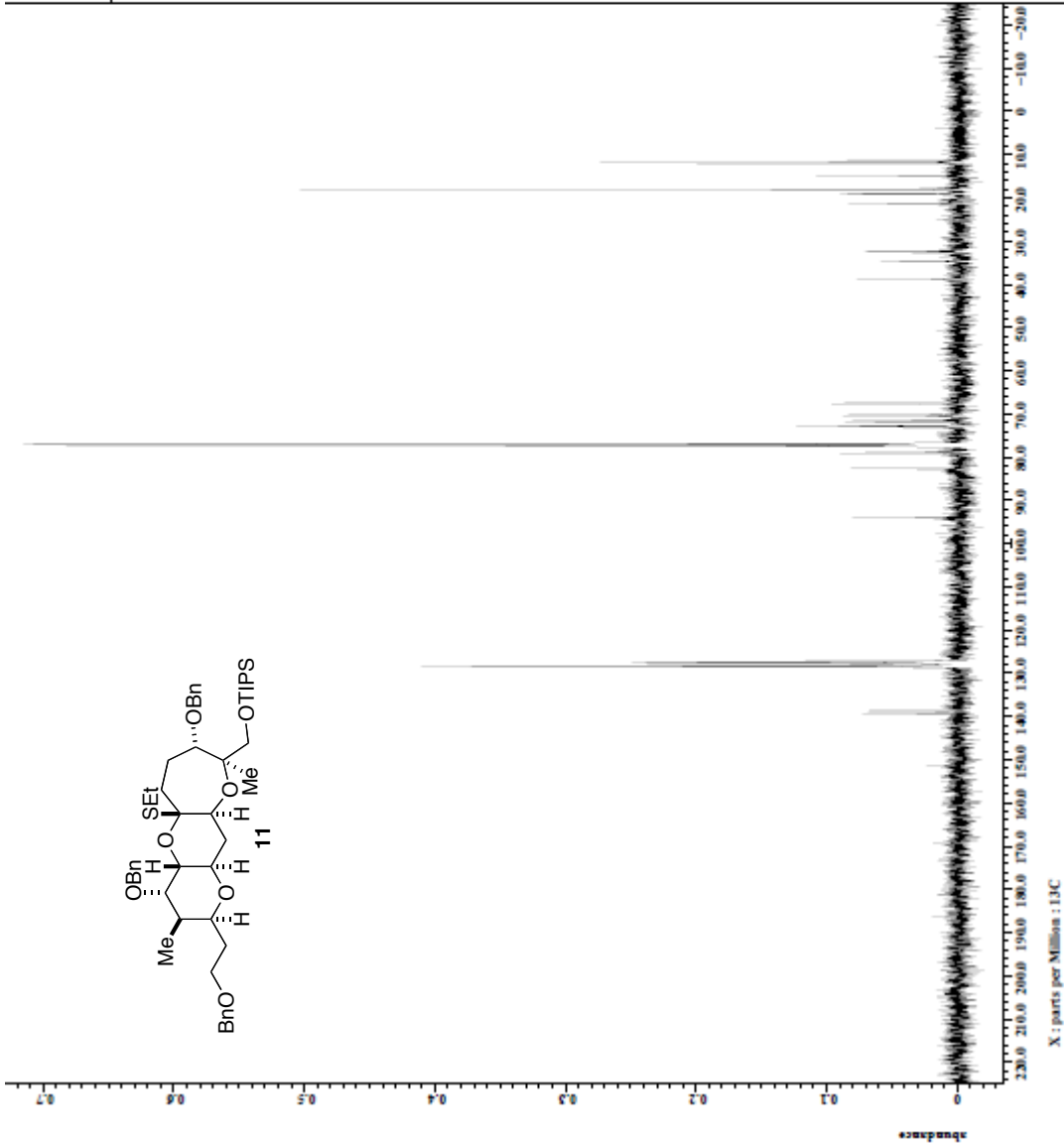
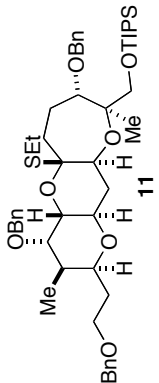


mixed thioacetal **11**



```

Filename = 16-100722-13C-5_1dE
Author = delta
Experiment = single_pulse_dec
Sample_ID = CHLOROPFORM-D
Solvent =
Creation_Time = 22-JUL-2010 02:41:31
Revision_Time = 2-DEC-2010 15:55:51
Current_Time = 2-DEC-2010 15:56:07
Comment = single pulse decouple
Data_Format = 1D COMPLETE
Dir_Size = 26214
Dir_Title = 13C
Dir_Units = [ppm]
Dimensions = 654x400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C
F2_domain = 100.62830333 [MHz]
F1_offset = 327.8 [ppm]
F2_offset = 327.8 [ppm]
F1_points = 4
F2_points = 4
F1_resolution = 0.95846665 [Hz]
F2_resolution = 31.40703518 [MHz]
F1_sweep = 18.78219838 [MHz]
F1_domain_min = 100.62830333 [MHz]
F1_domain_max = 100.62830333 [MHz]
F1_offset_min = 327.8 [ppm]
F1_offset_max = 327.8 [ppm]
Mod_F return = 1
Scans = 141
Total_scans = 141
X_90_width = 10.8 [us]
X_90_time = 0.44333312 [s]
X_acq_time = 1.04333312 [s]
X_sweep = 3 [dm]
X_stn = 3.5 [us]
X_pulse = 20.276 [dB]
Irr_atn_dec = 20.276 [dB]
Irr_atn_noise = 20.276 [dB]
Irr_noise = WAURE
Spectraling = 1 [s]
Initial_wait = 1 [s]
Roc_time = 2 [s]
Rever_gain = 58
Relaxation_delay = 2 [s]
Repetition_time = 3.04333312 [s]
Temp_get = 31.0 [OC]
    
```





```

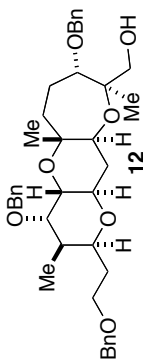
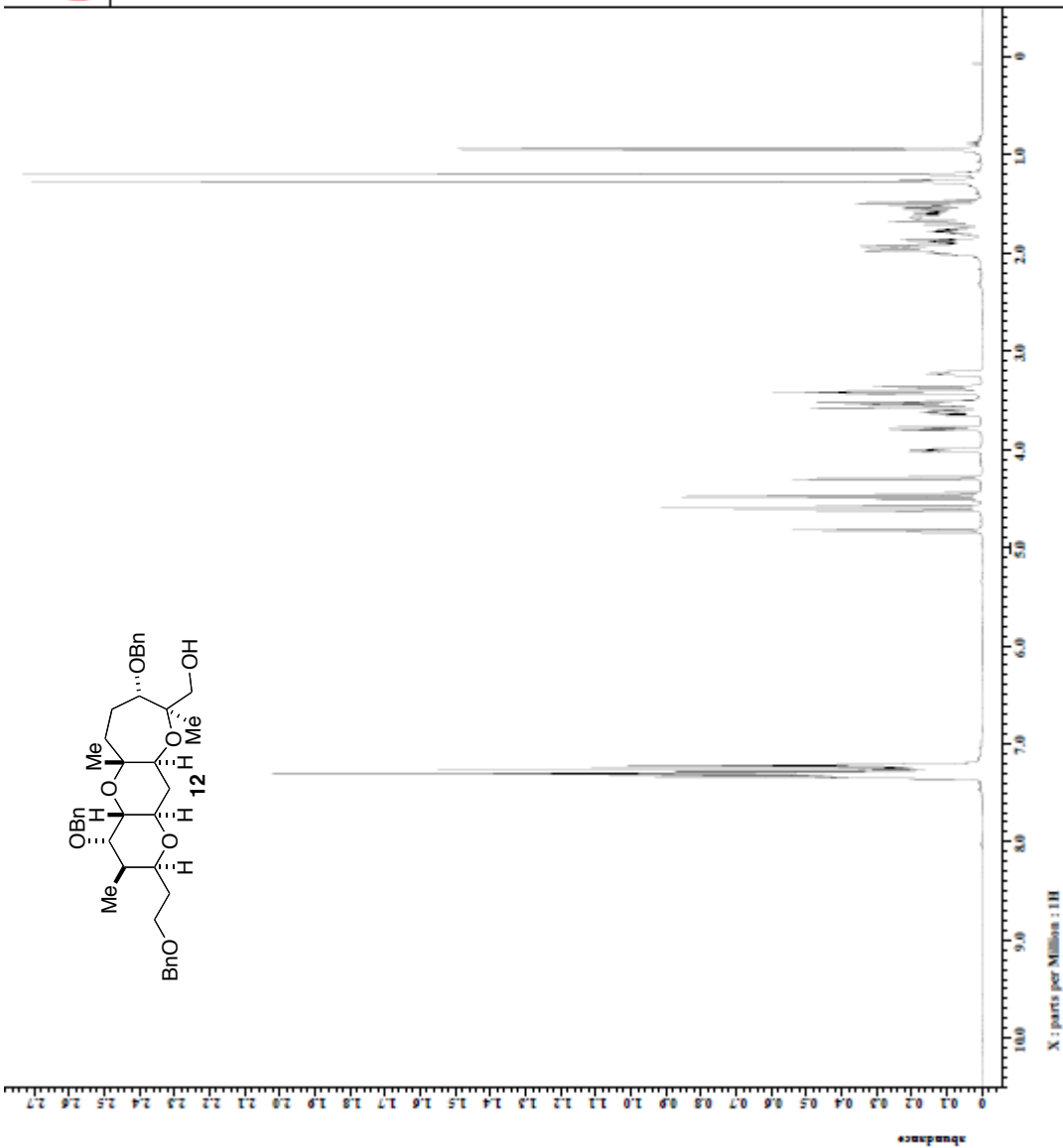
=====
Filename  = 15-100722-1H-5.fde
Author    = delta
Experiment = single_pulse.ac2
Sample_id = aas
Solvent   = CHLOROFORM-D
Creation_time = 22-JUN-2010 15:43:49
Revision_time = 2-JUL-2010 15:41:07
Current_time = 2-JUL-2010 15:41:26

=====
Comment   = single_pulse
Data_format = 1D COMPLETE
Data_size  = 13107
Data_title = 1H
Dim_units  = [ppm]
Dimensions = F2AS00
Spectrometer = DELTA2_NMR

=====
Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F2_domain      = 1H
F2_freq        = 500.15591521 [MHz]
F2_offset      = 163 [ppm]
F2_posits      = 1
F2_prescans    = 1
F2_resolution  = 0.42012084 [Hz]
F2_sweep       = 6.68325951 [kHz]
F2_domain      = 1H
F2_freq        = 500.15591521 [MHz]
F2_offset      = 5.0 [ppm]
F2_posits      = 1
F2_prescans    = 1
F2_resolution  = 0.42012084 [Hz]
F2_sweep       = 6.68325951 [kHz]
F2_domain      = 1H
F2_freq        = 500.15591521 [MHz]
F2_offset      = 5.0 [ppm]
F2_posits      = 1
F2_prescans    = 1
Mod_return     = 1
Scans          = 8
Total_scans    = 8

=====
F2_offset      = 6 [ppm]
F2_posits      = 2.38026752 [s]
F2_prescans    = 45 [deg]
F2_resolution  = 3.2 [cm]
F2_sweep       = 3 [ppm]
F2_posits      = Off
F2_prescans    = FWDH
F2_domain      = 1 [s]
F2_freq        = Recv_gain
F2_offset      = Relaxation_delay
F2_posits      = 4 [s]
F2_prescans    = 5.30026752 [s]
F2_resolution  = 22.9 [ppm]
=====

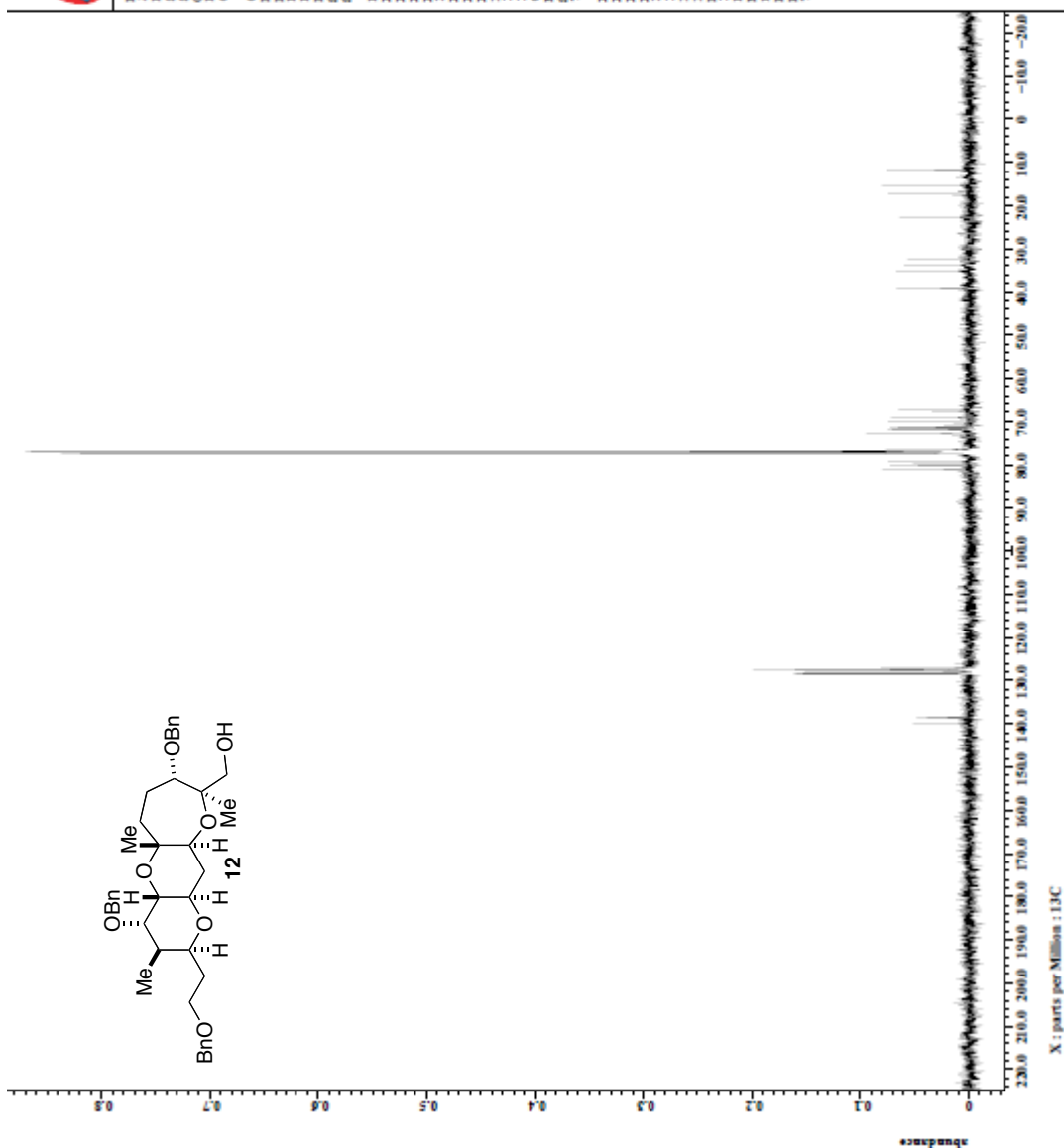
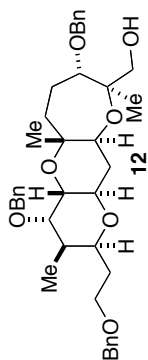
```





```

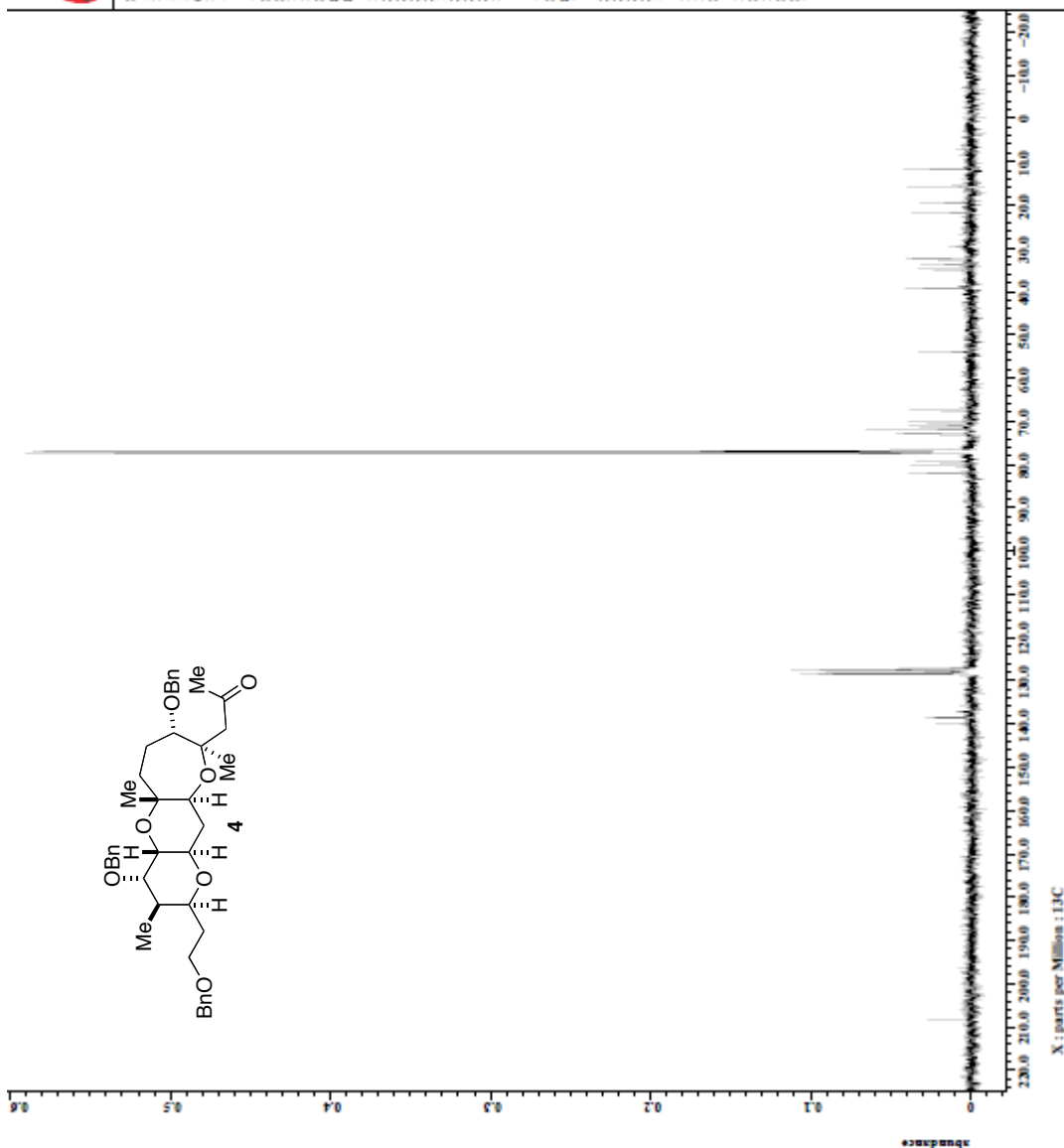
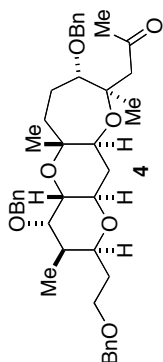
=====
Filenames  = 16-100722-13C-4_1JDE
Author     = delta
Experiment = single_pulse_dec
Sample_id  = sas
SOLVENT    = CHLOROFORM-D
Creation_Time = 22-JUN-2010 02:21:51
Revision_Time = 2-MAR-2010 15:15:15
Current_Time = 2-MAR-2010 15:15:13
Comment    = single pulse decouple
Data Format = 1D COMPLETE
Dir       = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 64x400
Spectrometer = DELTA2_NMR
Field Strength = 9.389766 [T] (400 [MHz])
Acq Duration = 1.04333312 [s]
F1 Domain = 13C
F2 Domain = 100.62830333 [MHz]
F1 Points = 32768
F2 Points = 4
F1 Prescans = 0.55846665 [Hz]
F2 Prescans = 31.40703518 [MHz]
IRF Domain = 18.78219838 [MHz]
IRF Gain = 5 [ppm]
IRF Offset = FALSE
Clipped = 1
Mod Return = 362
Scans = 362
Total Scans = 362
X30 Width = 10.8 [us]
X30 Acq Time = 0.04333312 [s]
X30 Delay = 3.0 [deg]
X30 Gain = 3 [dB]
X30 Pulse = 3.5 [us]
IRF Att Dec = 20.276 [dB]
IRF Att Nois = 20.276 [dB]
IRF Noise = WAURE
Sampling = 1 [Hz]
Initial Wait = 1 [s]
Rise Time = 2 [s]
Rever Gain = 60
Relaxation Delay = 2 [s]
Repetition Time = 3.04333312 [s]
Temp Set = 31.7 [degC]
=====
    
```



ketone 4



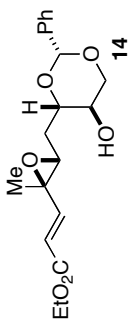
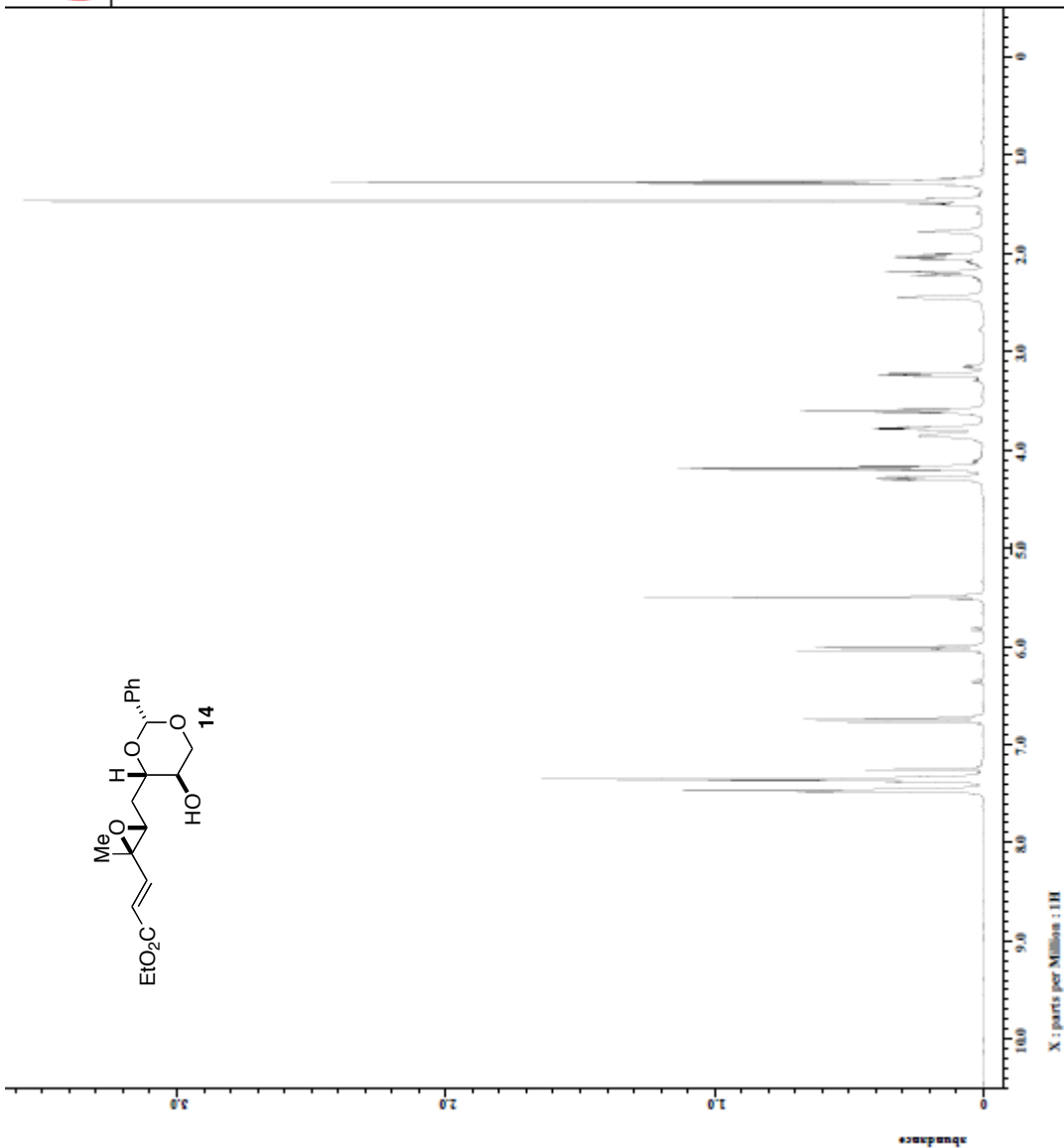
Filename 4-100402-13C-2.fde
Author delta
Experiment single_pulse_dec
Sample_id sas
CHLOROFORM-D
Creation_Time 2-SEP-2010 04:51:47
Revision_Time 2-DEC-2010 15:12:42
Current_Time 2-DEC-2010 15:12:19
Comment single_pulse decouple
Data_Format 1D COMPLEX
Date_Stamp 26214
Dir_title 13C
Dir_units [ppm]
Dimensions 4
Spectrometer CFX400
DELTA2_NMR
Field_strength 9.389766 [T] (400 [MHz])
Acq_duration 1.04333312 [s]
F1_domain 13C
F1_freq 100.62830333 [MHz]
F1_offset 3270 [ppm]
F1_phase 4
F1_prescans 4
F1_resolution 0.55846665 [Hz]
F1_sweep 31.40703518 [Hz]
F1_domain 18.78219838 [MHz]
F1_freq 5 [ppm]
F1_offset Clipped
F1_phase 780 [deg]
Mod_F return 1
Scans 626
Total_scans 626
F2_width 10.8 [us]
F2_acq_time 1.04333312 [s]
F2_offset 0 [deg]
F2_phase 3 [deg]
F2_pulse 3.5 [us]
F2_stn_dec 20.276 [dB]
F2_stn_noise 20.276 [dB]
F2_noise WAURE
F2_phase 1 [deg]
F2_offset Initial_wait
F2_phase 1 [deg]
F2_prescans 2 [s]
F2_sweep 58
F2_domain 2 [s]
F2_freq 3.04333312 [s]
F2_offset 2 [s]
F2_phase 21.1 [deg]



hydroxy epoxide 14



Filename = 21-100491-1R-3.fde
Author = delta
Experiment = single_pulse.ac2
Sample_id = #W613667
Solvent = CHLOROFORM-D
Creation_time = 31-03-2010 22:31:20
Revision_time = 2-DEC-2010 15:41:36
Current_time = 2-DEC-2010 15:41:30
Comment = single_pulse
Data_format = 1D COMPLETE
Data_size = 13107
Data_title = IR
Dim_units = [ppm]
Dimensions = FCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration = 2.38026752 [s]
X_domain = IR
X_freq = 500.15691521 [MHz]
X_points = 163 [ppm]
X_resolution = 1
X_swept = 0.42012084 [Hz]
IR_domain = IR
IR_freq = 6.68325951 [kHz]
IR_offset = 5.0 [ppm]
T1_domain = IR
T1_freq = 5.0 [ppm]
T1_offset = 5.0 [ppm]
Mod_return = PARSE
Scans = 1
Total_scans = 0
X_f0_width = 6 [Hz]
X_acq_time = 2.38026752 [s]
X_angle = 45 [deg]
X_str = 3.2 [dB]
X_pulse = 3 [Hz]
T1_mode = Off
Dantec_present = PARSE
Initial_wait = 1 [s]
Rever_gain = 54
Relaxation_delay = 1.5 [s]
Repetition_time = 1.80026752 [s]
Temp_set = 32.4 [C]



hydroxy epoxide 14



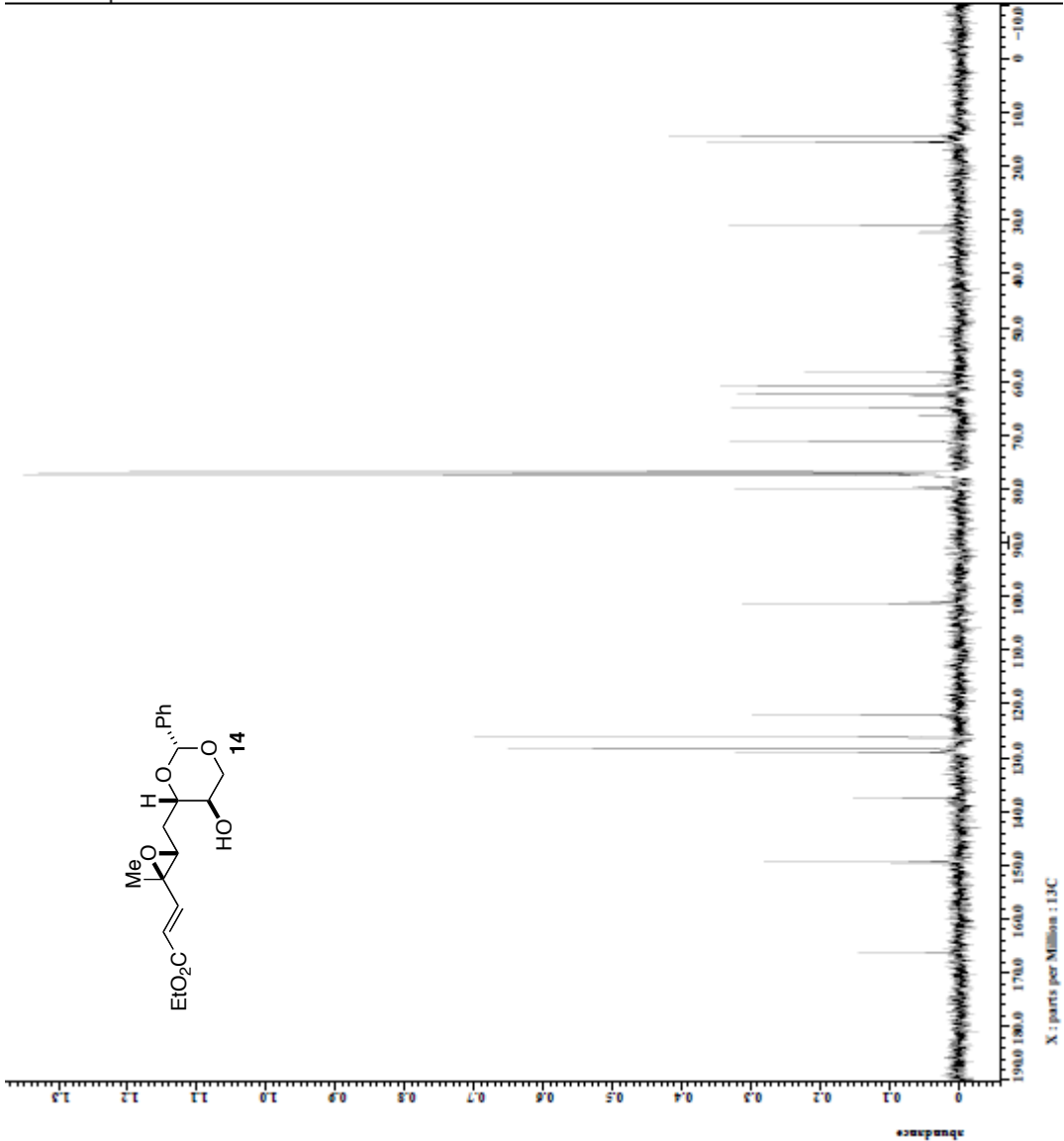
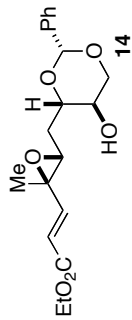
```

=====
File Name      * 81-1-27-100031-13C-3.
Author         * delta
Experiment     * single_pulse_dec
Sample_ID      * 8W036876
Solvent        * CHLOROFORM-D
Creation_Time  * 31-03-2010 05:17:40
Revision_Time  * 2-DEC-2010 16:03:52
Current_Time   * 2-DEC-2010 16:04:09

Comment        * single_pulse decouple
Data Format     * 1D COMPLEX
Dir Size       * 13107
Dir Title      * 13C
Dir Units       * [ppm]
Dimensions     * 627400
Spectrometer   * DELTA2_NMR

Field Strength * 9.389766 [T] (400 [MHz])
Acq Duration   * 0.65011712 [s]
F2 Domain      * 13C
F1 Freq        * 100.62830333 [MHz]
F1 Points      * 16394
F1 Prescans    * 4
F1 Resolution  * 1.53818438 [Hz]
F1 Sweep       * 25.2016125 [kHz]
F1 Domain      * 18.78219938 [MHz]
F1 Freq        * 5 [ppm]
F1 Offset      * 7808
Mod F return   * 1
Scans          * 216
Total Scans    * 216

X90 Width      * 0.8 [us]
X90 Delay       * 0.65011712 [s]
X90 Pulse       * 3.0 [deg]
X90 Phase       * 3 [deg]
X90 Amplitude   * 3.5 [us]
X90 Pulse Dec  * 20.276 [dB]
X90 Amplitude  * 20.276 [dB]
X90 Noise      * WAURE
X90 Frequency   * 1 [Hz]
X90 Initial Wait * 1 [s]
X90 No. Times   * 2 [s]
X90 Recvr Gain  * 60
X90 Relaxation Delay * 2 [s]
Repetition Time * 2.65011712 [s]
Temp [deg]     * 21.1 [deg]
=====
    
```



pyran 15



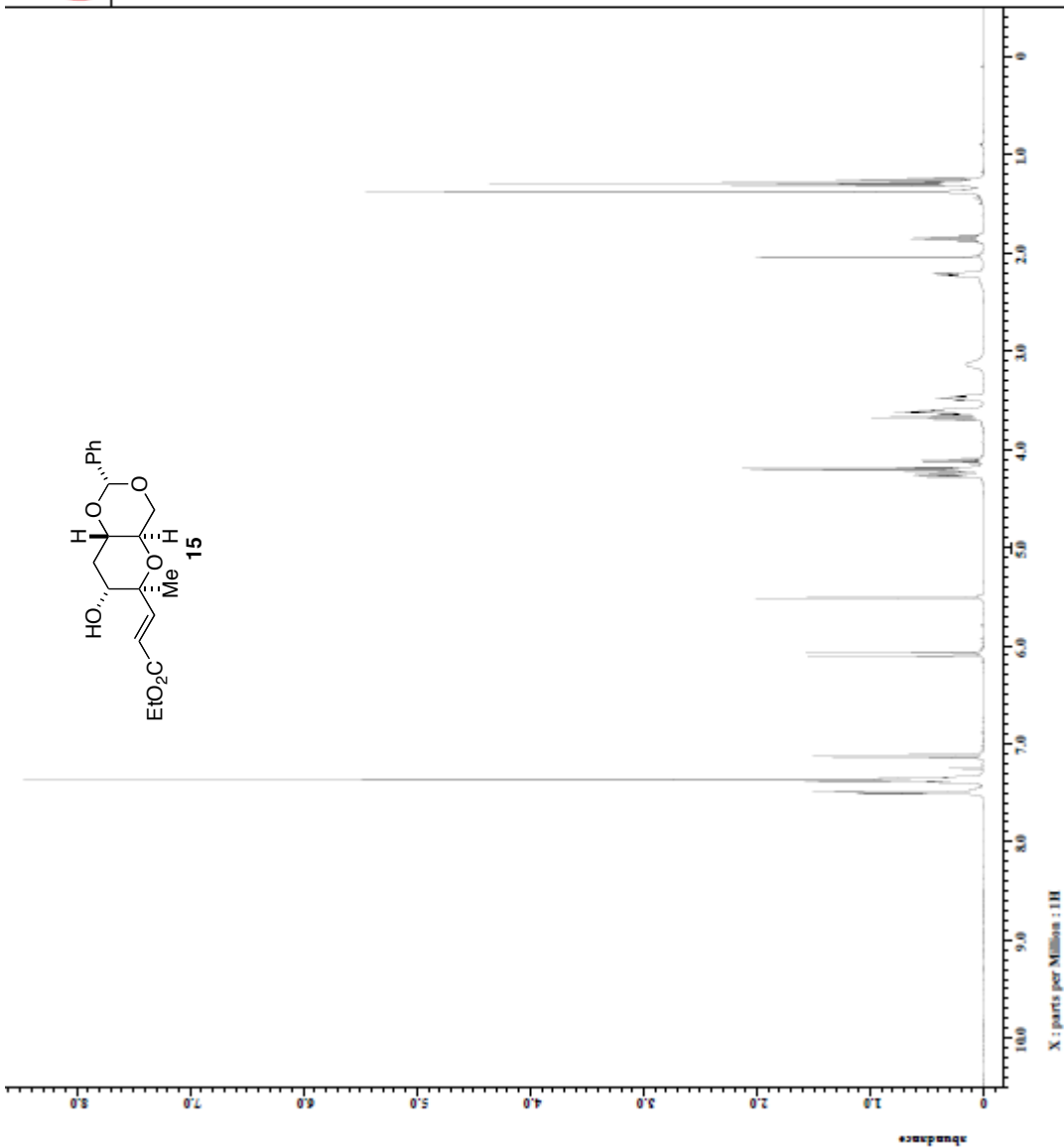
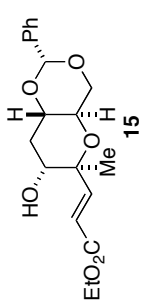
```

=====
Filenames  = 22-100802-1R-2.fde
Author    = delta
Experiment = single_pulse.ac2
Sample_id = sas
Solvent   = CHLOROFORM-D
Creation_time = 2-MS-2010 17:24:42
Revision_time = 2-MS-2010 15:41:55
Current_time = 2-MS-2010 15:42:00

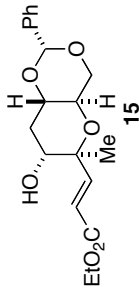
Comment   = single_pulse
Data_format = 1D COMPLETE
Dir_size  = 13107
Dir_title = 1R
Dir_units = [ppm]
Dimensions = F2AS00
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F2_domain      = 1R
F2_freq        = 500.15691521 [MHz]
F2_offset      = 163 [ppm]
F2_points      = 1
F2_resolution  = 0.42012084 [Hz]
F2_sweep       = 6.68325951 [kHz]
F2_domain      = 1R
F2_freq        = 50.15691521 [MHz]
F2_offset      = 5.0 [ppm]
F2_points      = 1
F2_resolution  = 500.15691521 [MHz]
F2_offset      = 5.0 [ppm]
Mod_return     = 1
Scans          = 8
Total_scans   = 8

F2_width       = 6 [us]
F2_acq_time    = 2.38026752 [s]
F2_angle       = 45 [deg]
F2_str         = 3.2 [dB]
F2_pulse       = 3 [us]
F2_presat      = Off
F2_mode        = Off
Dantec_presat = FALSH
Initial_wait   = 1 [s]
Recur_gain     = 4.0
Relaxation_delay = 5 [s]
Repetition_time = 3.30026752 [s]
Temp_get       = 32.7 [C]
=====
    
```

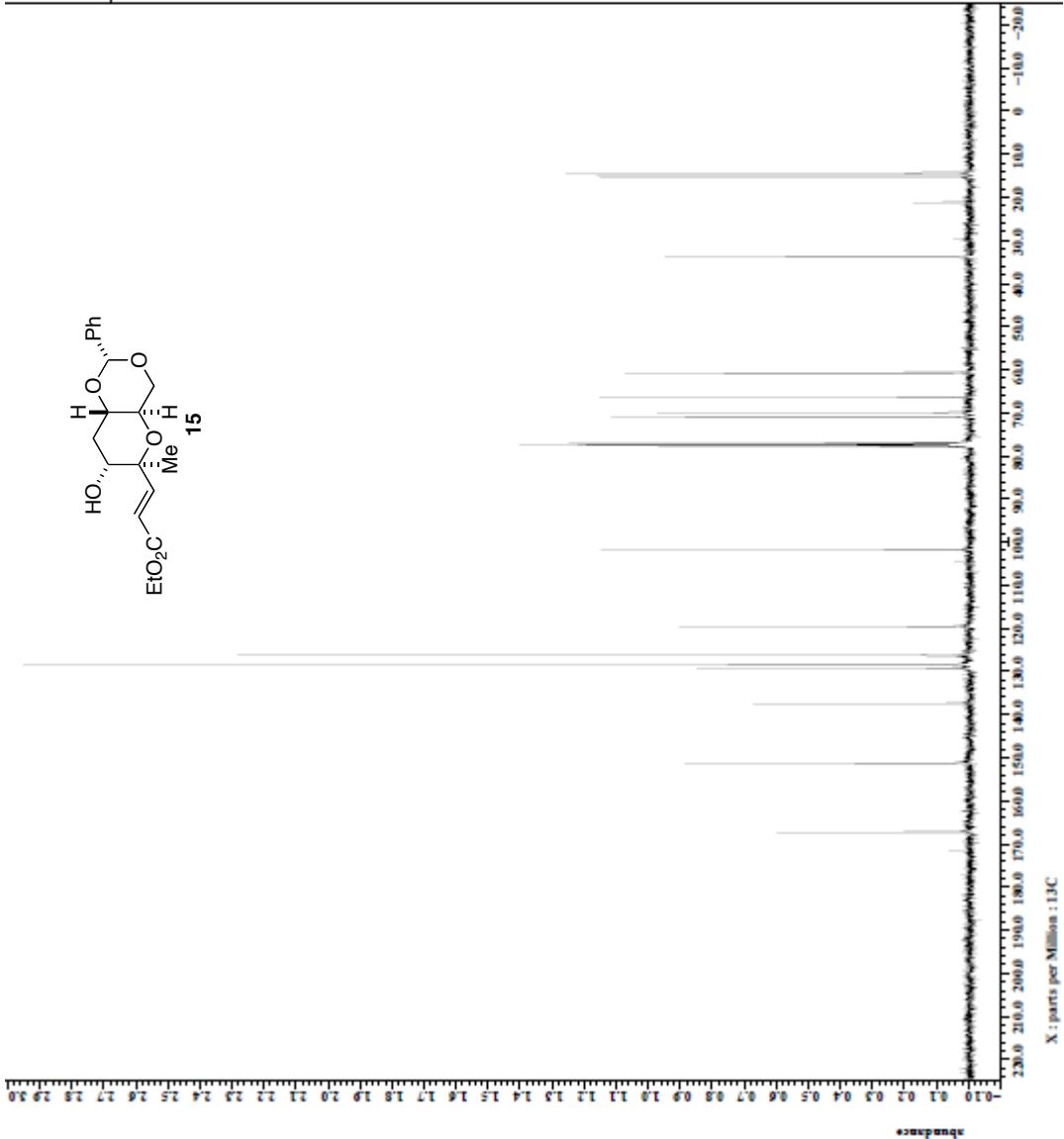


pyran 15



```

=====
F1ltnmms      = 22-100802-13C-2_1J6E
Author        = delta
Experiment    = single_pulse_dec
Sample_id     = aas
Solvent       = CHLOROFORM-D
Creation_Time = 2-MSJ-2010 00:10:42
Revision_Time = 2-MSJ-2010 15:15:42
Current_Time  = 2-MSJ-2010 15:17:01
=====
Comment       = single pulse decouple
Data Format    = 1D COMPLEX
Dir Size      = 26214
Dir Title     = 13C
Dir Units     = [ppm]
Dimensions    = 654400
Spectrometer = DELTA2_NMR
=====
Field strength = 9.389766 [T] (400 [MHz])
Acq duration   = 1.04333312 [s]
F1 domain      = 13C
F2 domain      = 100.62830333 [MHz]
F3 domain      = 327.8 [MHz]
F4 domain      = 4 [MHz]
F5 domain      = 0.95846665 [Hz]
F6 domain      = 31.40703518 [MHz]
F7 domain      = 18.78219938 [MHz]
F8 domain      = 5 [MHz]
F9 domain      = 5 [MHz]
Mod F return   = F4DRR
Scans          = 1
Total scans    = 76
=====
X10 width      = 10.8 [us]
X10 delay      = 0.04333312 [s]
X10 rise       = 10 [dec]
X10 fall       = 3 [dm]
X10 gate       = 3.5 [us]
X10 pulse      = 20.276 [dB]
X10 pulse dec = 20.276 [dB]
X10 noise      = 20.276 [dB]
X10 waure      = WAURE
X10 sampling   = 1 [Hz]
X10 initial_wat = 1 [dB]
X10 rse_time   = 2 [s]
X10 rsevr_gain = 60
X10 relax_time = 2 [s]
X10 rep_time   = 3.04333312 [s]
X10 temp_jct   = 31.4 [0C]
=====
  
```





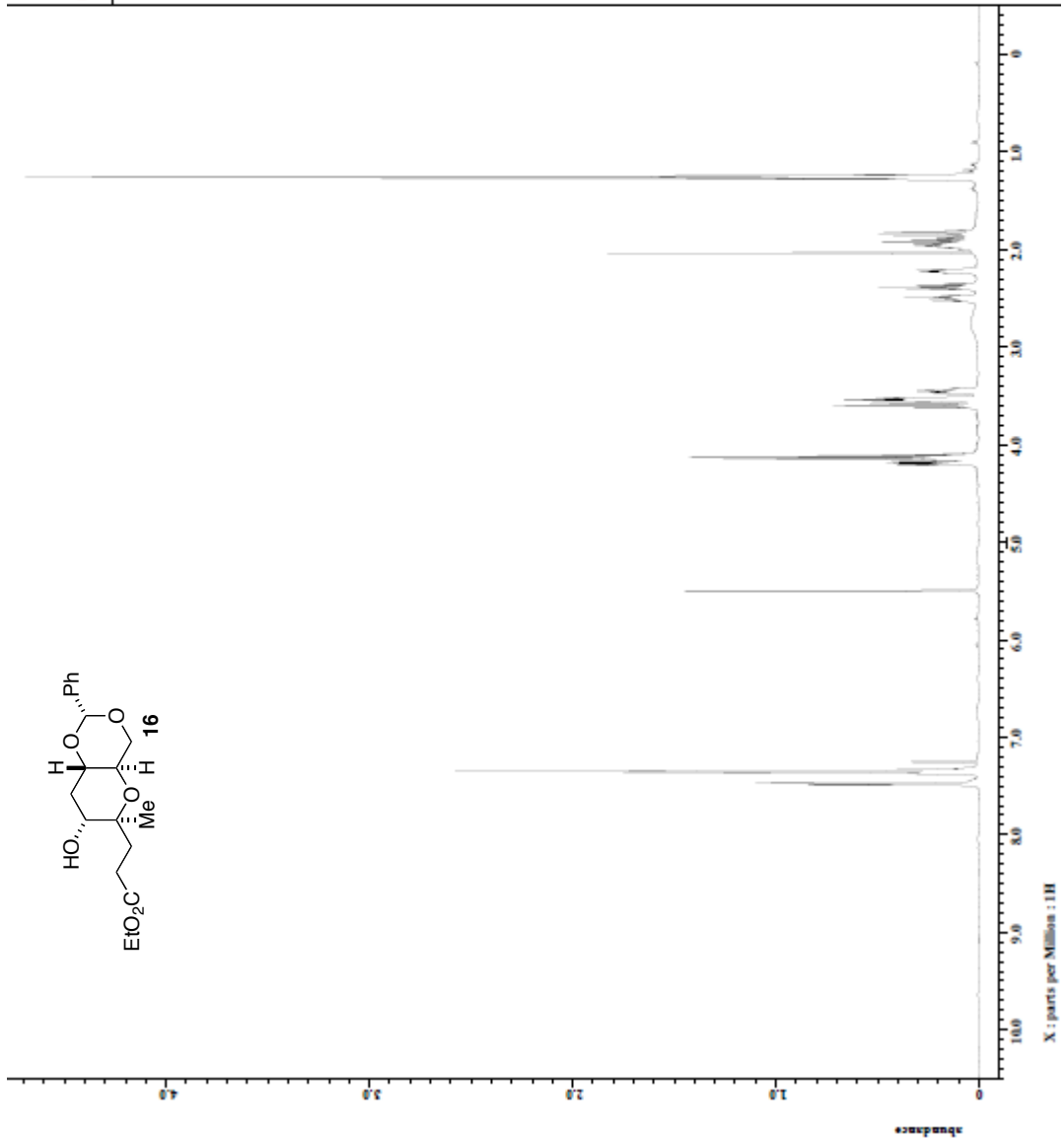
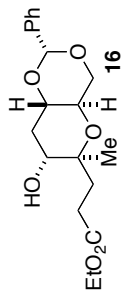
```

=====
Filename      = 23-100802-1R-2.fde
Author       = delta
Experiment   = single_pulse.ac2
Sample_id    = as3
Solvent      = CDCl3/POEM-D
Creation_time = 2-MS-2010 17:44:06
Revision_time = 2-MS-2010 15:42:13
Current_time  = 2-MS-2010 15:42:13

Comment       = single_pulse
Data_format   = 1D COMPLETE
Dir_size      = 13107
Dir_title     = 1R
Dir_units     = [ppm]
Dimensions    = F24500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F2_domain      = 1R
F2_freq        = 500.15591521 [MHz]
F2_offset      = 163 [ppm]
F2_points      = 1
F2_prescans    = 1
F2_resolution  = 0.42012084 [Hz]
F2_sweep       = 6.46925951 [kHz]
F2_domain_min = 0.15091521 [MHz]
F2_domain_max = 5.0 [ppm]
F2_freq_min    = 1R
F2_freq_max    = 500.15591521 [MHz]
F2_offset_min  = 5.0 [ppm]
F2_offset_max  = F2_OFFSET
Mod_return     = 1
Scans          = 8
Total_scans    = 8

F2_f0_width    = 6 [kw]
F2_acq_time     = 2.38026752 [s]
F2_angle        = 45 [deg]
F2_str          = 3.2 [dB]
F2_pulse        = 3 [kw]
F2_presat       = Off
F2_mode         = Off
F2_mode2        = F2_MODE
Dantec_presat   = 1 [s]
Initial_wait    = 1 [s]
Recur_gain      = 4 [s]
Relaxation_delay = 5 [s]
Repetition_time = 3.80026752 [s]
Temp_set        = 22.9 [degC]
    
```





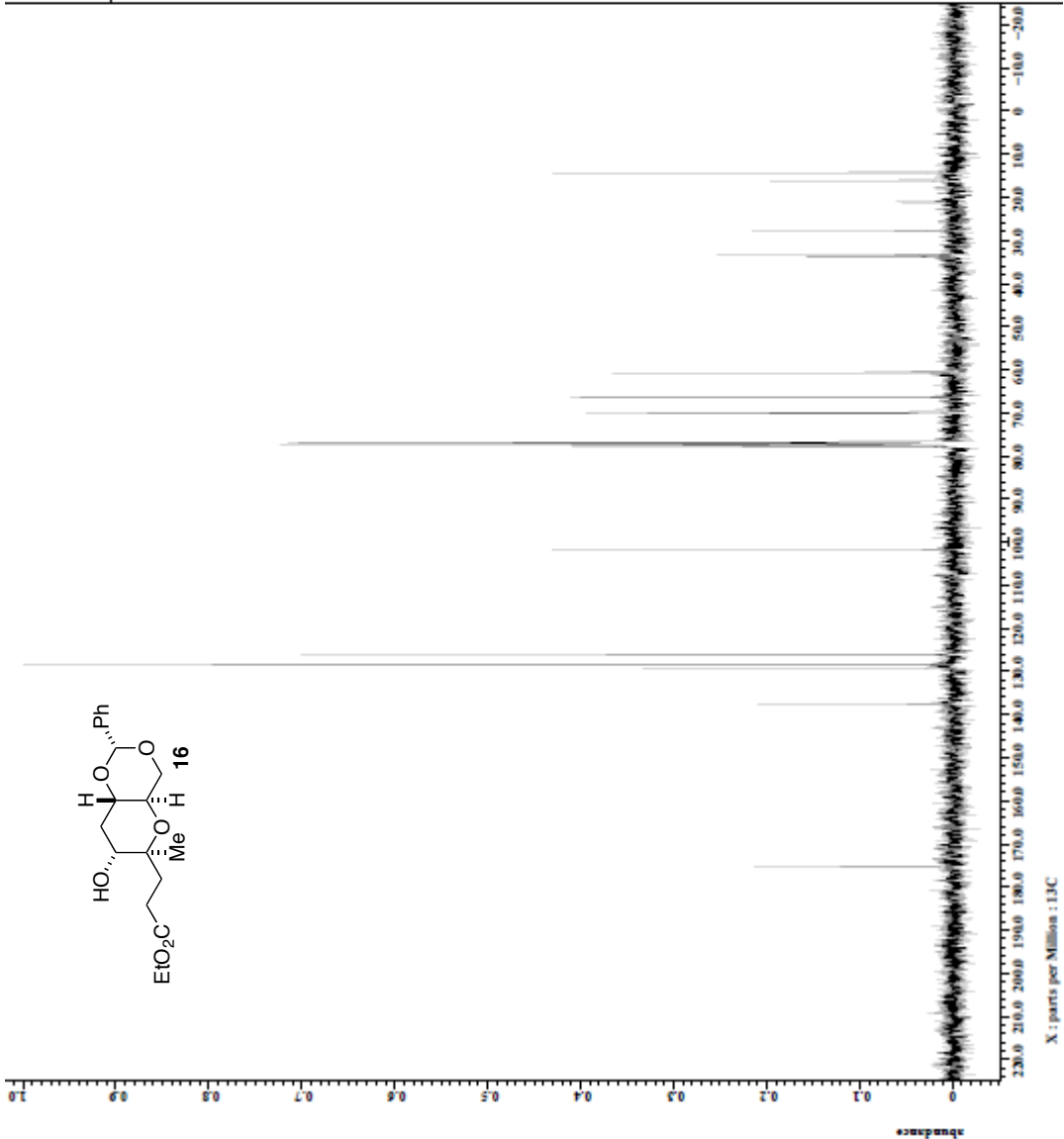
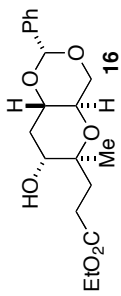
```

Filename      = 23-100802-13C-2_16E
Author       = Delta
Experiment   = single_pulse_dec
Sample_id    = sas
Solvent      = CHLOROFORM-D
Creation_time = 1-05-2010 21:58:14
Revision_time = 2-08C-2010 15:15:10
Current_time = 2-08C-2010 15:17:24

Comment      = single pulse decouple
Data_format  = 1D COMPLETE
Dir_size     = 26214
Dir_title    = 13C
Dir_units    = [ppm]
Dimensions   = 627400
Spectrometer = DELTA2_NMR

Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration   = 1.0433312 [s]
F1_domain      = 13C
F1_freq        = 100.62830333 [MHz]
F1_offset      = 3270 [ppm]
F1_pulses      = 4
F1_prescans    = 4
F1_resolution  = 0.95846665 [Hz]
F1_sweep       = 31.40703518 [MHz]
F1_domain_min = 18.78219838 [MHz]
F1_domain_max = 57 [MHz]
F1_offset_min = Clipped
F1_offset_max = FUDGE
Mod_f_return   = 1
Scans         = 117
Total_scans    = 117

X_90_width    = 10.8 [us]
X_90_time     = 1.0433312 [s]
X_pulse       = 3.5 [us]
X_pulse_freq  = 3 [dm]
X_pulse_gain  = 3.5 [us]
Irr_atn_dec   = 20.276 [dB]
Irr_atn_noise = 20.276 [dB]
Waltz16      = waltz16
Sweeping      = 1 [Hz]
Initial_wait  = 1 [s]
Roc_time      = 2 [s]
Rever_gain    = 60
Relaxation_delay = 2 [s]
Repetition_time = 3.104333312 [s]
Temp_jpt      = 31.4 [0C]
    
```





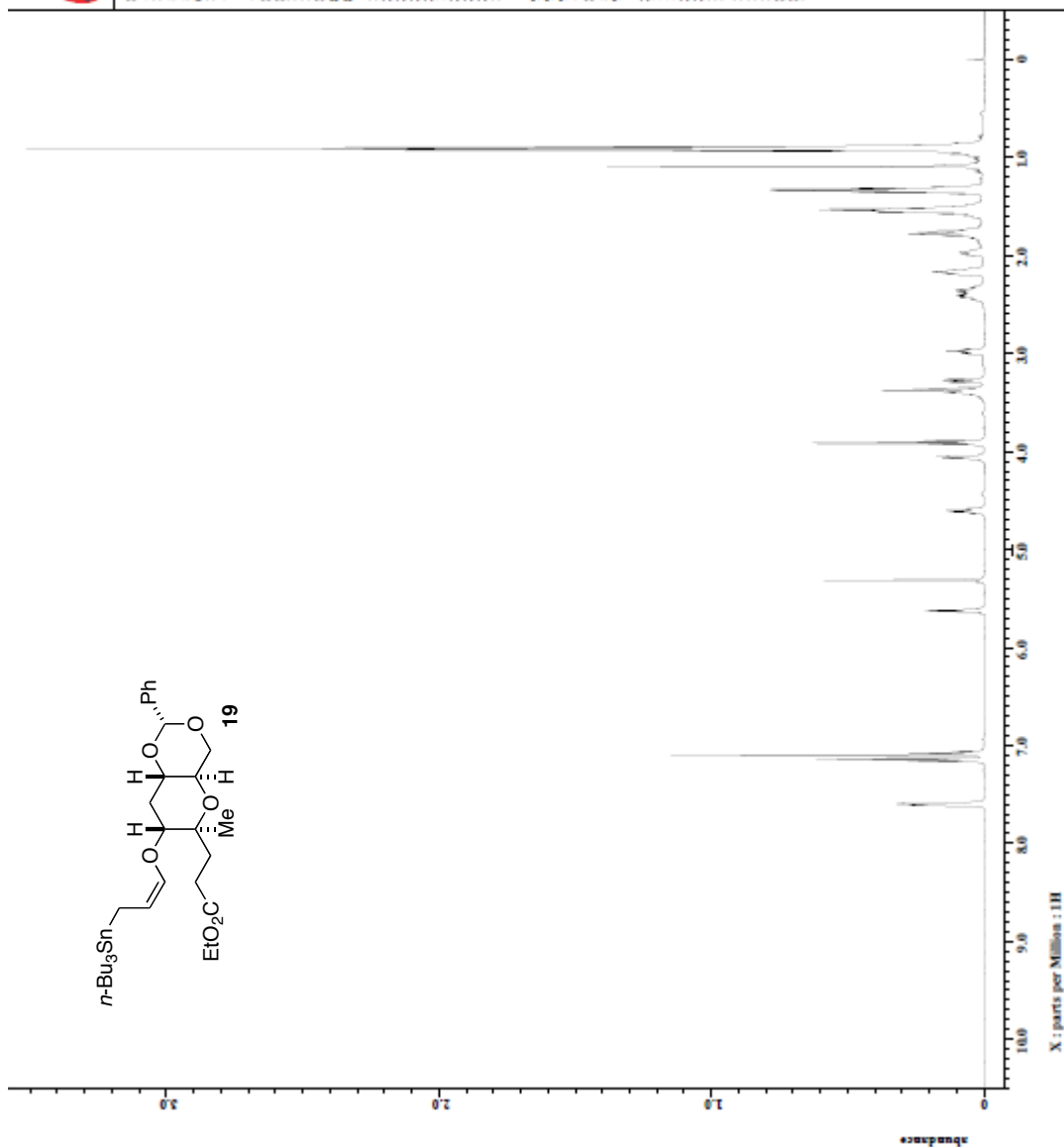
```

=====
Filename      = 26-100722-IN-2.fde
Author        = delta
Experiment    = single_pulse.ac2
Sample_ID     = sas
Solvent       = H2O/DMSO-D6
Creation_Time = 22-JUN-2010 16:12:30
Revision_Time = 2-MAR-2010 16:42:42
Current_Time  = 2-MAR-2010 16:43:01

=====
Comment       = single_pulse
Data_Format   = 1D COMPLEX
Dir_Size      = 13107
Dir_Title     = IR
Dir_Units     = [ppm]
Dimensions    = FCA500
Spectrometer  = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain      = IR
F2_domain      = 500.15591521 [MHz]
F1_offset      = 163 [ppm]
F2_offset      = 163 [ppm]
F1_resolution  = 1
F2_resolution  = 0.42012084 [Hz]
IR_sweep       = 6.46932591 [kHz]
IR_domain      = IR
IR_offset      = 5.0 [ppm]
IR1_domain     = IR
IR1_offset     = 5.0 [ppm]
IR1_resolution = 500.15591521 [MHz]
IR1_offset     = 5.0 [ppm]
Mod_return     = PARSE
Scans          = 1
Total_scans   = 8

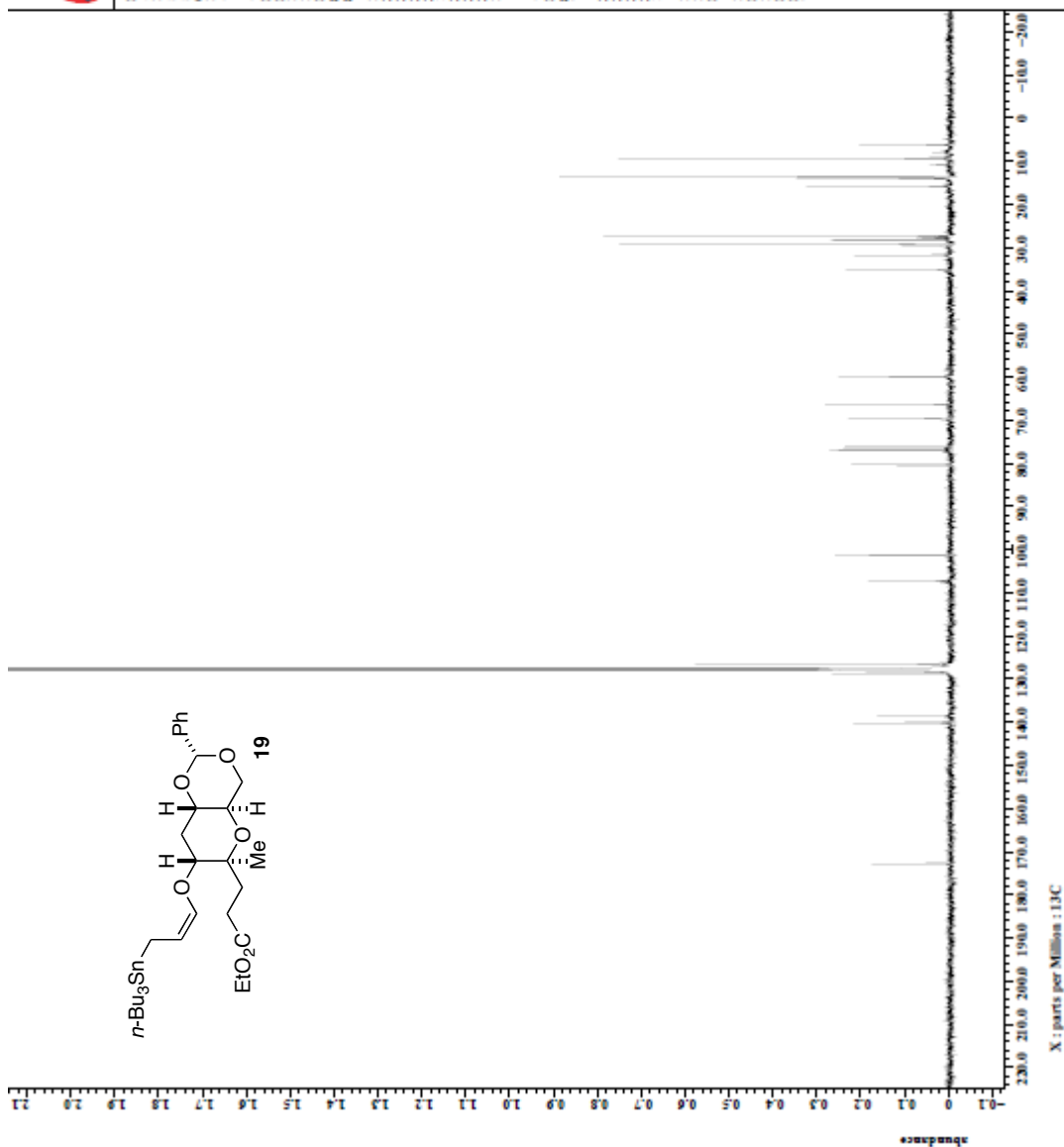
=====
F1_f0_width   = 6 [us]
F1_acq_time    = 2.38026752 [s]
F1_angle       = 45 [deg]
F1_str         = 3.2 [dB]
F1_pulse       = 3 [us]
F1_mode        = Off
F1_mode        = Off
Dantec_preset = PARSE
Initial_wait   = 1 [s]
Rever_gain     = 1 [s]
Relaxation_delay = 4 [s]
Repetition_time = 5.180026752 [s]
Temp_set       = 23.4 [degC]
=====
  
```





```

File Name      = 26-100722-13C-2_1.f6E
Author         = delta
Experiment     = single_pulse_dec
Sample_ID     = sas
Solvent       = BMEKMS-D6
Creation_Time = 22-JUL-2010 01:24:59
Revision_Time = 2-MAR-2010 15:15:13
Current_Time  = 2-MAR-2010 15:17:52
Comment       = single pulse decouple
Data Format    = 1D COMPLEX
Dir Size      = 26214
Dir Title     = 13C
Dir Units     = [ppm]
Dimensions    = 62x400
Spectrometer = DELTA2_NMR
Field Strength = 9.389766 [T] (400 [MHz])
Acq Duration  = 1.04333312 [s]
F1 Domain     = 13C
F2 Domain     = 100.62830333 [MHz]
F1 Points     = 3278 [pt]
F2 Points     = 4
F1 Prescans   = 4
F2 Prescans   = 0.95846665 [Hz]
IRF Sweep     = 31.40703518 [MHz]
IRF Domain    = 18.78219938 [MHz]
IRF Acq       = 5 [sec]
IRF Offset    = Clipped
Mod F Return  = 1
Scans         = 162
Total Scans   = 162
X30 Width     = 10.8 [us]
X30 Acq Time  = 0.04333312 [s]
X30 Delay     = 3.0 [deg]
X30 Gain      = 3 [dB]
X30 Pulse     = 3.5 [us]
IRF Stn Dec   = 20.276 [dB]
IRF Stn Nois = 20.276 [dB]
WALTZ         = wALTZ
Sweeping      = 1 [Hz]
Initial Wait  = 1 [s]
Roc Time      = 2 [s]
Rever Gain    = 2 [s]
Relaxation Delay = 2 [s]
Repetition Time = 3.04333312 [s]
Temp Set      = 32.4 [0C]
  
```





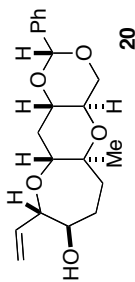
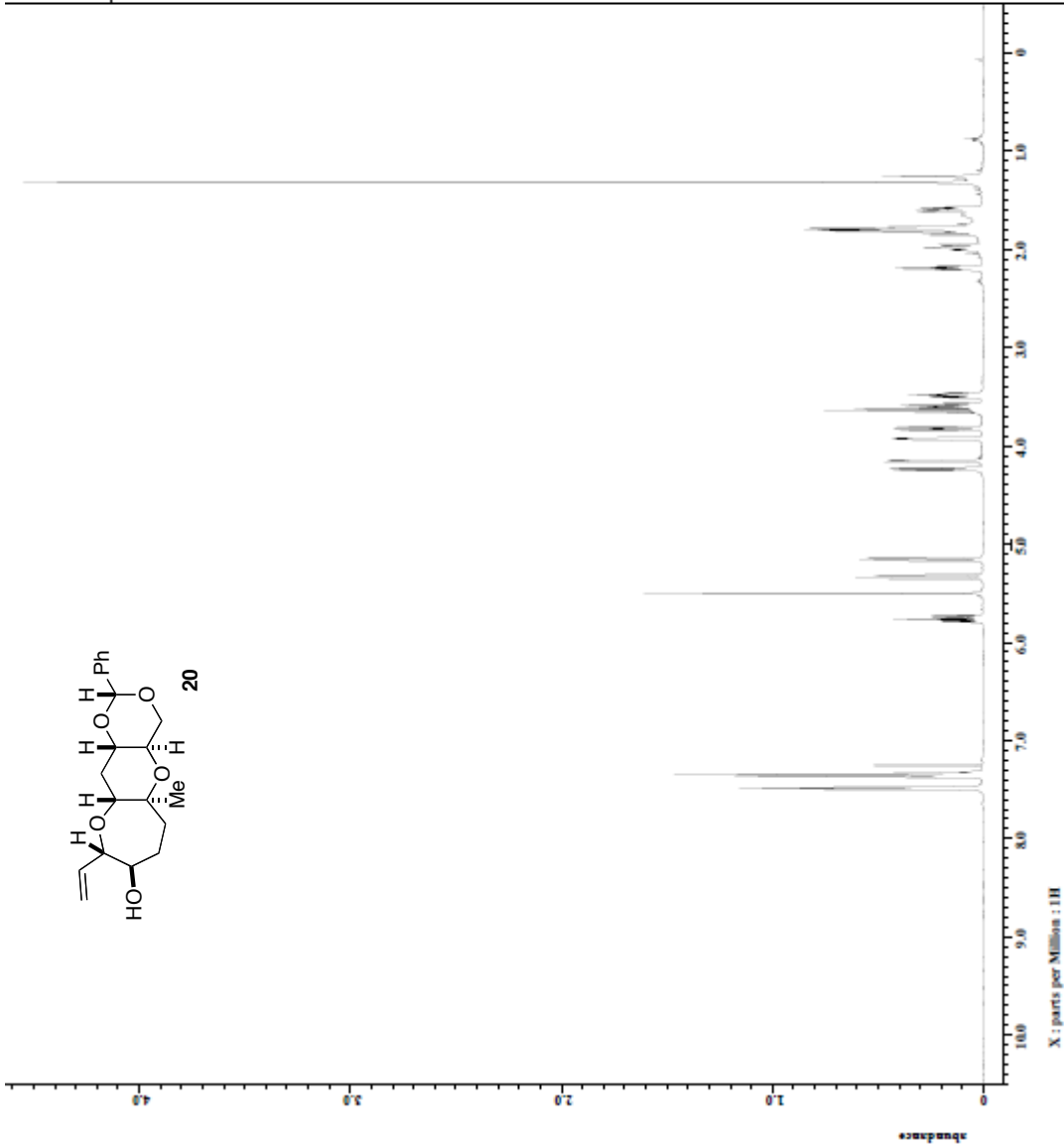
```

File Name      = 27-100802-1R-2.fde
Author         = delta
Experiment     = single_pulse.ac2
Sample_ID     = sas
Solvent       = CHLOROFORM-D
Creation_Time  = 2-MS-2010 17:13:46
Revision_Time  = 2-MS-2010 15:43:07
Current_Time   = 2-MS-2010 15:43:21

Comment       = single_pulse
Data_Format   = 1D COMPLETE
Dir_Size     = 13107
Dir_Title    = 1R
Dim_Units    = [ppm]
Dimensions   = FCA500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
X_domain      = 1R
F1_freq       = 500.15691521 [MHz]
X_points      = 163 [ppm]
X_resolution  = 1
X_prescans    = 1
X_resolution  = 0.42012084 [Hz]
X_sweep       = 1R
F2_domain     = 1R
F2_freq       = 50.15691521 [MHz]
X_resolution  = 1R
F2_offset     = 5.0 [ppm]
F2_freq       = 500.15691521 [MHz]
Tri_offset    = 5.0 [ppm]
Mod_return    = 1
Scans         = 8
Total_scans   = 8

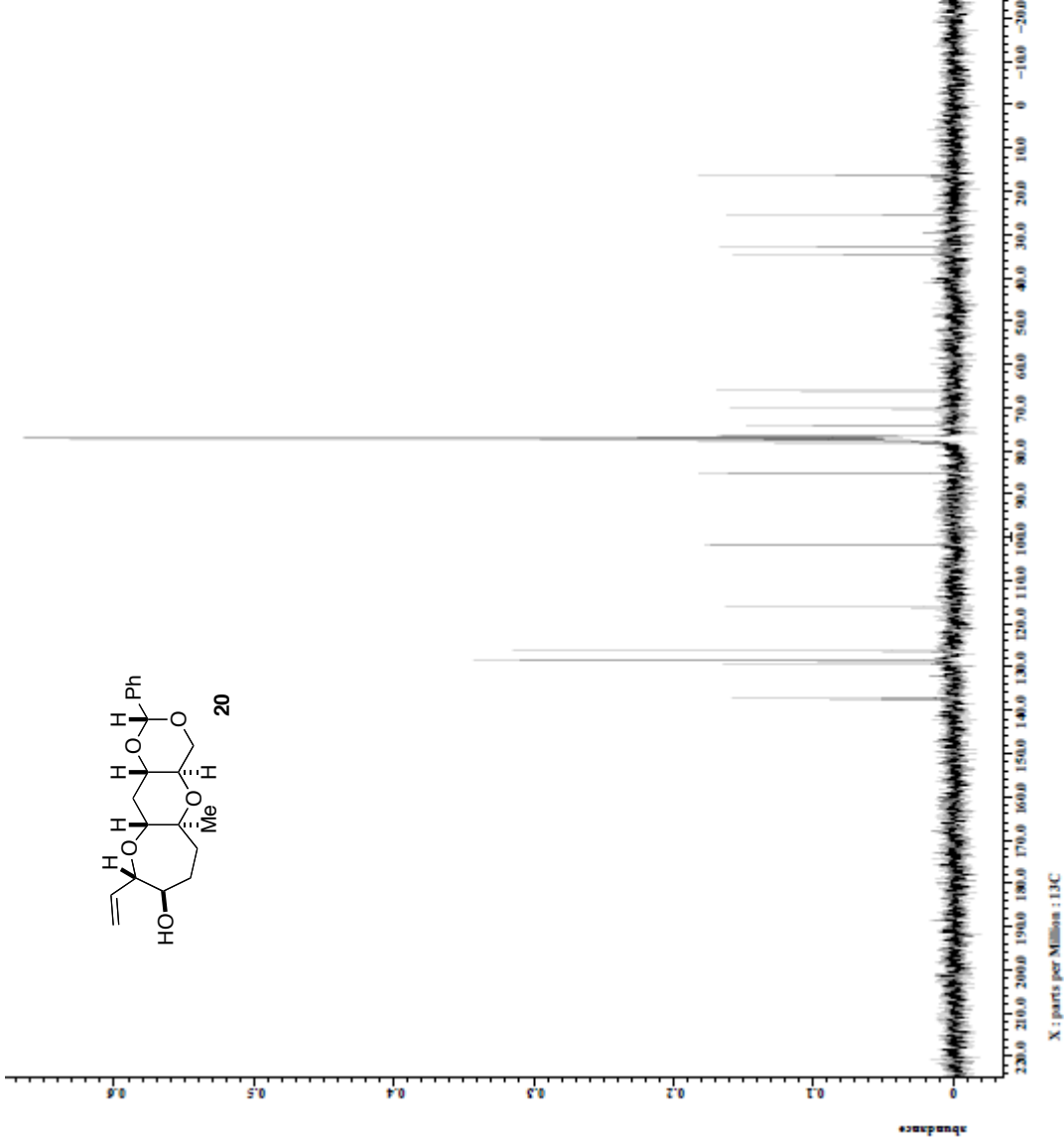
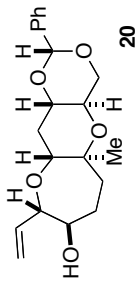
X_90_width    = 6 [us]
X_acq_time    = 2.38026752 [s]
X_angle       = 45 [deg]
X_str         = 3.2 [dB]
X_pulse       = 8 [us]
Tri_mode      = Off
Dantec preset = FALSH
Initial wait  = 1 [s]
Rever_gain    = 50
Relaxation_delay = 5 [s]
Repetition_time = 3.30026752 [s]
Temp_set      = 32.9 [degC]
    
```





```

Filename = 27-100802-13C-2_1.fde
Author =
Experiment =
  single_pulse_dec
Sample_id =
  sas
Solvent = CHLOROFORM-D
Creation_Time = 2-MS-2010 00:24:27
Revision_Time = 2-MS-2010 15:17:55
Current_Time = 2-MS-2010 15:18:13
Comment =
  single_pulse decouple
Data_Format = 1D COMPLEX
Dir_size = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 627400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C
F1_freq = 100.62830333 [MHz]
F1_offset = 3270 [ppm]
F1_pulses = 4
F1_resolution = 0.55846665 [Hz]
F1_sweep = 31.40703518 [MHz]
F1_domain_min = 18.78219938 [MHz]
F1_domain_max = 57 [ppm]
F1_offset_min = 0
F1_offset_max = FALSE
Mod_return = 1
Scans = 141
Total_scans = 141
F2_width = 10.8 [ppm]
F2_acq_time = 1.04333312 [s]
F2_resolution = 10.4 [ppm]
F2_offset = 3 [ppm]
F2_pulses = 3.5 [us]
F2_resolution_min = 20.276 [dB]
F2_resolution_max = 20.276 [dB]
F2_noise = WAURE
F2_offset_min = 1 [ppm]
F2_offset_max = Initial_wait
F2_resolution_min = 2 [ppm]
F2_resolution_max = 2 [ppm]
Relaxation_delay = 2 [s]
Repetition_time = 3.04333312 [s]
Temp_pct = 31.5 [degC]
  
```





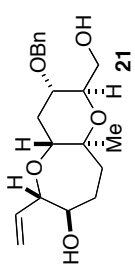
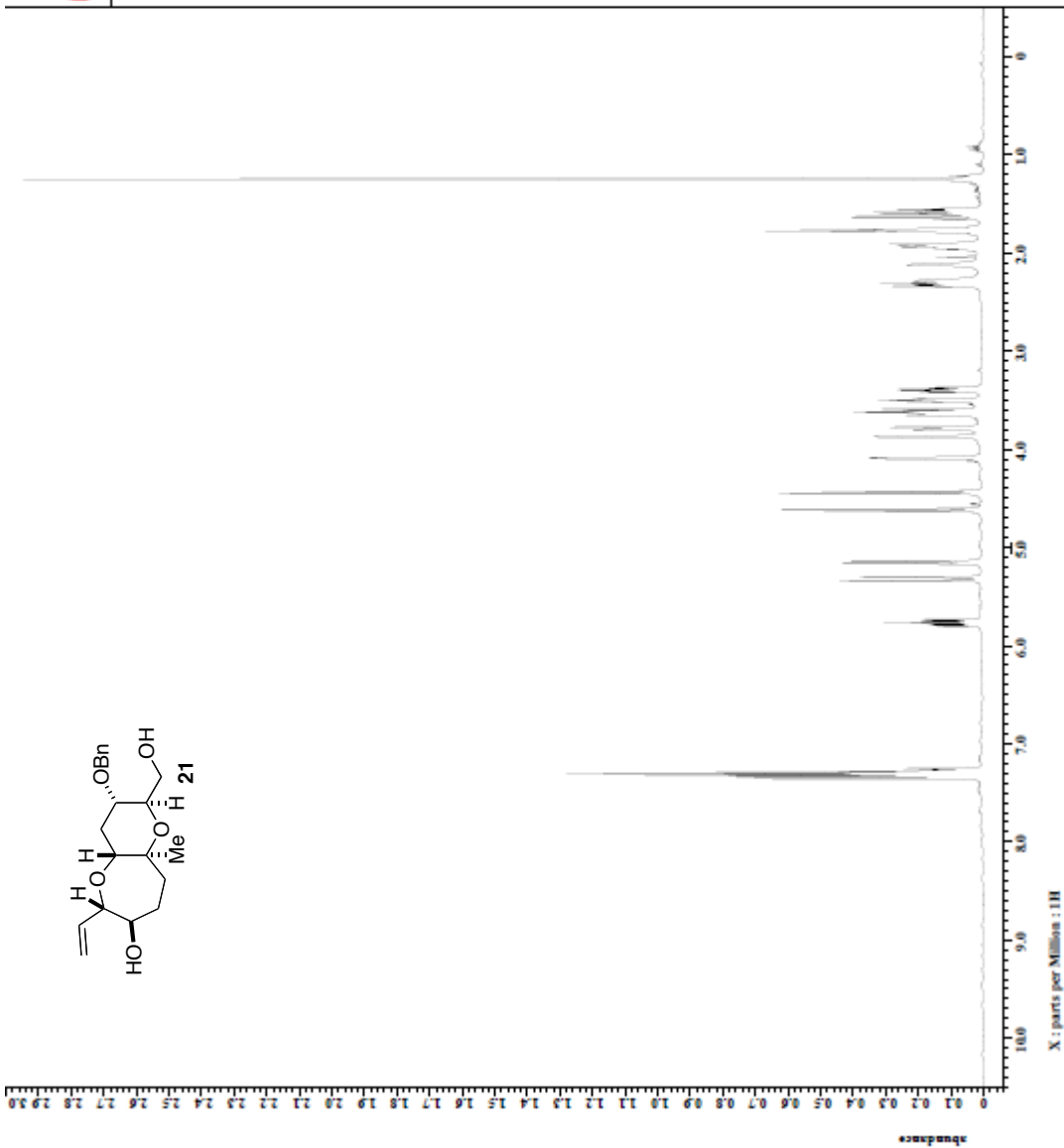
```

=====
Filename      = 26-100802-IN-2.fde
Author        = delta
Experiment    = single_pulse.ac2
Sample_id     = aas
Solvent       = CHLOROFORM-D
Creation_time = 2-MS-2010 17:56:35
Revision_time = 2-MS-2010 18:43:29
Current_time  = 2-MS-2010 18:43:40

=====
Comment      = single_pulse
Data Format   = 1D COMPLETE
Dir Size     = 13107
Dir Title    = IR
Dir Units    = [ppm]
Dimensions   = F2ASQ
Spectrometer = DELTA2_NMR

Field strength = 11.7473579 [T] (500 [MHz])
Acq duration   = 2.38026752 [s]
F2 domain      = IR
F1 freq        = 500.15691521 [MHz]
X_posits      = 163 [ppm]
X_resolution   = 1
X_prescans     = 1
X_resolution   = 0.42012084 [Hz]
X_sweep        = 6.68625951 [kHz]
IR_domain      = IR
IR_freq        = 50.15691521 [MHz]
IR_offset      = 5.0 [ppm]
IR1_domain     = IR
IR1_freq       = 500.15691521 [MHz]
IR1_offset     = 5.0 [ppm]
Clipped       = PARSE
Mod_return     = 1
Scans         = 8
Total_scans    = 8

X_90_width    = 6 [us]
X_acq_time     = 2.38026752 [s]
X_angle        = 45 [deg]
X_str          = 3.2 [dB]
X_pulse        = 3 [us]
X_prescans     = 1
X_mode         = Off
Dantle preset = PARSE
Initial wait   = 1 [s]
Rever_gain     = 44
Relaxation_delay = 5 [s]
Repetition_time = 3.36026752 [s]
Temp_set       = 23 [C]
    
```





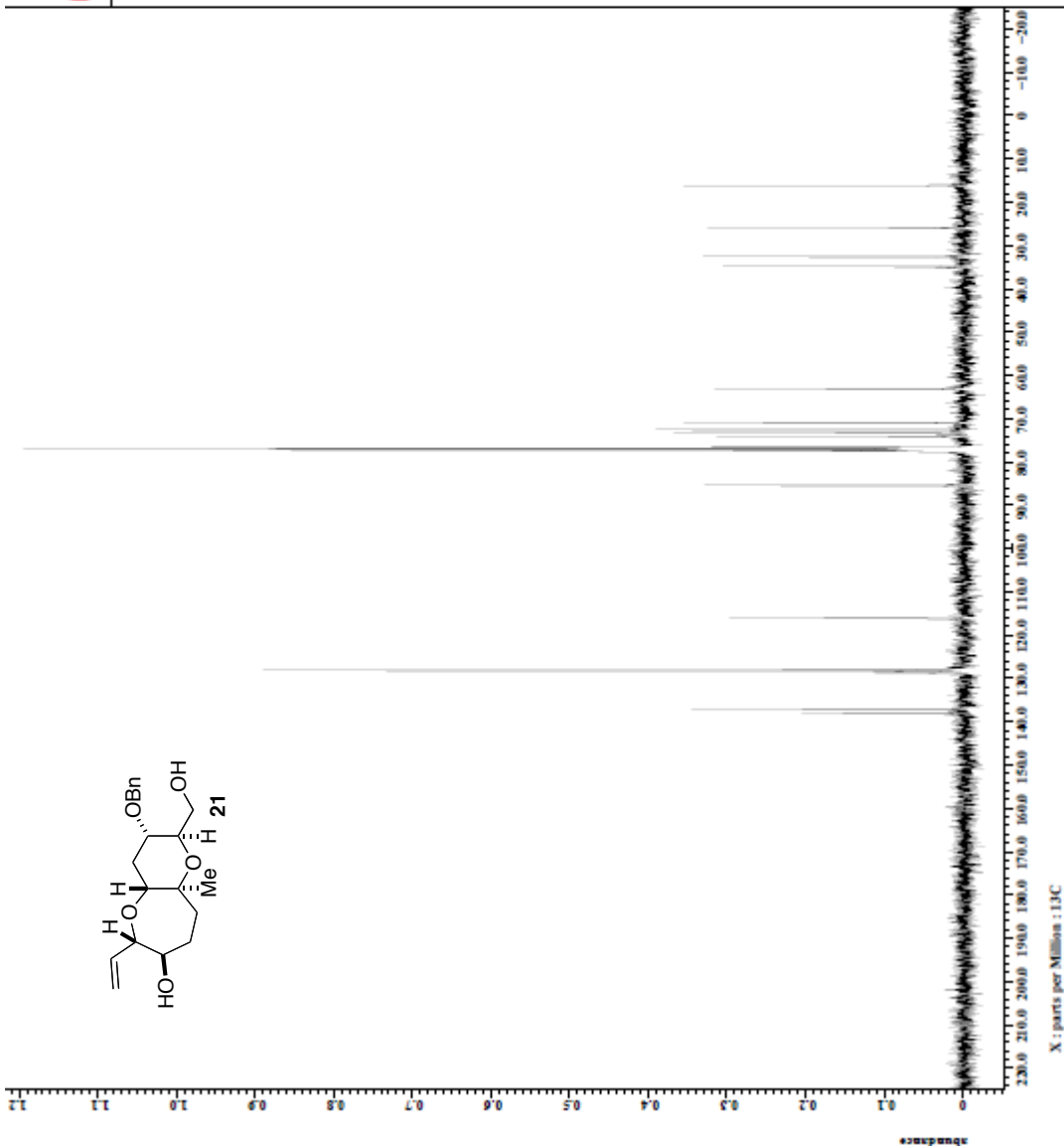
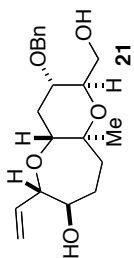
```

File Name      = 26-100802-13C-3_1.f6E
Author        = delta
Experiment    = single_pulse_dec
Sample_ID     = sas
Solvent       = CHLOROFORM-D
Creation_Time = 2-MS-2010 00:43:28
Revision_Time = 2-MS-2010 15:18:21
Current_Time  = 2-MS-2010 15:18:16

Comment       = single pulse decouple
Data Format   = 1D COMPLEX
Dir Size     = 26214
Dir Title    = 13C
Dir Units    = [ppm]
Dimensions   = 627400
Spectrometer = DELTA2_NMR

Field strength = 9.389766 [T] (400 [MHz])
Acq duration   = 1.0433312 [s]
F2 domain     = 13C
F1 freq       = 100.62830333 [MHz]
F2 offset     = 3270 [ppm]
F1 offset     = 3270 [ppm]
Prescans      = 4
Resolution    = 0.95846665 [Hz]
F sweep       = 31.40703518 [MHz]
IRF domain    = 1H
IRF freq      = 500.136247 [MHz]
IRF offset    = 5 [ppm]
Clipped      = 0
Mod F return  = 1
Scans         = 131
Total scans   = 131

X90 width     = 10.8 [us]
X90 offset    = 0.0433312 [s]
X90 delay     = 10 [deg]
X flip        = 3 [dm]
X pulse       = 3.5 [us]
IRF att dec   = 20.276 [dB]
IRF att nois = 20.276 [dB]
IRF noise     = WAURE
Sweeping      = 1 [Hz]
Initial wait  = 1 [s]
RGW time      = 2 [s]
Rever gain    = 60
Relaxation delay = 2 [s]
Repetition time = 3.0433312 [s]
Temp_jct      = 31.5 [deg]
    
```



tosylate 22



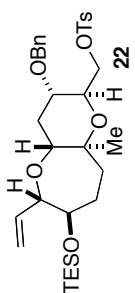
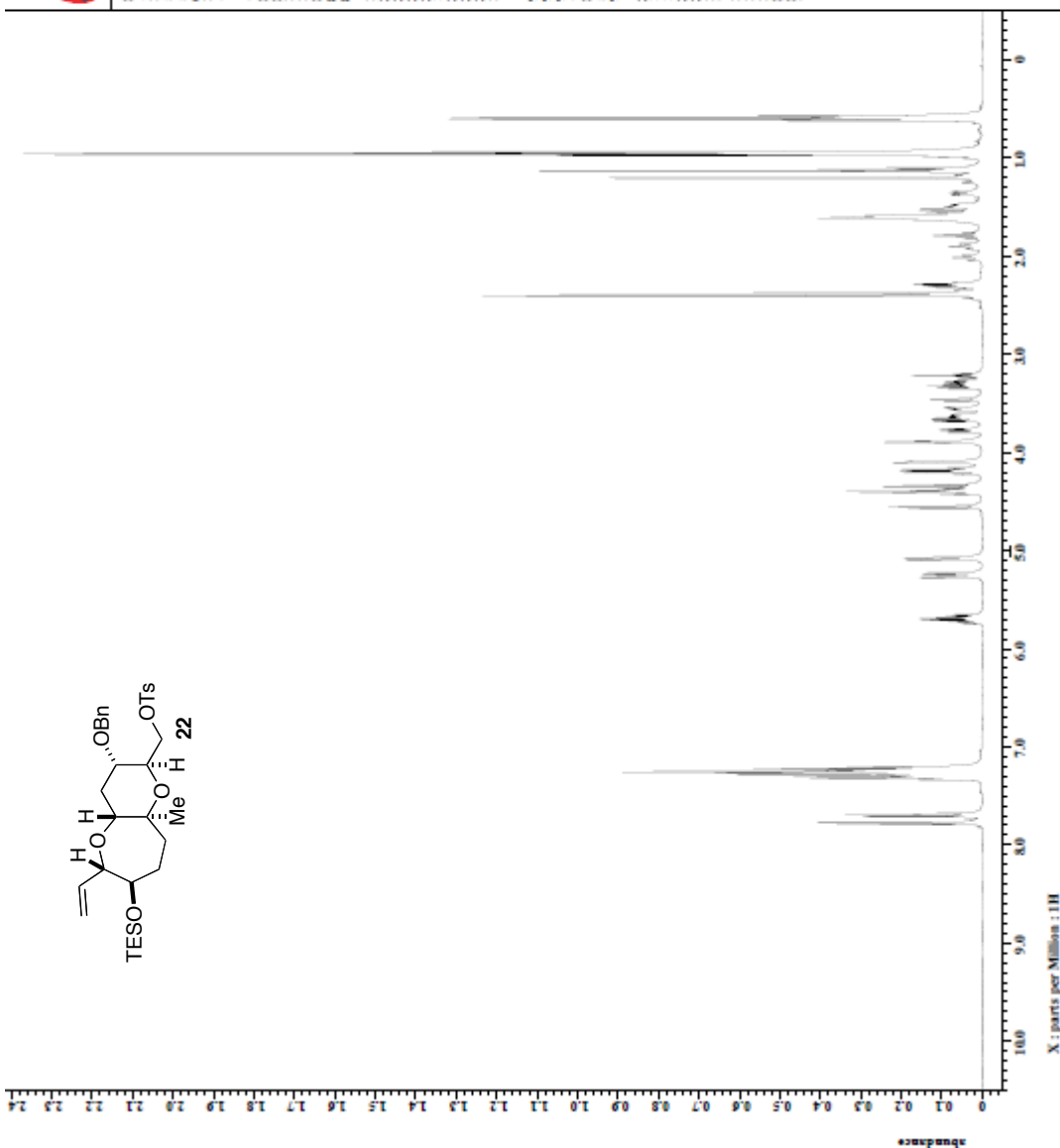
```

=====
Filenames  = 26-100902-IN-2.fde
Author     = delta
Experiment = single_pulse.ac2
Sample_id  = sas
Solvent    = CHLOROFORM-D
Creation_time = 2-SEP-2010 21:58:46
Revision_time = 2-DEC-2010 15:43:55
Current_time = 2-DEC-2010 15:44:11

Comment    = single_pulse
Data_format = 1D COMPLETE
Dir_size   = 13307
Dir_title  = IR
Dir_units  = [ppm]
Dimensions = FID4500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain      = IR
F1_freq        = 500.15691521 [MHz]
F1_offset      = 163 [ppm]
F1_resolution  = 1
F1_sweeps      = 0.42012084 [Hz]
F2_domain      = IR
F2_freq        = 6.489325991 [MHz]
F2_offset      = 5.0 [ppm]
F2_resolution  = 1
F2_sweeps      = 0.15991521 [MHz]
F3_domain      = IR
F3_freq        = 5.0 [ppm]
F3_offset      = 500.15691521 [MHz]
F3_resolution  = 1
Mod_return     = 1
Scans          = 8
Total_scans    = 8

F0_width      = 6 [us]
Acq_time      = 2.38026752 [s]
Angle         = 45 [deg]
Str           = 3.2 [dB]
Pulse        = 3 [us]
Pulse_prog   = Off
Tri_mode     = Off
Dantec_preat = FLD2H
Initial_wait = 1 [s]
Rever_gain   = 54
Relaxation_delay = 3 [s]
Repetition_time = 5.38026752 [s]
Temp_set     = 32.5 [degC]
=====
  
```





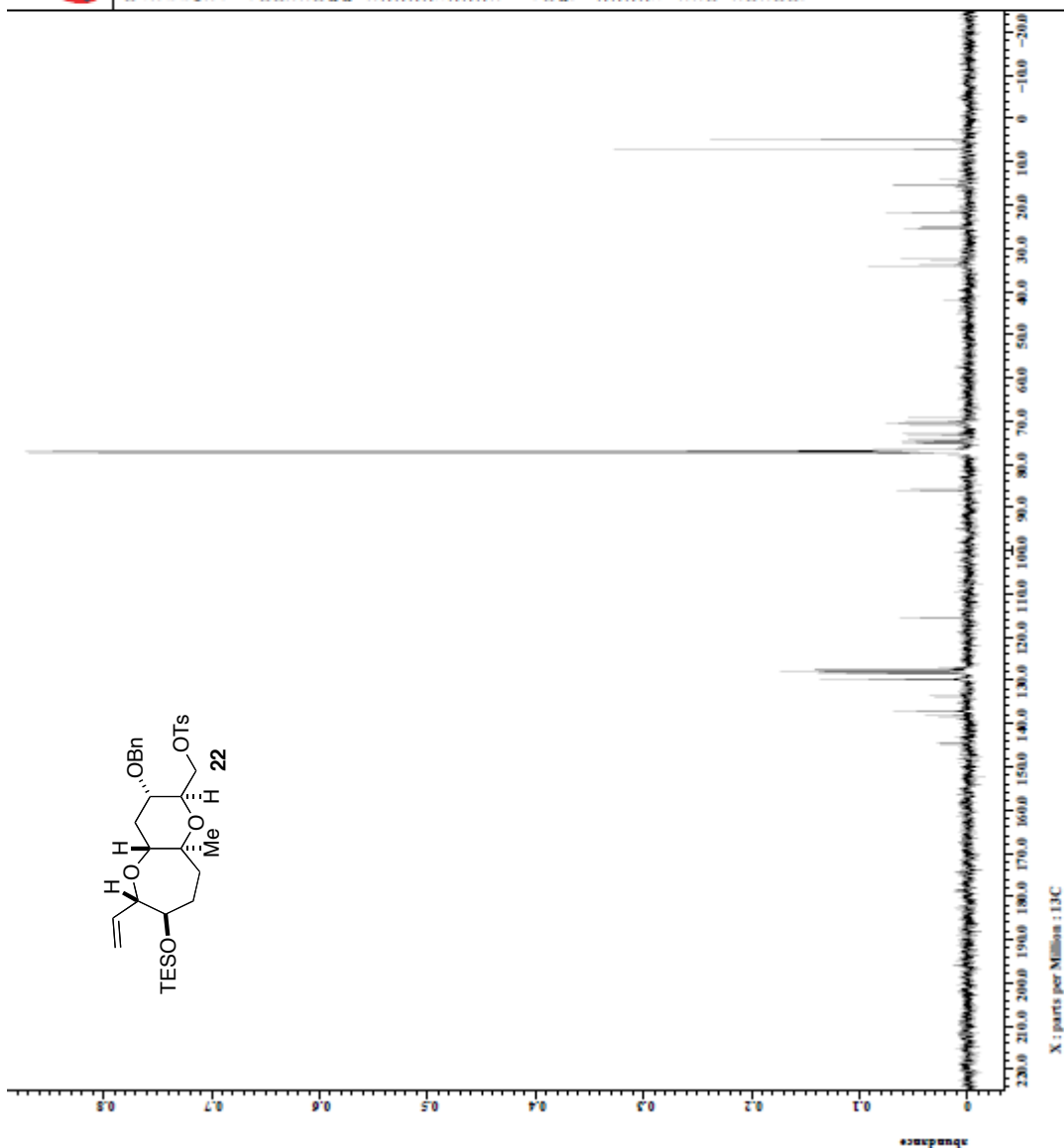
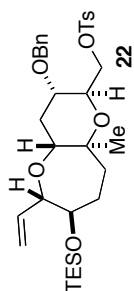
```

Filename      = 26-100902-13C-3_1.f6E
Author       = delta
Experiment   = single_pulse_dec
Sample_id    = sas
Solvent      = CHLOROFORM-D
Creation_time = 2-SEP-2010 04:10:26
Revision_time = 2-DEC-2010 15:18:44
Current_time = 2-DEC-2010 15:19:01

Comment      = single pulse decouple
Data Format   = 1D COMPLEX
Dir_size     = 26214
Dir_title    = 13C
Dir_units    = [ppm]
Dimensions   = 654x60
Spectrometer = DELTA2_NMR

Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration   = 1.04333312 [s]
F1_domain      = 13C
F2_domain      = 100.62830333 [MHz]
F1_offset      = 327.0 [ppm]
F2_offset      = 327.0 [ppm]
F1_prescans    = 4
F2_prescans    = 0.55846665 [Hz]
F1_sweep       = 31.40703518 [MHz]
F1_domain_min = 18.78219838 [MHz]
F1_domain_max = 57.0 [ppm]
F1_offset_min = Clipped
F1_offset_max = FAULT
Mod_return     = 1
Scans         = 428
Total_scans    = 428

X90_width     = 10.8 [us]
X90_time      = 0.04333312 [s]
X_acq_time    = 1.0 [dec]
X_sfn         = 3 [dB]
X_pulse       = 3.5 [us]
Irr_atn_dec   = 20.276 [dB]
Irr_atn_noise = 20.276 [dB]
WALTZ         = waltz
Sensitivity    = 1 [dB]
Initial_wait  = 1 [s]
Roc_time      = 2 [s]
Rever_gain    = 2 [s]
Relaxation_delay = 2 [s]
Repetition_time = 3.04333312 [s]
Temp_jvt      = 31.1 [0C]
    
```





```

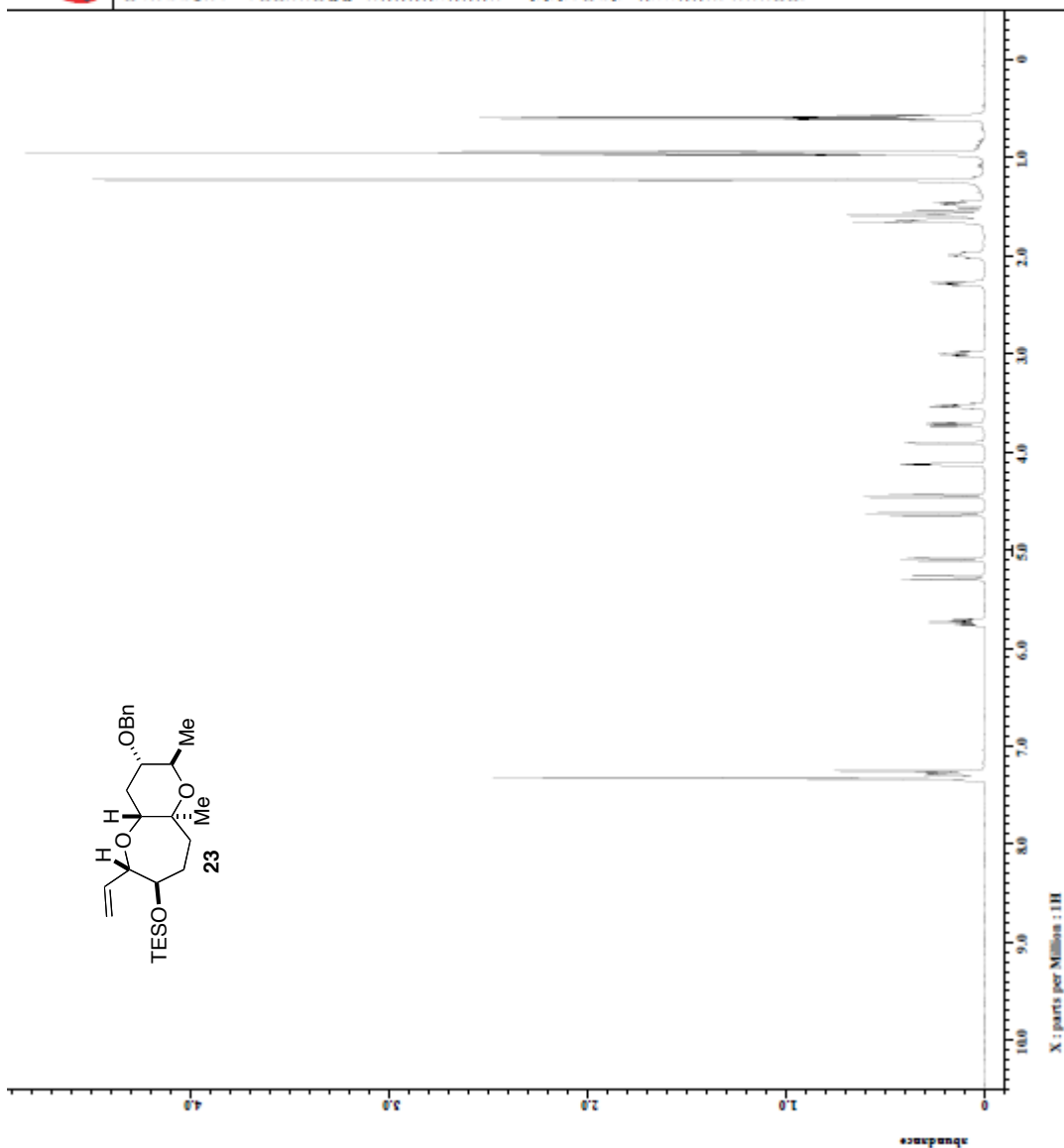
Filename = 20-100802-IN-4.fde
Author = delta
Experiment = single_pulse.ac2
Sample_ID = sss
Solvent = CHLOROFORM-D
Creation_Time = 2-MS-2010 16:14:22
Revision_Time = 2-MS-2010 16:44:19
Current_Time = 2-MS-2010 16:44:41

Comment = single_pulse
Data_Format = 1D COMPLEX
Data_Size = 13107
Dim_title = IR
Dim_units = [ppm]
Dimensions = FCA500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration = 2.38026752 [s]
X_domain = IR
X_freq = 500.15691521 [MHz]
X_posits = 163 [ppm]
X_prescans = 1
X_resolution = 0.42012084 [Hz]
X_sweep = IR
X_domain = IR
X_freq = 500.15691521 [MHz]
X_posits = 5.0 [ppm]
X_resolution = 0.42012084 [Hz]
X_sweep = IR
X_domain = IR
X_freq = 500.15691521 [MHz]
X_posits = 5.0 [ppm]
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 6 [us]
X_acq_time = 2.38026752 [s]
X_angle = 45 [deg]
X_str = 3.2 [dB]
X_pulse = 3 [us]
X_prescans = 1
X_mode = Off
Dantec_preset = FALSH
Initial_wait = 1 [s]
Rever_gain = 54
Relaxation_delay = 5 [s]
Repetition_time = 3.30026752 [s]
Temp_set = 12.9 [C]

```

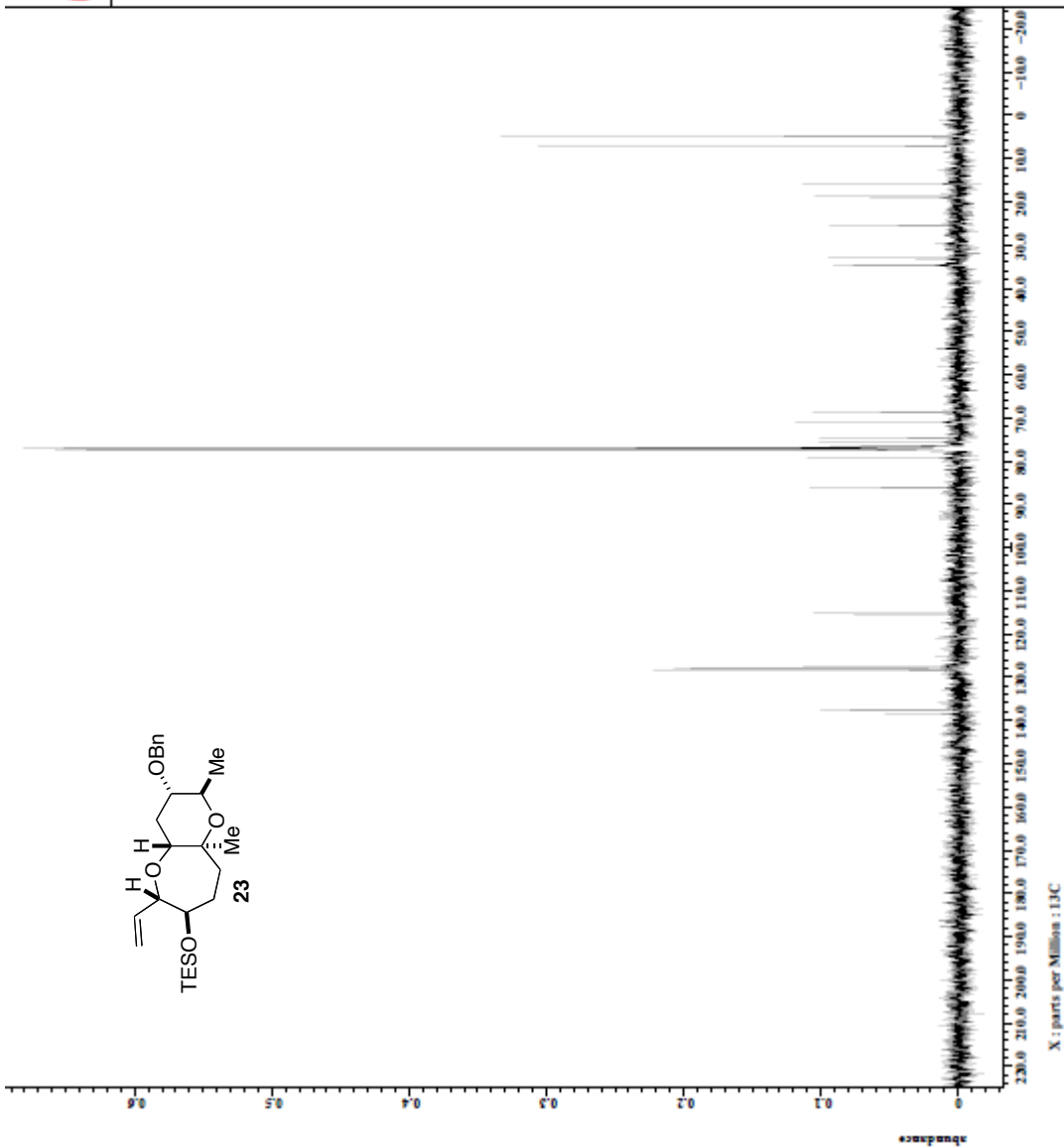
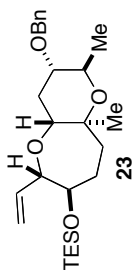




```

Filename      = 20-100802-13C-2_1.f6E
Author
Experiment    = single_pulse_dec
Sample_id     = aas
Solvent       = CHLOROFORM-D
Creation_Time = 2-APR-2010 01:00:16
Revision_Time = 2-APR-2010 15:15:10
Current_Time  = 2-APR-2010 15:19:10
Comment       = single pulse decouple
Data Format   = 1D COMPLEX
Dir Size     = 26214
Dir Title    = 13C
Dir Units    = [ppm]
Dimensions   = 627400
Spectrometer = DELTA2_NMR
Field Strength = 9.389766 [T] (400 [MHz])
Acq Duration  = 1.0433312 [s]
F1 Domain    = 13C
F2 Domain    = 100.62830333 [MHz]
F3 Domain    = 327.80 [MHz]
F4 Domain    = 4 [MHz]
F5 Domain    = 0.95846665 [Hz]
F6 Domain    = 31.40703518 [MHz]
F7 Domain    = 18.78219838 [MHz]
F8 Domain    = 5 [MHz]
F9 Domain    = 5 [MHz]
Clipped      = FALSE
Mod Return   = 1
Scans        = 145
Total Scans  = 145
X90 Width    = 10.8 [us]
X90 Delay    = 0.0433312 [s]
X90 Pulse    = 10 [deg]
X90 Phase    = 3 [deg]
X90 Amplitude = 3.5 [us]
X90 Power    = 20.276 [dB]
X90 Noise    = 20.276 [dB]
X90 Wait     = WAUTE
X90 Delay    = 1 [s]
X90 Delay    = 1 [s]
X90 Delay    = 2 [s]
X90 Delay    = 5 [s]
Relaxation Delay = 2 [s]
Repetition Time = 3.0433312 [s]
Temp Set     = 21.5 [degC]

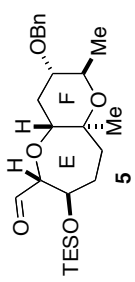
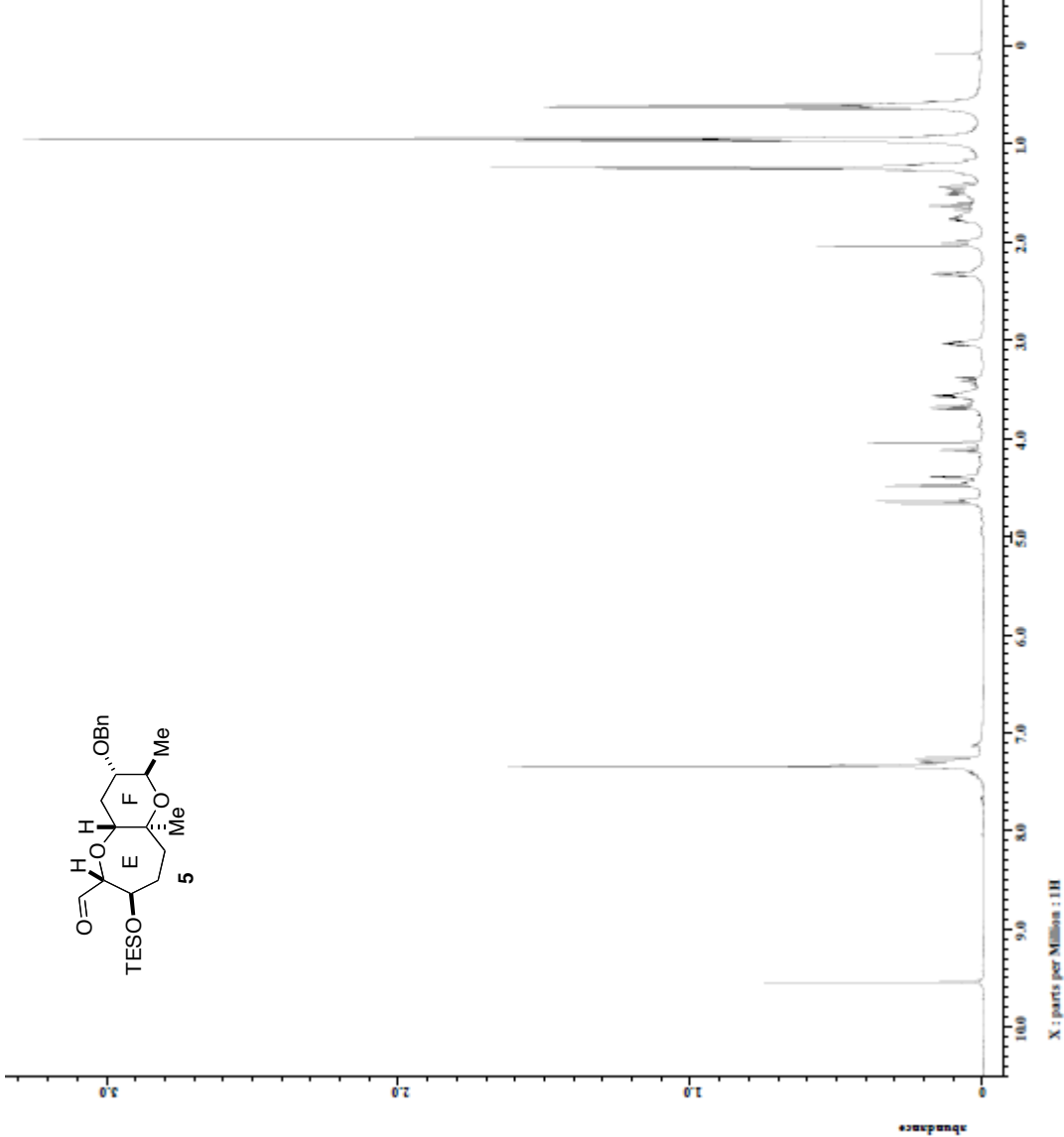
```



aldehyde 5



```
Filename = 5-100720-1H-0.jdf
Author =
Experiment =
  single_pulse.exe2
Sample_ID =
  aas
Solvent = CHLOROFORM-D
Creation_Time = 20-JUL-2010 21:18:34
Revision_Time = 2-MAR-2010 15:17:47
Current_Time = 2-MAR-2010 15:18:03
Comment = single_pulse
Data_Format = 1D COMPLETE
Dir_Size = 13107
Dir_Title =
Dir_Units = [ppm]
Dimensions =
Spectrum1 = FID1500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579 [T] (500 MHz)
Acq_duration = 2.38026752 [s]
X_domain = 1H
X_freq = 500.15591521 [MHz]
X_posits = 163 [ppm]
X_prescans = 1
X_resolution = 0.42012084 [Hz]
X_sweep = 6.68325991 [kHz]
F1_domain = 1H
F1_freq = 500.15591521 [MHz]
F1_offset = 1H (ppm)
F1_domain = 1H
F1_freq = 500.15591521 [MHz]
F1_offset = 5.0 [ppm]
Mod_return = PAR2H
Scans = 1
Total_scans = 8
X_f0_width = 6 [Hz]
X_acq_time = 2.38026752 [s]
X_angle = 45 [deg]
X_str = 3.2 [cm]
X_pulse = 3 [Hz]
X_prescans = 1
X_mode = Off
Dantec_preset = PAR2H
Initial_wait = 1 [s]
Rever_gain = 4.0
Relaxation_delay = 4 [s]
Repetition_time = 5.16026752 [s]
Temp_pct = 52 [0C]
```



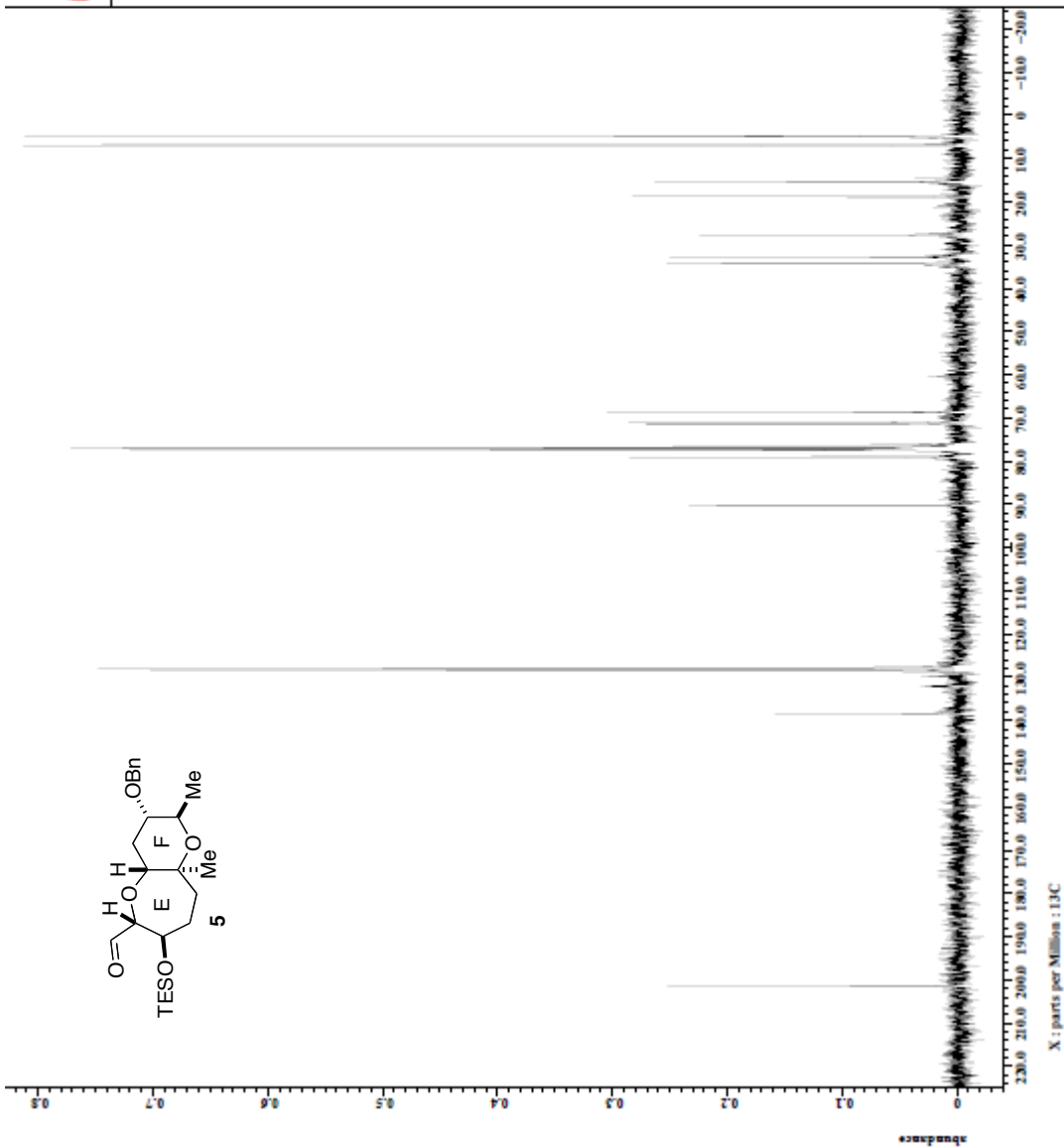
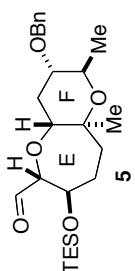
aldehyde 5



```

=====
Filename      = 5-100721-13C-7.fde
Author       = delta
Experiment   = single_pulse_dec
Sample_ID    = sas
CHLOROPFORM = CHLOROPFORM-D
Creation_Time = 20-JUL-2010 21:52:56
Revision_Time = 2-DEC-2010 15:53:06
Current_Time = 2-DEC-2010 15:53:15
=====
Comment      = single pulse decouple
Data Format   = 1D COMPLETE
Dir Size     = 26214
Dir Title    = 13C
Dir Units    = [ppm]
Dimensions   = 512x400
Spectrometer = DELTA2_NMR
=====
Field strength = 9.389766 [T] (400 [MHz])
Acq duration   = 1.04333312 [s]
F1 domain     = 13C
F2 domain     = 100.62830333 [MHz]
F1 freq       = 327.80 [MHz]
F2 freq       = 4.70 [MHz]
F1 prescans   = 4
F2 prescans   = 0.95846665 [Hz]
F1 resolution = 31.40703518 [MHz]
F2 resolution = 18.78219838 [MHz]
F1 sweep      = 5 [ppm]
F2 sweep      = 5 [ppm]
F1 offset     = Clipped
F2 offset     = F2OFF
Mod F return  = 1
Scans        = 172
Total scans  = 172
=====
X10 width     = 10.8 [ppm]
X10 offset    = 64.333312 [s]
X10 delay     = 10 [dec]
X10 gain      = 3 [dB]
X10 pulse     = 3.5 [us]
X10 pulse dec = 20.276 [dB]
X10 noise     = 20.276 [dB]
X10 waltz     = wALTZ
X10 nutting   = 1 [Hz]
X10 nutting wait = 1 [s]
X10 nutting gain = 2 [s]
X10 nutting delay = 60
X10 nutting relaxation delay = 2 [s]
X10 nutting repetition time = 3.04333312 [s]
X10 nutting temp_jct = 31.2 [C]
=====

```



X : parts per Million : 13C

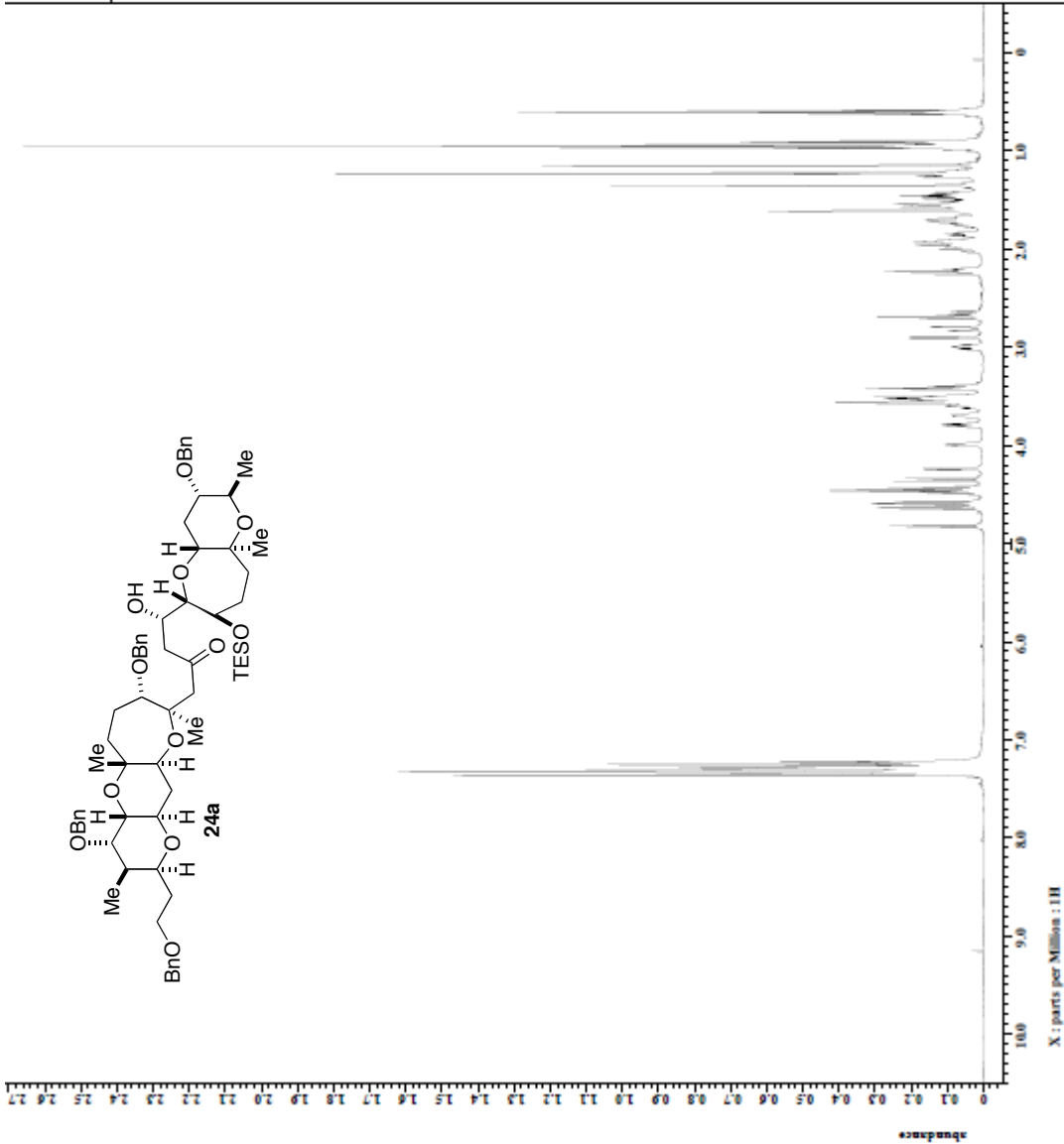
ketone 24a



```

=====
Filenames      * 31e-1009100-1E-6-.f0E
Author        * daiba
Experiment    * single_pulse.ac2
Sample_id     * sas
Solvent       * CHLOROFORM-D
Creation_time * 2010-10-18 11:52:19
Revision_time * 2010-10-18 15:44:40
Current_time  * 2010-10-18 15:11:10
=====
Comment       * single_pulse
Data_format   * 1D COMPLETE
Dim_size      * 13107
Dim_title     * IR
Dim_units     * [ppm]
Dimensions    * F0A500
Spectrometer  * DELTA2_NMR
=====
Field_strength      * 11.7473579 [T] (500 [MHZ])
Acq_duration        * 2.38026752 [s]
F1_domain           * IR
F1_freq             * 500.15591521 [MHz]
F2_domain           * 163 [ppm]
F2_freq             * 163.044
F3_domain           * IR
F3_freq             * 0.42012084 [Hz]
F4_domain           * 6.68325951 [MHz]
F4_freq             * 6.68325951 [MHz]
F5_domain           * 8.0 [ppm]
F5_freq             * 8.0 [ppm]
F6_domain           * IR
F6_freq             * 500.15591521 [MHz]
F7_domain           * 5.0 [ppm]
F7_freq             * 5.0 [ppm]
Mod_offset         * PAR42H
Mod_resolution     * 1
Mod_rearm         * 0
Scans              * 0
Total_scans       * 0
=====
F0_width          * 6 [us]
F0_acq_time       * 2.38026752 [s]
F0_angle          * 45 [deg]
F1_sfn            * 3.2 [GHz]
F1_pulse         * 3 [us]
F1_offset        * Off
F1_mode          * Off
F2_pulse         * Off
F2_offset        * Off
F2_mode          * Off
F3_pulse         * Off
F3_offset        * Off
F3_mode          * Off
F4_pulse         * Off
F4_offset        * Off
F4_mode          * Off
F5_pulse         * Off
F5_offset        * Off
F5_mode          * Off
F6_pulse         * Off
F6_offset        * Off
F6_mode          * Off
F7_pulse         * Off
F7_offset        * Off
F7_mode          * Off
=====
Relaxation_delay  * 5.0 [s]
Repetition_time  * 5.0 [s]
Repetition_delay * 5.0 [s]
Temp_set         * 30.0 [C]
=====

```

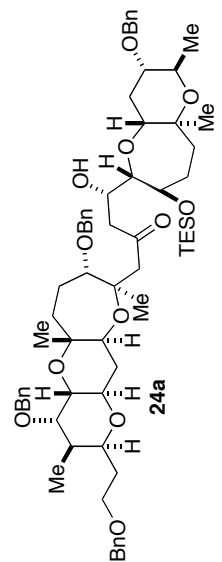
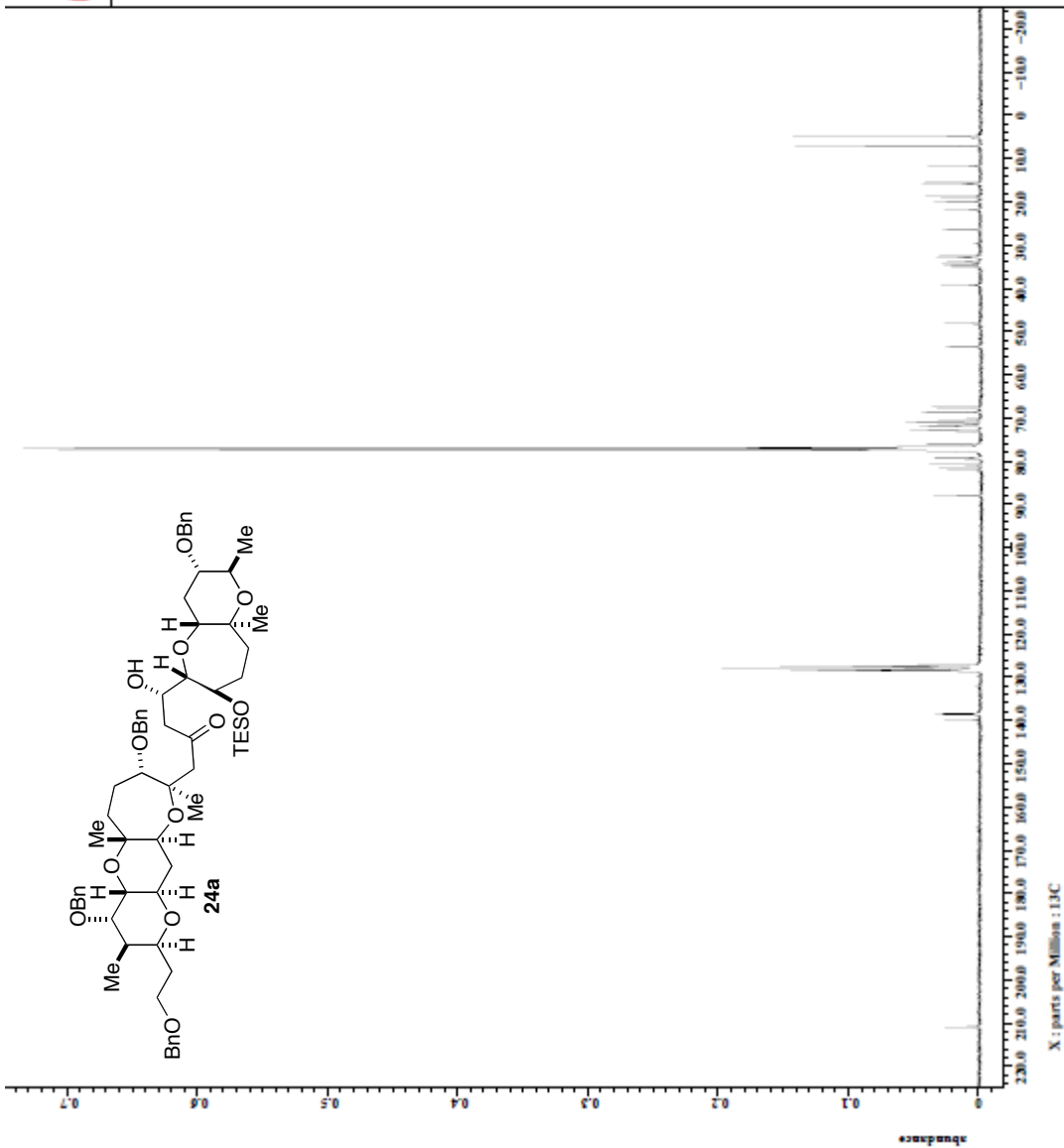


ketone 24a



```

File Name      = 31a-1009102-13C-2_1.jde
Author        = delta
Experiment    = single_pulse_dec
Sample_ID     = aas
Pulse_Prog   = CHLOROPDM-Q
Solvent       = 2-DBP-2010 15:15:57
Revision_Time = 2-DBP-2010 15:15:127
Current_Time  = 2-DBP-2010 15:15:143
Comment       = single pulse decouple
Data Format    = 1D COMPLETE
Dir Size      = 26214
Dir Title     = 13C
Dir Units     = [ppm]
Dimensions    = 627400
Spectrometer = DELTA2_NMR
Field Strength = 9.389766 [T] (400 [MHz])
Acq Duration  = 1.04333312 [s]
F2 Domain     = 13C
F2 Freq       = 100.62830333 [MHz]
F2 Offset     = 32700 [ppm]
F2 Points     = 4
F2 Prescans   = 4
F2 Resolution = 0.55846665 [Hz]
F2 Sweep      = 31.40703518 [MHz]
F1 Domain     = 1H
F1 Freq       = 500.136237 [MHz]
F1 Offset     = 0 [ppm]
F1 Points     = 65536
F1 SSB        = 0
Mod F Return  = 1
Scans         = 12099
Total Scans   = 12099
X30 Width     = 10.8 [us]
X30 Acq Time  = 0.04333312 [s]
X30 Decoupl  = 10 [dec]
X30 Gain      = 3 [dB]
X30 Pulse     = 3.5 [us]
X30 Pulse Dec = 20.276 [dB]
X30 Acq Noise = 20.276 [dB]
X30 Noise     = WAURE
X30 Sampling  = 1 [Hz]
X30 Initial Wait = 1 [s]
X30 Rec Time  = 2 [s]
X30 Recvr Gain = 60
X30 Relaxation Delay = 2 [s]
X30 Repetition Time = 3.04333312 [s]
X30 Temp [C]  = 21.2 [C]
    
```



ketone **24b**



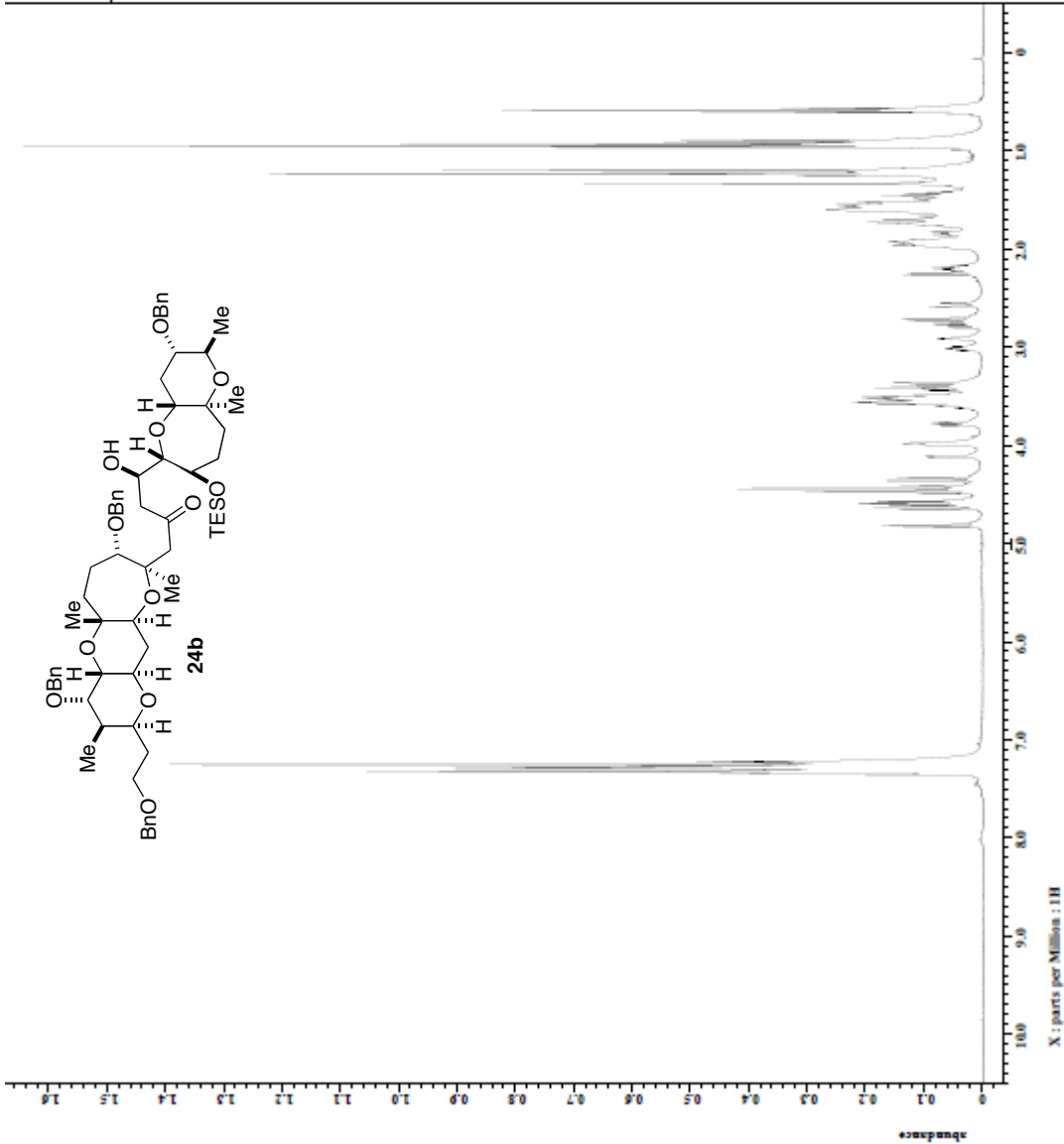
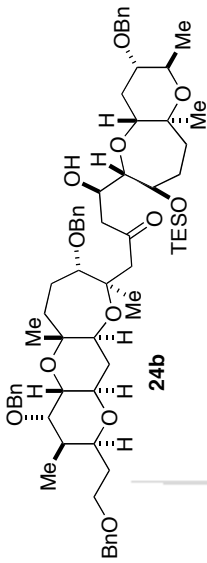
```

File Name  = 1h-100903-1E-2.fde
Author     =
Experiment = single_pulse.ac2
Sample_ID  =
Solvent    = CDCl3/POEM-D
Creation_Time = 3-SEP-2010 21:11:09
Revision_Time = 2-DEC-2010 15:45:22
Current_Time = 2-DEC-2010 15:45:36

Comment    = single_pulse
Data_Format = 1D COMPLEX
Dim Size   = 13107
Dim Title  =
Dim Units  = [ppm]
Dimensions =
Spectrum1  = F2A500
Spectrum2  = DELTA2_NMR

Field_strength = 11.7473579 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
X_domain       = 1H
F1_freq        = 500.15591521 [MHz]
X_posits      = 163 [ppm]
X_prescans     = 1
X_resolution   = 0.42012084 [Hz]
X_sweep        = 6.68925991 [kHz]
F2_domain      = 1H
F2_freq        = 500.15591521 [MHz]
F2_offset      = 5.0 [ppm]
F21_domain     = 1H
F21_freq       = 500.15591521 [MHz]
F21_offset     = 5.0 [ppm]
Mod_return     = 1
Scans         = 8
Total_scans   = 8

X_f0_width    = 6 [Hz]
X_acq_time    = 2.38026752 [s]
X_angle       = 45 [deg]
X_str         = 3.2 [dB]
X_pulse       = 3 [uV]
X_prescans    = 1
X_mode        = Off
X_mode2       = Off
X_mode3       = Off
Dantec_preset = FALSH
Initial_wait  = 1 [s]
Rever_gain    = 60
Relaxation_delay = 3 [s]
Repetition_time = 5.28026752 [s]
Temp_set      = 22.9 [C]
    
```



ketone 24b



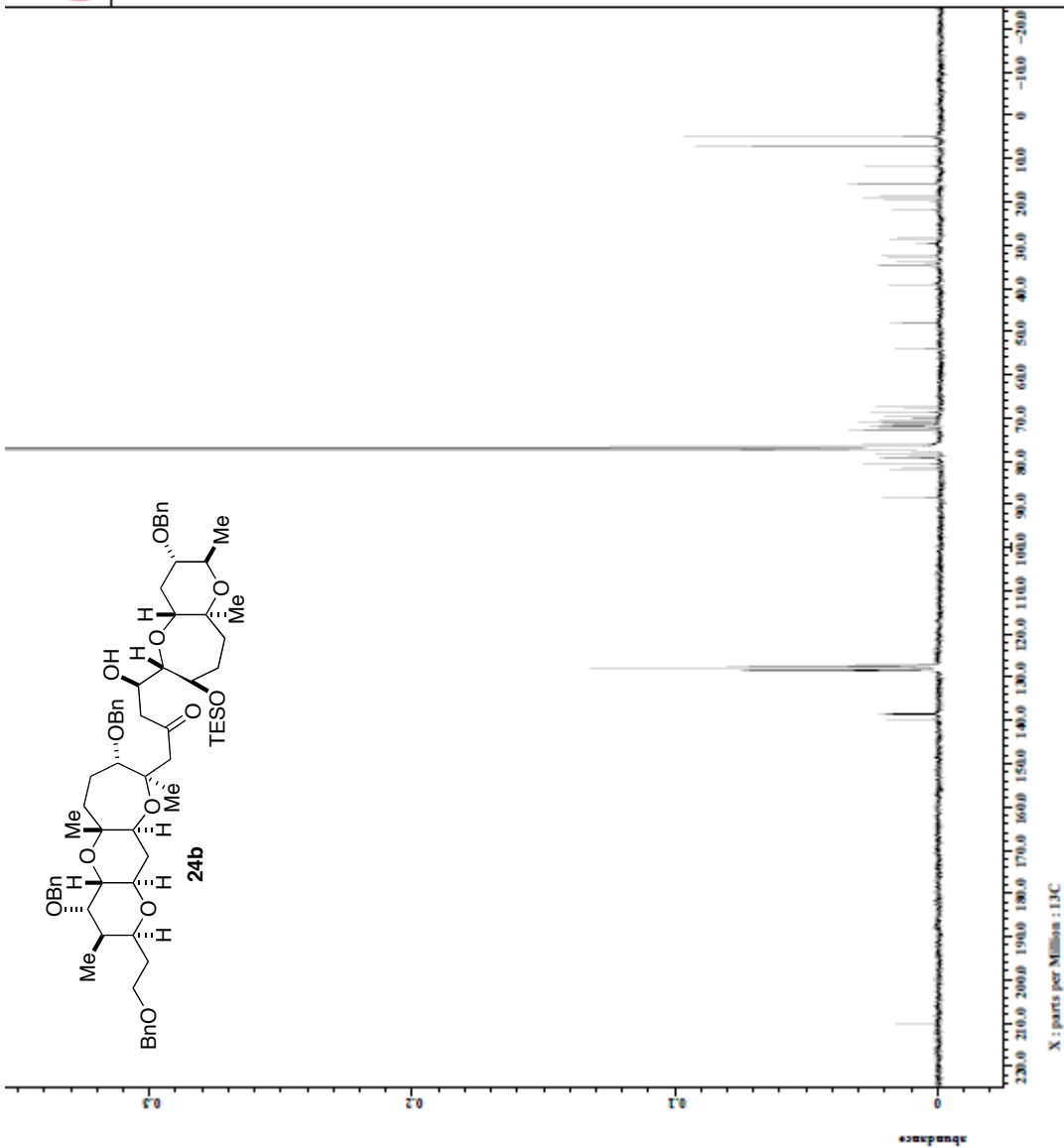
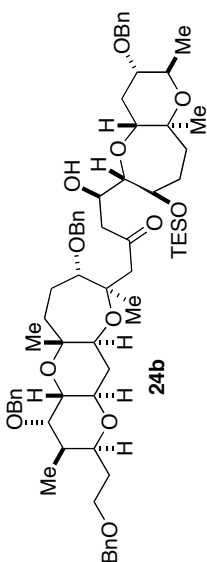
```

File Name      = 1h-100903-13C-2_1.jde
Author        =
Experiment    = single_pulse_dec
Sample_ID     = aas
Pulse_Prog    = CMLAOPDM-J
Creation_Time = 3-SEP-2010 15:19:50
Revision_Time = 3-DEC-2010 15:19:51
Current_Time  = 2-DEC-2010 16:00:05

Comment       = single pulse decouple
Data Format    = 1D COMPLEX
Dir Size      = 26214
Dir Title     = 13C
Dir Units     = [ppm]
Dimensions    = 627400
Spectrometer  = DELTA2_NMR

Field strength = 9.389766 [T] (400 [MHz])
Acq duration   = 1.0433312 [s]
F2 domain      = 13C
F2 freq        = 100.62830333 [MHz]
F2 offset      = 3270 [ppm]
F2 gain        = 3.76 [dB]
F2 prescans   = 4
F2 resolution  = 0.55846665 [Hz]
F2 sweep       = 31.40703518 [MHz]
F1 domain      = 1H
F1 freq        = 499.78219938 [MHz]
F1 offset      = 5 [ppm]
F1 gain        = 23.0 [dB]
Mod F return   = 1
Scans         = 11212
Total scans   = 11212

X90 width     = 10.8 [us]
X90 offset    = 0.6433312 [s]
X90 delay     = 10 [deg]
X flip        = 3 [dB]
X pulse       = 3.5 [us]
Irr atn_dec   = 20.276 [dB]
Irr atn_noise = 20.276 [dB]
WALTZ16       = WALTZ16
NUC1         = 13C
NUC2         = 1H
Relax time    = 2 [s]
Recvr gain    = 60
Relaxation delay = 2 [s]
Repetition time = 3.0433312 [s]
Temp_jct     = 31.2 [degC]
    
```





```

----- PROCESSING PARAMETERS -----
dc balance : 0 : FALSE
sweep : 0.2[Hz] : 0.0[s]
trapacid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
machinesphase : YONE
ppm
    
```

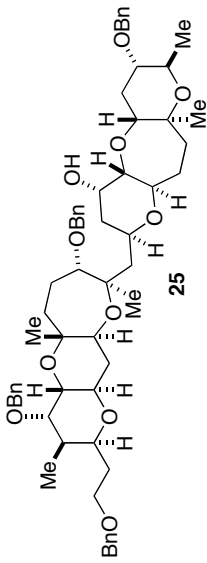
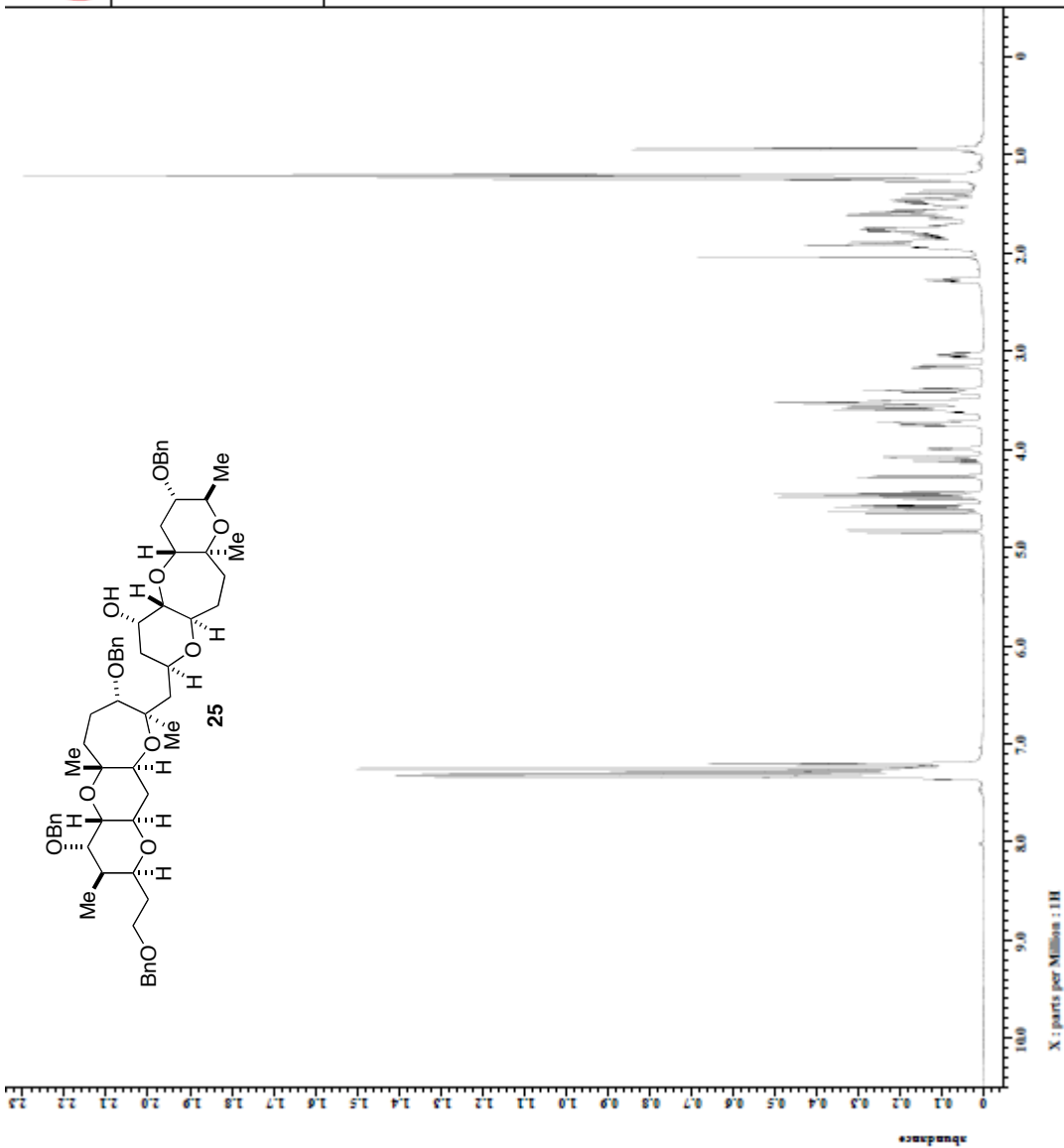
```

Filename = 32a-100907-1R-1.jdf
Author =
Experiment = single_pulse.exe2
Sample_id = 840813
Solvent = DMSO-d6
Chemical_shift = 7.088-2010 13:22:36
Revision_time = 27-05-2010 21:11:21
Current_time = 2-05-2010 15:46:19

Comment =
Data_format = single_pulse
Data_dir = 10 COMPLETE
Data_file = 1R107
Dim_units = [ppm]
Dimensions = X
Site = XCA500
Spectrometer = DEUTRA_NMR

Field_strength = 11.7473573[T] (500[MHz])
X_acq_duration = 2.30026752[s]
X_domain = 1R
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 1.43012684[Hz]
X_resolution_ppm = 0.00286057[ppm]
X_resolution_cycles = 6.46225991[MHz]
Irr_domain = 1R
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1R
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clip_start = 0.0[ppm]
Clip_end = 10.0[ppm]
Mod_return = 1
Scans = 0
Total_scans = 0

X_90_width = 5.1[us]
X_90_time = 5.1[us]
X_acq_time = 4.51[sec]
X_att = 3.2[db]
X_pulse = 3.1[us]
Irr_mode = Off
Tri_mode = Off
Dumps_preset = FALSE
Initial_wait = 1.0[s]
Relaxation_delay = 2.0[s]
Repetition_delay = 4.31026752[s]
Temp_pct = 22.4[degC]
    
```





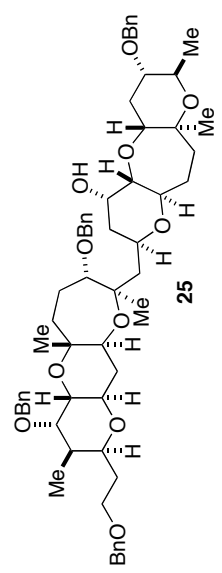
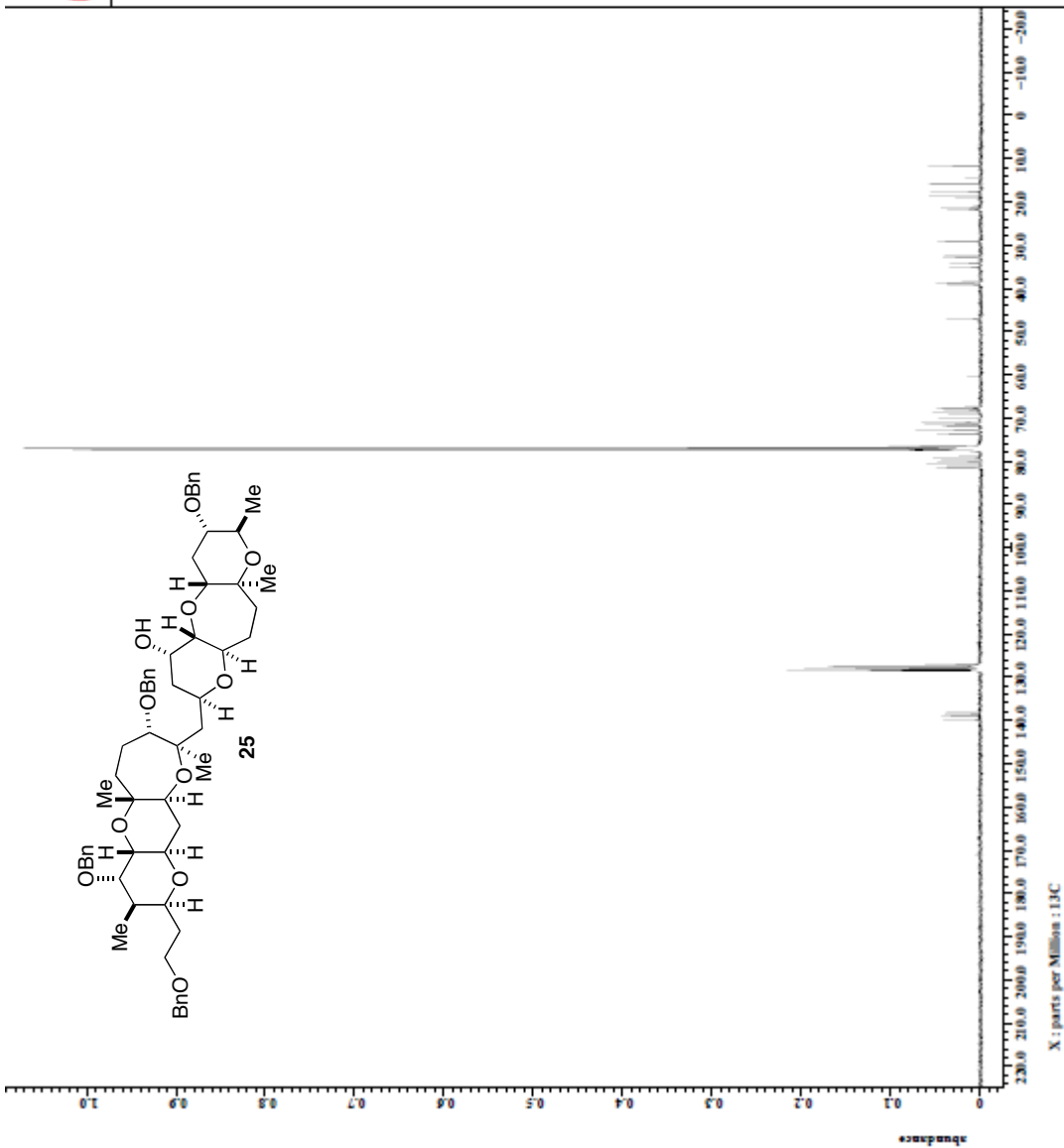
```

=====
Filename      = 2-100907-13C-2_1.f6E
Author        = Delta
Experiment    = single_pulse_dec
Sample_ID     = 04650731
Solvent       = CHLOROFORM-D
Creation_Time = 7-SEP-2010 05:26:34
Revision_Time = 2-DEC-2010 16:00:13
Current_Time  = 2-DEC-2010 16:00:32

Comment       = single pulse decouple
Data Format    = 1D COMPLEX
Dir Size      = 26214
Dir Title     = 13C
Dir Units     = [ppm]
Dimensions    = 627400
Spectrometer = DELTA2_NMR

Field strength = 9.389766 [T] (400 [MHz])
Acq duration   = 1.04333312 [s]
F2 domain     = 13C
F1 freq       = 100.62830333 [MHz]
X posits     = 3270 [ppm]
X prescans   = 4
X resolution = 0.95846665 [Hz]
X sweep      = 31.40703518 [MHz]
F1 domain     = 1H
F1 freq       = 500.13629999 [MHz]
X posits     = 5 [ppm]
X prescans   = 1
X resolution = 1.78219938 [MHz]
X sweep      = 270 [ppm]
Mod F return  = 1
Scans        = 4898
Total scans  = 4898

X90 width    = 10.8 [us]
X90 delay    = 0.04333312 [s]
X delay      = 3.0 [dec]
X gain       = 3 [dB]
X pulse      = 3.5 [us]
Irr_atn_dec = 20.276 [dB]
Irr_atn_noi = 20.276 [dB]
WALTZ16     = WAUZE
NUC1        = 13C
NUC2        = 1H
NUC3        = 13C
Noe time     = 2 [s]
Recvr gain   = 60
Relaxation_delay = 2 [s]
Repetition_time = 3.04333312 [s]
Temp_jct     = 31.9 [OC]
=====
    
```



alcohol S9



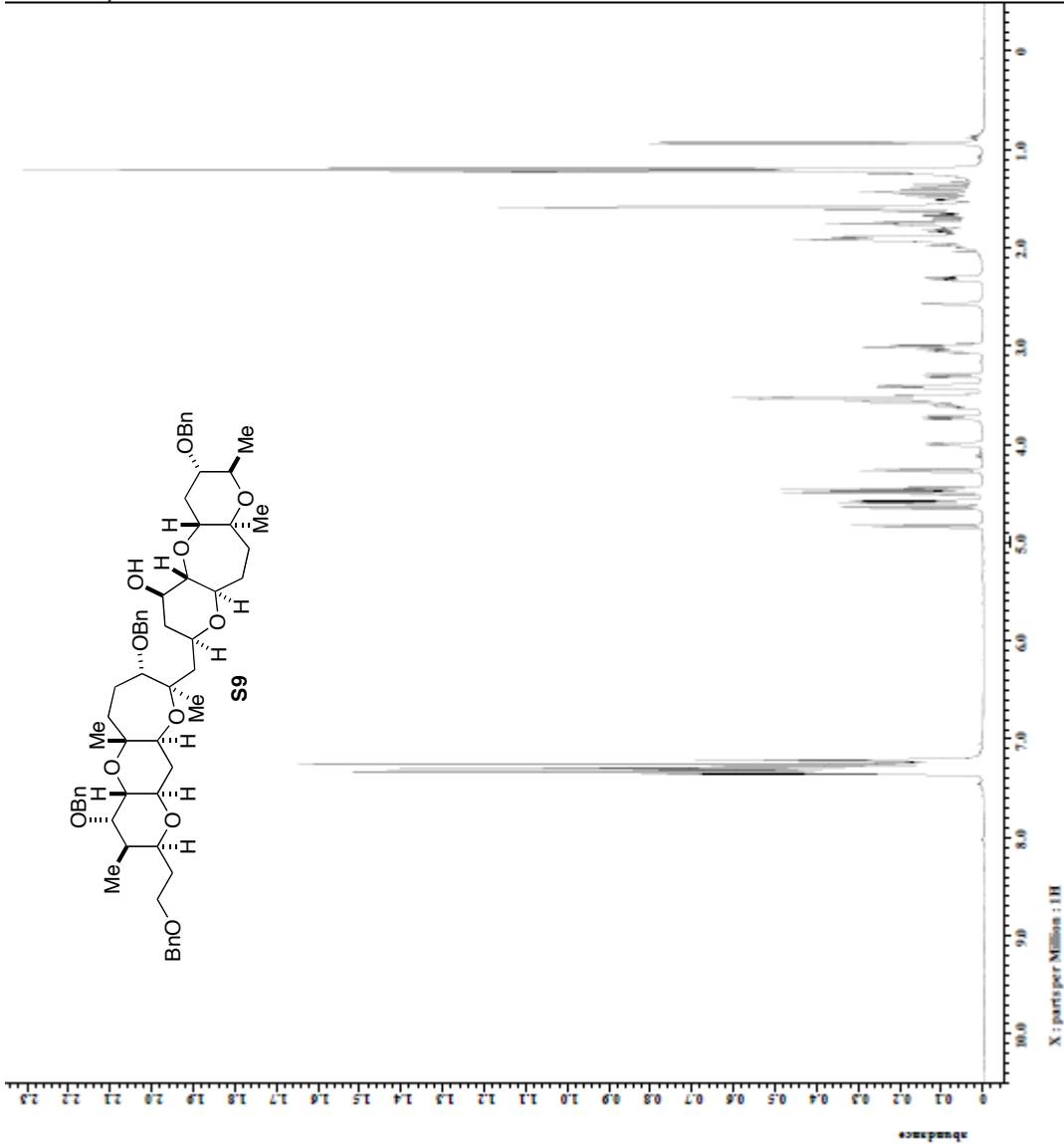
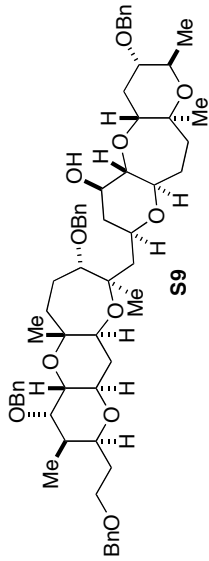
```

=====
Filesave  = 32b-100910-1H-6_3d4
Author    = delta
Experiment = single_pulse.exe2
Sample_id = 0446513
Solvent   = CDCl3
Creation_time = 10-SEP-2010 12:51:12
Revision_time = 2-DEC-2010 15:46:32
Current_time = 2-DEC-2010 15:46:45

Comment   = single_pulse
Data_format = 1D COMPLEX
Data_size  = 13107
Data_title = 1H
Data_units = [ppm]
Dimensions = 1
File       = DCAS00
Name       = DELTA2_1H
Spectrometer = DELTA2_NMR

Field_strength = 11.7473575 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain     = 100.15591521 [MHz]
F2_domain     = 5.0 [ppm]
F3_domain     = 163884
F4_domain     = 163884
X_resolution  = 1
X_swept      = 0.42012084 [Hz]
X_resolution = 6.88325991 [kHz]
IR_sweep     = 1H
IR_domain    = 50.15591521 [MHz]
IR_freq     = 5.0 [ppm]
IR_domain   = 1H
IR_freq     = 500.15591521 [MHz]
Tri_offset  = 5.0 [ppm]
Clipped     = FALSE
Mod_return  = 1
Data_size   = 32
Total_scans = 32

X_f0_width   = 6 [Hz]
X_acq_time   = 2.38026752 [s]
X_angle     = 45 [deg]
X_p1       = 3.2 [dB]
X_p2       = 0 [dB]
X_pulse    = [Hz]
X_mode     = OFF
Data_preset = FALSH
Initial_wait = 1 [s]
Rever_gain  = 60
Relaxation_delay = 1.5 [s]
Repetition_time = 32 [sec]
Temp_jct    = 32 [deg]
    
```

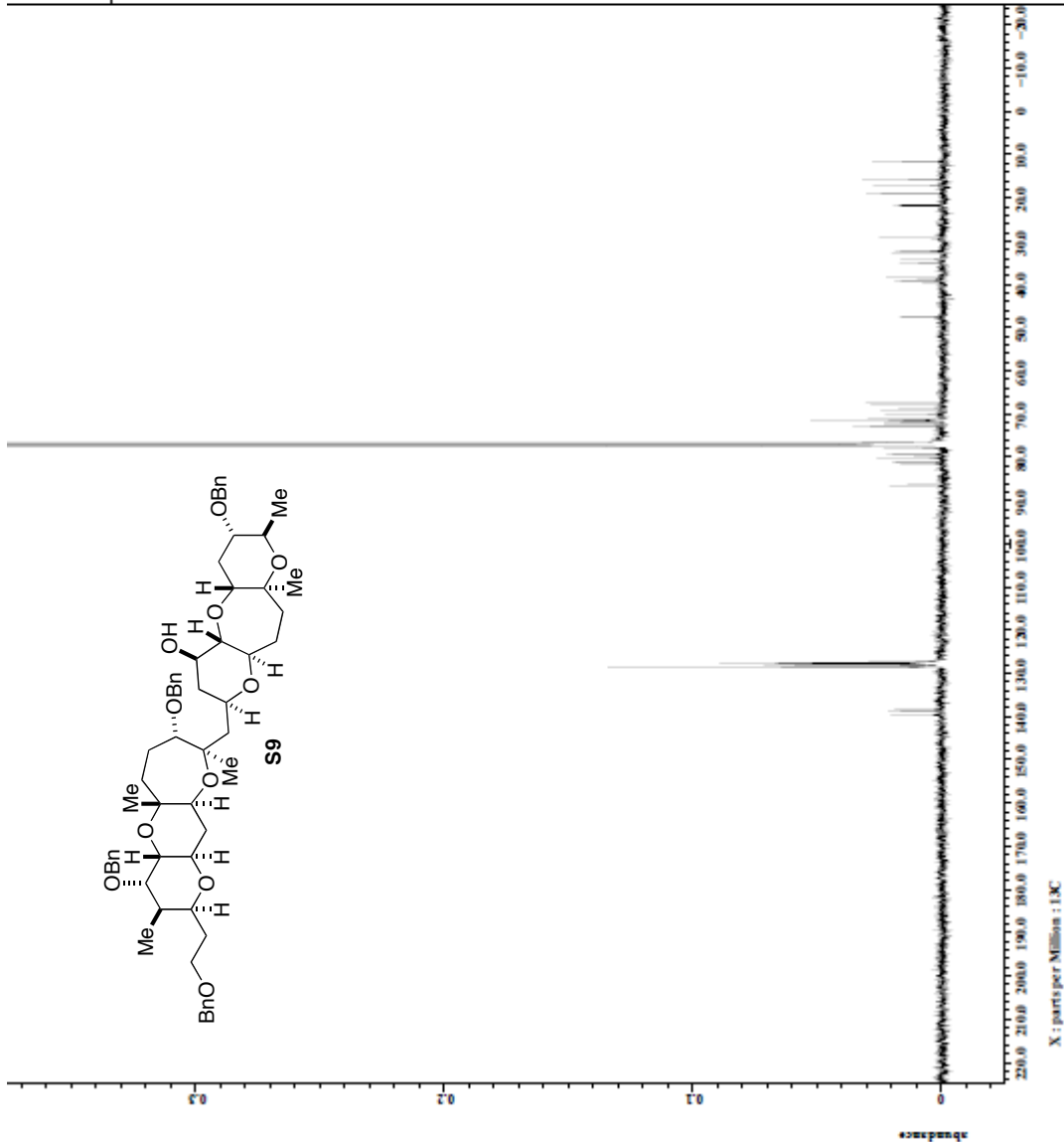
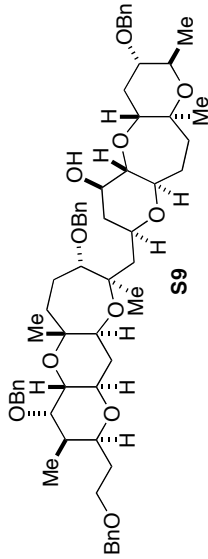


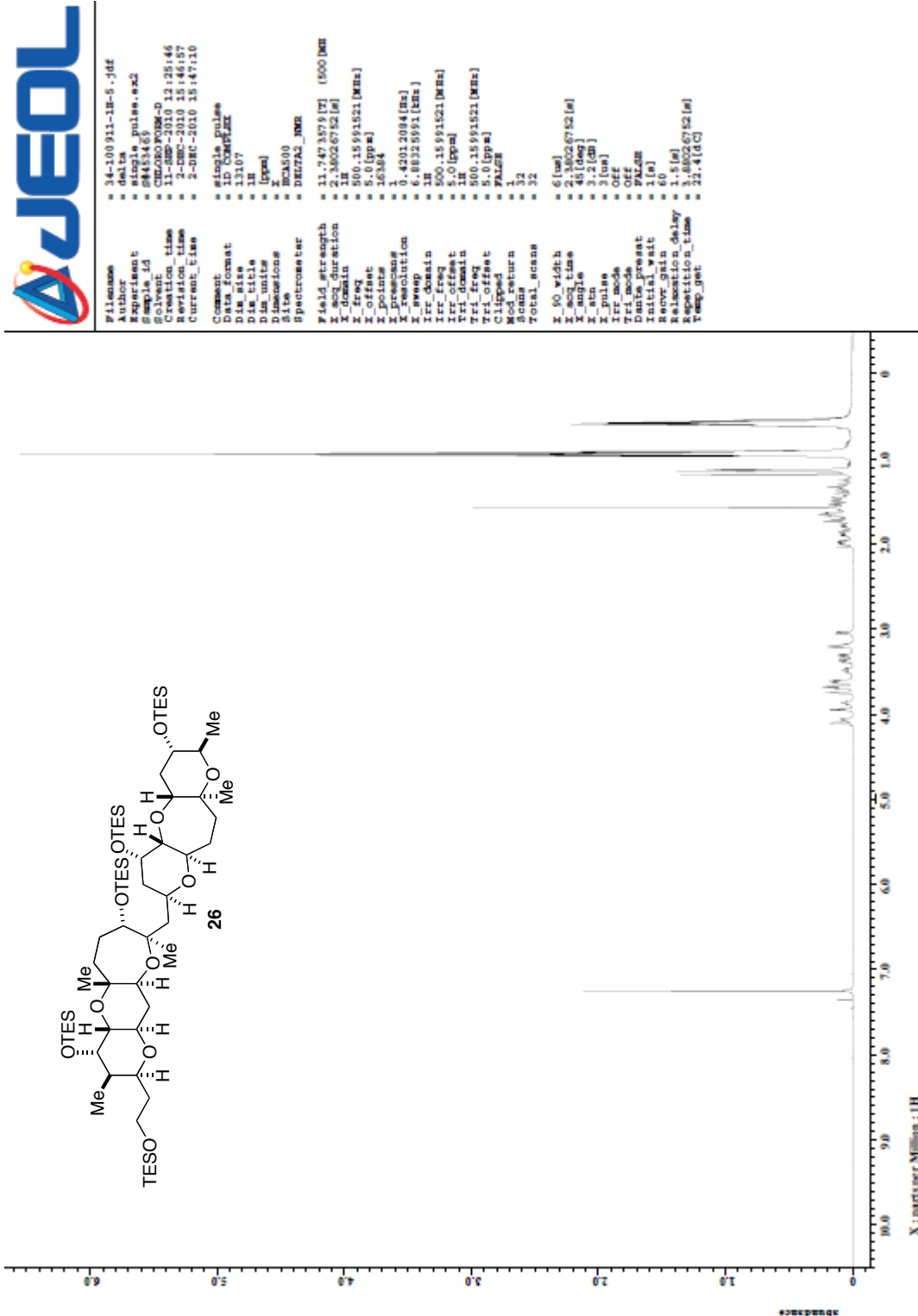
alcohol S9



```

=====
Filebase  = 89-100910-13C-2_9df
Author    = delta
Experiment = single_pulse_dec
Sample_id = 8448435
Solvent   = CDCl3
Creation_time = 9-Mar-2010 22:05:02
Revision_time = 2-Dec-2010 16:03:27
Current_time = 2-Dec-2010 10:02:43
Comment   = single_pulse decouple
Data_format = 1D COMPTX
Dir_size  = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 655x400
File      = 89X400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 82453033 [MHz]
F2_domain = 100 [ppm]
F1_offset = 52768
F2_offset = 52768
X_points = 4
X_prescans = 0.95846665 [Hz]
X_resolution = 31.40703518 [Hz]
X_sweep = 18.76219830 [MHz]
IR_domain = 51 [ppm]
IR_freq = 5160
Clipped = TRUE
Mod_return = 1
Scans = 3240
Total_scans = 3240
X_90_width = 10.5 [us]
X_acq_time = 1.04333312 [s]
X_solve = 30 [dec]
X_atn = 3 [db]
X_pulse = 3.5 [us]
IR_atn_dec = 20.276 [db]
IR_atn_noise = 20.276 [db]
IR_noise = 20.276 [db]
IR_wait = 20.276 [db]
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 58
Relaxation_delay = 2 [s]
Repetition_time = 21.4 [s]
Temp_jct = 31.4 [dC]
=====
    
```

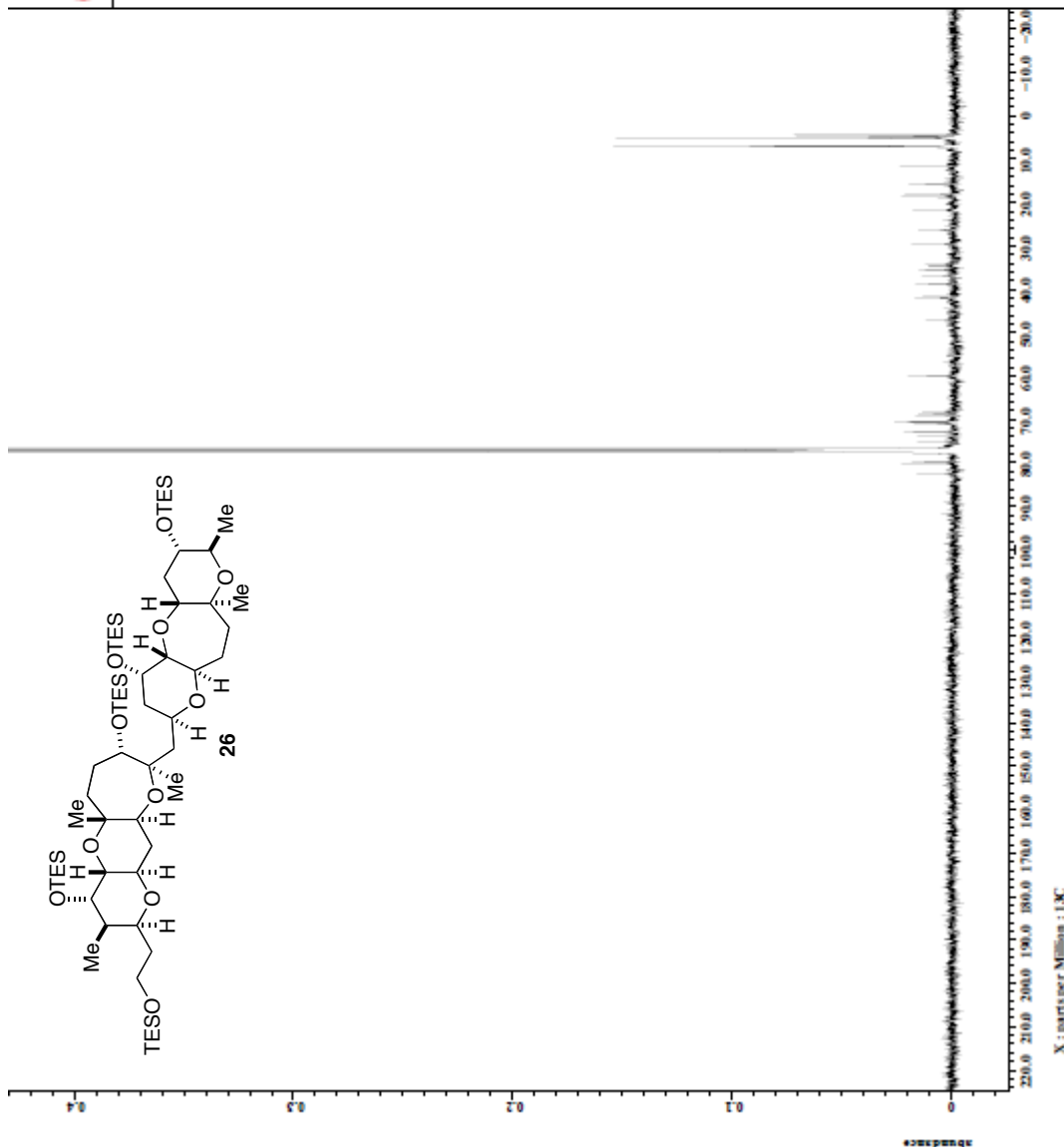
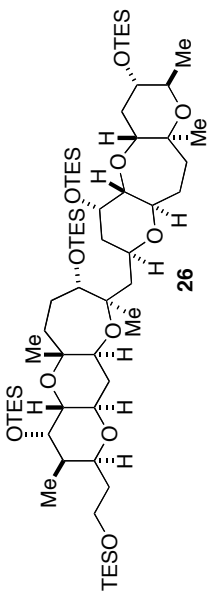






```

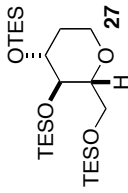
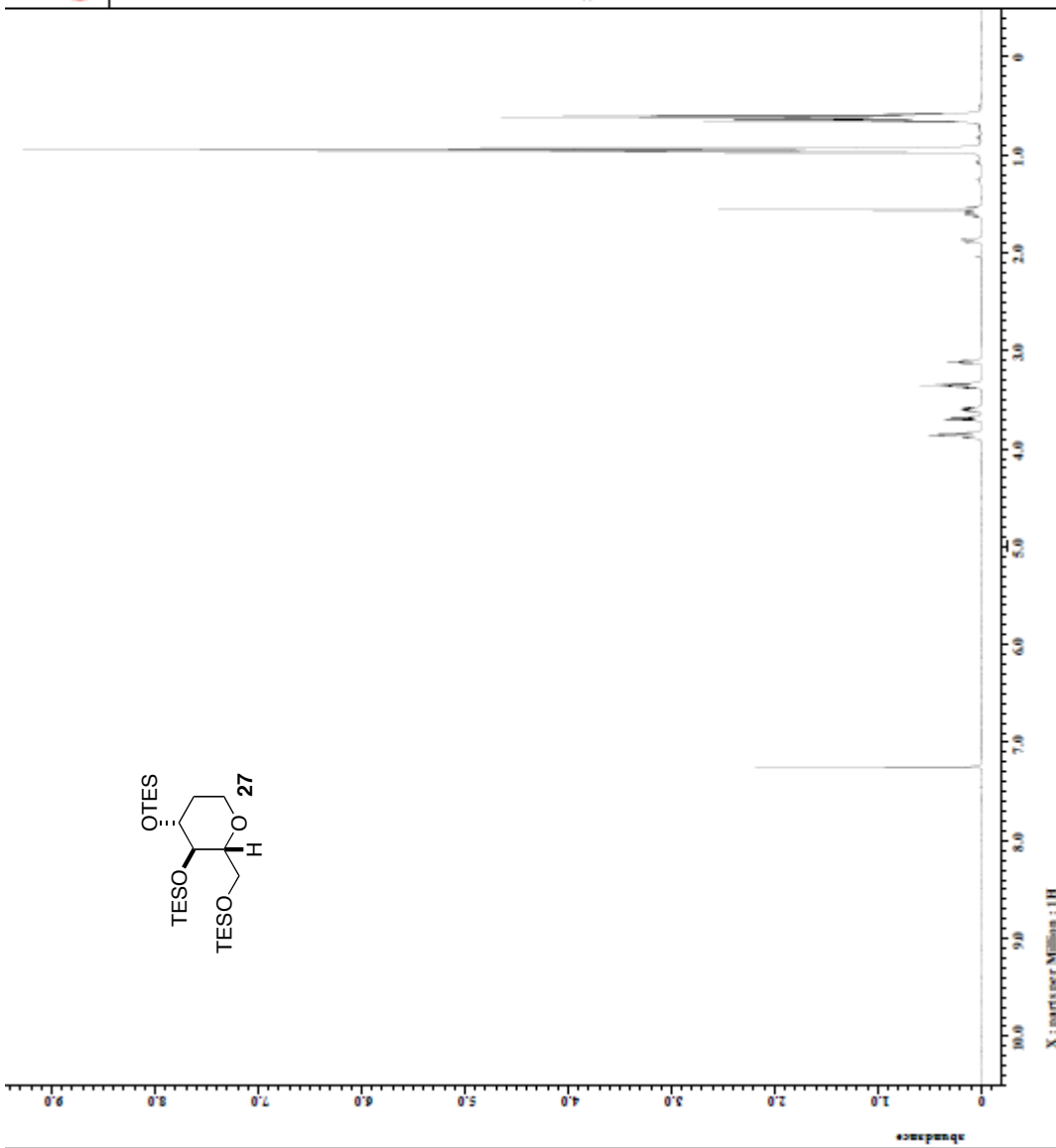
Filename = 34-100911-13C-2.jdt
Author = delta
Experiment = single_pulse_dec
Sample_id = 04352031
Solvent = CDCl3
Creation_time = 10-SEP-2010 10:37:30
Revision_time = 2-DEC-2010 16:00:37
Current_time = 2-DEC-2010 10:00:54
Comment = single_pulse decouple
Data_format = ID COMPTX
Dir_size = 26214
Dir_title = 13C
Dir_units = [ppm]
Dir_extensions =
File = DCX400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 42430333 [MHz]
F2_domain = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665 [Hz]
X_sweep = 31.40703518 [Hz]
IR_domain =
IR_freq = 9.78219830 [MHz]
Clipped =
Mod_return = 1
Scans = 3500
Total_scans = 3500
X_90_width = 10.5 [us]
X_acq_time = 1.04333312 [s]
X_angle = 30 [deg]
X_atn = 3 [dB]
X_pulse = 3.5 [us]
IR_atn_dec = 20.276 [dB]
IR_atn_noise = 20.276 [dB]
D1_delay = 0.000 [s]
D11_delay = 0.000 [s]
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 60
Relaxation_delay = 2 [s]
Repetition_time = 2.000 [s]
Temp_jct = 31.9 [dC]
    
```





```

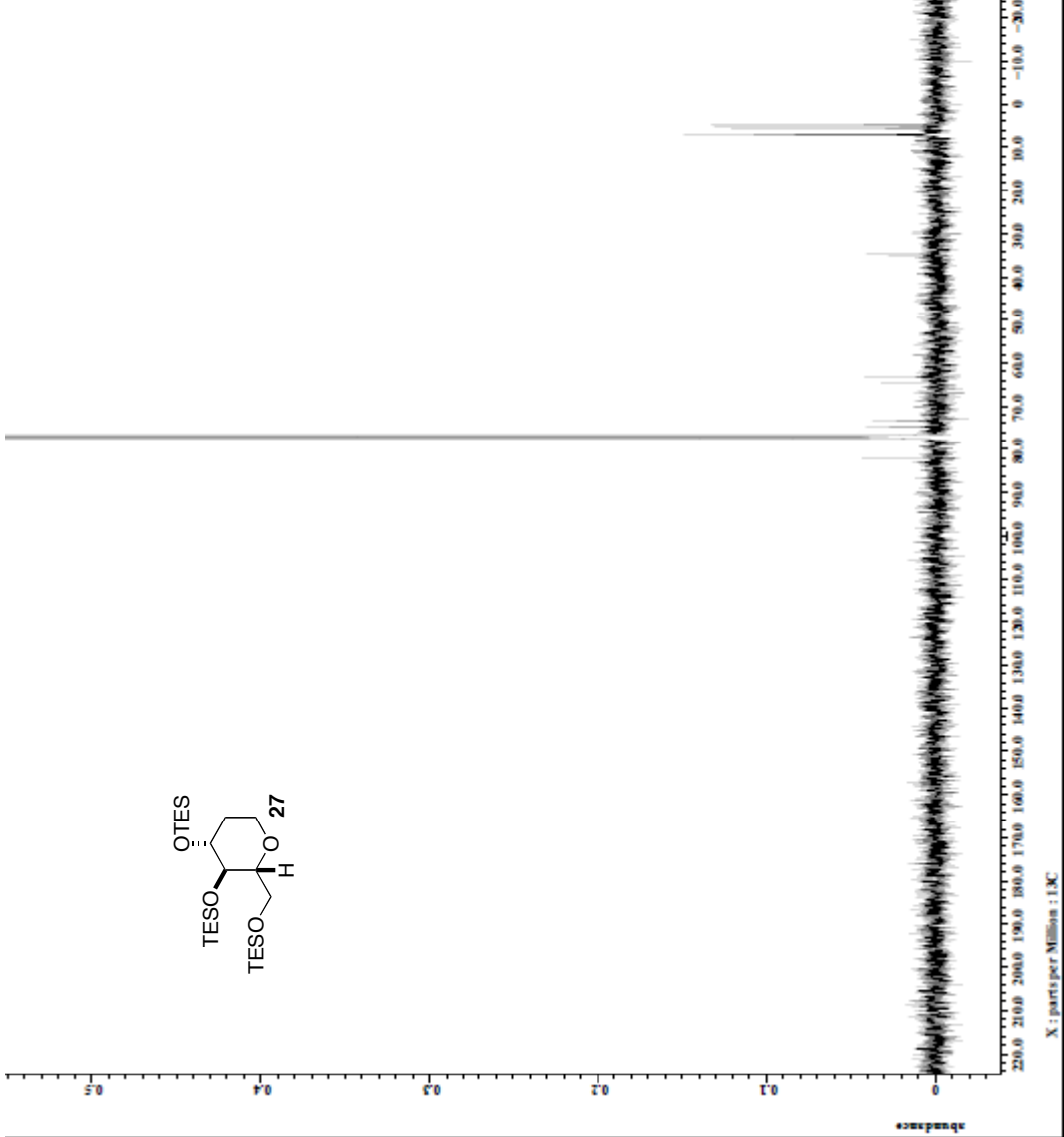
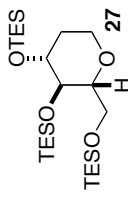
=====
* 35-100905-1R-2_3.f4f
* delta
* single_pulse.exe2
* 047921
* CHLOROFORM-D
* 5-SEP-2010 22:04:40
* 2-DEC-2010 15:47:13
* 2-DEC-2010 15:47:32
*
*
* single_pulse
* ID COMPLEX
* 13107
* IN
* [ppm]
* ECAS00
* SPECTRA
* DELTA2_NMR
*
* Field_strength = 11.7473579 [T] (500 [MH
* I_acq_duration = 2.38026752 [s]
* I_domain = 10.015591521 [MHz]
* I_offset = 5.0 [ppm]
* I_points = 16384
* I_prescans = 1
* I_resolution = 0.42012084 [Hz]
* I_sweep = 6.88325991 [kHz]
* I1_domain = 50.15591521 [MHz]
* I1_freq = 50.15591521 [MHz]
* I1_offset = 5.0 [ppm]
* I1_resolution = 500.15591521 [MHz]
* I1_sweep = 5.0 [ppm]
* Mod_return = 1
* Total_scans = 8
*
* I_50_width = 6 [Hz]
* I_acq_time = 2.38026752 [s]
* I_angle = 45 [deg]
* I_sca = 3.2 [dB]
* I_pulse = [µs]
* I1_pulse = [µs]
* I1_mode = OFF
* Data_presat = FALSE
* Initial_wait = 1 [s]
* Recvr_gain = 62
* Relaxation_delay = 1.5 [s]
* Relaxation_time = 32.5 [dC]
* Temp_jct =
=====
    
```





```

Filebase = 36-100905-13C-2.jdt
Author = delta
Experiment = single_pulse_dec
Sample_id = 04051914
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2010 05:43:06
Revision_time = 2-DEC-2010 16:01:01
Current_time = 2-DEC-2010 16:01:22
Comment = single_pulse decouple
Data_format = 1D COMPTX
Dir_size = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 1Dx400
Site = DEUT400
Spectrometer = DEUT400_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 82430333 [MHz]
F2_domain = 100 [ppm]
F1_offset = 32768
F2_offset = 0.95846665 [Hz]
F1_resolution = 31.40703518 [Hz]
F2_resolution = 18.76219830 [MHz]
IR_domain = 5 [cm]
IR_freq = 5100 [cm]
IR_offset = 0
IR_clipped = 1
Mod_return = 1
Scans = 191
Total_scans = 191
X_90_width = 10.5 [us]
X_acq_time = 1.04333312 [s]
X_pulse = 30 [deg]
X_atn = 3 [dB]
X_atn_delay = 3.5 [us]
IR_atn_dec = 20.276 [dB]
IR_atn_noise = 20.276 [dB]
IR_atn_delay = 0.000 [us]
IR_atn_noise_delay = 0.000 [us]
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 58
Relaxation_delay = 2 [s]
Repetition_time = 21.33333312 [s]
Temp_jct = 31.3 [dC]
    
```





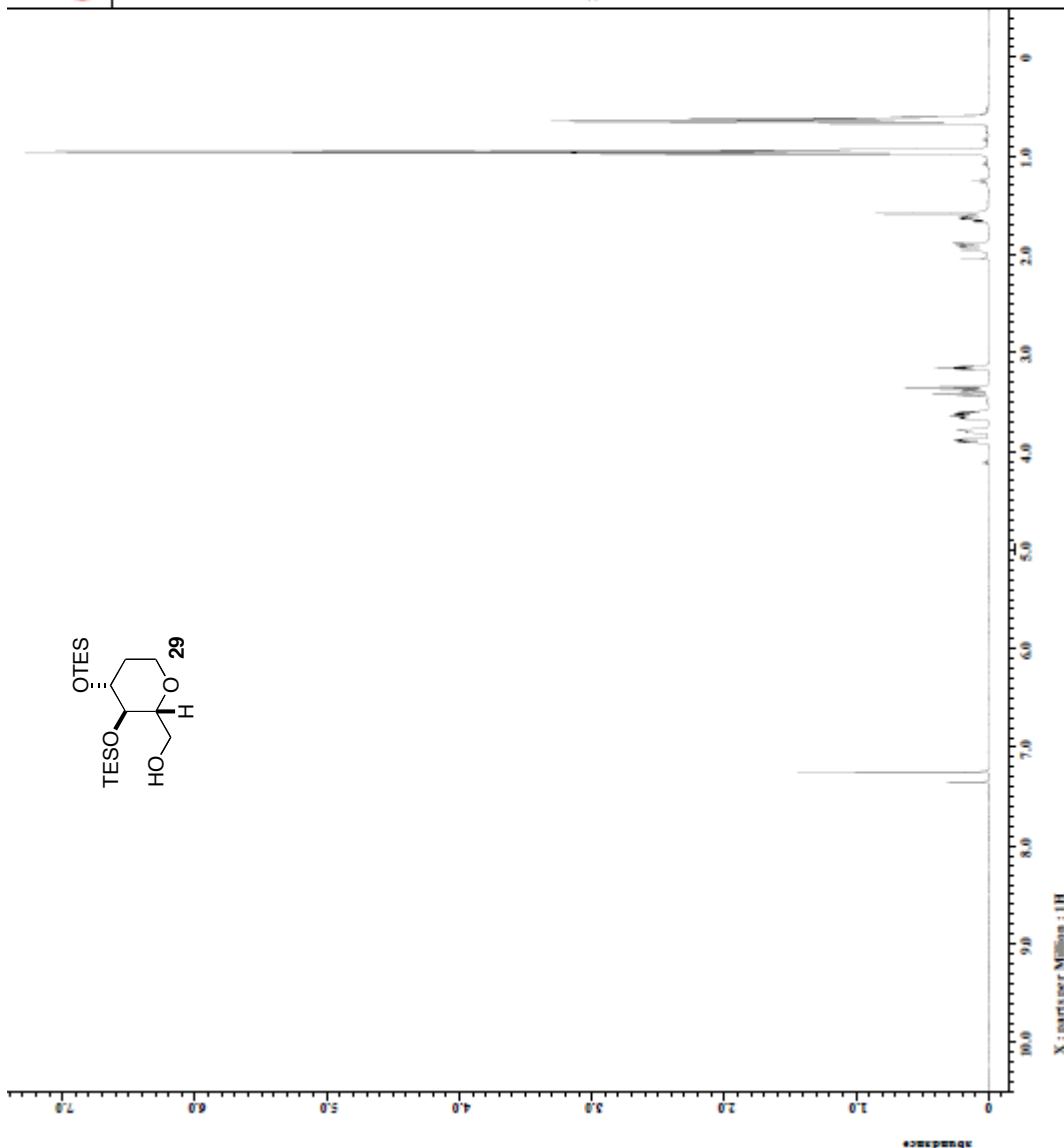
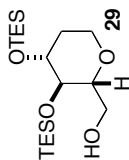
```

Filebase      = 37-100905-1R-2_3d4
Author        = delta
Experiment    = single_pulse.ex2
Sample_id     = 0475455
Solvent       = CHLOROFORM-D
Creation_time = 5-SEP-2010 21:59:27
Revision_time = 2-DEC-2010 15:47:39
Current_time  = 2-DEC-2010 15:47:38

Comment       = single_pulse
Data_format   = ID COMPLEX
Data_size     = 13107
Data_title    = 1R
Data_units    = [ppm]
Dimensions    = F2AS100
Site          = JEOL500
Spectrometer = DELTA2_NMR

Field_strength = 11.7473575 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain      = 100.15591521 [MHz]
F2_domain      = 5.0 [ppm]
F1_offset      = 163884
F2_offset      = 0.42012084 [Hz]
Prescans       = 1
X_resolution   = 6.88325991 [kHz]
X_sweep        = 50.15591521 [MHz]
IR_domain     = 5.0 [ppm]
IR_freq       = 500.15591521 [MHz]
Tri_domain    = 5.0 [ppm]
Tri_freq      = 500.15591521 [MHz]
Tri_offset    = 1
Mod_return    = 1
Total_scans   = 8

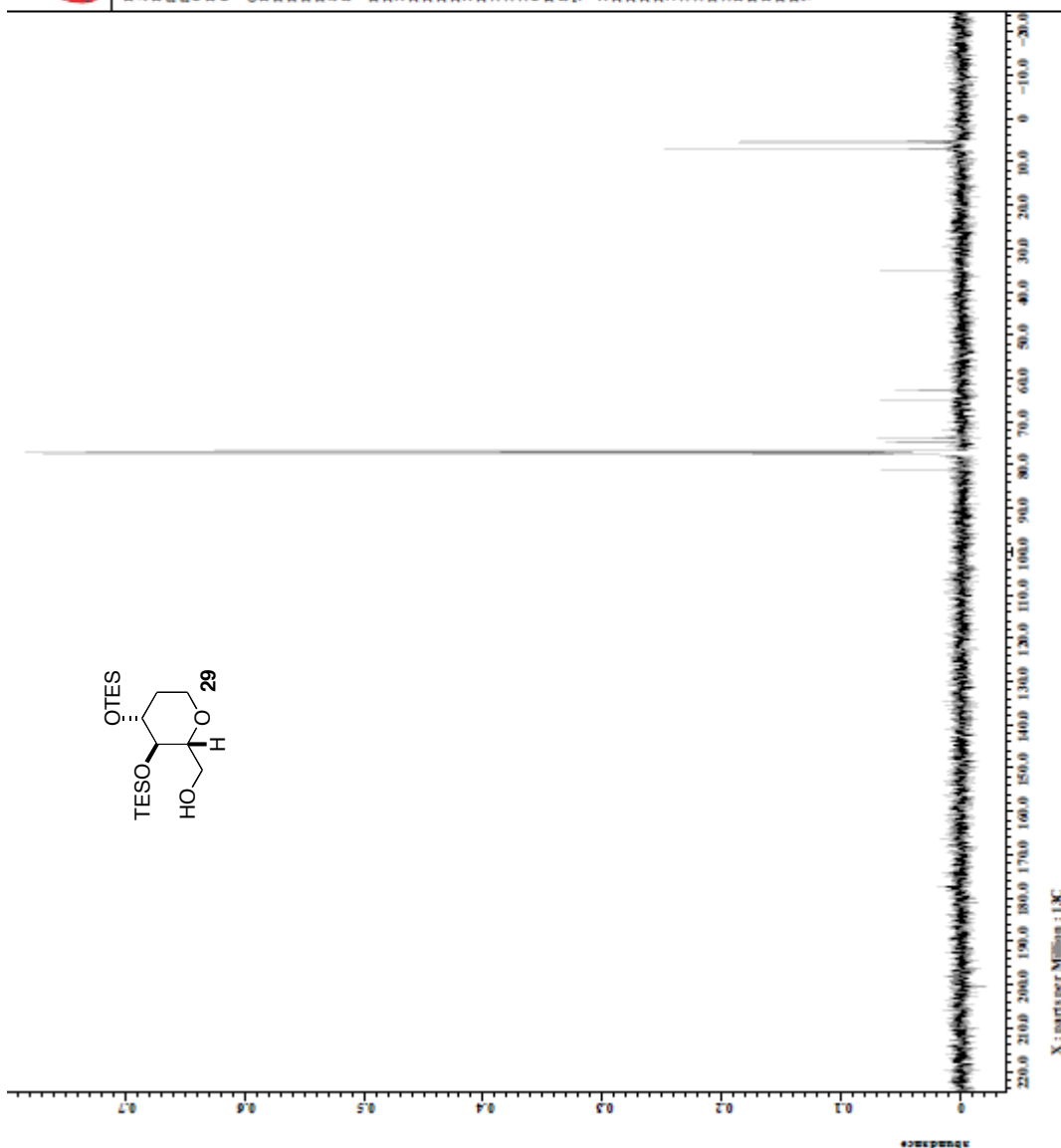
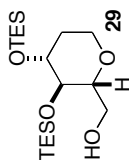
X_f0_width    = 6 [Hz]
X_acq_time    = 2.38026752 [s]
X_angle       = 45 [deg]
X_p1          = 3.2 [dB]
X_p2          = 0 [dB]
X_pulse       = OFF
X_mode        = OFF
Data_preset   = FALSH
Initial_wait  = 1 [s]
Recvr_gain    = 60
Relaxation_delay = 1.5 [s]
Repetition_time = 32.6 [s]
Temp_jct      = 32.6 [dC]
    
```





```

Filebase = 37-100905-13C-2_3dft
Author = delta
Experiment = single_pulse_dec
Sample_id = 2484146
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2010 05:28:26
Revision_time = 2-DEC-2010 16:01:27
Current_time = 2-DEC-2010 16:01:43
Comment = single pulse decouple
Data_format = ID COMPTX
Dir_size = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 655x400
Site = DEUTZ02
Spectrometer = DEUTZ02_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 82430333 [MHz]
F2_domain = 100 [ppm]
K_points = 32768
K_prescans = 4
K_resolution = 0.29846665 [Hz]
K_sweep = 31.40703518 [Hz]
IR_domain = 18.78219830 [MHz]
IR_freq = 5160
IR_clip = 5160
Mod_return = 1
Scans = 248
Total_scans = 248
K_90_width = 10.5 [us]
K_acq_time = 1.04333312 [s]
K_angle = 30 [deg]
K_atn = 3 [dB]
K_pulse = 3.5 [us]
IR_atn_dec = 20.276 [dB]
IR_atn_noise = 20.276 [dB]
K_gain = 2000
K_offset = 0
K_phase = 0
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 60
Relaxation_delay = 2 [s]
Relaxation_time = 21.33333312 [s]
Temp_jct = 31.3 [dC]
    
```

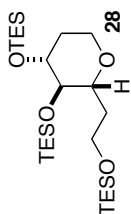
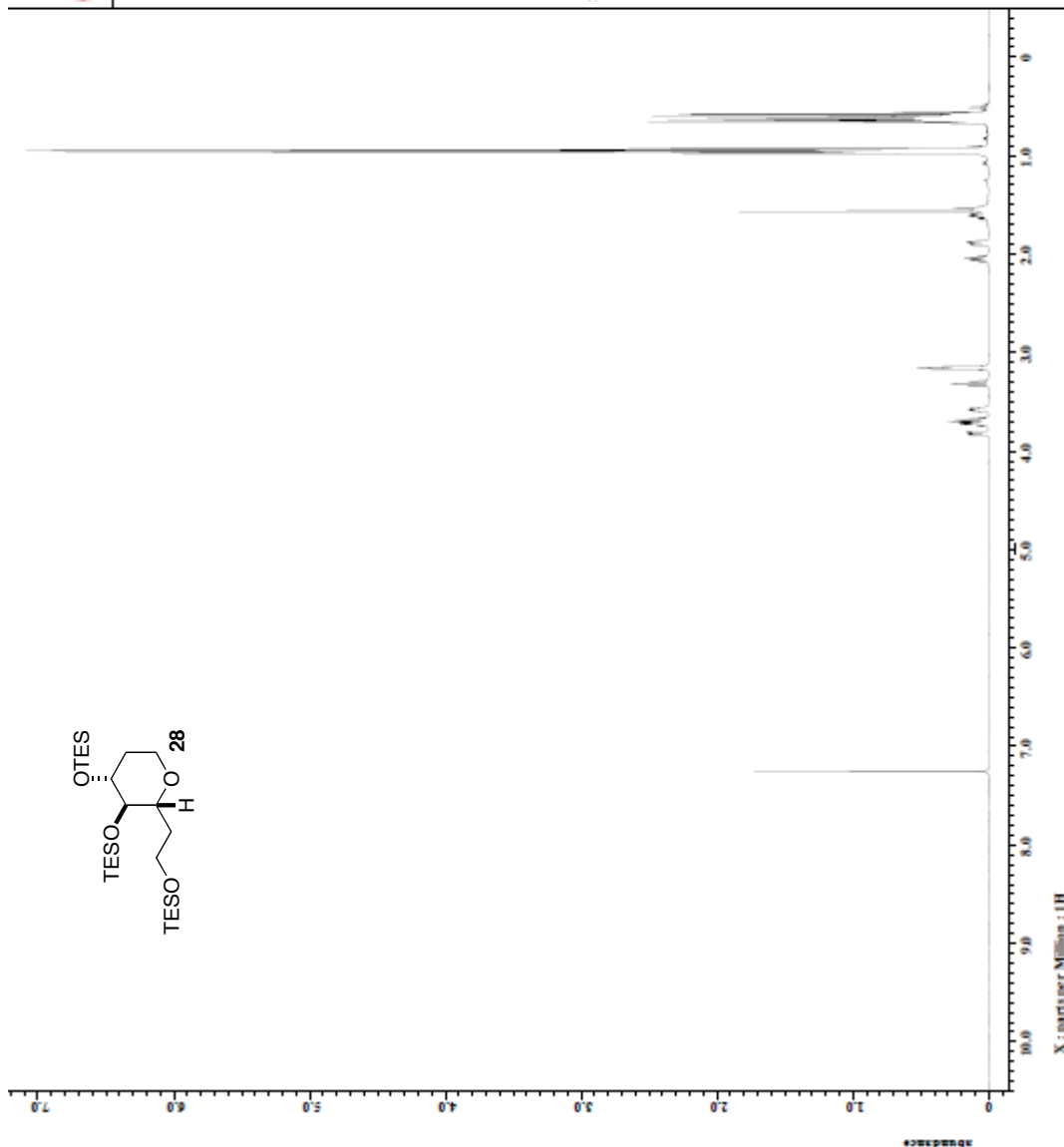




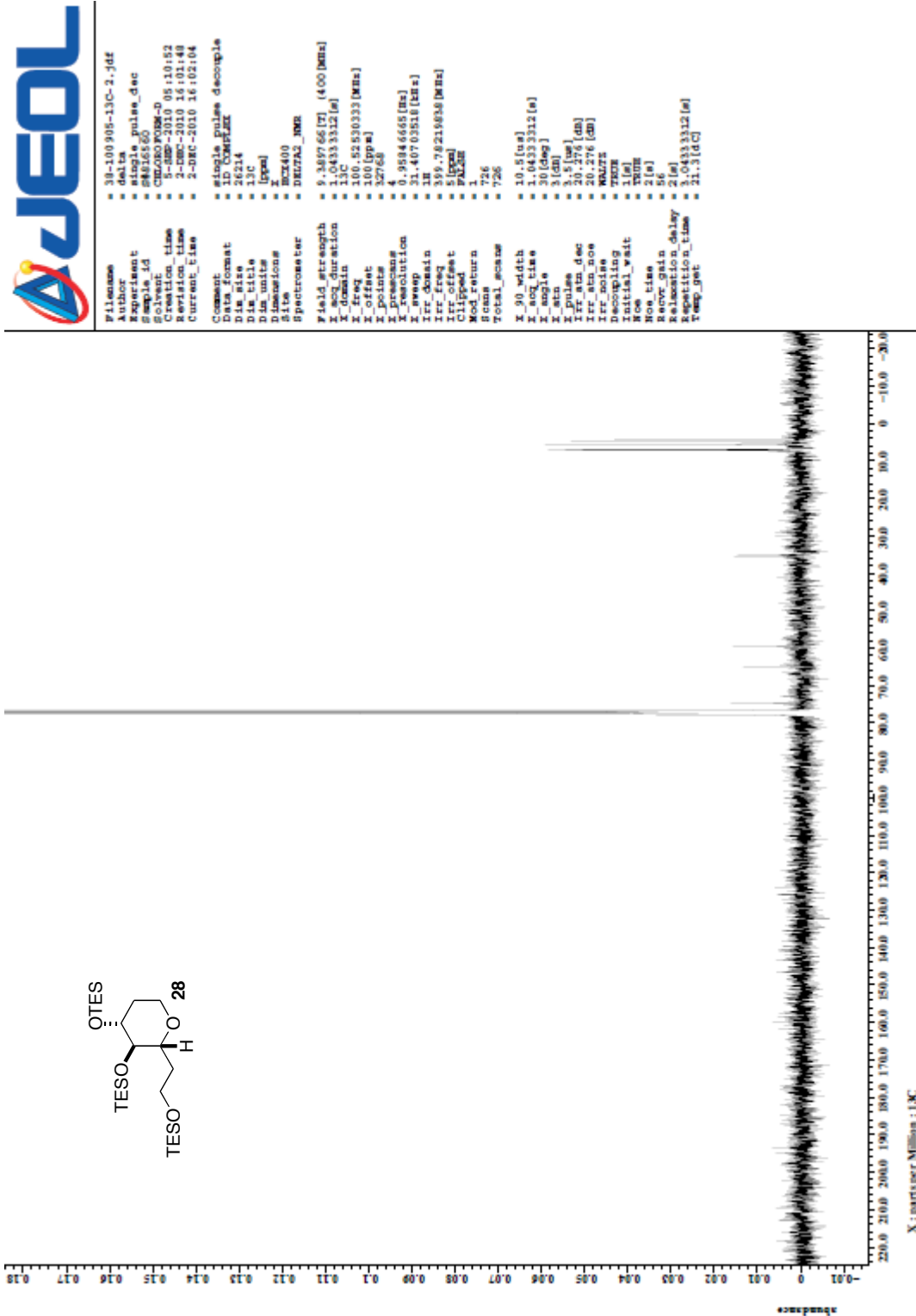
```

# 30-100930-1H-2_3.f4f
# delta
# single_pulse.ex2
# 04/07/12
# CHLOROFORM-D
# 30-NOV-2010 16:50:57
# 2-DEC-2010 15:48:04
# 2-DEC-2010 13:48:13
# single_pulse
# ID COMPLEX
# 133107
# 1H
# [ppm]
# ECAS00
# DEUTAO_NMR
# Spectrometer
# Field_strength = 11.7473575 [T] (500 [MH]
# Acq_duration = 2.38026752 [s]
# F1_domain = 100.15591521 [MHz]
# F2_domain = 5.0 [ppm]
# F2_offset = 163884
# F2_resolution = 1
# F2_swept = 0.42012084 [Hz]
# F2_resolution = 6.88325991 [kHz]
# IR_domain = 50.15591521 [MHz]
# IR_freq = 5.0 [ppm]
# IR_domain = 500.15591521 [MHz]
# IR_offset = 5.0 [ppm]
# Mod_return = 1
# Total_scans = 8
# 50_width = 6 [Hz]
# Acq_time = 2.38026752 [s]
# Angle = 45 [deg]
# Aq = 3.2 [dB]
# Pulse = [Hz]
# Pulse = OFF
# Tri_mode = OFF
# Data_presat = PALSH
# Initial_wait = 1 [s]
# Recvr_gain = 60
# Relaxation_delay = 1.5 [s]
# Relaxation_time = 32.8 [dC]
# Temp_jct =

```



tris-TES ether 28





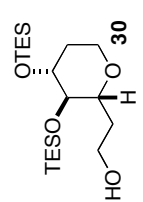
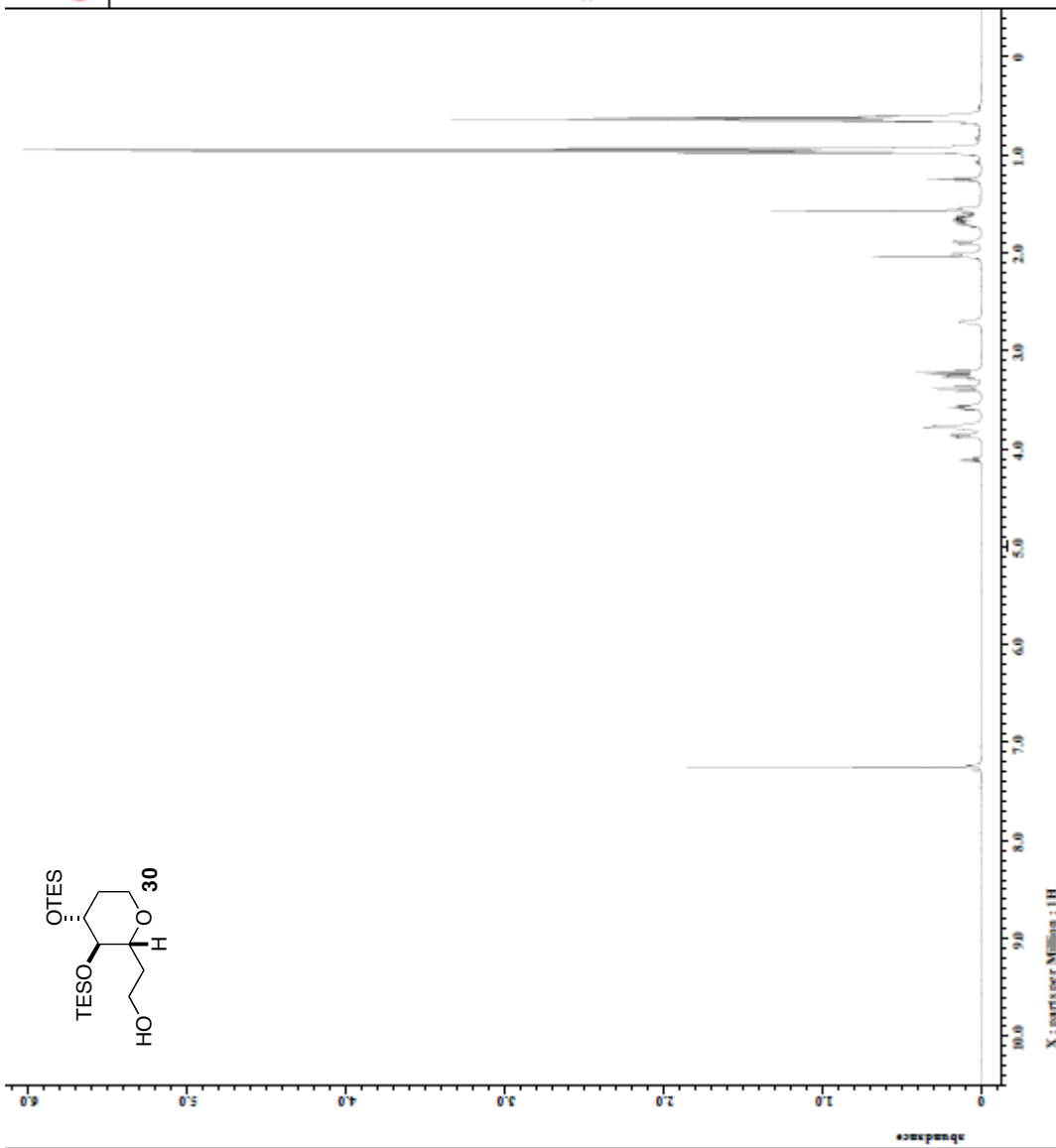
```

Filebase      = 39-100831-1R-2_3df
Author        = delta
Experiment    = single_pulse.ex2
Sample_id     = 84724172
Solvent       = CHLOROFORM-D
Creation_time = 31-AUG-2010 20:02:11
Revision_time = 2-DEC-2010 15:48:25
Current_time  = 2-DEC-2010 15:48:56

Comment       = single_pulse
Data_format   = ID COMPLEX
Data_size     = 13107
Data_title    = 1H
Data_units    = [ppm]
Dimensions    = F2AS100
Site          = DEUTAS100
Spectrometer  = DELTA2_NMR

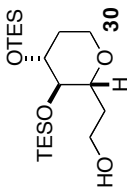
Field_strength = 11.7473575 [T] (500 [MHz])
Acq_duration   = 2.38026752 [s]
F1_domain     = 100.15591521 [MHz]
F2_domain     = 5.0 [ppm]
F1_offset     = 163884
F2_offset     = 0.42012084 [Hz]
Prescans      = 1
Resolution    = 6.88325991 [kHz]
Sweep         = 50.15591521 [MHz]
IR_domain    = 5.0 [ppm]
IR_freq      = 500.15591521 [MHz]
Tri_domain   = 5.0 [ppm]
Tri_freq     = 500.15591521 [MHz]
Tri_offset   = 1
Mod_return    = 1
Total_scans   = 8

X_50_width    = 6 [um]
X_acq_time    = 2.38026752 [s]
X_angle       = 45 [deg]
X_sca         = 3.2 [dB]
X_pulses      = 6 [um]
X_pulse_prog  = OFF
X_tri_mode    = OFF
Data_preset   = FALSH
Initial_wait  = 1 [s]
Recvr_gain    = 64
Relaxation_delay = 1.5 [s]
Relaxation_time = 32.6 [dC]
Temp_jct      = 32.6 [dC]
    
```



OTES

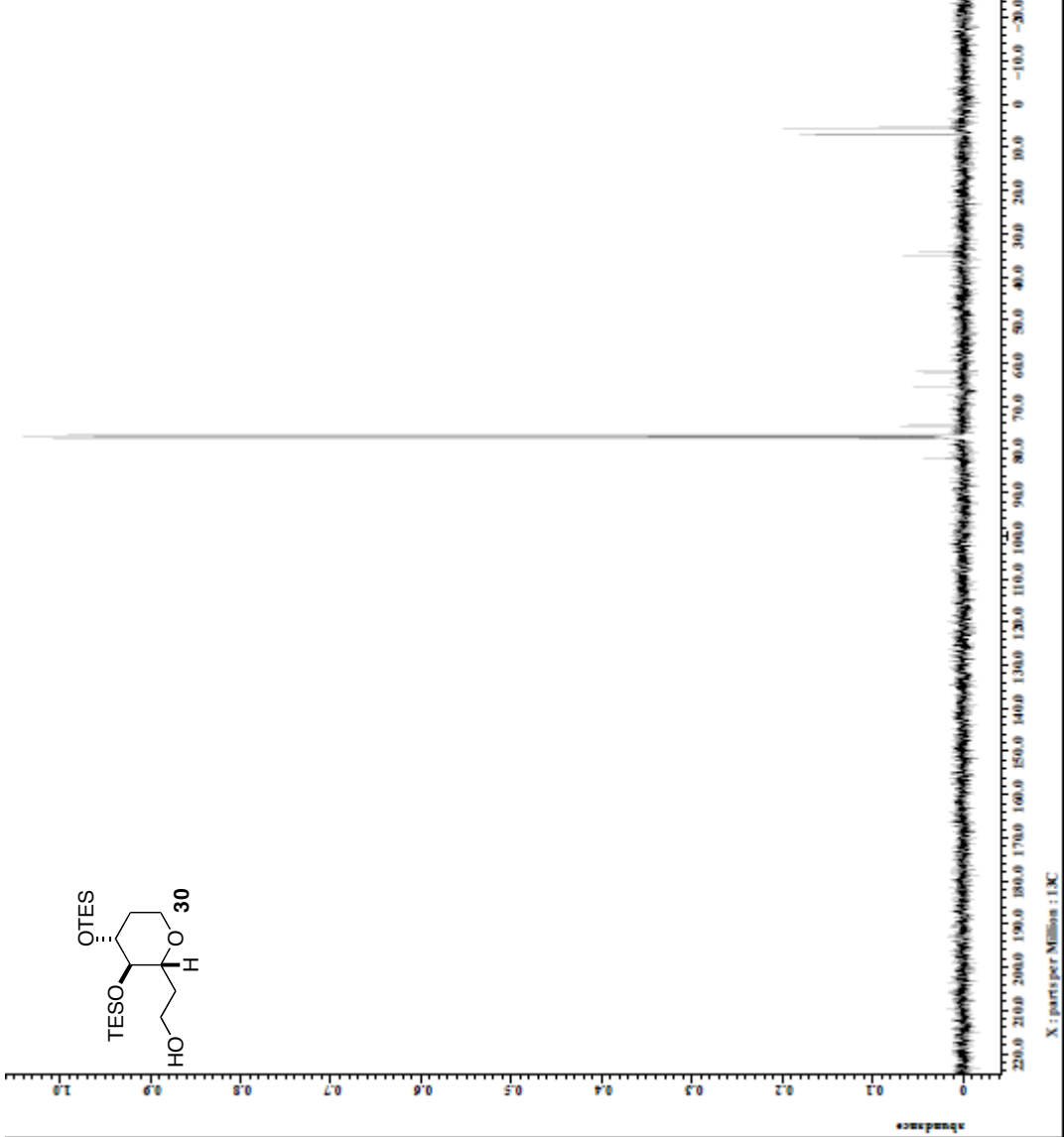
30



```

Filebase = 39-100905-13C-2.jdt
Author = delta
Experiment = single_pulse_dec
Sample_id = 04005875
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2010 04:28:16
Revision_time = 2-DEC-2010 16:02:10
Current_time = 2-DEC-2010 16:02:26
Comment = single_pulse decouple
Data_format = ID COMPTX
Data_size = 26214
Data_title = 13C
Data_units = [ppm]
Dimensions = 655x400
Site = DEUTZ02
Spectrometer = DEUTZ02_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 82430333 [MHz]
F2_domain = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.29846665 [Hz]
X_sweep = 31.40703518 [Hz]
IR_domain = 18.78219830 [MHz]
IR_freq = 5162.5
Clipped = FALSE
Mod_return = 1
Scans = 207.0
Total_scans = 207.0
X_90_width = 10.8 [us]
X_acq_time = 1.04333312 [s]
X_pulse = 30 [deg]
X_atn = 3 [dB]
X_atn = 3.5 [us]
IR_atn_dec = 20.276 [dB]
IR_atn_noise = 20.276 [dB]
Sweep = 180
Dwell = 2000
Initial_wait = 1 [s]
Nox_time = 2 [s]
Relaxr_gain = 60
Relaxation_delay = 2 [s]
Relaxation_time = 21.33333312 [s]
Temp_jct = 31.3 [dC]

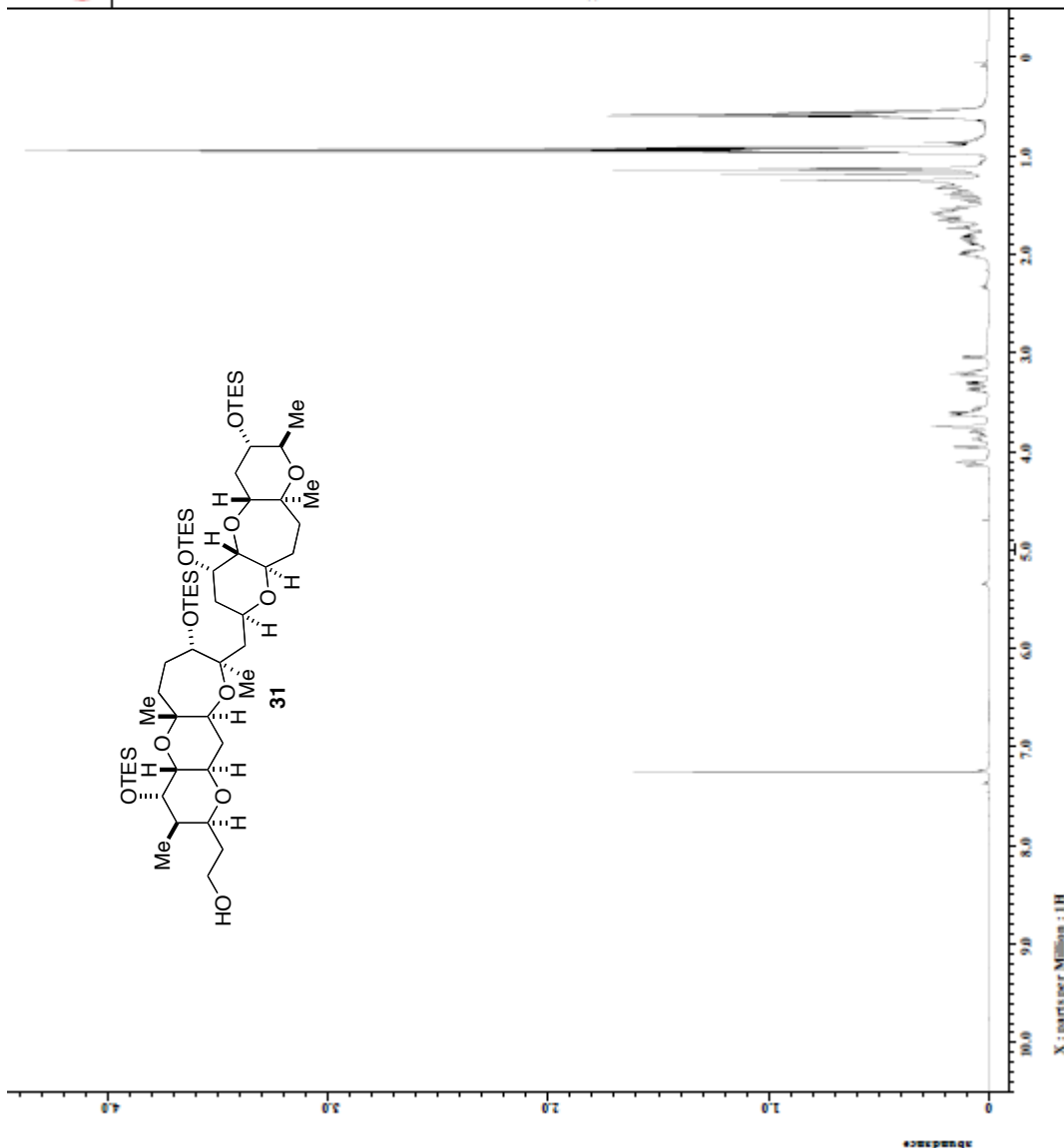
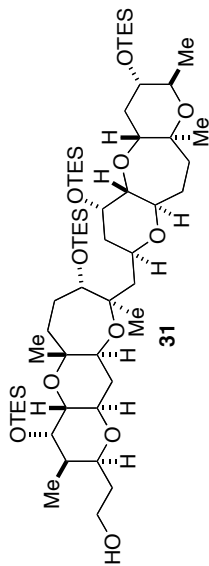
```





```

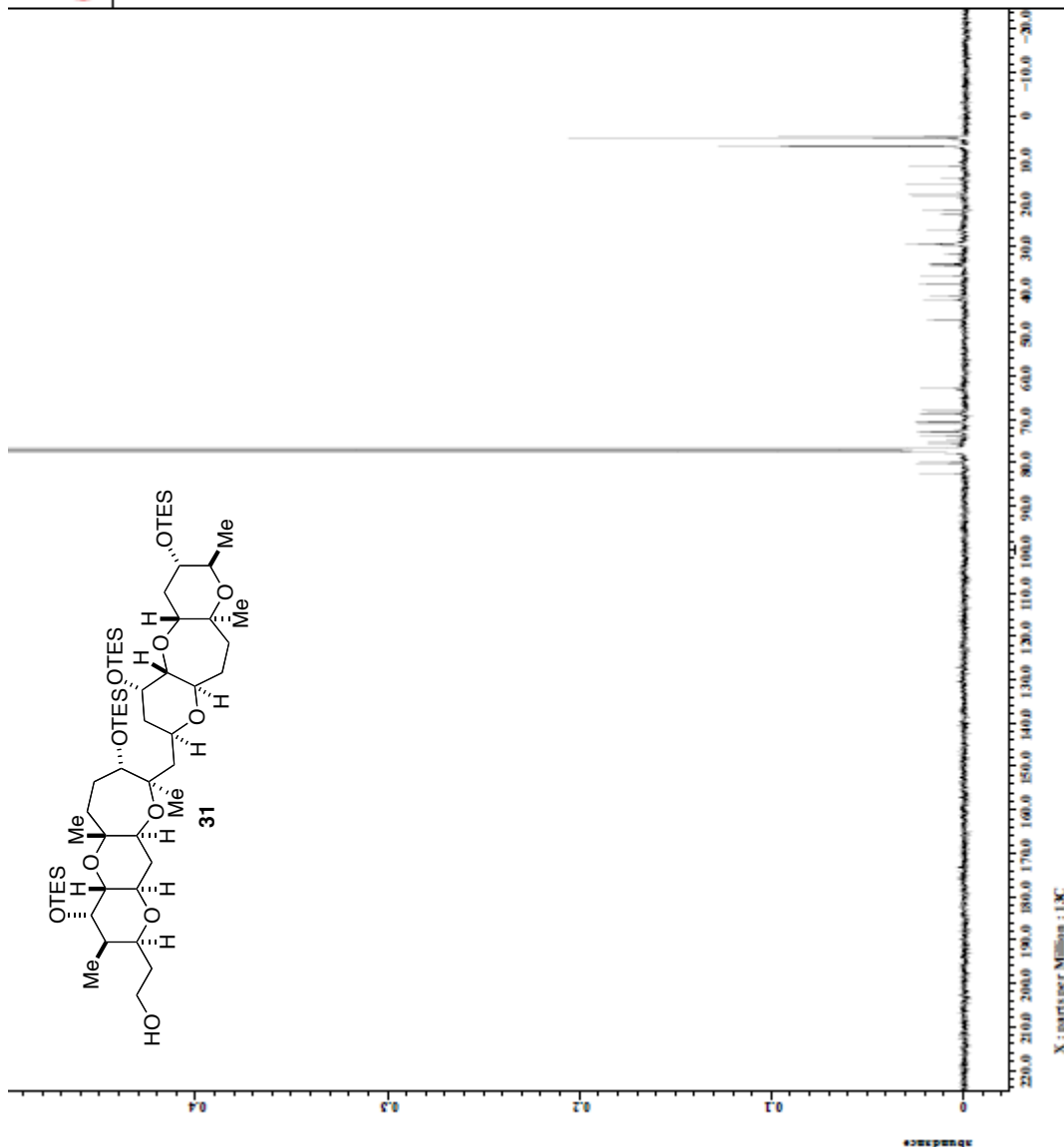
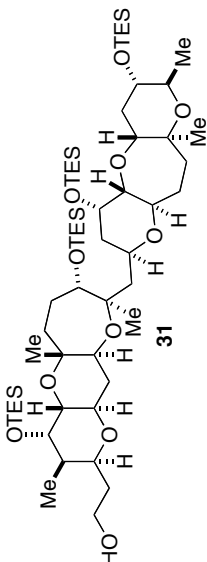
Filebase = 40-100909-1E-6_3d4
Author = delta
Experiment = single_pulse.ex2
Sample_id = 04754525
Solvent = CHLOROFORM-D
Creation_time = 9-SEP-2010 20:49:11
Revision_time = 2-DEC-2010 15:49:10
Current_time = 2-DEC-2010 15:49:22
Comment = single_pulse
          ID COMPLET
Data_format = 13107
Dia_size = IN
Dia_units = [ppm]
Dimensions = 1Dx500
Site = DELTA2_NMR
Spectrometer = DELTA2_NMR
Field_strength = 11.7473575 [T] (500 [MHz])
Acq_duration = 2.38026752 [s]
F1_domain = 100.15591521 [MHz]
F2_domain = 5.0 [ppm]
F3_domain = 163884
X_points = 1
X_prescans = 0.42012084 [Hz]
X_resolution = 6.88325991 [kHz]
X_sweep = IN
IR_domain = 50.15591521 [MHz]
IR_freq = IN
IR_domain = 5.0 [ppm]
Tri_domain = 500.15591521 [MHz]
Tri_freq = PALSE
Tri_offset = 1
Mod_return = 1
Total_scans = 64
X_50_width = 6 [Hz]
X_acq_time = 2.38026752 [s]
X_angle = 45 [deg]
X_sca = 3.2 [dB]
X_pulse = [Hz]
X_mode = OFF
Data_preset = PALSE
Initial_wait = 1 [s]
Recvr_gain = 58
Relaxation_delay = 1.5 [s]
Repetition_time = 33.1 [dC]
Temp_jct =
  
```



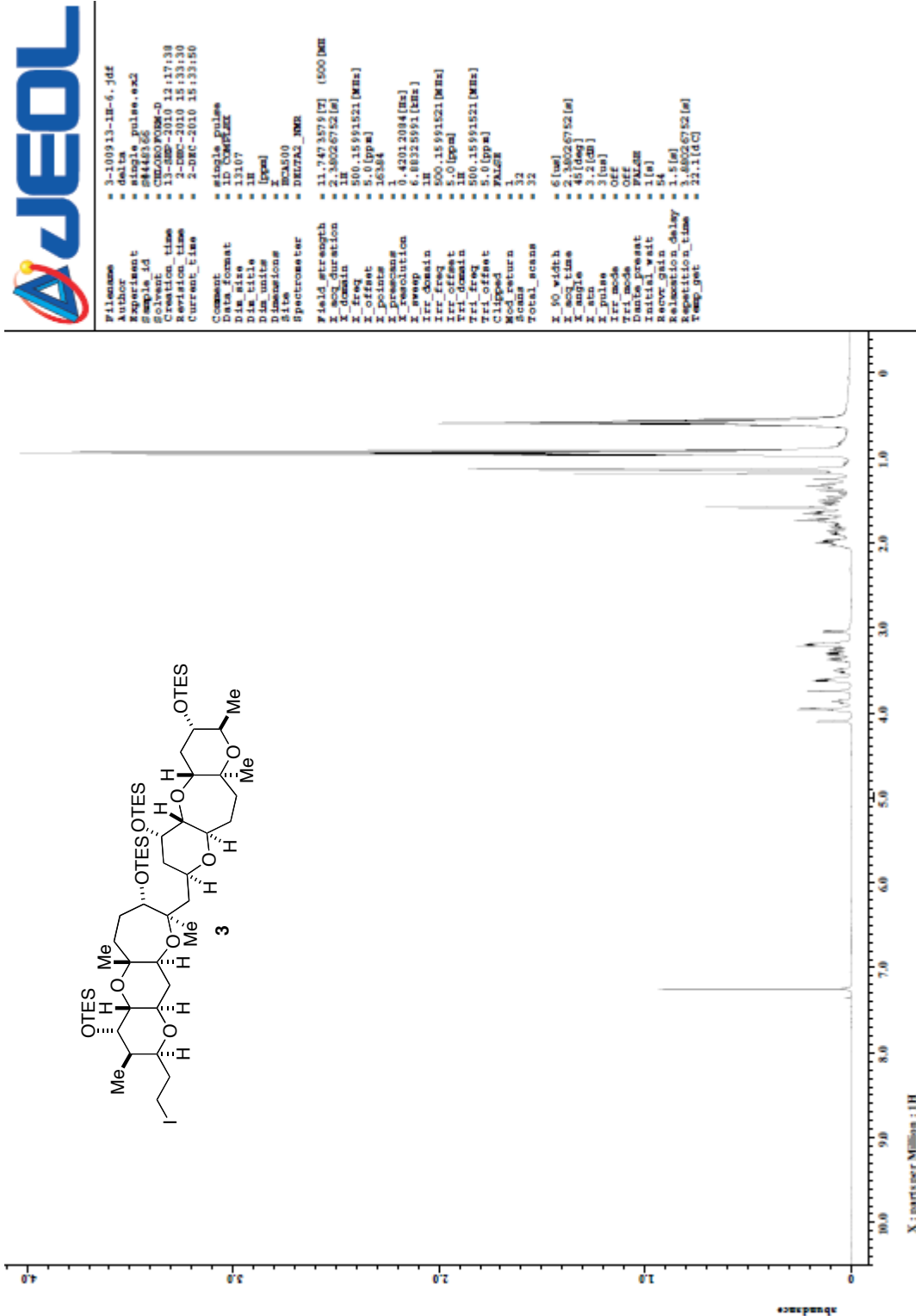


```

Filebase = 40-100909-13C-2_2dat
Author = delta
Experiment = single_pulse_dec
Sample_id = 04616176
Solvent = CDCl3
Creation_time = 9-SEP-2010 02:46:35
Revision_time = 2-DEC-2010 16:02:33
Current_time = 2-DEC-2010 16:02:33
Comment = single_pulse decouple
Data_format = 1D COMPTX
Dir_size = 26214
Dir_title = 13C
Dir_units = [ppm]
Dimensions = 655x400
File = 02x400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 824530333 [MHz]
F2_domain = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.29846665 [Hz]
X_sweep = 31.40703518 [Hz]
IR_domain = 18.78219030 [MHz]
IR_freq = 5 [cm]
Clipped = TRUE
Mod_return = 1
Scans = 4469
Total_scans = 4469
X_90_width = 10.5 [us]
X_acq_time = 1.04333312 [s]
X_spla = 30 [dec]
X_atn = 3 [dB]
X_pulse = 3.5 [us]
IR_atn_dec = 20.276 [dB]
IR_atn_no = 20.276 [dB]
IR_gain = 2000
Dc_offset = 0.00000000
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 60
Relaxation_delay = 2 [s]
Repetition_time = 2.1 [s]
Temp_jct = 31 [C]
    
```



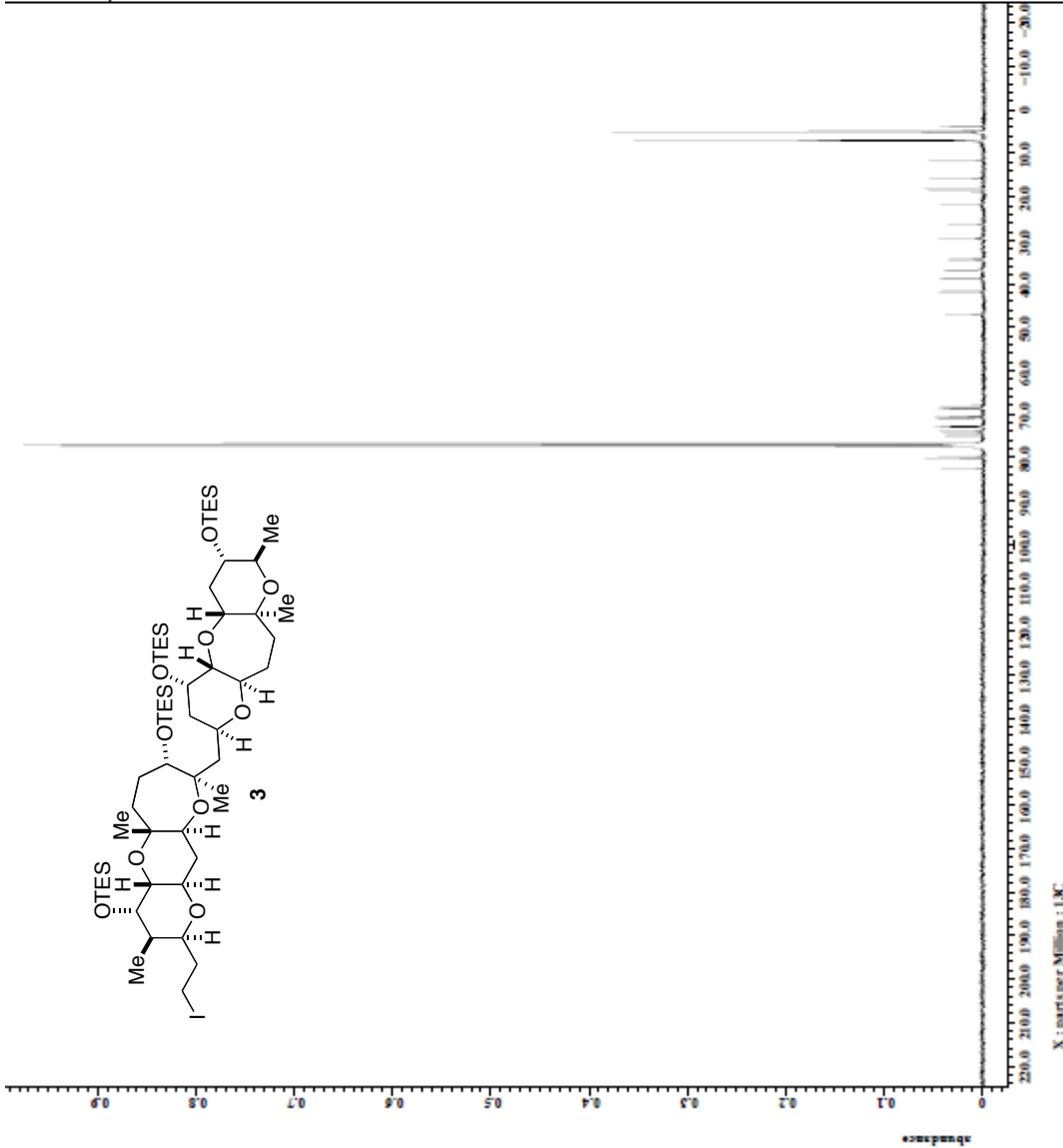
iodide 3



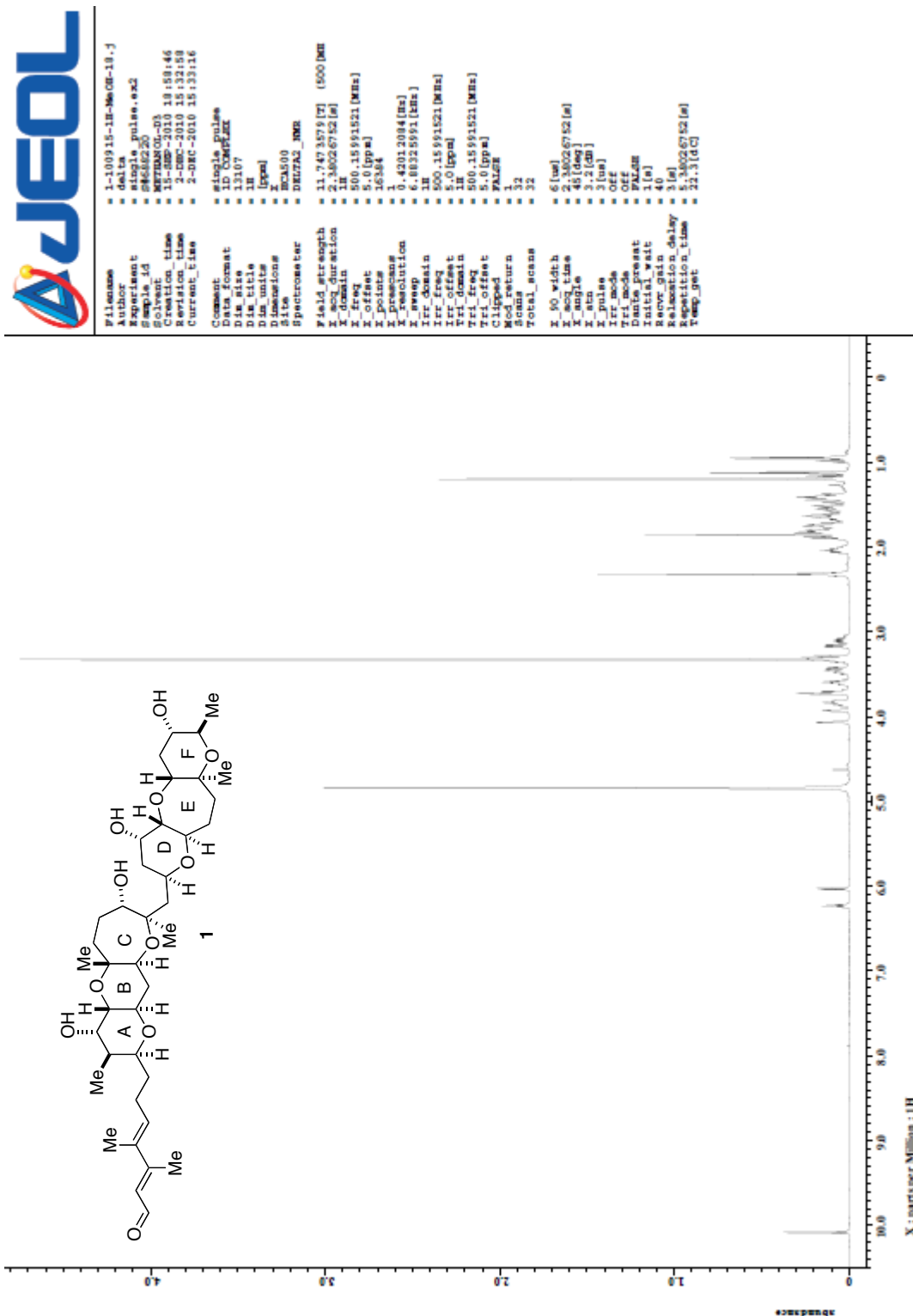


```

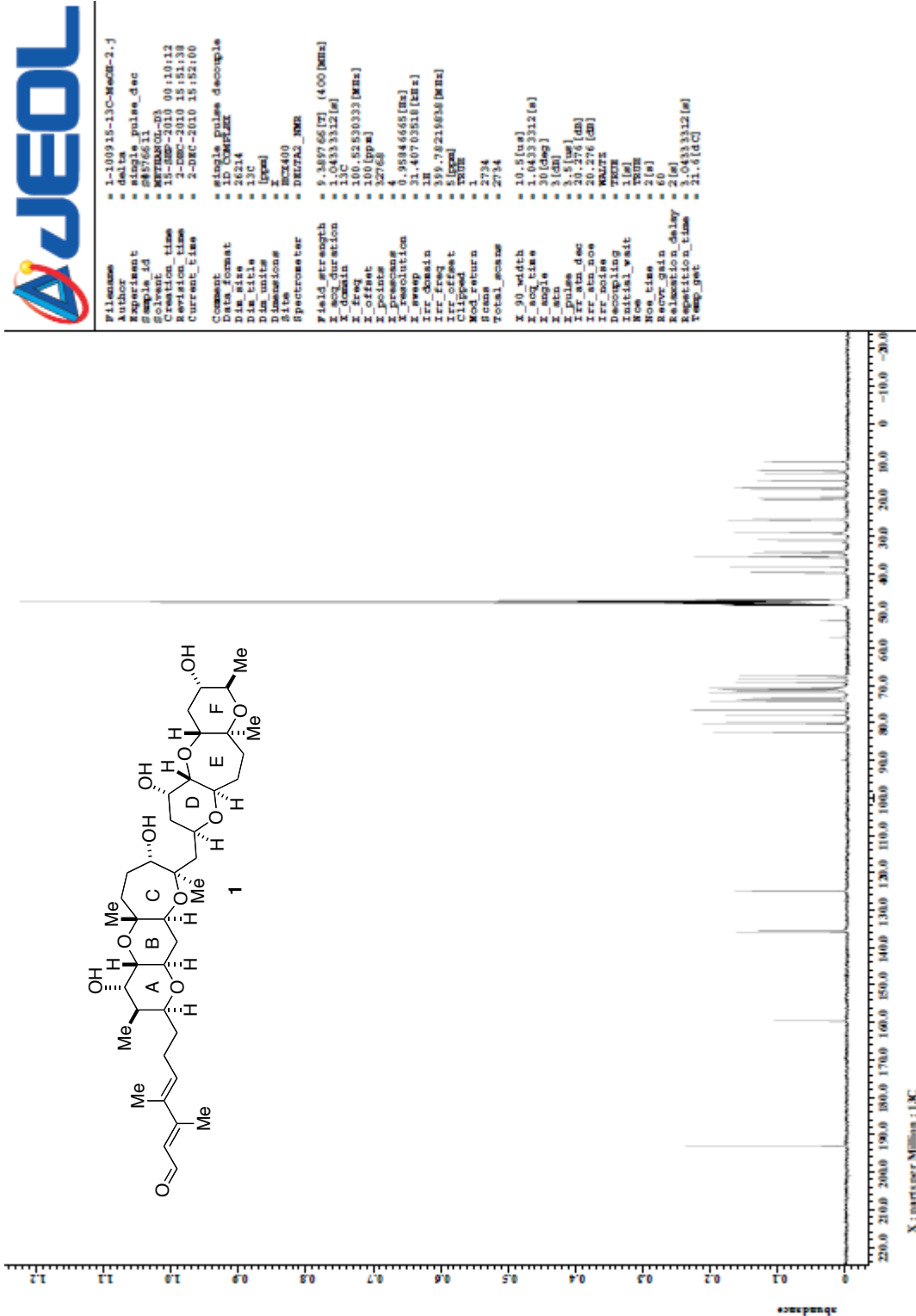
Filebase = 3-100913-13C-2_3df
Author = delta
Experiment = single_pulse_dec
Sample_id = 0434752
Solvent = CDCl3
Creation_time = 13-SEP-2010 18:29:28
Revision_time = 2-DEC-2010 18:52:09
Current_time = 2-DEC-2010 19:52:12
Comment = single_pulse decouple
Data_format = 1D COMPTX
Dir_size = 26214
Dir_title = 13C
Dir_units = lppm
Dimensions = 655x400
Size = DEUT2A2_NMR
Spectrometer = DEUT2A2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
Acq_duration = 1.04333312 [s]
F1_domain = 13C 125.030333 [MHz]
F2_domain = 100 [ppm]
X_points = 52768
X_prescans = 4
X_resolution = 0.25846665 [Hz]
X_sweep = 31.40703518 [Hz]
IR_domain = 18.78219830 [MHz]
IR_freq = 5 [ppm]
Clipped = 0
Mod_return = 1
Scans = 3479
Total_scans = 3479
X_90_width = 10.8 [us]
X_acq_time = 1.04333312 [s]
X_spla = 30 [dec]
X_atn = 3 [db]
X_pulse = 3.5 [us]
IR_atn_dec = 20.276 [db]
IR_atn_nox = 20.276 [db]
D1_delay = 0.000 [s]
Initial_wait = 1 [s]
Nox_time = 2 [s]
Recvr_gain = 60
Relaxation_delay = 2 [s]
Repetition_time = 1.04333312 [s]
Temp_jct = 31 [C]
    
```



brevisin (1)



brevisin (1)



¹³C NMR spectrum of natural brevisin

