Supporting Information for

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

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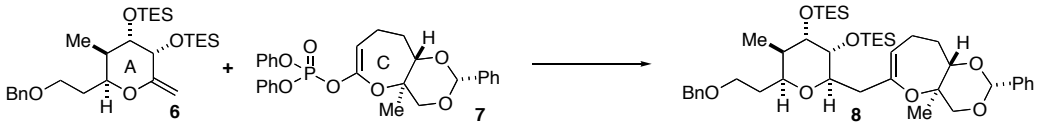
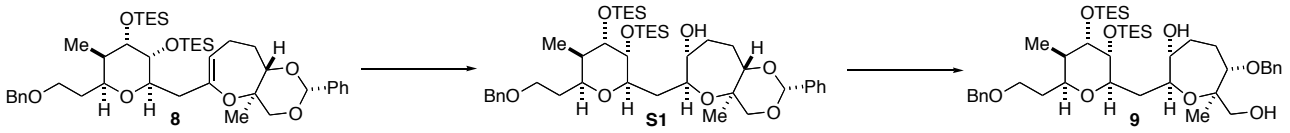
General methods: All moisture and/or air sensitive reactions were carried out in oven-dried (>100 °C) glassware under argon atmosphere unless otherwise noted. Anhydrous dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Inc. Other solvents 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 F_{254} 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 ^{13}C spectra were recorded on a JEOL ECA-500 and ECX-400 spectrometer and calibrated with residual undeuterated solvent as an internal reference [^1H NMR, $CHCl_3$ (7.24), C_6HD_5 (7.15), CHD_2OD (3.31), C_5HD_4N (7.58); ^{13}C NMR, $CDCl_3$ (77.0), C_6D_6 (128.0), CD_3OD (49.0), C_5D_5N (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 Cs_2CO_3 (5.5 mL), the ketene acetal phosphate **7** (1.35 g, 2.73 mmol) in DMF (15 mL + 9.0 mL rinse) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (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 Et_2O. The combined organic fractions were washed with brine, dried over Na_2SO_4, 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 Et_3N, 2nd: 2% acetone/hexane, containing 0.5% of Et_3N) to afford the enol ether **8** (1.76 g, 86%) as a colorless oil: $[\alpha]_D^{28}$ 73.4 (*c* 0.0273, C_6H_6); IR (film) 2952, 2875, 2360, 1750, 1698, 1540, 1454, 1105, 1017, 734, 696, 670 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 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); ^{13}C NMR (100 MHz, C_6D_6) 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 $C_{43}H_{68}O_7Si_2$ $[M+H]^+$ 753.4576, found 753.4578.

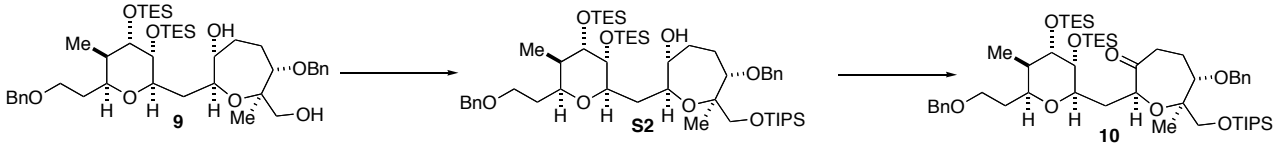
diol **9**



To a solution of the enol ether **8** (31.0 mg, 0.0412 mmol) in THF (1 mL) was added $BH_3 \cdot SMe_2$ (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: $[\alpha]_D^{28}$ –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 $C_{43}H_{70}O_8Si_2Na$ $[M+Na]^+$ 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: $[\alpha]_D^{27}$ –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 $C_{43}H_{72}O_8Si_2Na$ $[M+Na]^+$ 795.4658, found 795.4677.

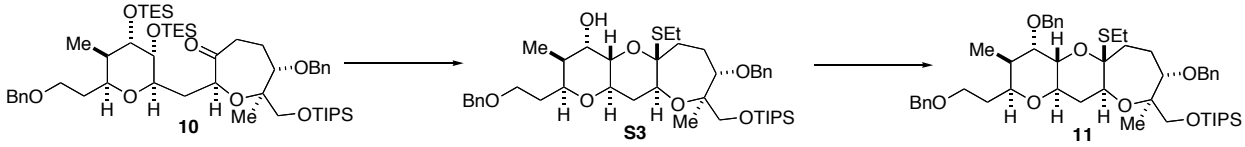
ketone **10**



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 $MgSO_4$, 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 CH_2Cl_2 (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: $[\alpha]_D^{27}$ –49.1 (*c* 0.402, $CHCl_3$); IR (film) 2952, 2875, 2360, 1716, 1540, 1456, 1106, 1004, 734, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{52}H_{90}O_8Si_3Na$ $[M+Na]^+$ 949.5836, found 949.5864.

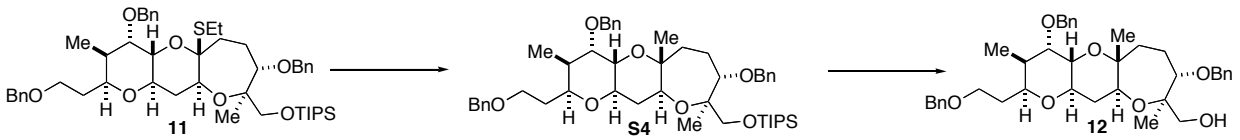
mixed thioacetal **11**



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 Et_3N 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 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 (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, $CHCl_3$); IR (film) 3747, 2939, 2865, 2360, 1650, 1540, 1455, 1108, 885, 808, 737, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{49}H_{72}O_7SSiNa$ $[M+Na]^+$ 855.4660, found 855.4670.

alcohol **12**

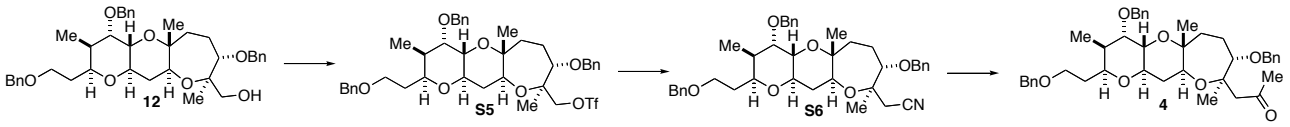


*m*CPBA (65%, 1.10 g, 4.14 mmol) in CH_2Cl_2 (20 mL) was washed twice with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (8 mL), which was used in the next reaction.

To a solution of mixed thioacetal **11** (670 mg, 0.804 mmol) in CH_2Cl_2 (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 Me_3Al (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 $MgSO_4$, 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 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 (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, $CHCl_3$); IR (film) 3748, 2933, 2868, 2360, 1650, 1560, 1457, 1097, 1064, 737, 699, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{39}H_{51}O_7$ $[M+H]^+$ 631.3629, found 631.3618.

ketone **4**

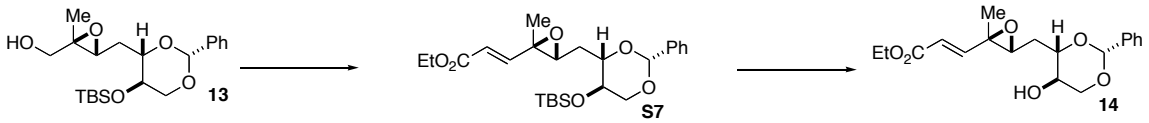


To a solution of alcohol **12** (30.3 mg, 0.0481 mmol) in CH_2Cl_2 (2 mL) at –78 °C were added 2,6-lutidine (0.10 mL, 0.86 mmol) and Tf_2O (0.050 mL, 0.30 mmol). The resultant solution was stirred for 15 min and quenched with Et_3N and saturated aqueous $NaHCO_3$. The aqueous phase was extracted three 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 °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 °C. After stirring at the same temperature for 20 min, the reaction mixture was allowed to warm to 0 °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: $[\alpha]_D^{28}$ 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 $C_{41}H_{52}O_7Na$ $[M+Na]^+$ 679.3605, found 679.3597.

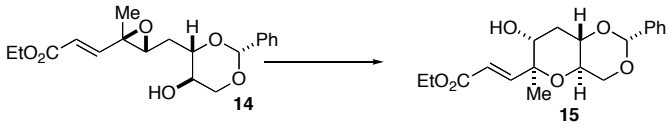
hydroxy epoxide **14**



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, $Ph_3P{=}CHCO_2Me$ (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.

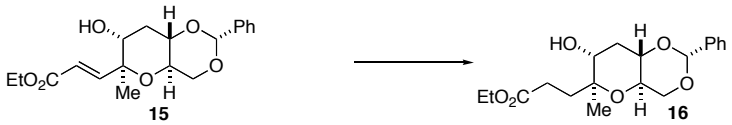
To a solution of **S7** was added a stock solution of TBAF/AcOH [0.1 M solution prepared from TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol), AcOH (0.30 mL, 5.2 mmol), and THF (44.7 mL), 50.0 mL, 5.0 mmol] at room temperature. The reaction mixture was stirred at room temperature for 13 h, and then quenched with 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: $[\alpha]_D^{28}$ –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 $C_{19}H_{24}O_6Na$ $[M+Na]^+$ 349.1465, found 349.1450.

pyran **15**



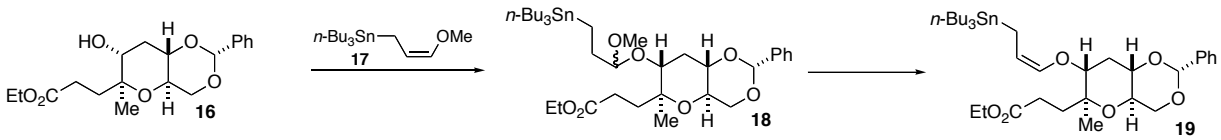
To a solution of the hydroxy epoxide **14** (3.52 g, 10.1 mmol) in CH_2Cl_2 (200 mL) at room temperature was added PPTS (3.51 g, 14.0 mmol). After stirring for 4 h, PPTS (1.54 g, 6.13 mmol) was added. The resultant mixture was stirred for 1 h, quenched with Et_3N and concentrated under reduced pressure. 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, $CHCl_3$); IR (film) 3748, 3463, 2982, 2360, 1715, 1653, 1456, 1369, 1305, 1187, 1092, 1019, 985, 754, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{19}H_{25}O_6$ $[M+H]^+$ 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, $CHCl_3$); IR (film) 3838, 3747, 3446, 2980, 2945, 2360, 1731, 1540, 1455, 1374, 1290, 1186, 1098, 1017, 754, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{19}H_{27}O_6$ $[M+H]^+$ 351.1802, found 351.1808.

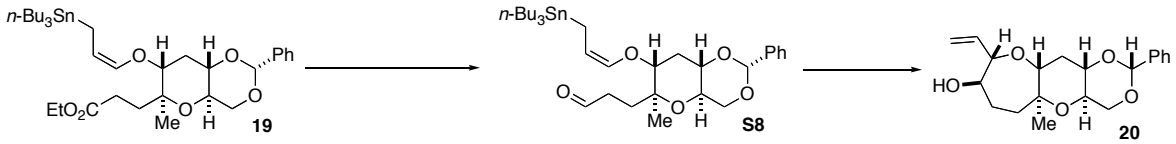
allylstannane **19**



To a solution of ester **16** (43.2 mg, 0.123 mmol) in CH_2Cl_2 (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 Et_3N and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (10% ethyl acetate/hexane, containing 0.5% of Et_3N) 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 CH_2Cl_2 (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 $NaHCO_3$ was added. 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. The residue was subjected to column chromatography on silica gel (3–5% ethyl acetate/hexane, containing 0.5% of Et_3N) to afford allylstannane **19** (44.0 mg, 56% for 2 steps) as a colorless oil: $[\alpha]_D^{28}$ 28.7 (*c* 0.0516, C_6H_6); IR (film) 3747, 2959, 2360, 1735, 1650, 1457, 1374, 1181, 1094, 1020, 750, 693 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 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); ^{13}C NMR (100 MHz, C_6D_6) 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 $C_{34}H_{57}O_6Sn$ $[M+H]^+$ 681.3172, found 681.3171.

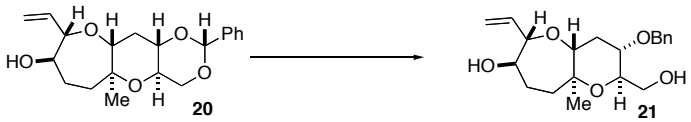
alcohol **20**



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.

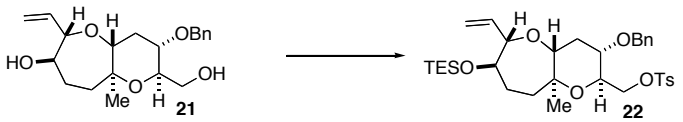
To a solution aldehyde **S8** in CH_2Cl_2 (3 mL) was added $BF_3{\cdot}Et_2O$ (0.010 mL, 0.079 mmol) at –78 °C. After stirring at the same temperature for 5 min, the resultant mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous phase was extracted three times with EtOAc. The combined organic 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: $[\alpha]_D^{25}$ –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 $C_{20}H_{27}O_5$ $[M+H]^+$ 347.1853, found 347.1867.

diol **21**



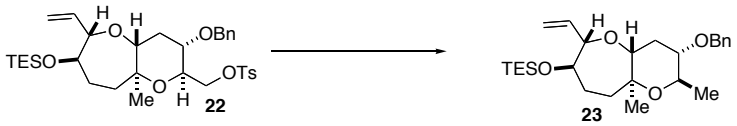
To a solution of alcohol **20** (205 mg, 0.592 mmol) in CH_2Cl_2 (6 mL) was added DIBALH (1.0 M in hexane, 3.0 mL, 3.0 mmol) at 0 °C. After stirring at room temperature for 22 h, the reaction was quenched with saturated aqueous potassium sodium tartrate. The mixture was diluted with ethyl acetate and 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: $[\alpha]_D^{25}$ 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 $C_{20}H_{29}O_5$ $[M+H]^+$ 349.2010, found 349.2009.

tosylate **22**



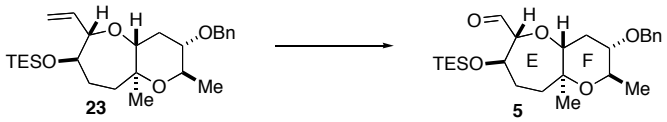
To a solution of diol **21** (101 mg, 0.290 mmol) in CH_2Cl_2 (6 mL) at 0 °C were added Et_3N (0.20 mL, 1.43 mmol), DMAP (4.5 mg, 0.037 mmol) and *p*-TsCl (65.0 mg, 0.341 mmol). After stirring at the same temperature for 14.5 h, *p*-TsCl (60.0 mg, 0.315 mmol) was added. The resultant mixture was stirred 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 NH_4Cl. The aqueous phase was extracted twice 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 twice (1st and 2nd: 10% ethyl acetate/hexane) to afford tosylate **22** (136 mg, 76%) as a colorless oil: $[\alpha]_D^{25}$ 38.6 (*c* 0.0230, $CHCl_3$); IR (film) 3447, 2920, 2360, 1650, 1540, 1093, 808, 748, 671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{33}H_{48}O_7SiSNa$ $[M+Na]^+$ 639.2782, found 639.2784.

olefin **23**



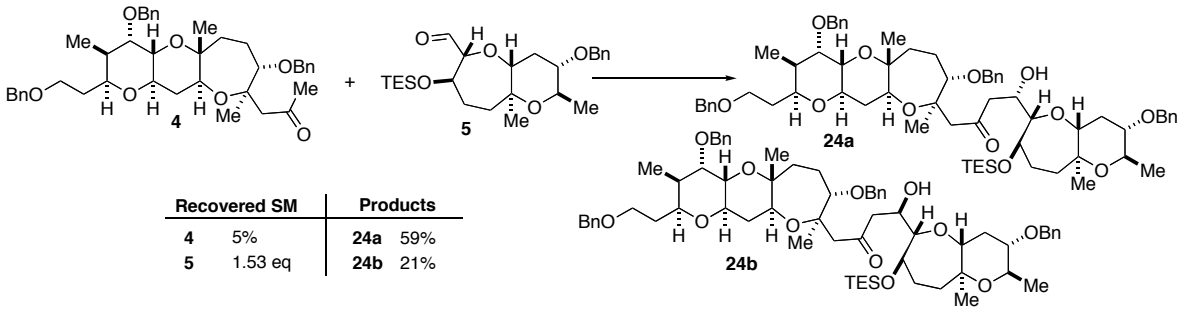
To a solution of tosylate **22** (136 mg, 0.221 mmol) in THF (5.5 mL) at 0 °C was added $LiAlH_4$ (101 mg, 2.66 mmol). The resultant mixture was gradually warmed to room temperature, stirred for 23 h, and then quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture was diluted 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 $MgSO_4$, 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: $[\alpha]_D^{28}$ 23.8 (*c* 0.138, $CHCl_3$); IR (film) 3447, 2945, 2882, 2360, 1650, 1457, 1096, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{26}H_{43}O_4Si$ $[M+H]^+$ 447.2925, found 447.2931.

aldehyde **5**



A solution of olefin **23** (58.0 mg, 0.130 mmol) in CH_2Cl_2 (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 PPh_3 (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: $[\alpha]_D^{25}$ 36.7 (*c* 1.35, $CHCl_3$); IR (film) 2952, 2879, 1736, 1455, 1376, 1239, 1097, 1002, 812, 739, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{25}H_{41}O_5Si$ $[M+H]^+$ 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 °C. After stirred at 0 °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 °C. After stirring at 0 °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 °C. The reaction mixture was stirred at –78 °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.

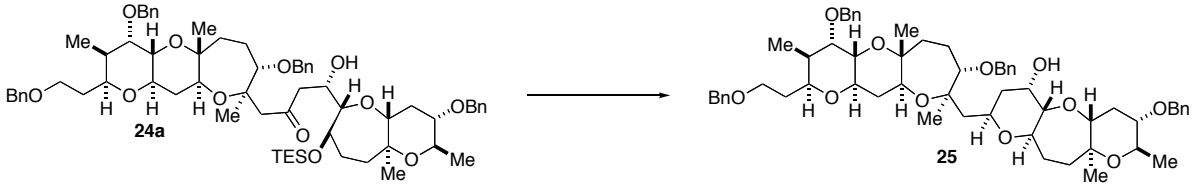
data for **24a**: $[\alpha]_D^{28}$ 2.33 (*c* 0.166, $CHCl_3$); IR (film) 3743, 3455, 2947, 2882, 2360, 1697, 1457, 1380, 1096, 1065, 735, 699, 676 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.31 (m, 8H), 7.29–7.25 (m, 8H), 7.22–7.21 (m, 4H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.3 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.34 (d, *J* = 11.8 Hz, 1H), 4.23 (d, *J* = 6.3 Hz, 1H), 3.98 (ddd, *J* = 9.2, 2.9, 2.9 Hz, 1H), 3.78 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.68 (dddd, *J* = 8.0, 8.0, 4.6, 2.9 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 Hz, 1H), 2.89 (d, *J* = 5.0 Hz, 1H), 2.80 (dd, *J* = 17.6, 2.5 Hz, 1H), 2.69 (d, *J* = 13.0 Hz, 1H), 2.65 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.23 (d, *J* = 13.4 Hz, 1H), 2.20 (ddd, *J* = 11.8, 4.6, 4.6 Hz, 1H), 2.02–1.88 (m, 3H), 1.84 (ddd, *J* = 11.3, 4.6, 4.6 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 Hz, 3H), 1.13 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.90 (d, *J* = 7.6 Hz, 3H), 0.59 (q, *J* = 8.0 Hz, 6H); ^{13}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 $C_{66}H_{92}O_{12}SiNa$ $[M+Na]^+$ 1127.6250, found 1127.6234.

data for **24b**:

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

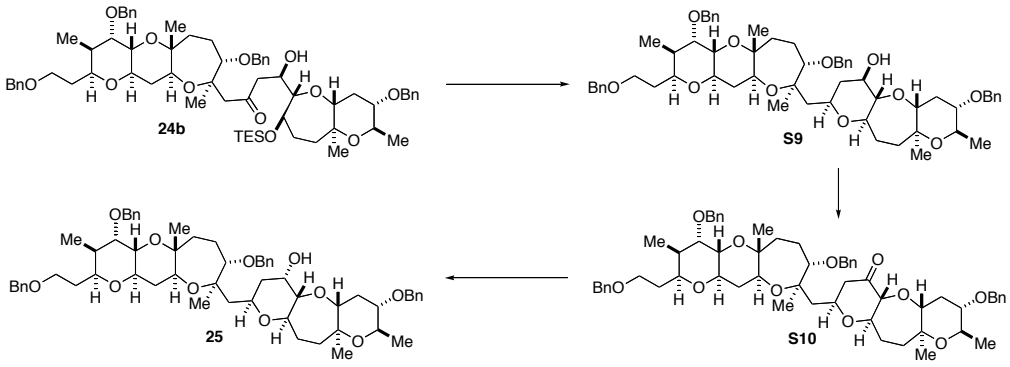
693, 671 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 8H), 7.29–7.25 (m, 8H), 7.23–7.20 (m, 4H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 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 $C_{66}H_{92}O_{12}SiNa$ $[M+Na]^+$ 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 °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: $[\alpha]_D^{28}$ 13.1 (*c* 0.106, $CHCl_3$); IR (film) 3743, 3447, 2933, 2868, 2360, 1650, 1560, 1453, 1381, 1082, 737, 699, 676 cm^{-1}; ^1H 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}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 $C_{60}H_{78}O_{11}Na$ $[M+Na]^+$ 997.5436, found 997.5430.

alcohol **25** (**24b** → **25**)

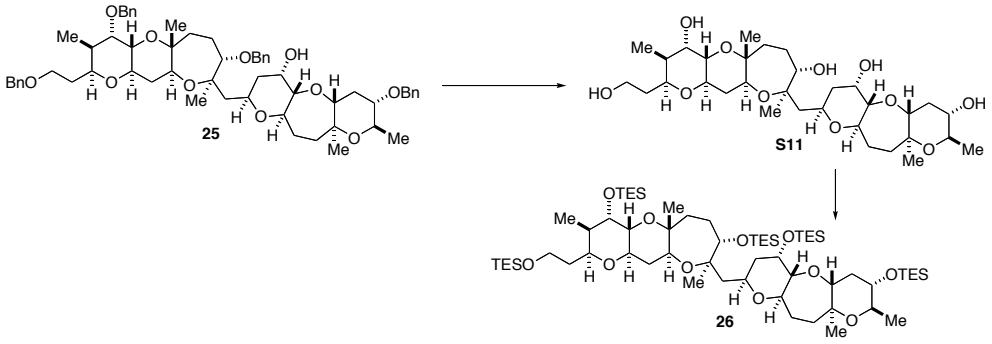


To a solution of the ketone **24b** (36.5 mg, 0.0330 mmol) in CH_2Cl_2 (6 mL) and Et_3SiH (2.0 mL) at –78 °C was added dropwise TMSOTf (0.1 M in CH_2Cl_2, 2.0 mL, 0.20 mmol). After stirring for 20 min, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted three times 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 $C_{60}H_{78}O_{11}Na$ $[M+Na]^+$ 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 °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).

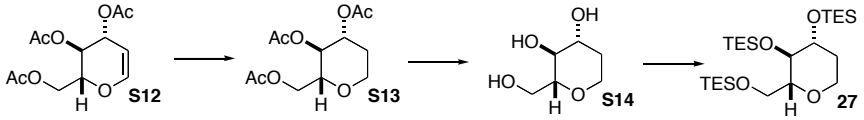
pentakis-TES ether **26**



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/$CHCl_3$) to afford crude pentaol **S11**, which was used in the next reaction without further purification.

To a solution of **S11** in CH_2Cl_2 (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 $NaHCO_3$. The aqueous phase was extracted twice 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 twice (1st: 5% ethyl acetate/hexane, 2nd: 2% ethyl acetate/hexane) to afford pentakis-TES ether **26** (882 mg, 84%) as a colorless oil: $[\alpha]_D^{28}$ 8.89 (*c* 0.0970, $CHCl_3$); IR (film) 3743, 3438, 2945, 2868, 2360, 1650, 1560, 1451, 1386, 1084, 1014, 827, 744, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{62}H_{124}O_{11}Si_5Na$ $[M+Na]^+$ 1207.7882, found 1207.7870.

tris-TES ether **27**

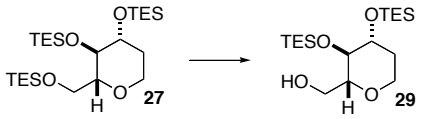


To a solution of tri-*O*-acetyl-D-glucal (**S12**) (820 mg, 3.01 mmol) in EtOAc (20 mL) was added 5% Pd/C (110 mg). The reaction mixture was stirred at room temperature for 6 h under a hydrogen atmosphere. The mixture was filtered through a pad of Celite® and concentrated under reduced pressure to afford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

To a solution of **S13** in MeOH (15 mL) was added K_2CO_3 (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.

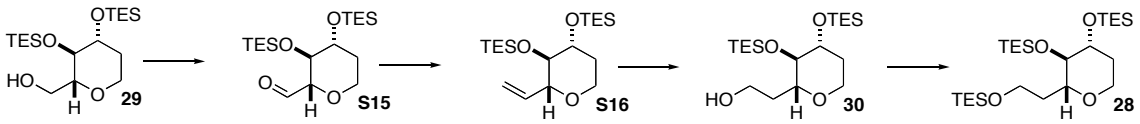
To a solution of **S14** in CH_2Cl_2 (60 mL) at 0 °C were added 2,6-lutidine (2.80 mL, 24.2 mmol) and TESOTf (2.70 mL, 12.0 mmol). The resultant solution was stirred for 20 min and quenched with saturated aqueous $NaHCO_3$. The aqueous phase was extracted twice with EtOAc. The combined organic fractions were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel twice (1st and 2nd: 3% ethyl acetate/hexane) to afford tris-TES ether **27** (780 mg, 53% for 3 steps) as a colorless oil: $[\alpha]_D^{28}$ 8.64 (*c* 0.754, $CHCl_3$); IR (film) 2954, 2907, 2360, 1459, 1239, 1129, 1105, 1007, 981, 811, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{24}H_{54}O_4Si_3Na$ $[M+Na]^+$ 513.3222, found 513.3212.

alcohol **29**



To a solution of tris-TES ether **27** (780 mg, 1.59 mmol) in CH_2Cl_2 (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 $MgSO_4$, 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, $CHCl_3$); IR (film) 3469, 2954, 2877, 2360, 1459, 1415, 1380, 1239, 1127, 1103, 1007, 943, 808, 739, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{18}H_{40}O_4Si_2Na$ $[M+Na]^+$ 399.2357, found 399.2369.

tris-TES ether **28**



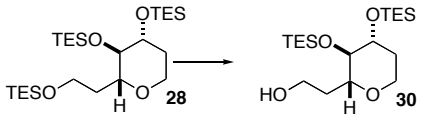
To a solution of alcohol **29** in CH_2Cl_2–DMSO (3:1, 8.0 mL) were added Et_3N (0.83 mL, 5.94 mmol) and SO_3·pyridine (601 mg, 3.78 mmol) at 0 °C. The resultant solution was stirred at room temperature for 1.5 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered, and concentrated to afford crude aldehyde **S15**, which was used in the next reaction without further purification.

To a suspension of $Ph_3P^+CH_3Br^-$ (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 NH_4Cl. The aqueous phase was extracted twice 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 (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% H_2O_2 (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 $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (20% ethyl acetate/hexane) to afford alcohol **30**, which was used in the next reaction.

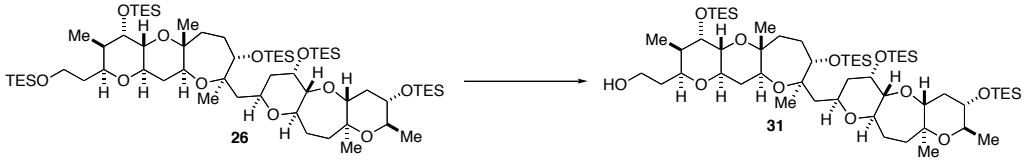
To a solution of alcohol **30** in CH_2Cl_2 (4.0 mL) at 0 °C were added 2,6-lutidine (0.073 mL, 0.632 mmol) and TESOTf (0.11 mL, 0.505 mmol). The resultant solution was stirred for 15 min and quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted twice with EtOAc. The combined organic 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 (5% ethyl acetate/hexane) to afford tris-TES ether **28** (210 mg, 87% for 2 steps) as a colorless oil: $[\alpha]_D^{28}$ 7.02 (*c* 0.246, $CHCl_3$); IR (film) 2954, 2877, 2360, 1458, 1412, 1380, 1239, 1127, 1103, 1007, 809, 739, 673 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{25}H_{57}O_4Si_3$ $[M+H]^+$ 505.3559, found 505.3559.

alcohol **30**



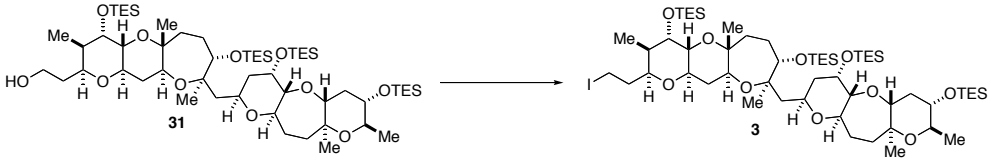
To a solution of tris-TES ether **28** (201 mg, 0.398 mmol) in CH_2Cl_2 (4.0 mL) was added DIBALH (1.0 M in hexane, 2.0 mL, 2.0 mmol) at –40 °C. After stirring at the same temperature for 30 min, the resultant mixture was quenched with EtOAc and saturated aqueous potassium sodium tartrate. The mixture 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: $[\alpha]_D^{28}$ 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 $C_{19}H_{42}O_4Si_2Na$ $[M+Na]^+$ 413.2514, found 413.2529.

alcohol **31**



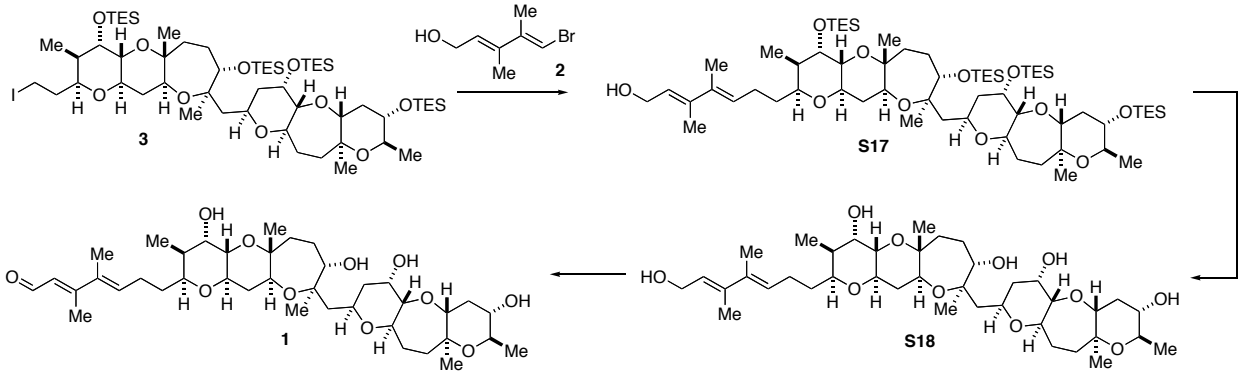
To a solution of pentakis-TES ether **26** (201 mg, 0.169 mmol) in CH_2Cl_2 (5.0 mL) was added DIBALH (1.0 M in hexane, 1.7 mL, 1.7 mmol) at –40 °C. After stirring at the same temperature for 30 min, the mixture was gradually warmed up to –20 °C over 20 min and stirred at –20 °C for 1 h. Then the resultant 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: $[\alpha]_D^{28}$ 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 $C_{56}H_{110}O_{11}Si_4Na$ $[M+Na]^+$ 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), PPh_3 (145 mg, 0.553 mmol), and I_2 (240 mg, 0.946 mmol). After stirring at room temperature for 30 min, the reaction was quenched with saturated aqueous Na_2SO_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/hexane) to afford iodide **3** (171 mg, 97%) as a colorless oil: $[\alpha]_D^{28}$ 14.8 (*c* 0.118, $CHCl_3$); IR (film) 3441, 2952, 2875, 2361, 1460, 1376, 1236, 1106, 1085, 1057, 997, 959, 831, 727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{56}H_{109}IO_{10}Si_4Na$ $[M+Na]^+$ 1203.6035, found 1203.6085.

brevisin (**1**)



To a solution of iodide **3** (159 mg, 0.134 mmol) in Et_2O (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 Cs_2CO_3 (0.90 mL), bromodienol **2** (99.0 mg, 0.518 mmol) in DMF (2.0 mL + 1.0 mL rinse) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (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 $MgSO_4$, 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 NH_4Cl. The aqueous phase was extracted five 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 (5–10% MeOH/$CHCl_3$) to afford crude **S18**, which was used in the next reaction without further purification.

To the solution of **S18** in CH_2Cl_2 (5 mL) was added MnO_2 (290 mg) at 0 °C. After stirring for 15 min, MnO_2 (310 mg) was added to the solution. The mixture was stirred at 0 °C for 1 h, MnO_2 (310 mg) was added. After stirring for 1 h, the reaction mixture was directly subjected to column chromatography on silica gel (3–5% MeOH/$CHCl_3$) to afford brevisin **1** (71.2 mg, 75% for 3 steps) as a colorless amorphous solid.

Data for synthetic **1**:

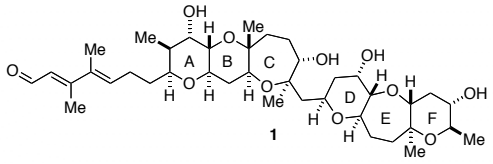
$[\alpha]_D^{28}$ –25.6 (*c* 0.0620, MeOH)
IR (film) 3442, 2933, 2360, 1647, 1458, 1420, 1380, 1123, 1084, 1046 cm^{-1}

^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 $C_{39}H_{62}O_{11}Na$ $[M+Na]^+$ 729.4184, found 729.4192.

ıthetic

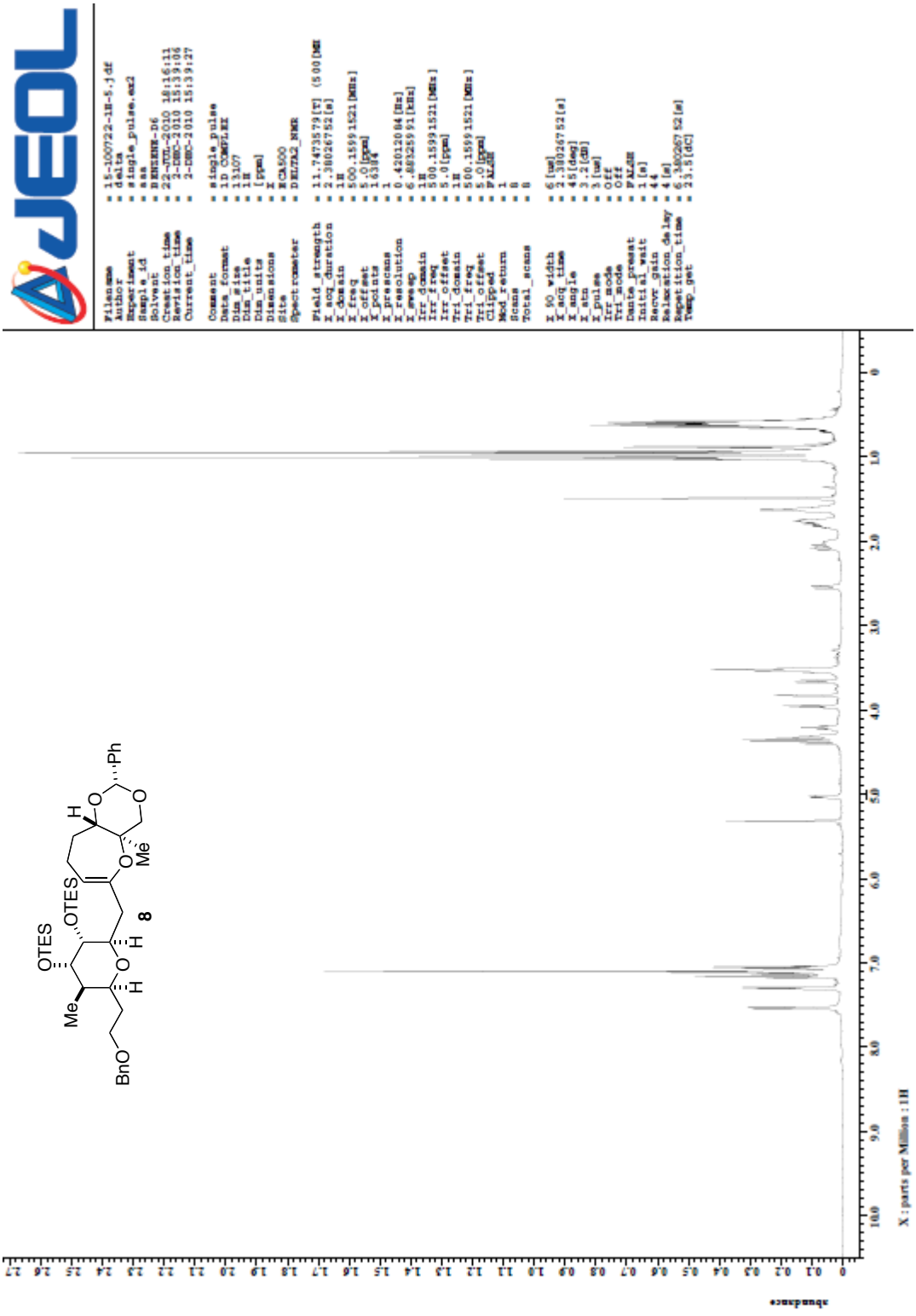


tural

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

^{1}H NMR in Methanol-d_4 (500 M Hz)

enol **8**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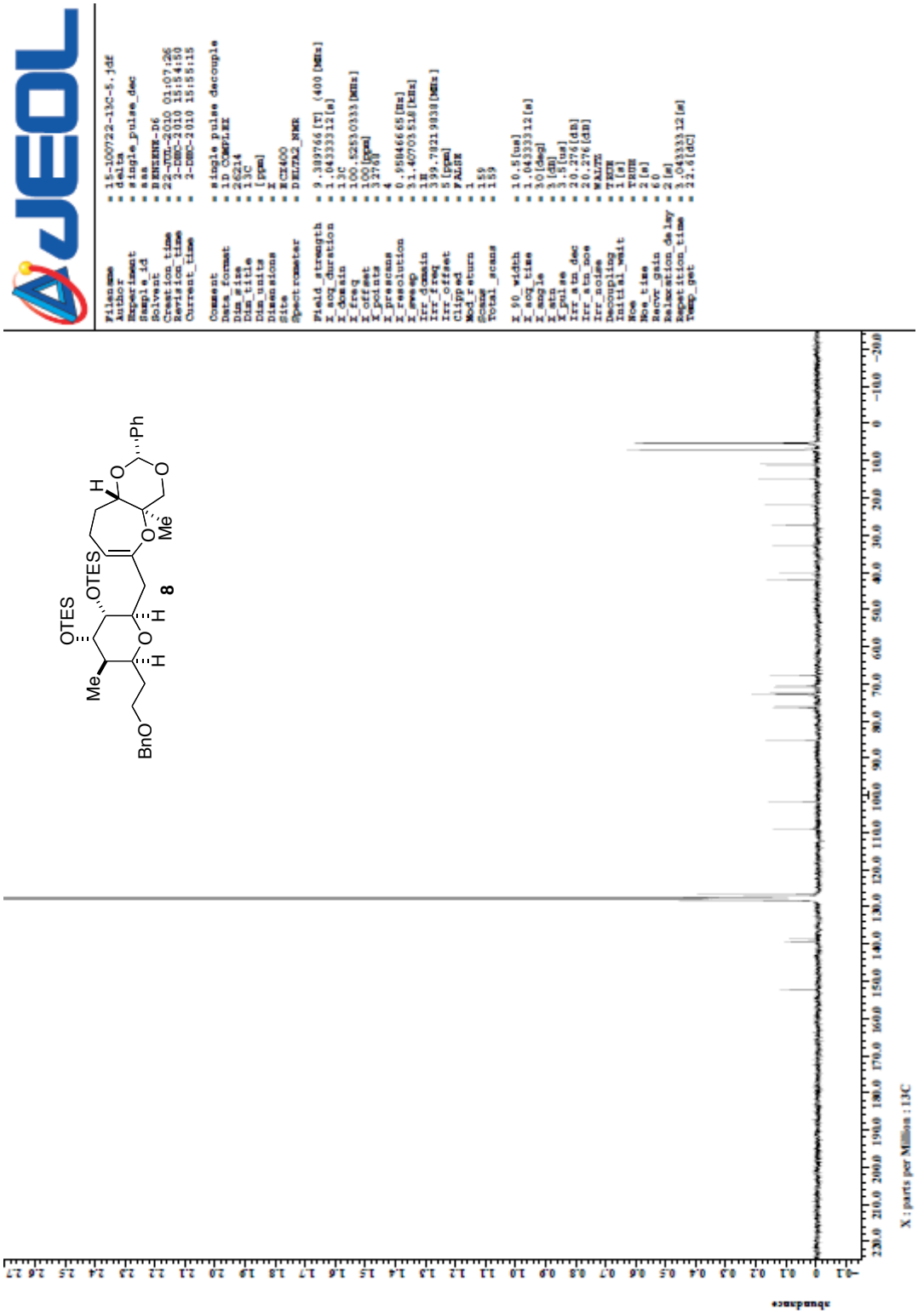
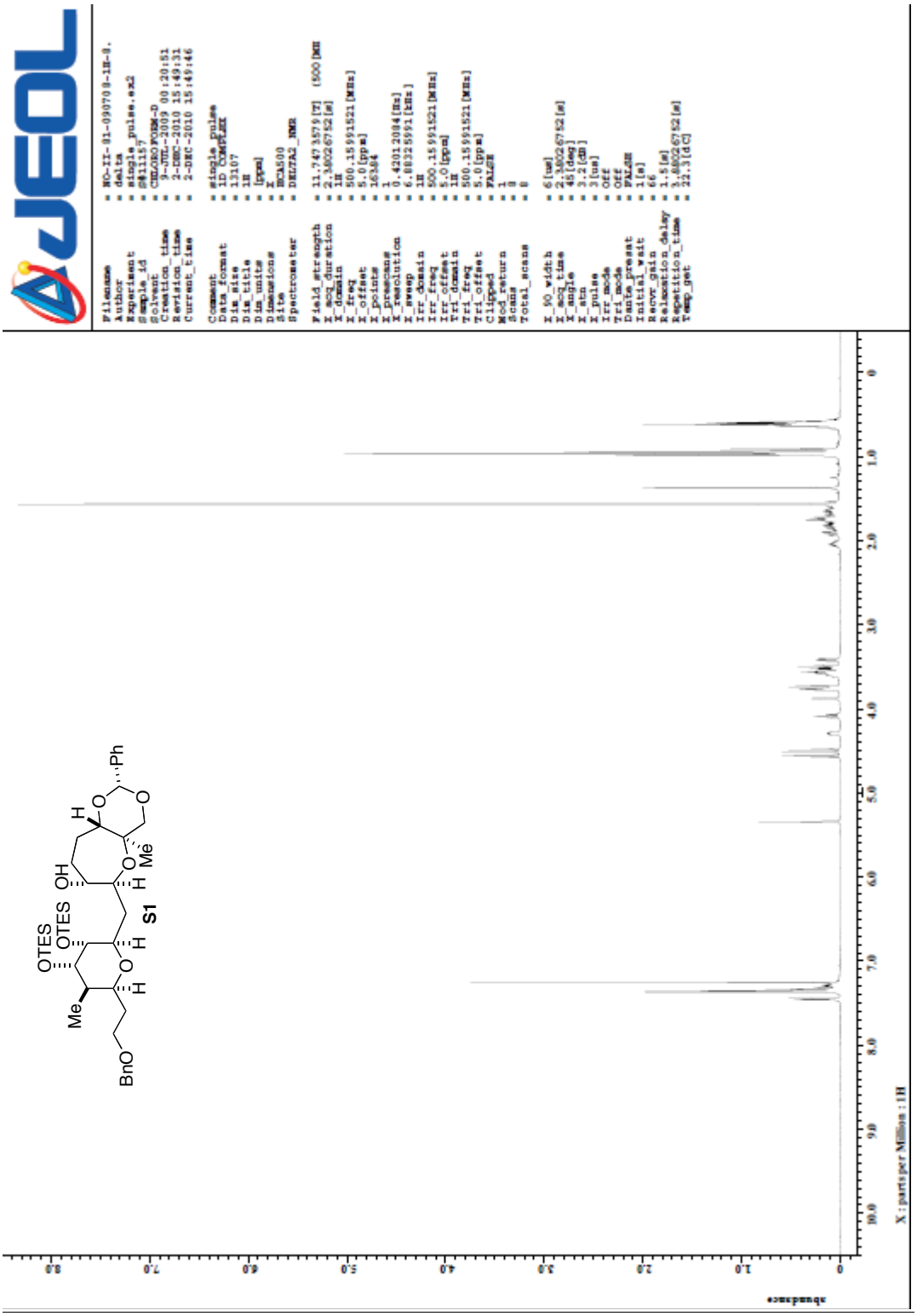
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Data_format = FALSE
Initial_wait = 1[s]
Recve_gain = 44
Relaxation_delay = 4[s]
Repetition_time = 6.3802675 2[s]
Temp_get = 23.5[deg]
OTES
OTES
Me
H
O
H
8
H
O
O
Ph
O
Me
BnO
abundance
X : parts per Million : 1H

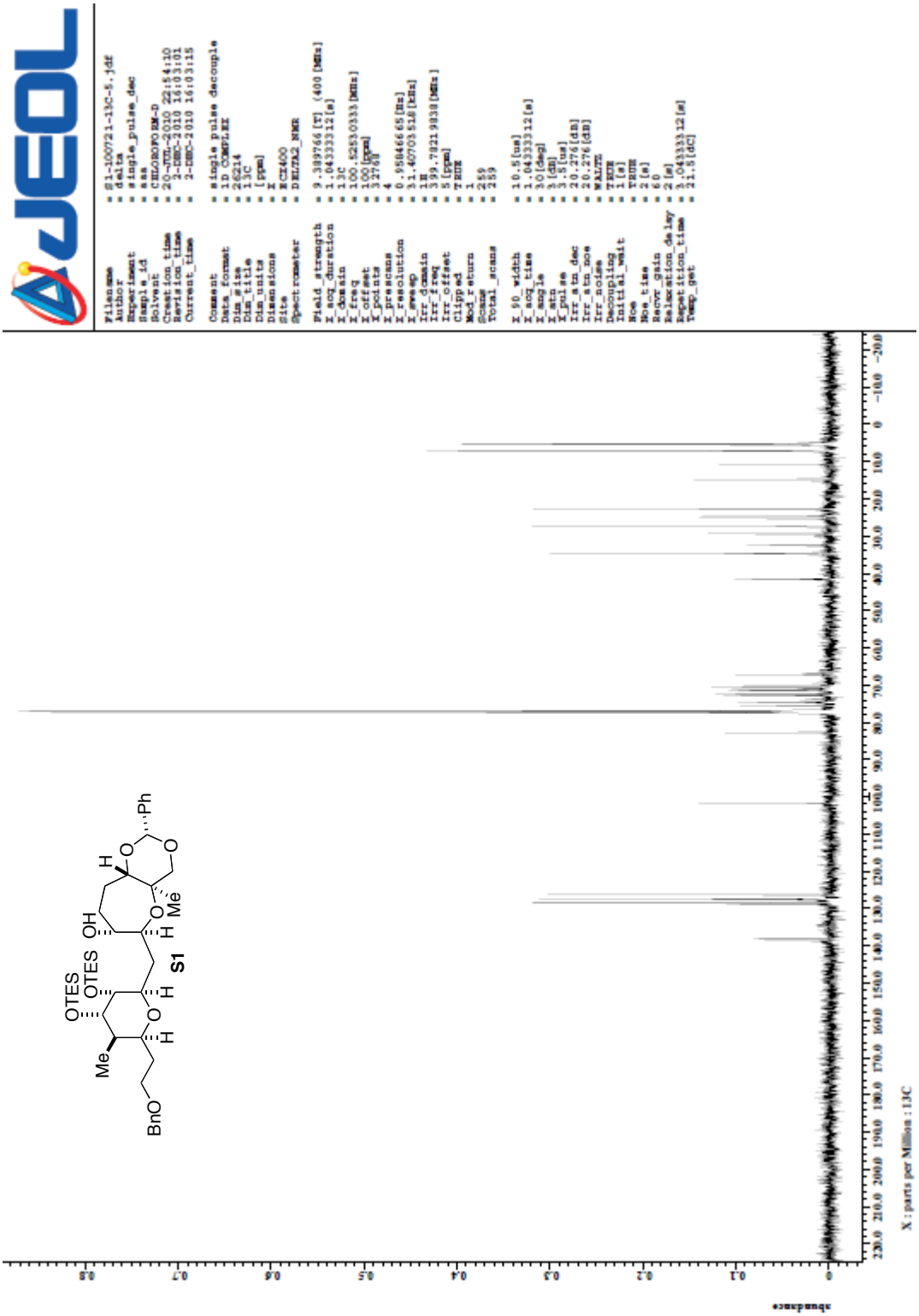
enol **8**


Ph
O
H
O
O
Me
OTES
OTES
8
H
O
H
Me
BnO
Filename = 15-100722-13C-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
Solvent = DMSOEM-D6
Creation_time = 22-JUL-2010 01:07:26
Revision_time = 2-DEC-2010 15:15:50
Current_time = 2-DEC-2010 15:15:15
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 24214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RX2400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.5253033[MHz]
X_offset = 3276[Hz]
X_points = 4
X_prescans = 0
X_resolution = 0.958466 65[Hz]
X_sweep = 31.40703 516[kHz]
Irr_domain = 1H
Irr_freq = 399.7821 9838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@nuc = 159
Total_scans = 159
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]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recy_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.0433331 2[s]
Temp_get = 22.6[dC]
abundance
X : parts per Million : 13C

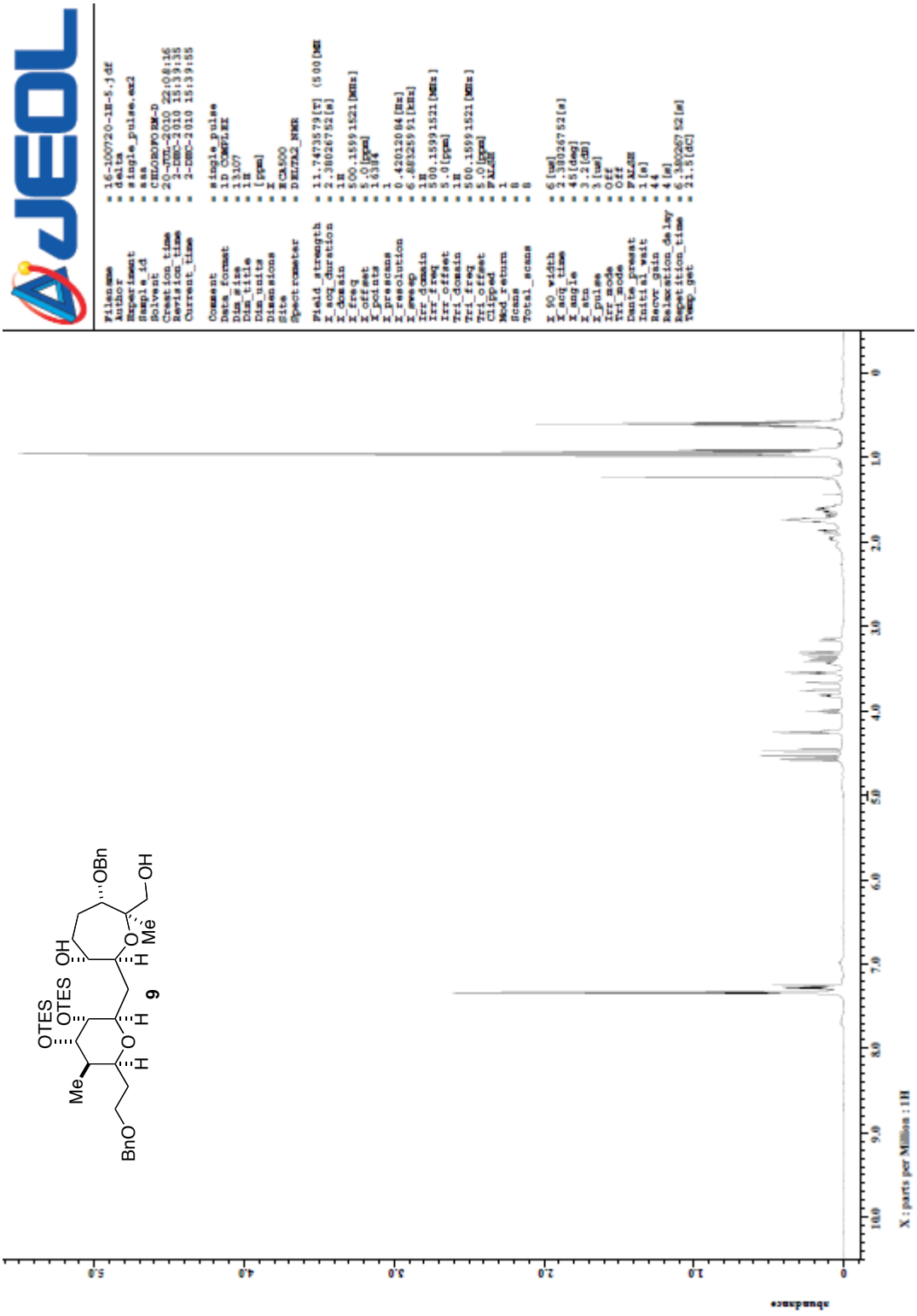
alcohol **S1**


JEOL
Filename = MO-II-01-090708-1H-8.
Author = delta
Experiment = single_pulse.ex2
Sample_id = #811157
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2009 00:20:51
Revision_time = 2-DEC-2010 15:49:31
Current_time = 2-DEC-2010 15:49:46
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = NCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.747357[T] (500[MH
X_acq_duration = 2.3602675[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325991[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.3602675[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decoupler_preset = PW60M
Initial_wait = 1[s]
Relaxation_delay = 6[s]
Repetition_time = 1.5[s]
Temp_get = 3.6602675[s]
= 22.3[dC]
OTES
OTES
OH
Me
BnO
Ph
S1
abundance
X : parts per Million : 1H

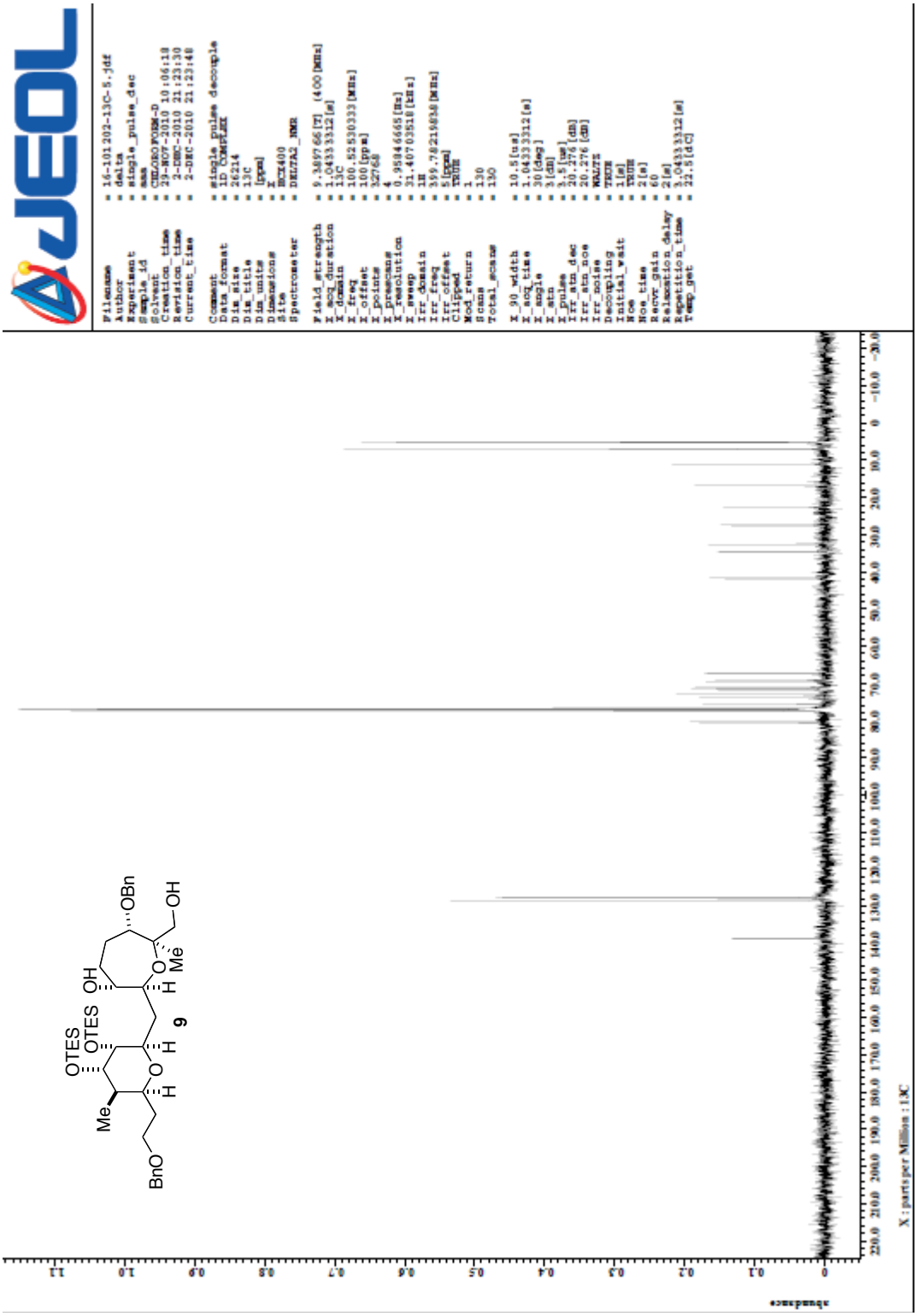
alcohol **S1**


JEOL
Filename = S1-100721-13C-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 20-JUL-2010 22:54:10
Revision_time = 2-DEC-2010 16:03:01
Current_time = 2-DEC-2010 16:03:15
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 259
Total_scans = 259
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.5[deg]
OTES
OTES
OH
Me
BnO
S1
Ph
Me
X : parts per Million : 13C
Abundance

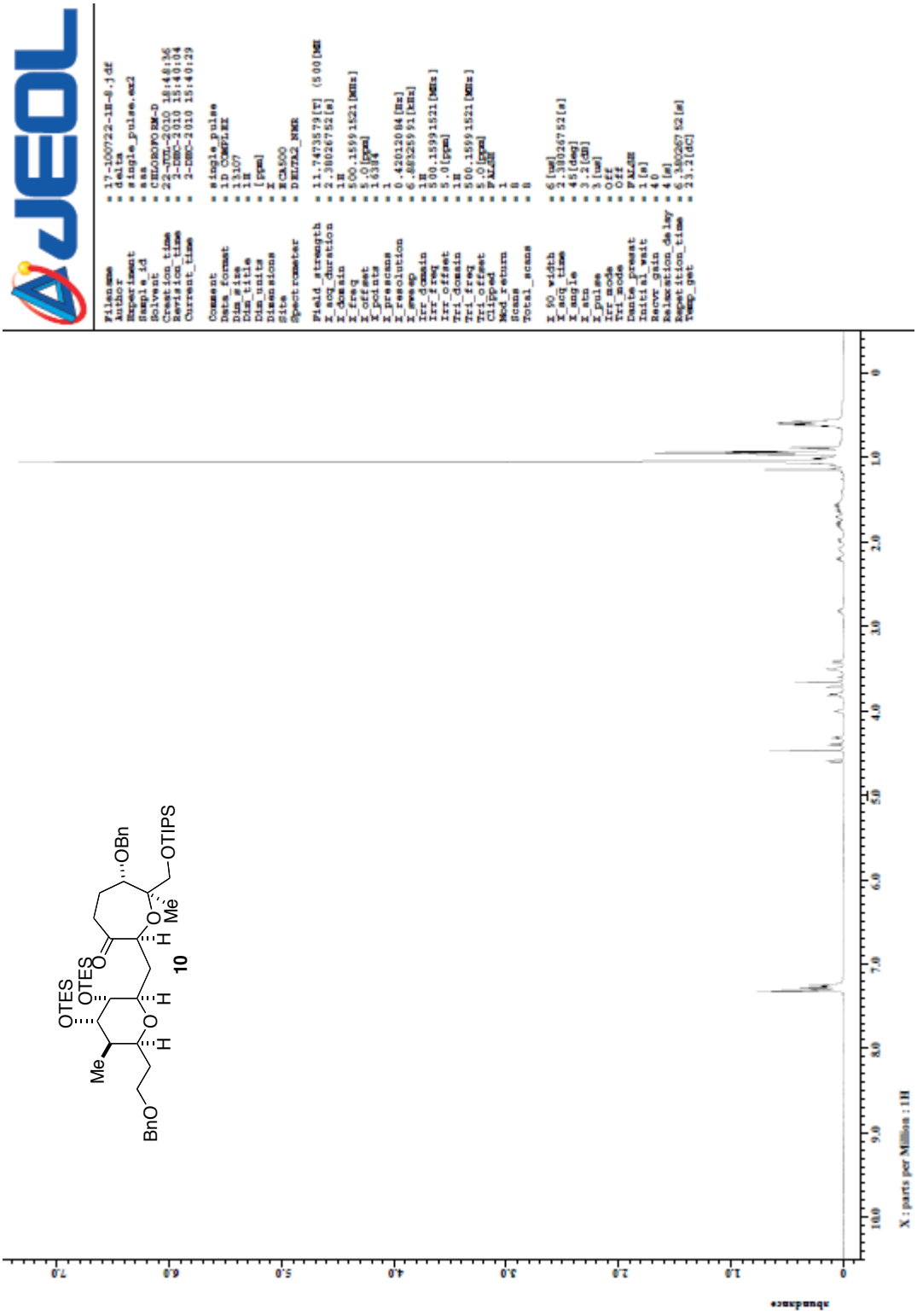
diol **9**


JEOL
Filename = 16-100720-1H-5.jdf
Author = delta
Experiment = single_pulse.exz
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 20-JUL-2010 22:08:16
Revision_time = 2-DEC-2010 15:39:35
Current_time = 2-DEC-2010 15:39:55
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RECA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Data_format = FALSE
Initial_wait = 1[s]
Recve_gain = 44
Relaxation_delay = 4[s]
Repetition_time = 6.38026752[s]
Temp_get = 21.5[dC]
OTES
OTES
OH
Me
BnO
OBn
OH
Me
9
abundance
X : parts per Million : 1H

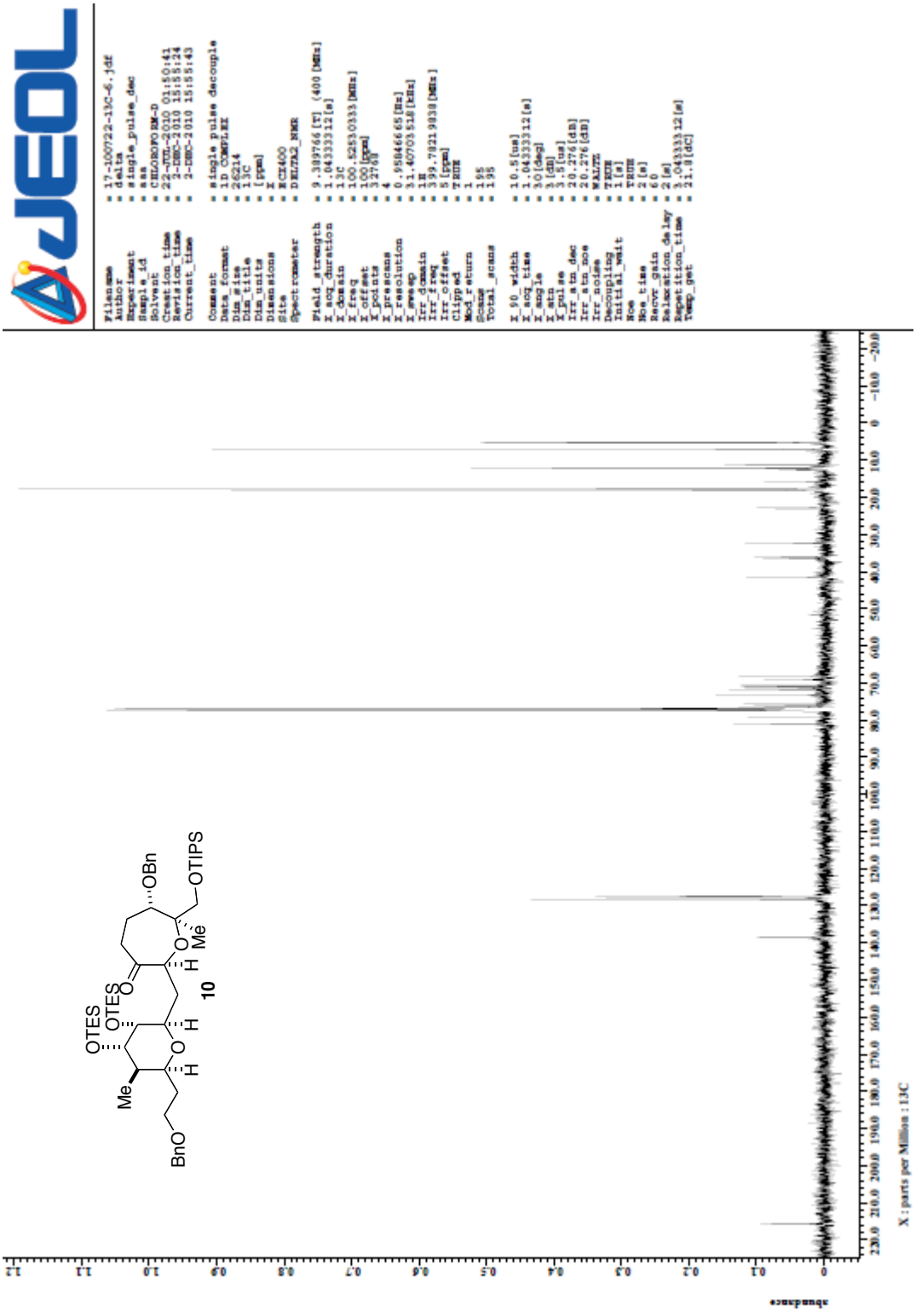
diol **9**


OTES
OTES
OH
OBn
OH
Me
H
H
H
O
O
H
Me
9
BnO
Abundance
X : parts per Million : 13C

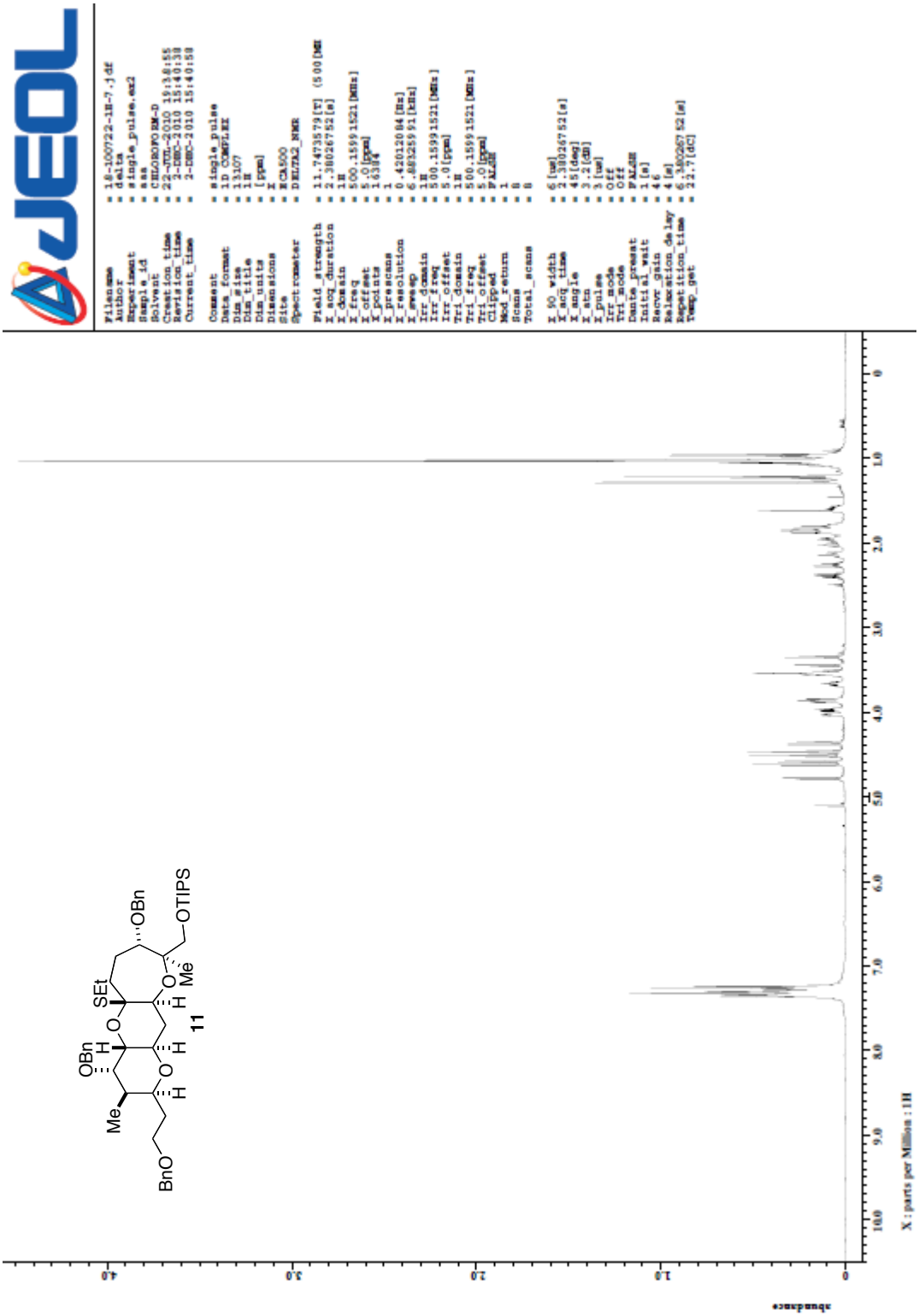
ketone **10**


JEOL
Filename = 17-100722-1H-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2010 18:48:36
Revision_time = 2-DEC-2010 15:40:04
Current_time = 2-DEC-2010 15:40:29
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Data_format = FALSE
Initial_wait = 1[s]
Recve_gain = 40
Relaxation_delay = 4[s]
Repetition_time = 6.38026752[s]
Temp_get = 23.2[dC]
OTES
OTES
Me
BnO
OBn
OTIPS
Me
10
abundance
X : parts per Million : 1H

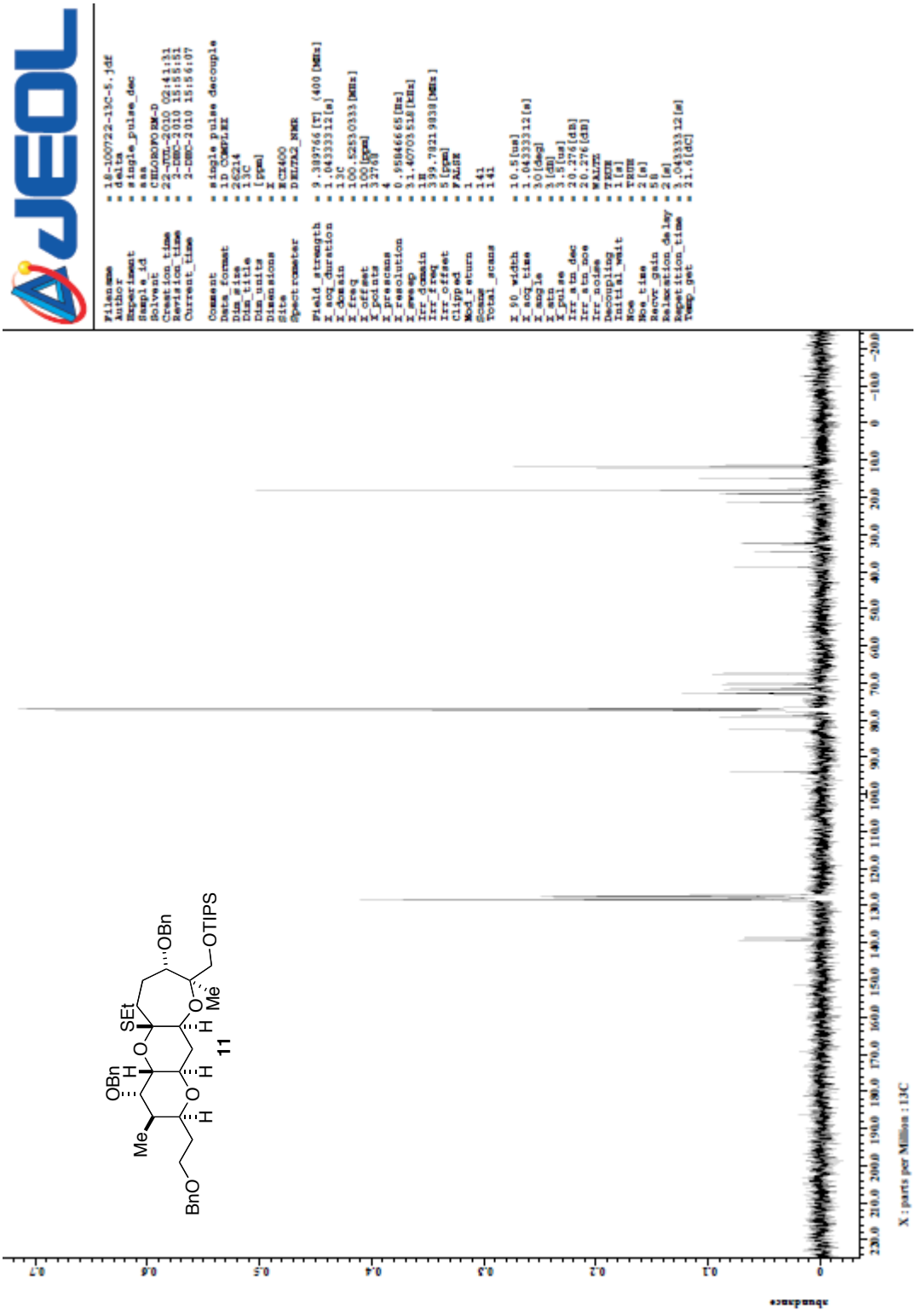
ketone **10**


JEOL
Filename = 17-100722-13C-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
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
Dim_size = 2214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 195
Total_scans = 195
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.8[degC]
OTES
OTES
Me
BnO
OBn
OTIPS
Me
10
abundance
X : parts per Million : 13C

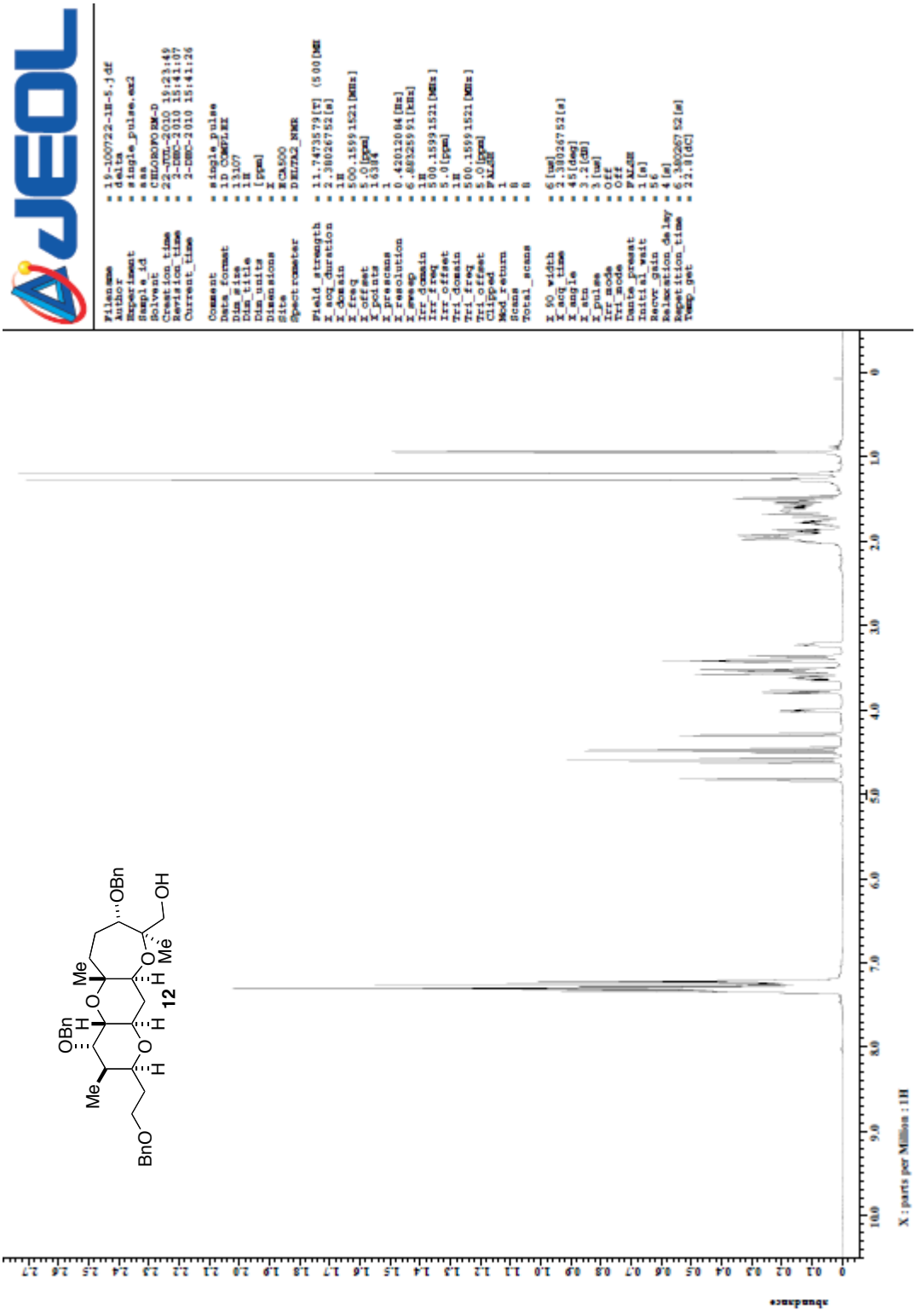
mixed thioacetal **11**



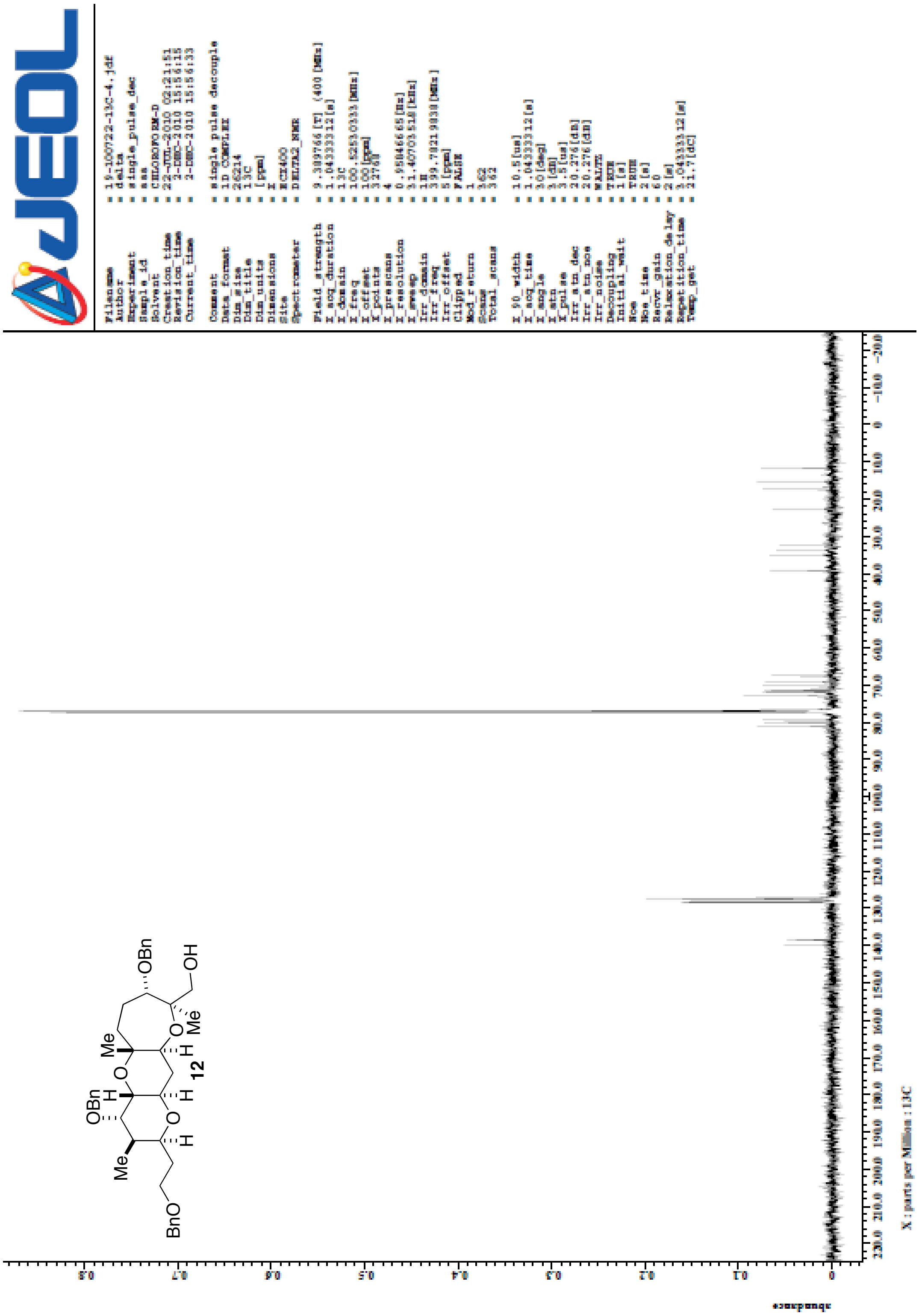
mixed thioacetal **11**



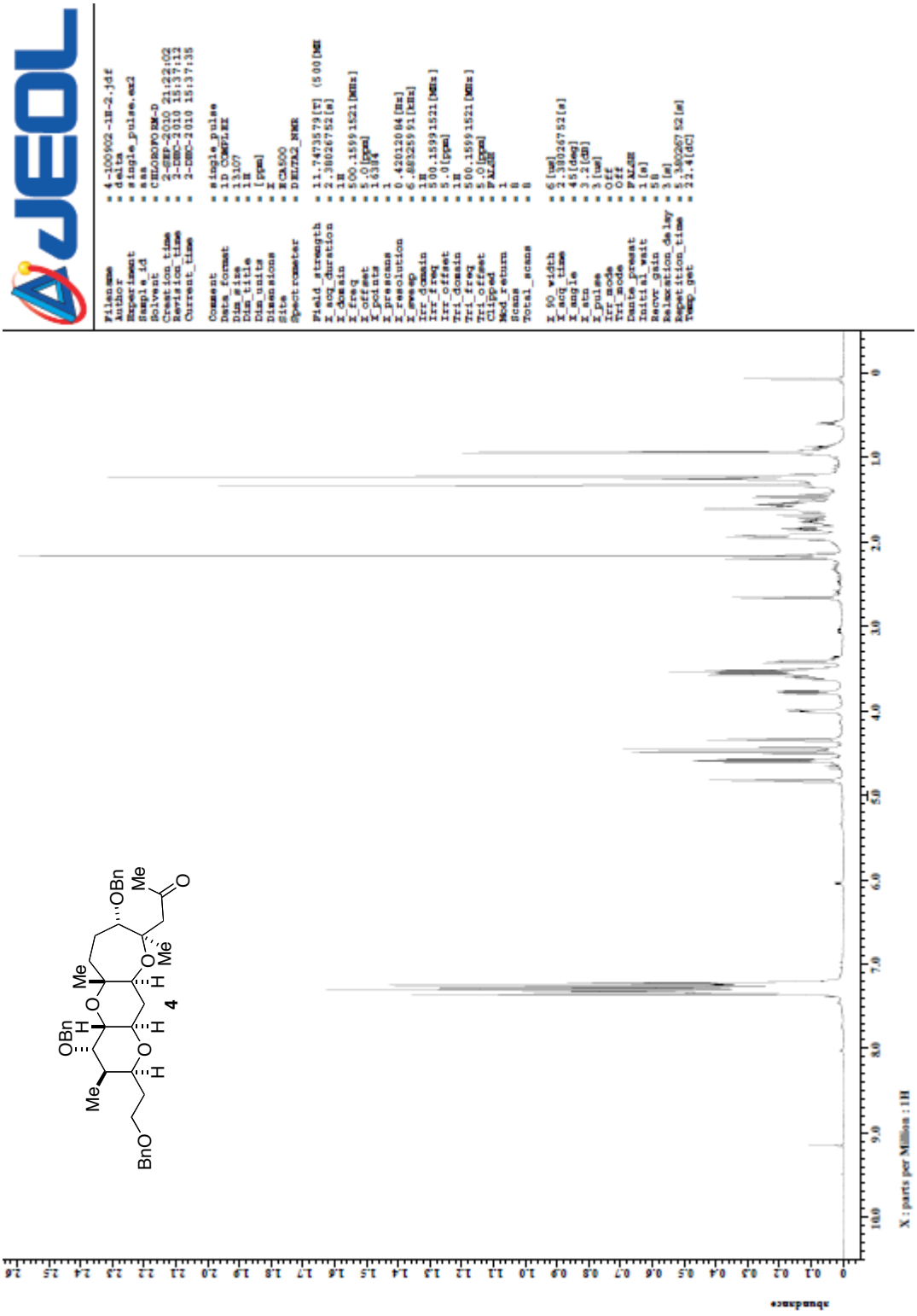
alcohol **12**


Filename = 19-100722-1H-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2010 19:23:49
Revision_time = 2-DEC-2010 15:41:07
Current_time = 2-DEC-2010 15:41:26
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = JEOL500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decm_present = FALSE
Initial_wait = 2[s]
Recyc_gain = 5.6
Relaxation_delay = 4[s]
Repetition_time = 6.38026752[s]
Temp_get = 23.0[deg]
OBn
OH
Me
O
H
12
BnO
abundance
X : parts per Million : 1H

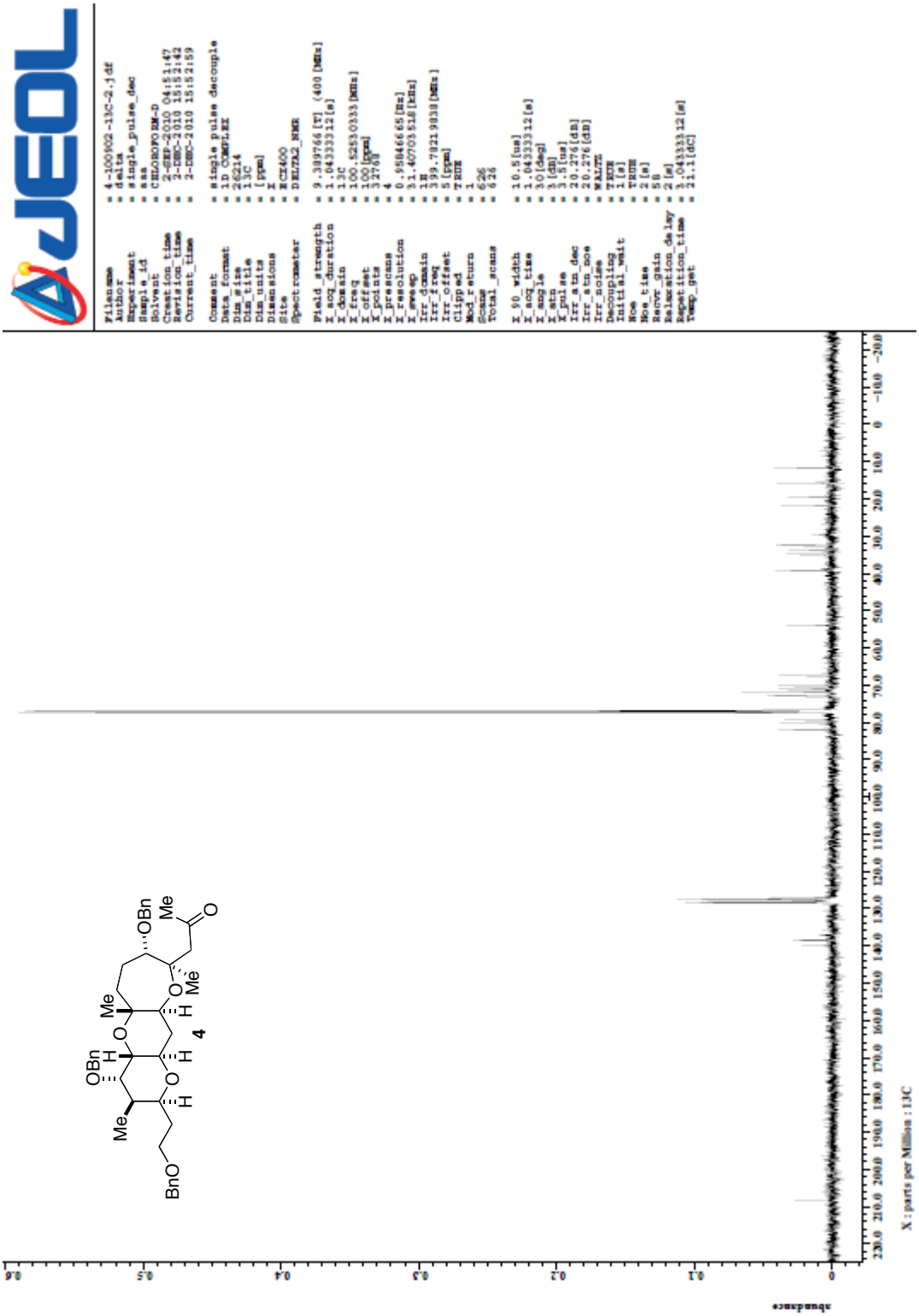
alcohol **12**



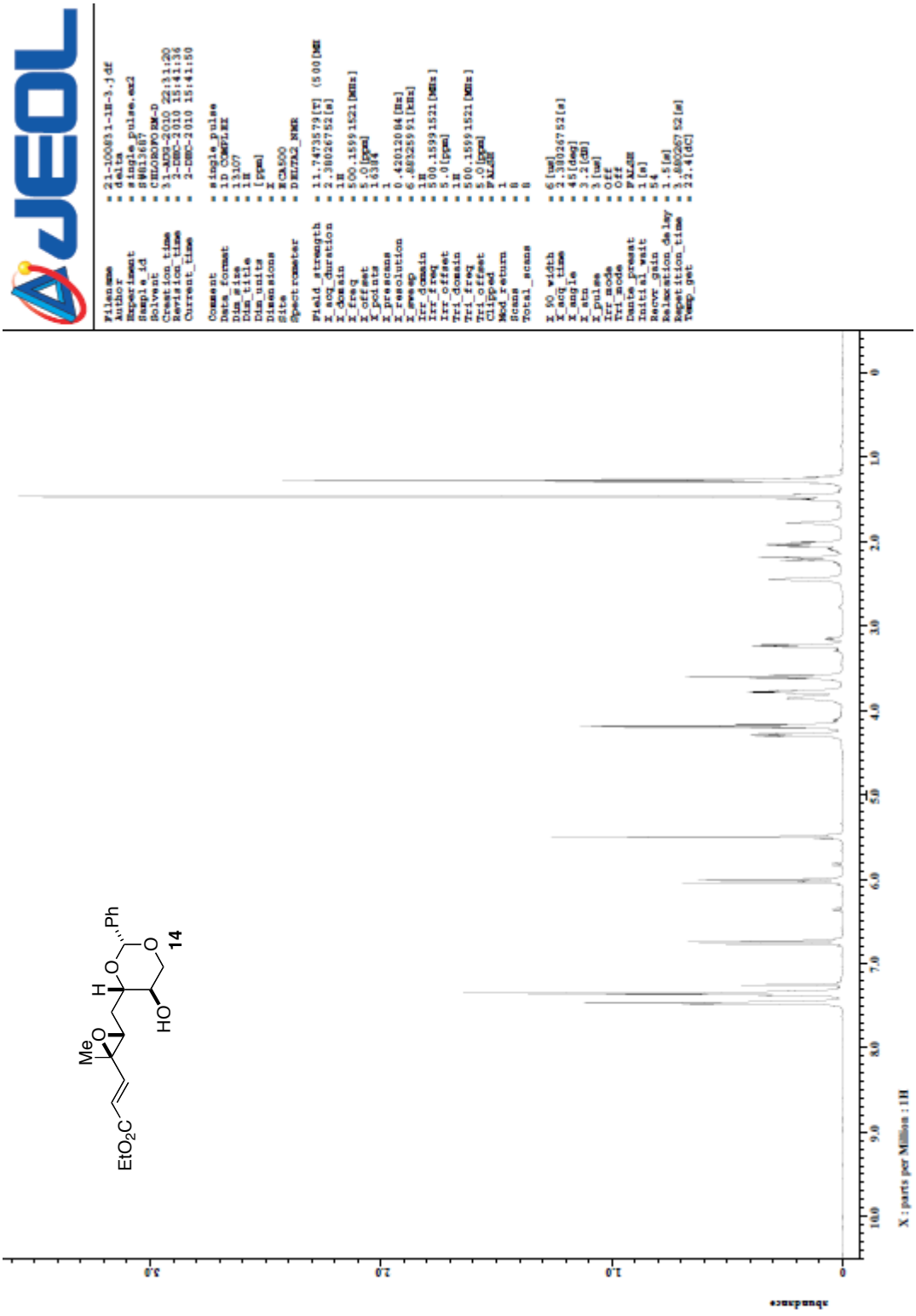
ketone **4**


Filename = 4-100902-1H-2.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-SEP-2010 21:22:02
Revision_time = 2-DEC-2010 15:17:12
Current_time = 2-DEC-2010 15:37:35
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.3802675 2[s]
X_domain = 1H
X_freq = 500.1599 1521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.4201208 4[Hz]
X_sweep = 6.8825899 1[kHz]
Irr_domain = 1H
Irr_freq = 500.1599 1521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.1599 1521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.3802675 2[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decm_present = FALSE
Initial_wait = 2[s]
Recve_gain = 58
Relaxation_delay = 3[s]
Repetition_time = 5.3802675 2[s]
Temp_get = 23.4[deg]
OBn
Me
O
Me
O
H
H
Me
OBn
H
O
H
Me
BnO
4
abundance
X : parts per Million : 1H

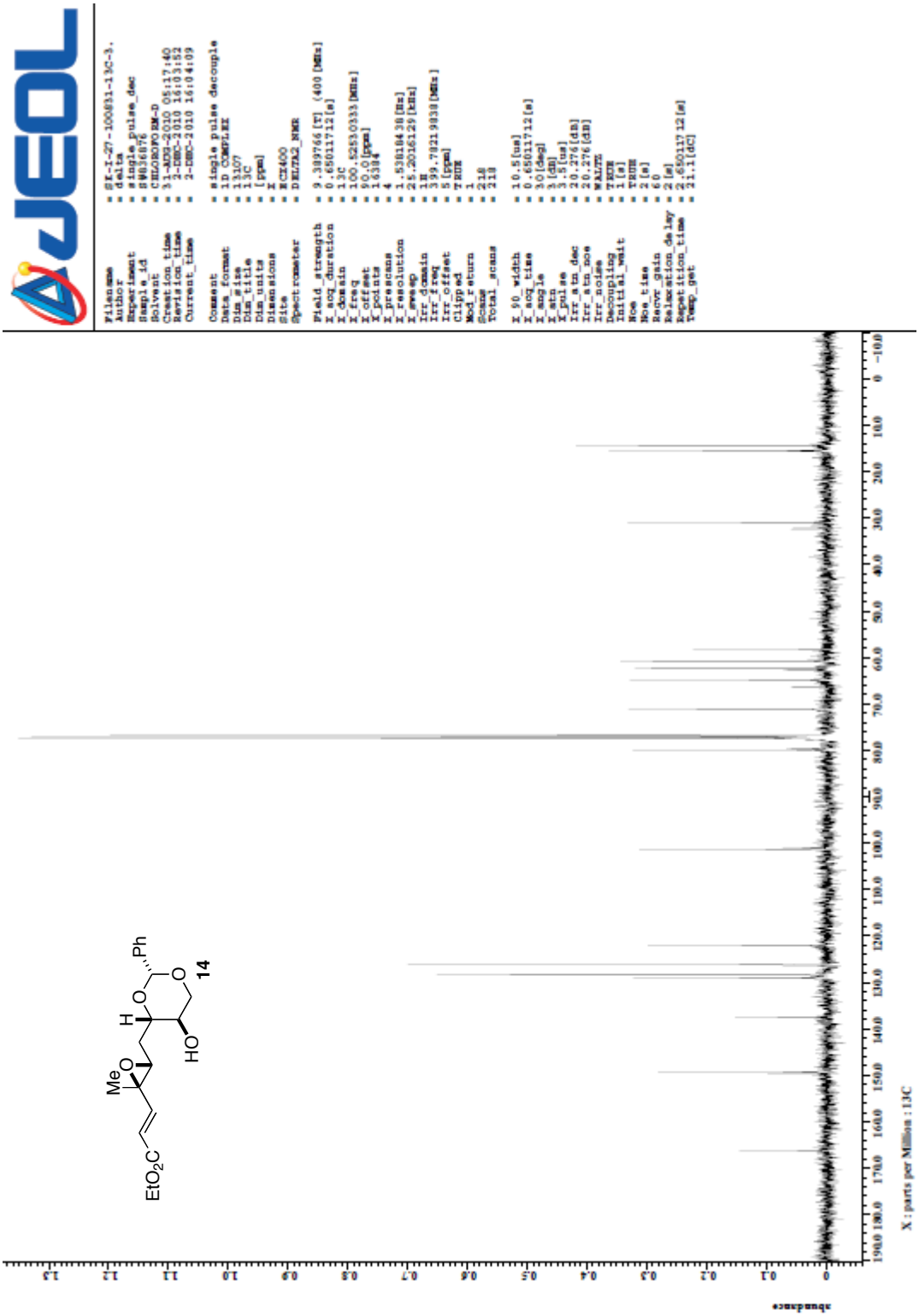
ketone **4**


Filename = 4-100902-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
Solvent = CHLOROFORM-D
Creation_time = 2-SEP-2010 04:51:47
Revision_time = 2-DEC-2010 15:52:42
Current_time = 2-DEC-2010 15:52:59
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32K
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 626
Total_scans = 626
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Recy_time = 2[s]
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.1[deg]
OBn
Me
O
Me
H
O
H
OBn
Me
O
H
Me
4
BnO
abundance
X : parts per Million : 13C

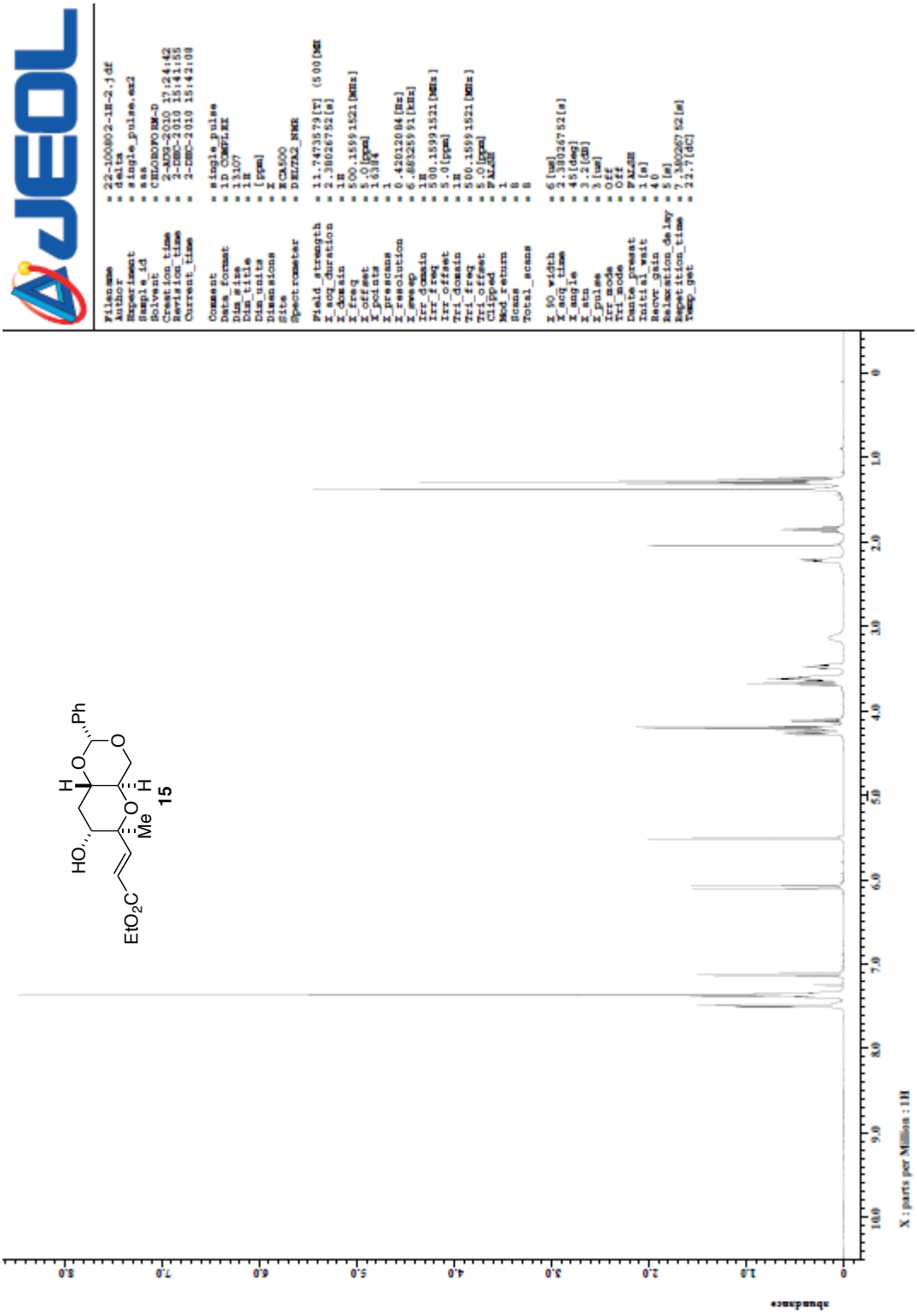
hydroxy epoxide **14**



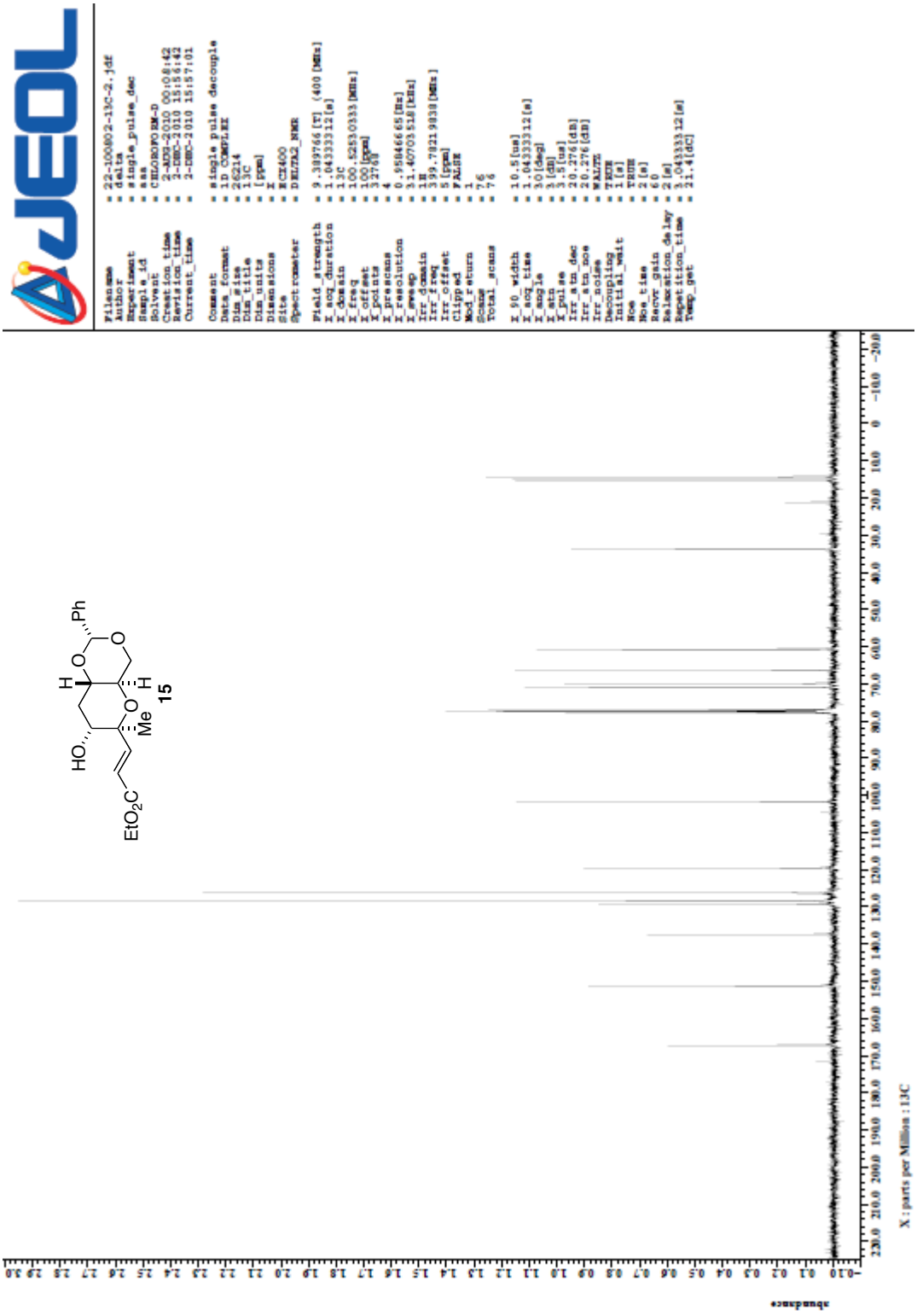
hydroxy epoxide **14**



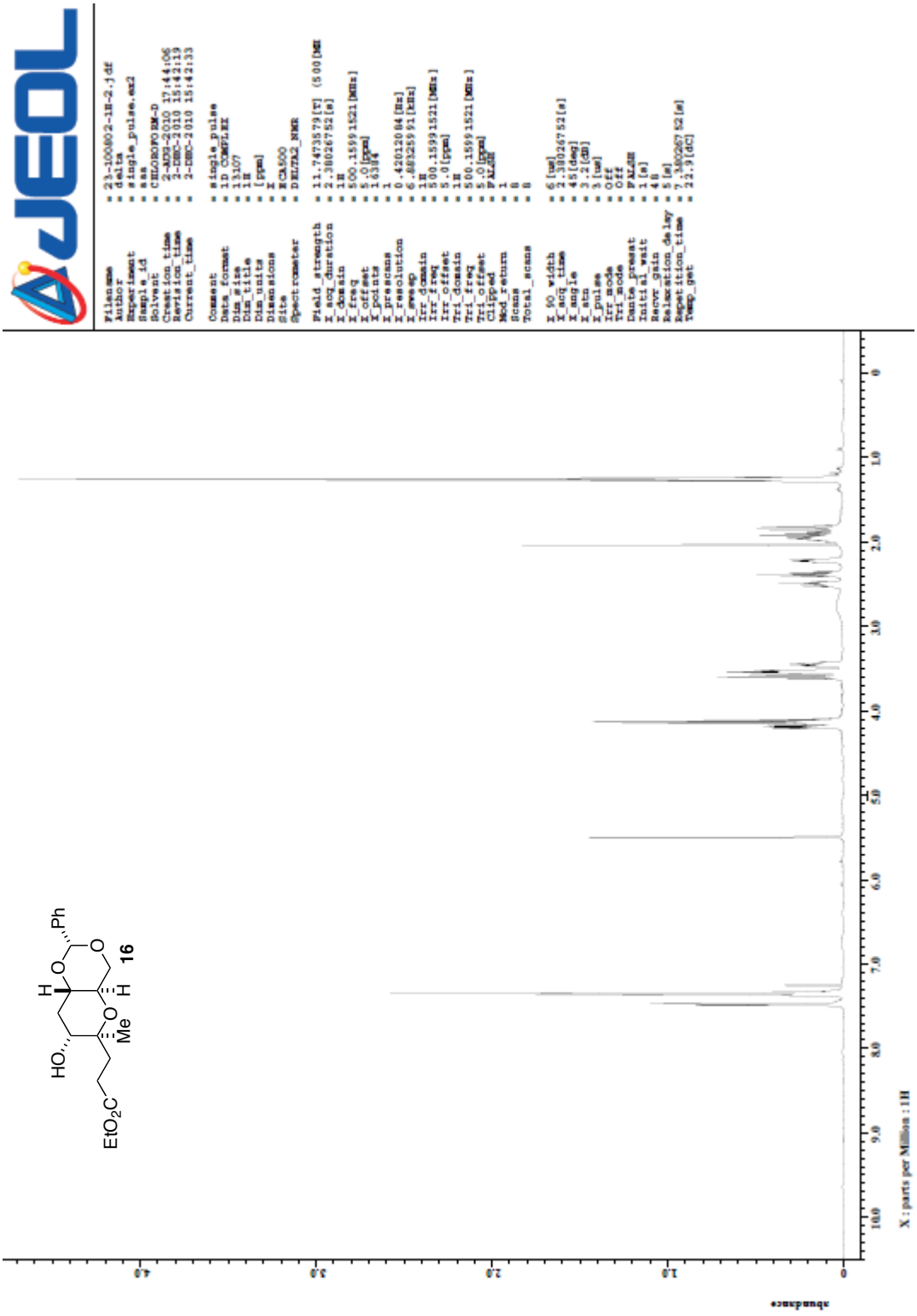
pyran **15**



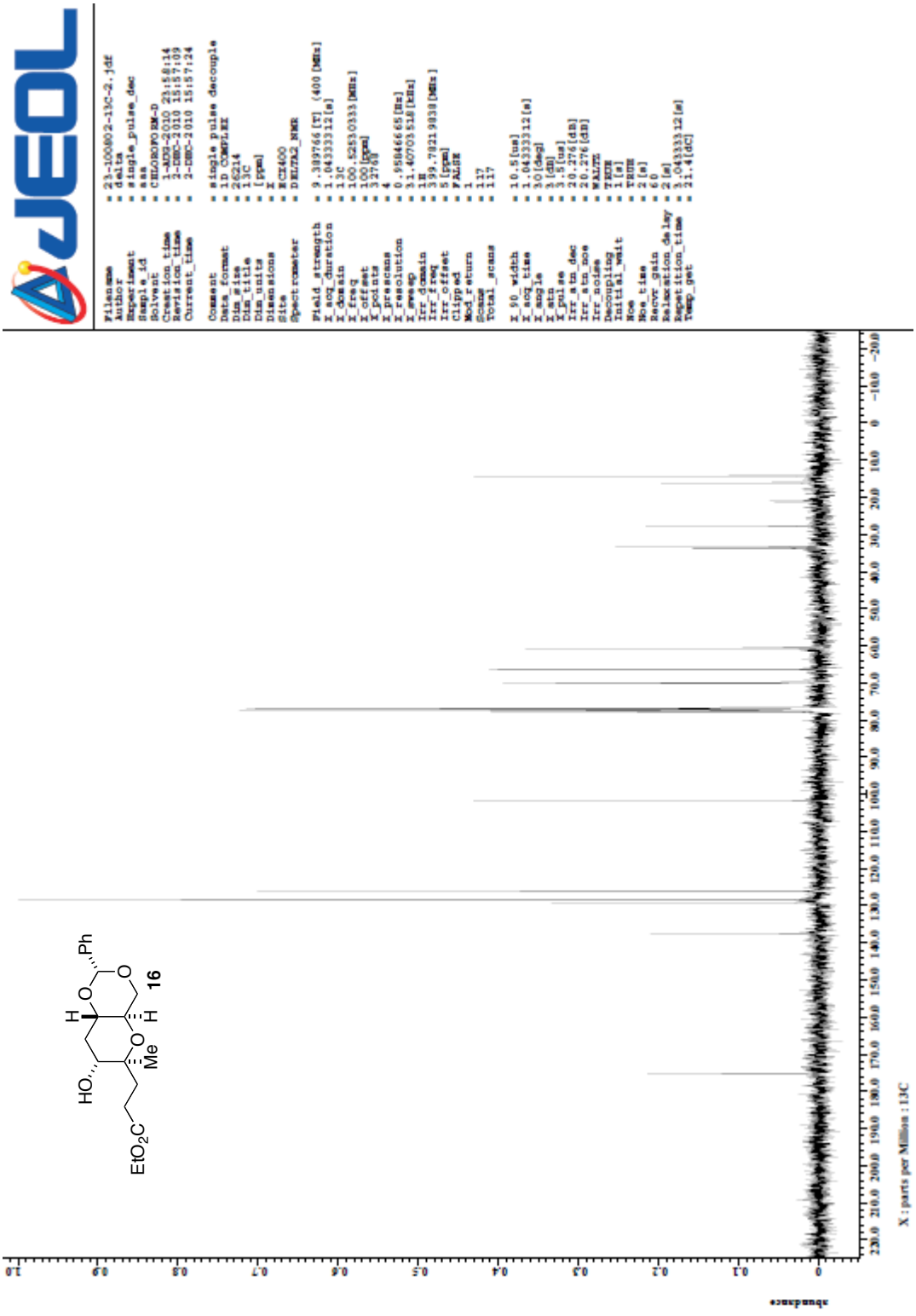
pyran **15**



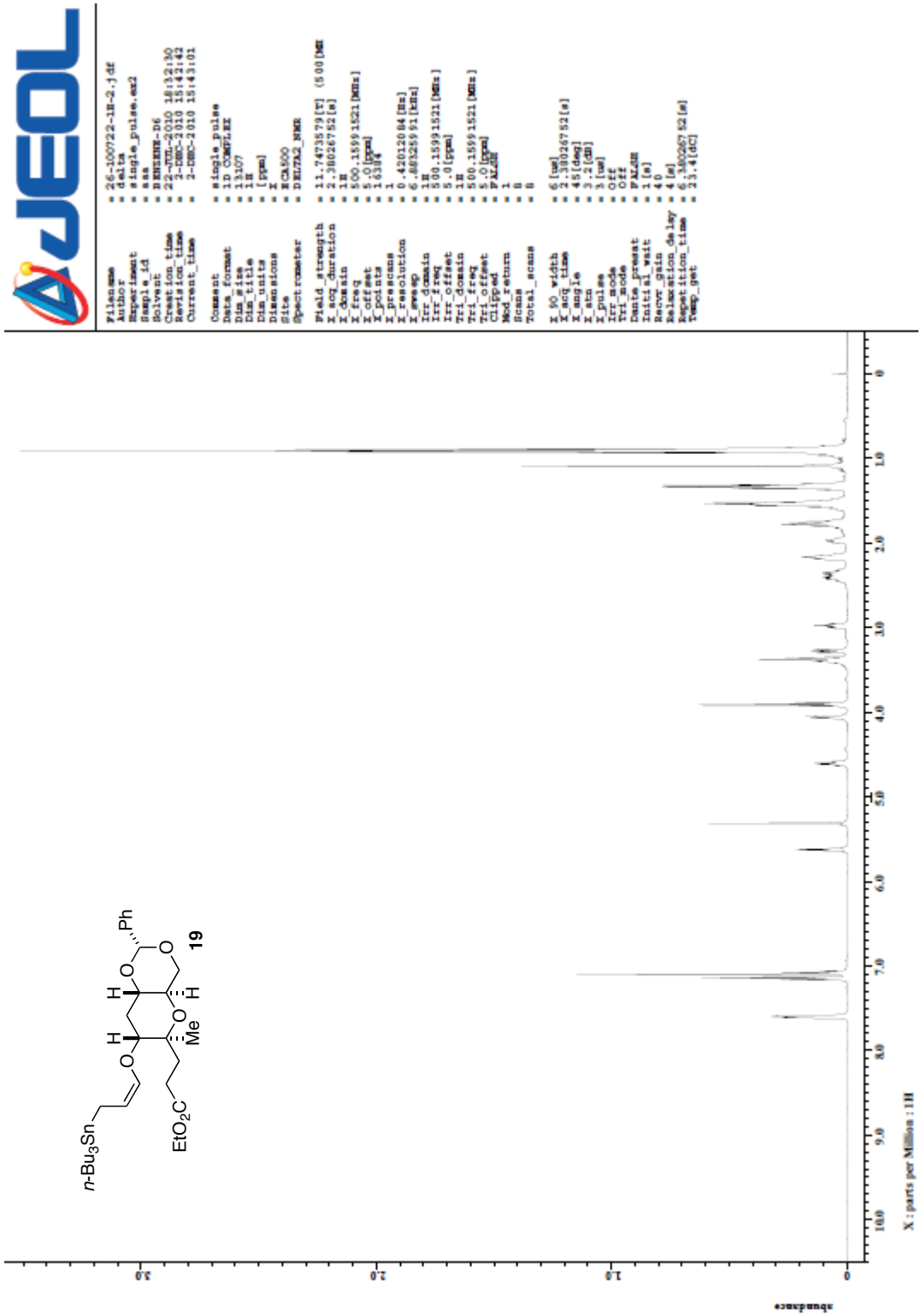
ester **16**



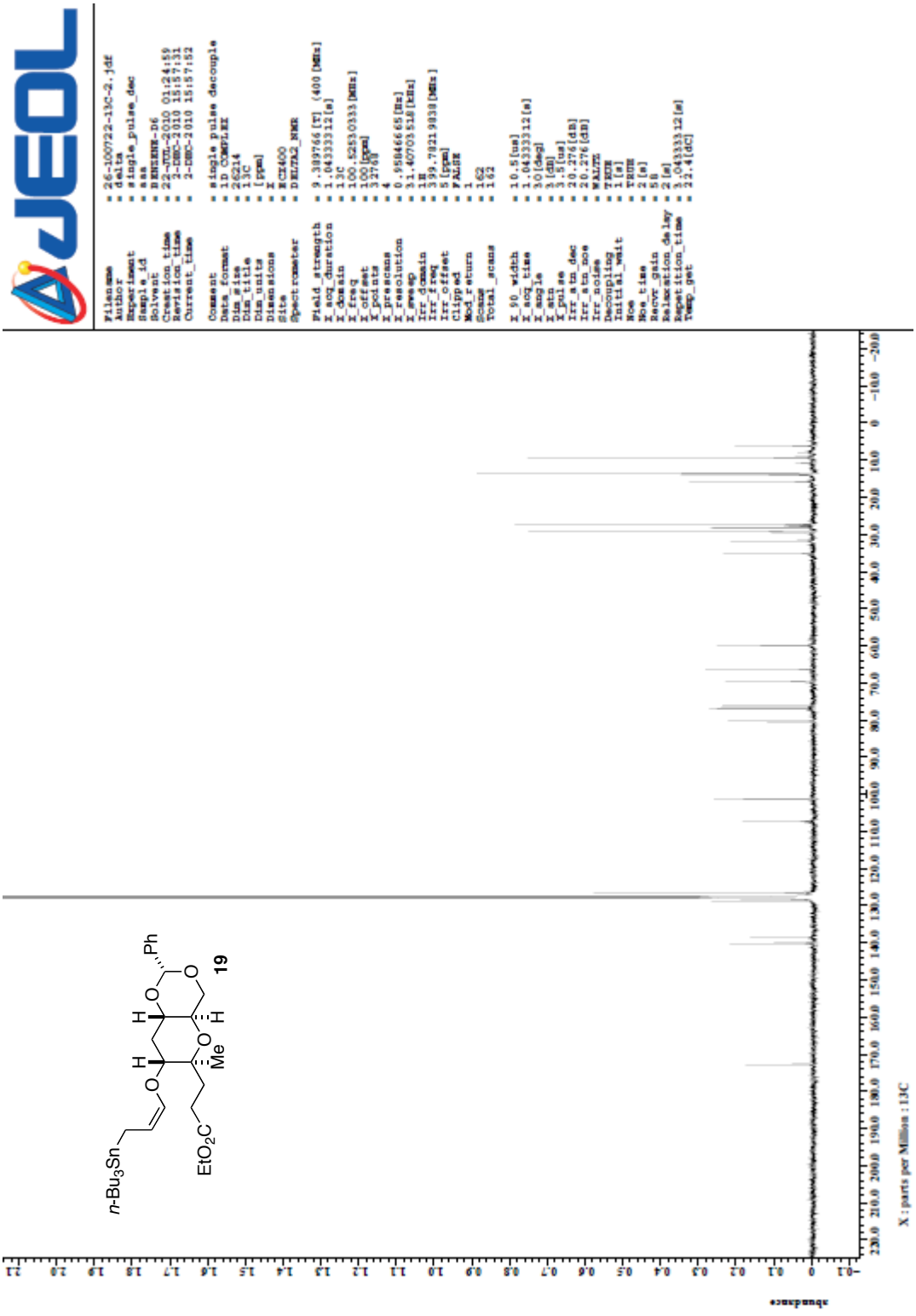
ester **16**


Filename = 23-100802-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
Solvent = CHLOROFORM-D
Creation_time = 1-AUG-2010 23:58:14
Revision_time = 2-DEC-2010 15:57:09
Current_time = 2-DEC-2010 15:57:24
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32k
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = NC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703516[kHz]
Irr_domain = 1H
Irr_freq = 399.78219833[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@case = 117
Total_scans = 117
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]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.4[deg]
abundance
X : parts per Million : 13C
HO
H
O
O
Ph
H
O
Me
EtO2C
16

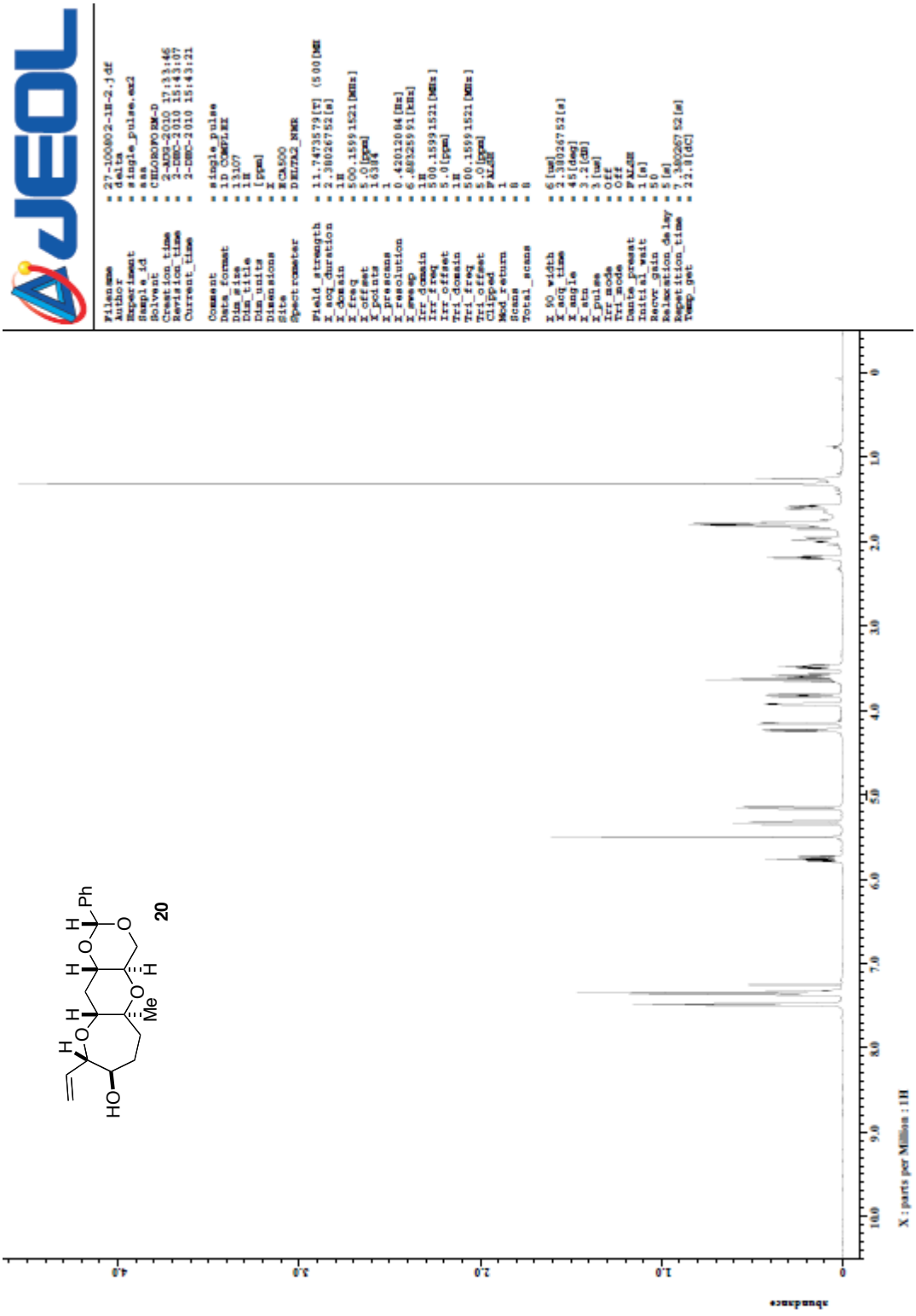
allylstannane **19**



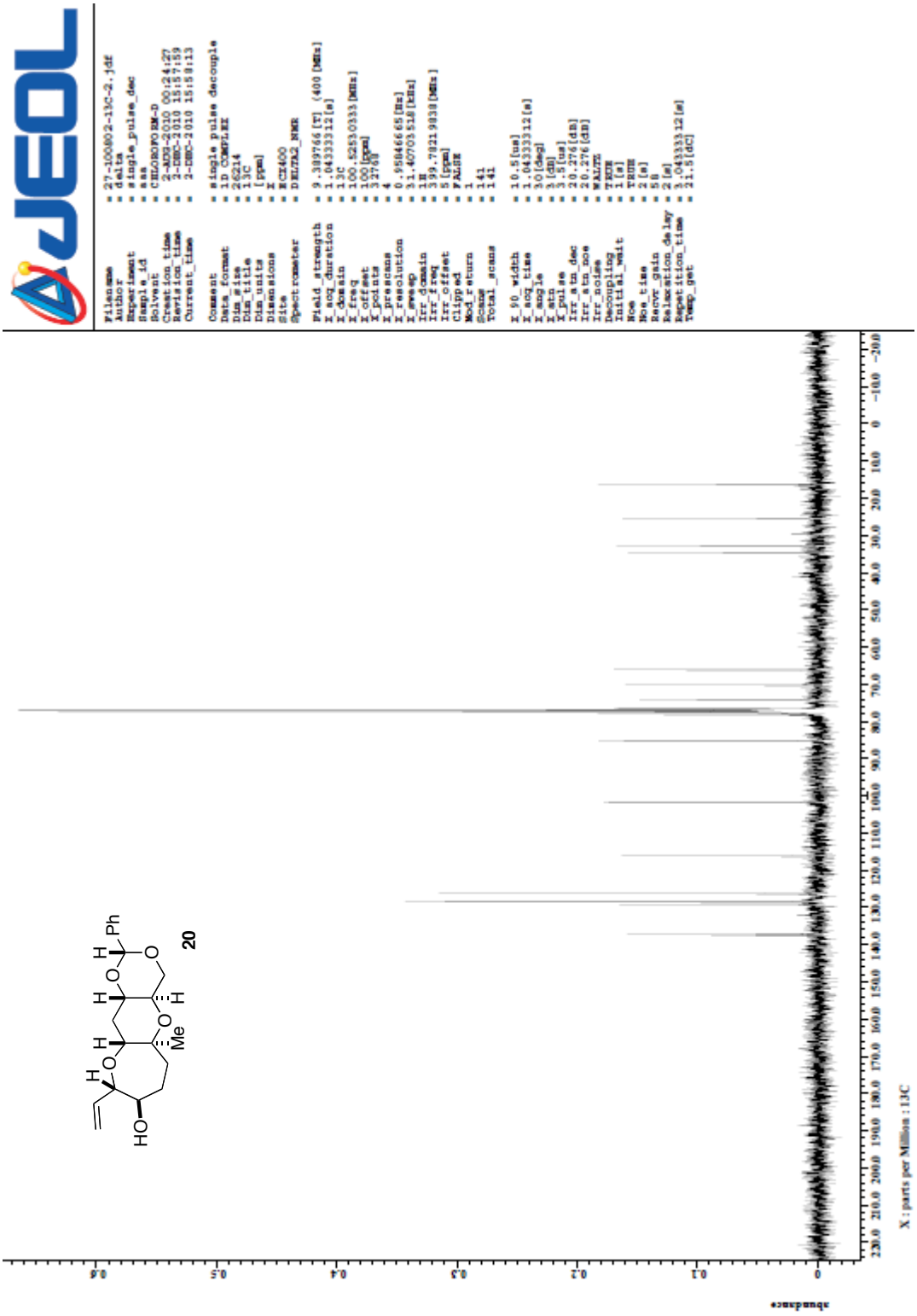
allylstannane **19**



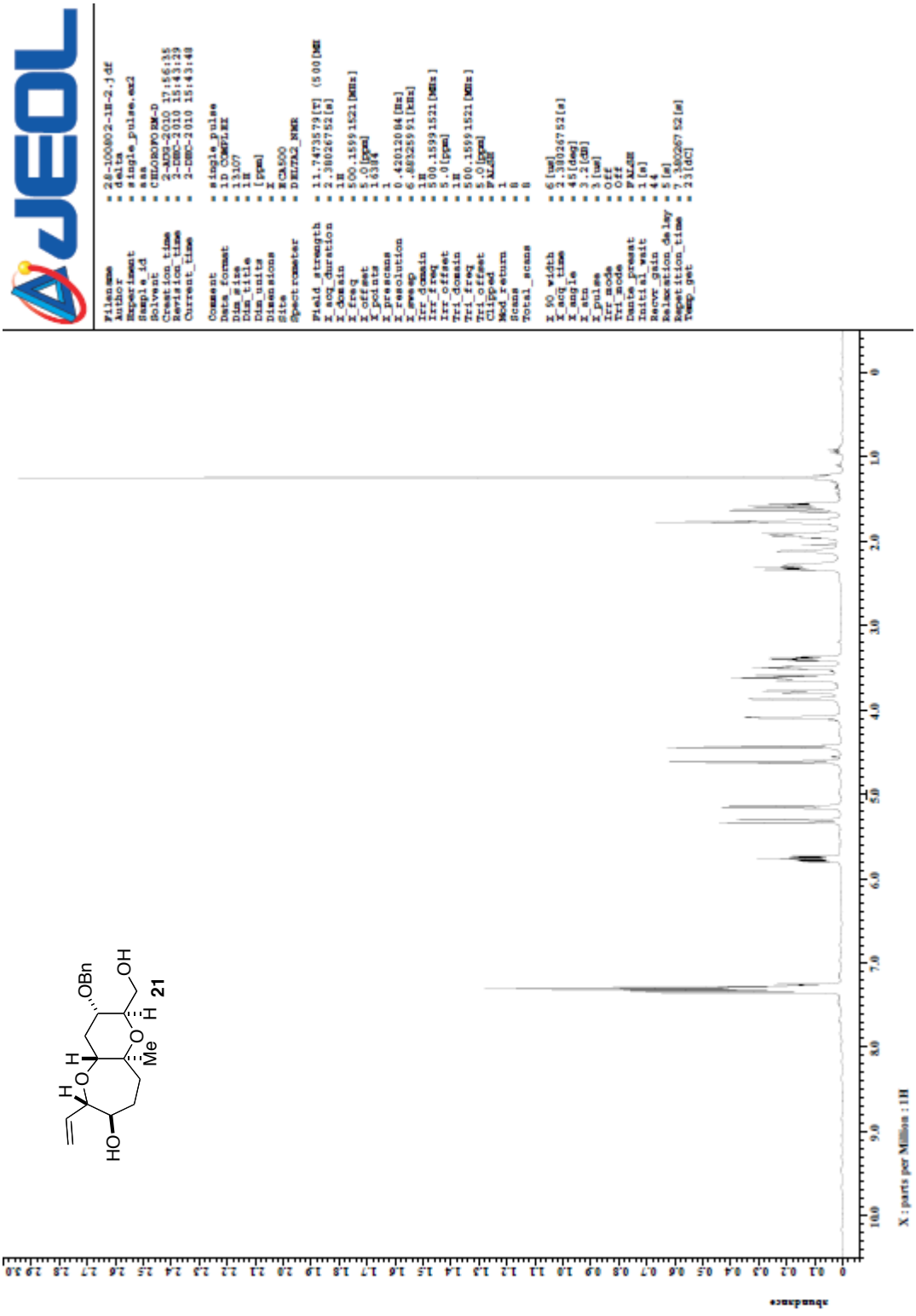
alcohol **20**


JEOL
Filename = 27-100802-1H-2.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 17:13:46
Revision_time = 2-DEC-2010 15:43:07
Current_time = 2-DEC-2010 15:43:21
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.3802675 2[s]
X_domain = 1H
X_freq = 500.1599 1521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.4201 2084[Hz]
X_sweep = 6.8832599 1[kHz]
Irr_domain = 1H
Irr_freq = 500.1599 1521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.1599 1521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.3802675 2[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decie_preset = FALSE
Initial_wait = 1[s]
Recve_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 7.3802675 2[s]
Temp_get = 23.0[dC]
20
HO
Me
Ph
abundance
X : parts per Million : 1H

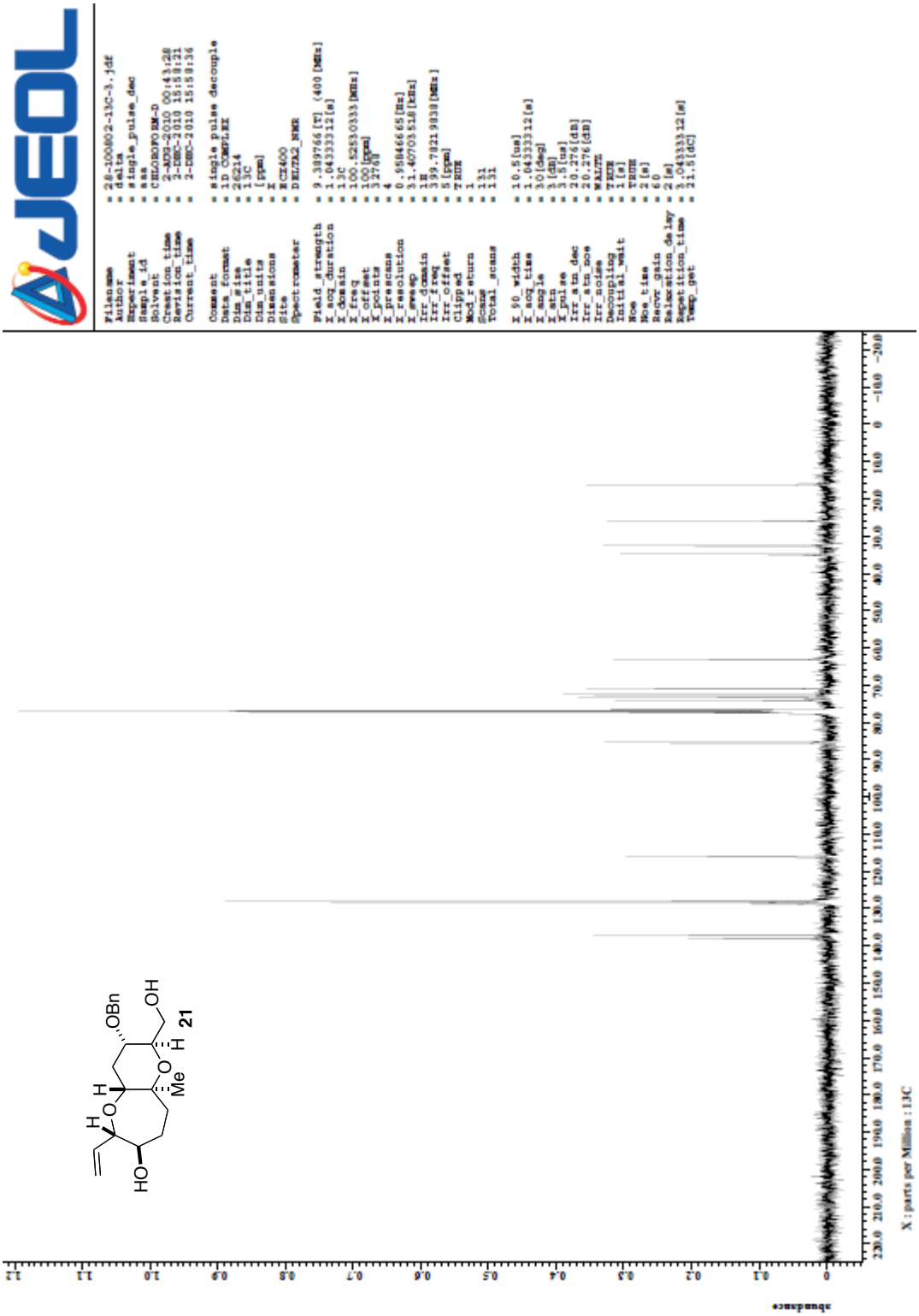
alcohol **20**


JEOL
Filename = 27-100802-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 00:24:27
Revision_time = 2-DEC-2010 15:57:59
Current_time = 2-DEC-2010 15:59:13
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 2214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@case = 141
Total_scans = 141
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recve_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.5[degC]
20
Me
HO
abundance
X : parts per Million : 13C

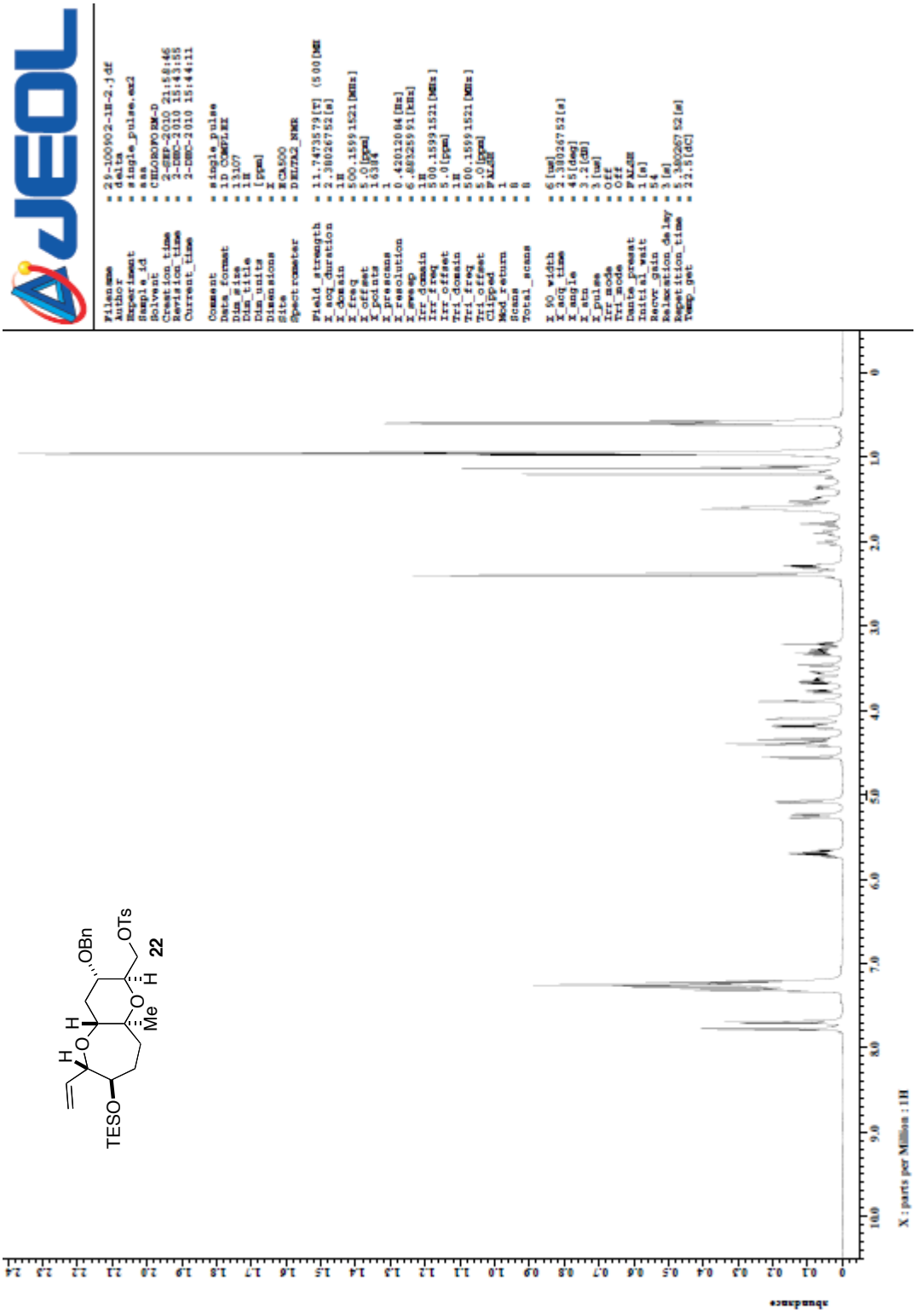
diol **21**


JEOL
Filename = 28-100802-1H-2.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 17:56:35
Revision_time = 2-DEC-2010 15:43:29
Current_time = 2-DEC-2010 15:43:48
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.68525591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = PARTLY
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decie_present = PARTLY
Initial_wait = 1[s]
Recve_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 7.38026752[s]
Temp_get = 23[dC]
OBn
OH
H
O
H
O
Me
H
21
HO
abundance
X : parts per Million : 1H

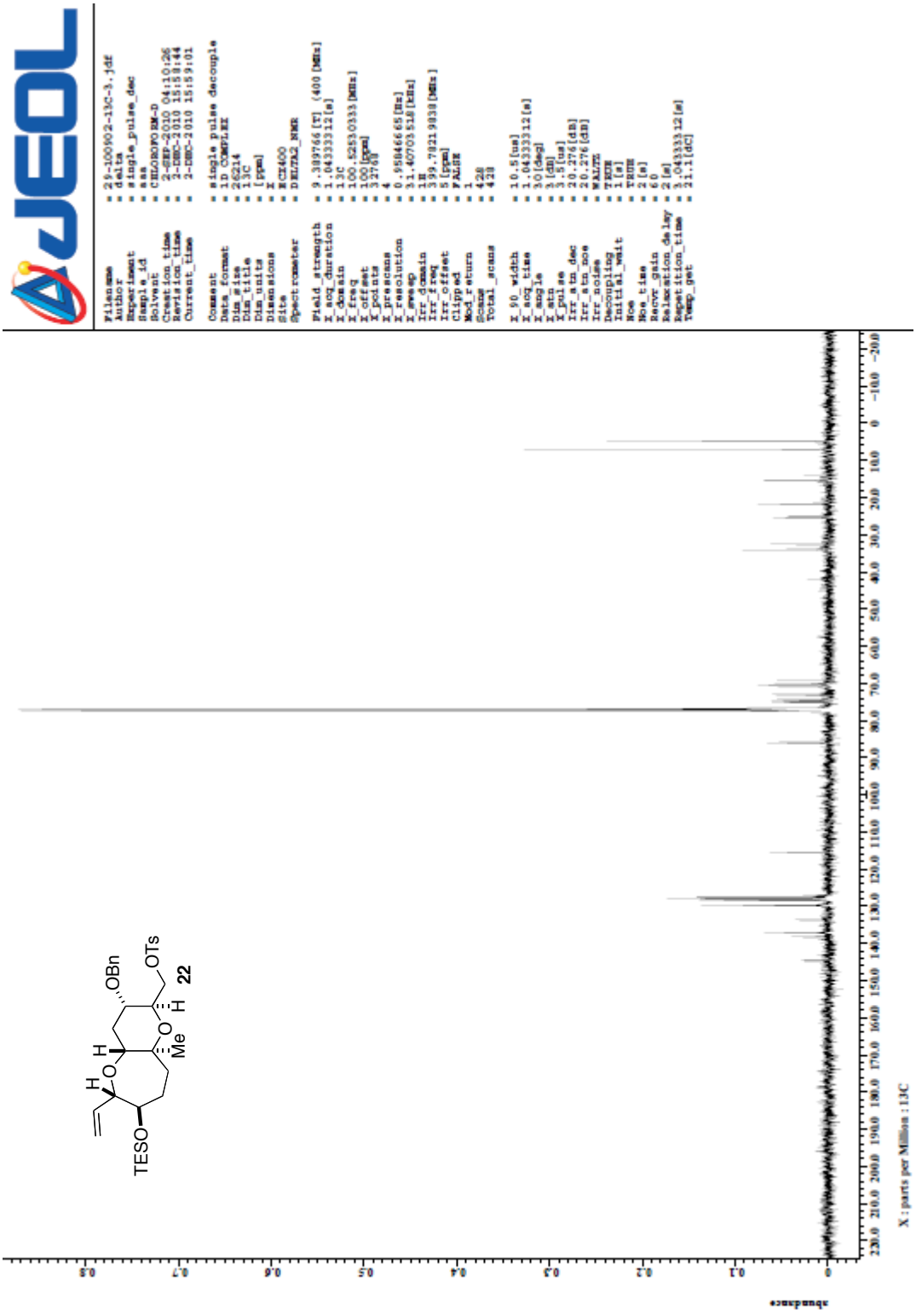
diol **21**


Filename = 28-100802-13C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 00:43:28
Revision_time = 2-DEC-2010 15:59:21
Current_time = 2-DEC-2010 15:59:36
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32314
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 3276.80[Hz]
X_points = 4
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5 [ppm]
Clipped = TRUE
Mod_return = 1
@case = 131
Total_scans = 131
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.5[deg]
OBn
OH
H
O
H
O
Me
H
21
HO
Abundance
X : parts per Million : 13C

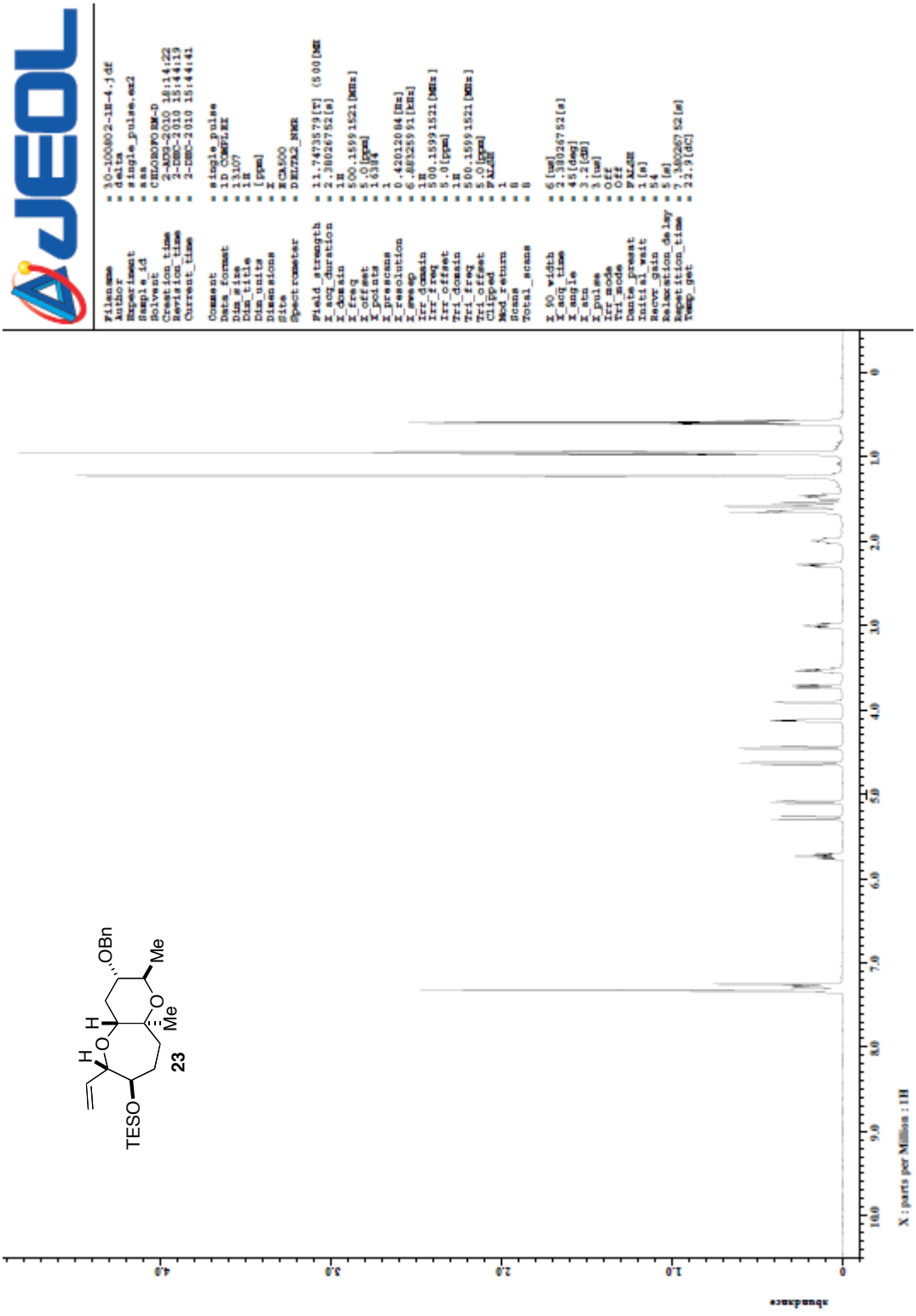
tosylate **22**


Filename = 29-100902-1H-2.jdf
Author = delta
Experiment = single_pulse.exz
Sample_id = sss
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 COMPLEX
Data_axis = 1H
Data_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = JEOL500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.380267552[s]
X_domain = 1H
X_freq = 500.1599152l[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.420120284[Hz]
X_sweep = 6.885259591[kHz]
Irr_domain = 1H
Irr_freq = 500.1599152l[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.1599152l[MHz]
Tri_offset = 5.0[ppm]
Clipped = PARTLY
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.380267552[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decim_present = PARTLY
Initial_wait = 1[s]
Recve_gain = 54
Relaxation_delay = 3[s]
Repetition_time = 5.380267552[s]
Temp_get = 23.5[dC]
OBn
OTs
H
O
H
O
Me
H
22
TESO
abundance
X : parts per Million : 1H

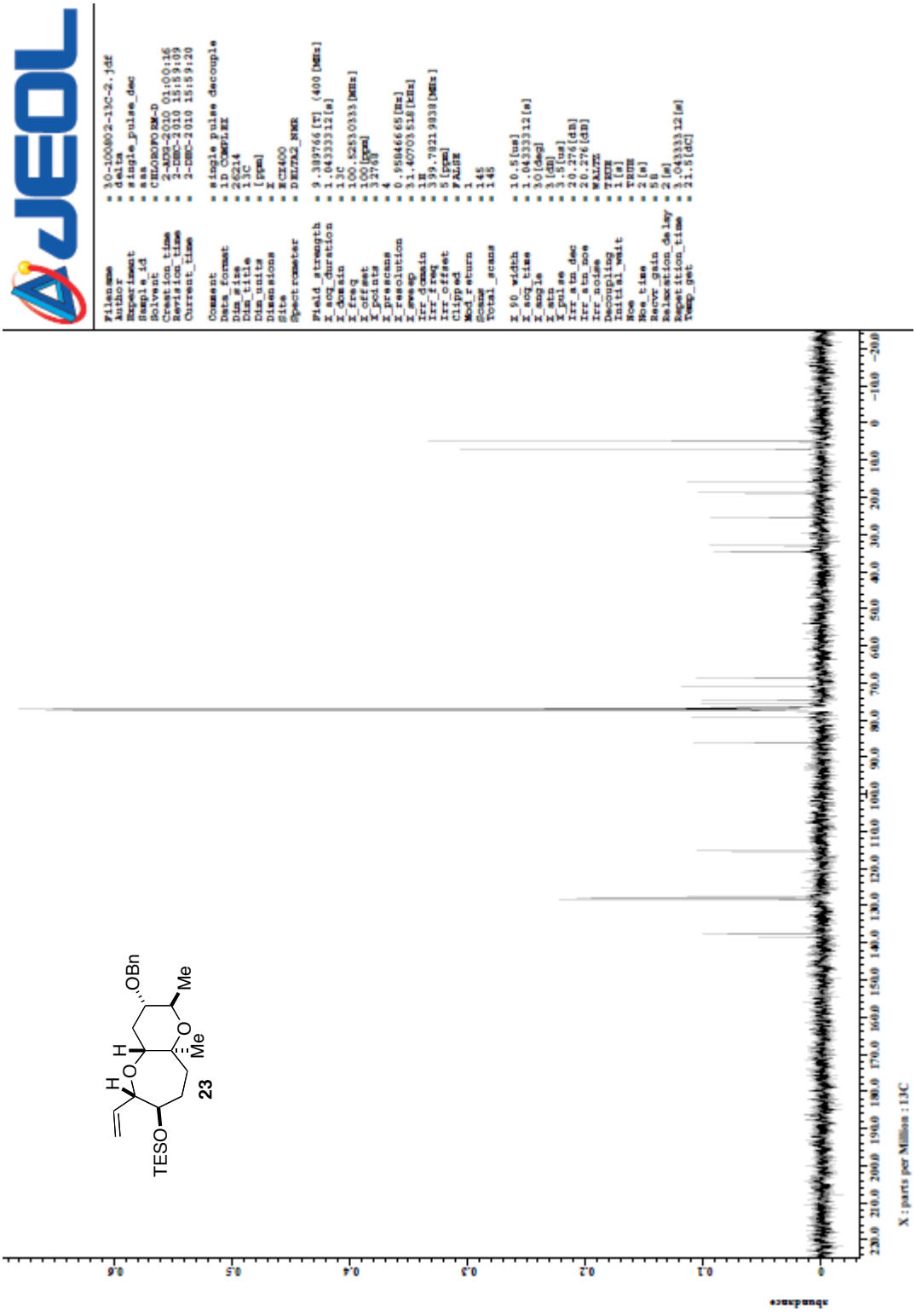
tosylate **22**


JEOL
Filename = 29-100902-13C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-SEP-2010 04:10:26
Revision_time = 2-DEC-2010 15:59:44
Current_time = 2-DEC-2010 15:59:01
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32k
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@case = 428
Total_scans = 428
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.1[deg]
OBn
OTs
H
O
Me
H
22
TESO
abundance
X : parts per Million : 13C

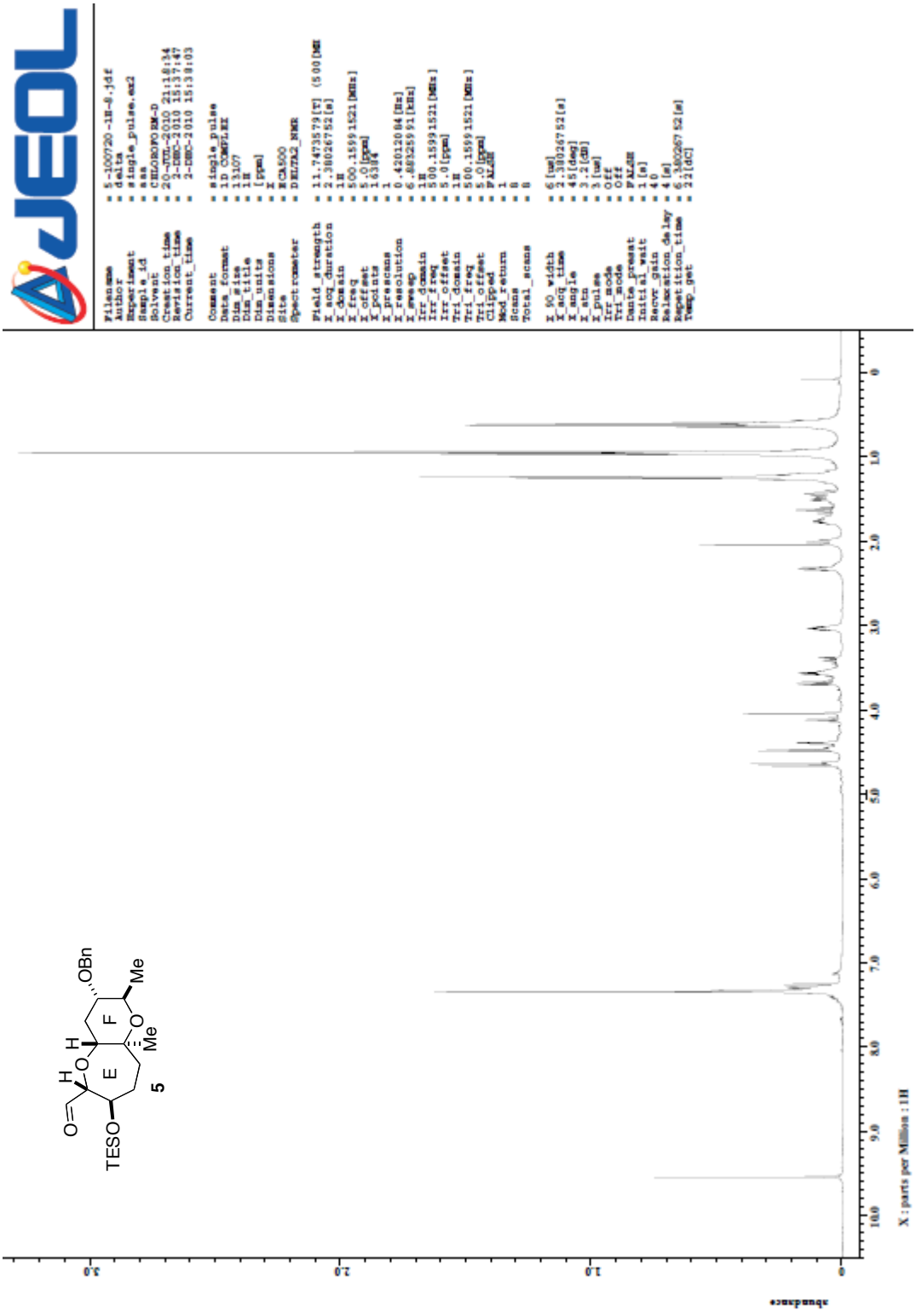
olefin **23**


JEOL
Filename = 30-100802-1H-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 18:14:22
Revision_time = 2-DEC-2010 15:44:13
Current_time = 2-DEC-2010 15:44:41
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = PARTLY
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decm_present = PARTLY
Initial_wait = 1[s]
Recve_gain = 54
Relaxation_delay = 5[s]
Repetition_time = 7.38026752[s]
Temp_get = 23.9[deg]
OBn
Me
O
Me
H
O
H
TESO
23
abundance
X : parts per Million : 1H

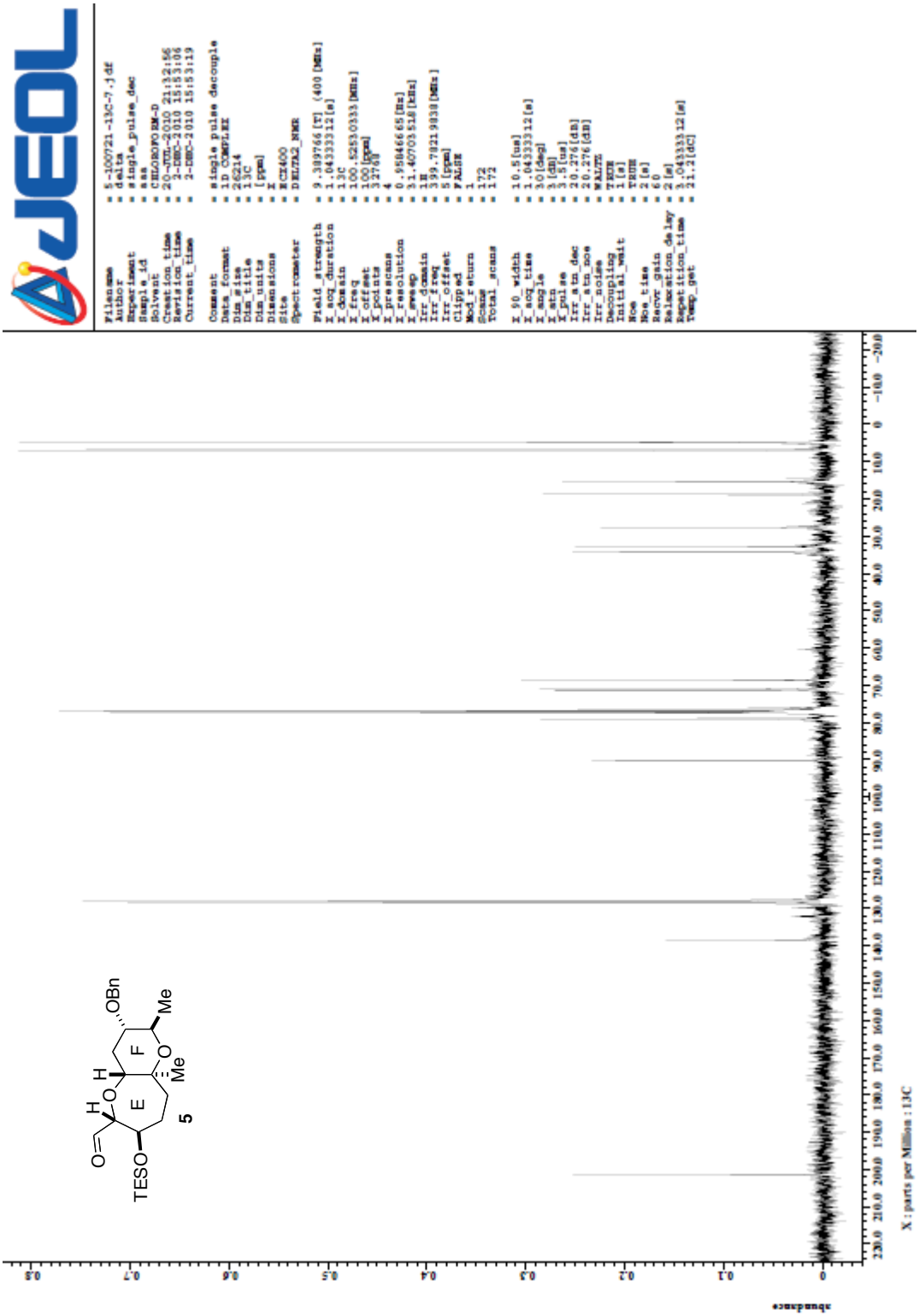
olefin **23**


JEOL
Filename = 30-100802-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = sm
Solvent = CHLOROFORM-D
Creation_time = 2-AUG-2010 01:00:16
Revision_time = 2-DEC-2010 15:59:09
Current_time = 2-DEC-2010 15:59:20
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32k
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = NC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@case = 145
Total_scans = 145
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 5%
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.5[deg]
OBn
Me
O
Me
H
O
H
TESO
23
abundance
X : parts per Million : 13C

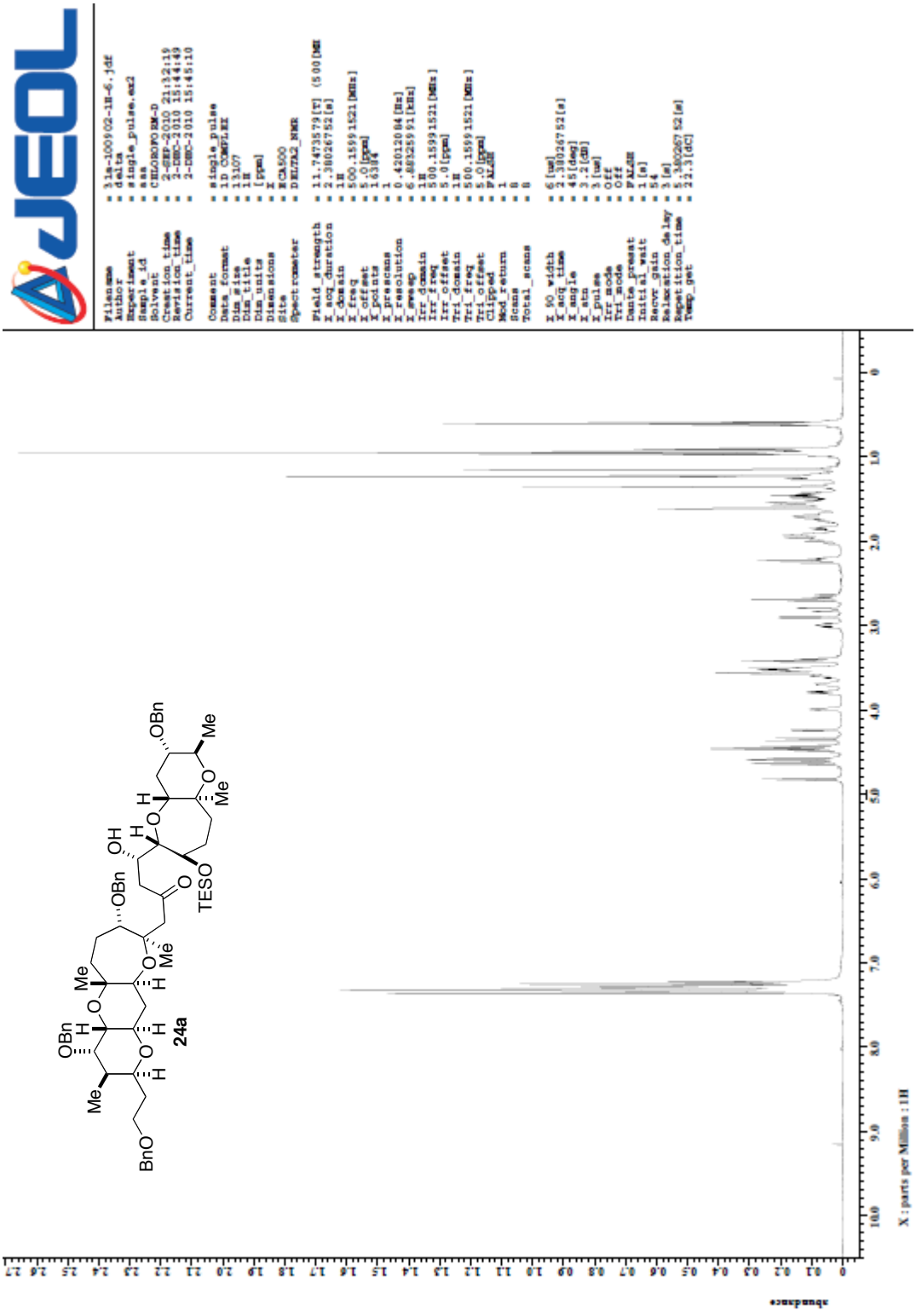
aldehyde **5**


JEOL
Filename = 5-100720-1H-8.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 20-JUL-2010 21:18:34
Revision_time = 2-DEC-2010 15:37:47
Current_time = 2-DEC-2010 15:39:03
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = JEOL ECA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88525591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decie_preset = FALSE
Initial_wait = 1[s]
Recve_gain = 4.0
Relaxation_delay = 4[s]
Repetition_time = 6.38026752[s]
Temp_get = 23[dC]
OBn
Me
Me
TESO
O=
H
O
H
O
E
F
5
abundance
X : parts per Million : 1H

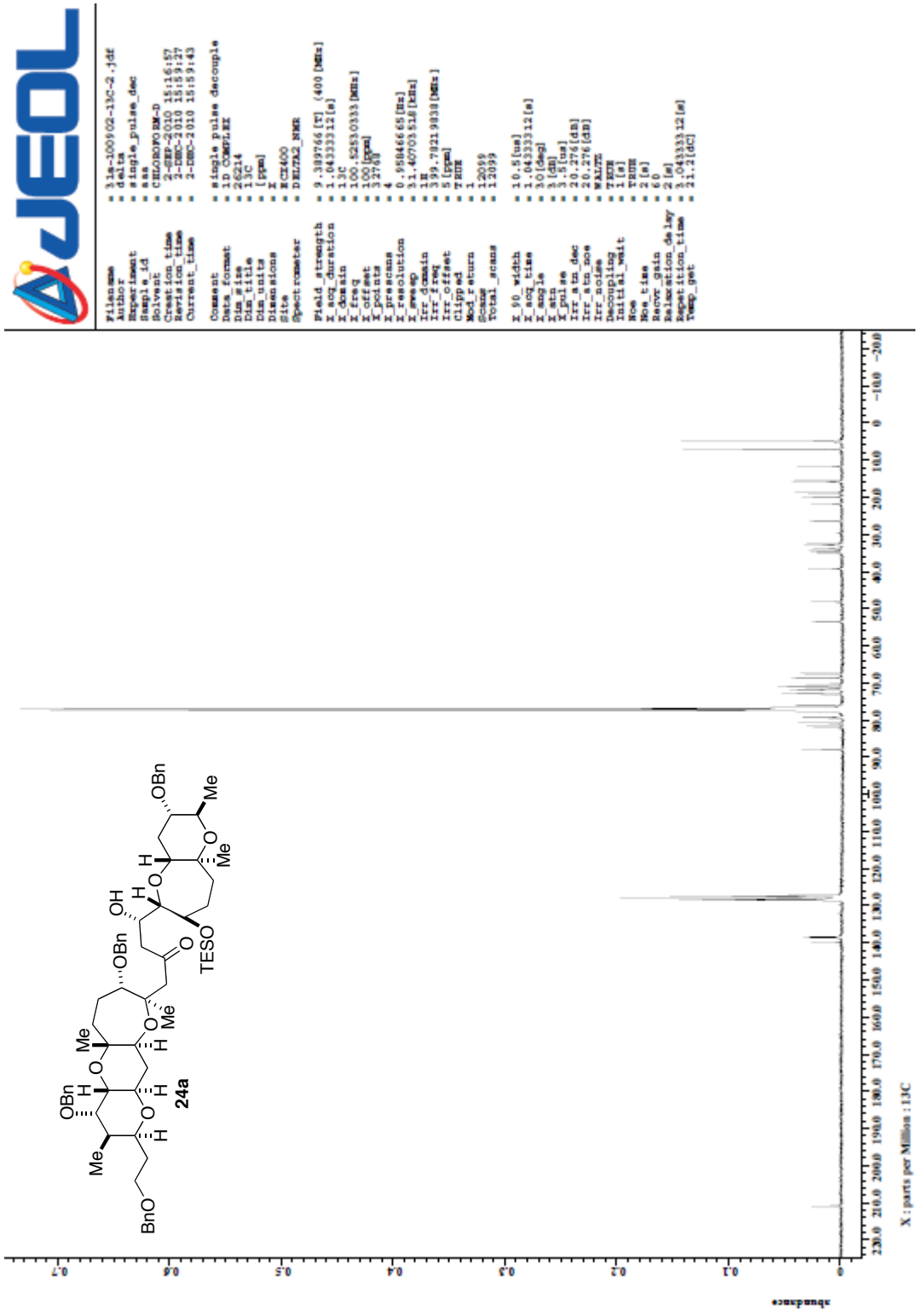
aldehyde **5**


Filename = 5-100721-13C-7.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aa
Solvent = CHLOROFORM-D
Creation_time = 20-JUL-2010 21:32:56
Revision_time = 2-DEC-2010 15:53:06
Current_time = 2-DEC-2010 15:53:13
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32314
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 3276[H]
X_points = 4
X_prescans = 0
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
@case = 172
Total_scans = 172
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.2[deg]
OBn
Me
H
O
F
O
Me
E
H
O
TESO
5
abundance
X : parts per Million : 13C

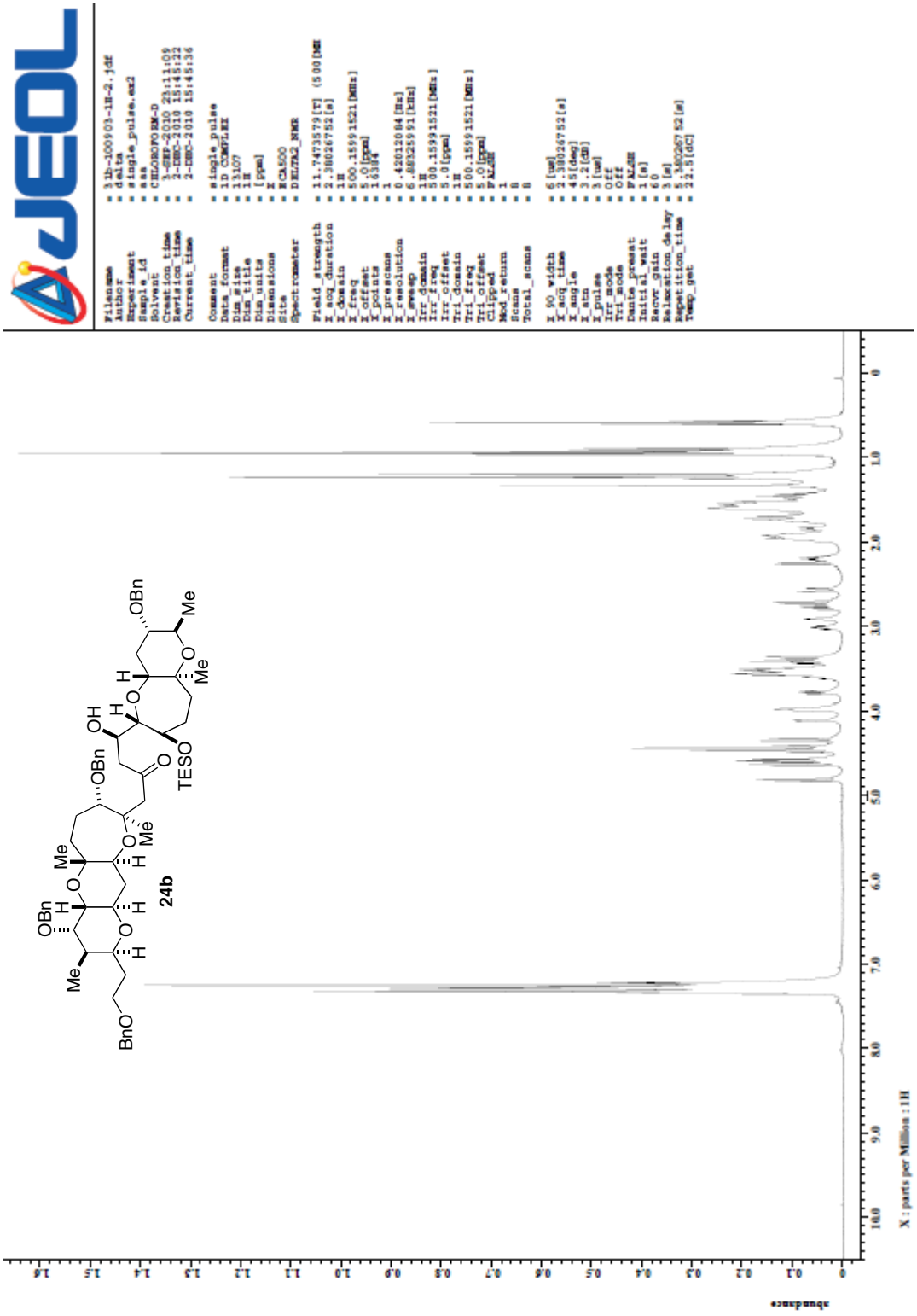
ketone **24a**


JEOL
Filename = 31a-100902-1H-6.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 2-SEP-2010 21:32:19
Revision_time = 2-DEC-2010 15:44:49
Current_time = 2-DEC-2010 15:45:10
Comment = single pulse
Data_format = 1D COMPLEX
Dim_size = 11307
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = RCA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.38026752[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.42012084[Hz]
X_sweep = 6.88325591[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = PARTIAL
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 6[us]
X_acq_time = 2.38026752[s]
X_angle = 45[deg]
X_atn = 3.2[dB]
X_pulse = 3[us]
Irr_mode = Off
Tri_mode = Off
Decpl_preset = PARTIAL
Initial_wait = 2[s]
Recve_gain = 54
Relaxation_delay = 3[s]
Repetition_time = 5.38026752[s]
Temp_get = 23.3[deg]
OBn
OH
TESO
Me
BnO
24a
abundance
X : parts per Million : 1H

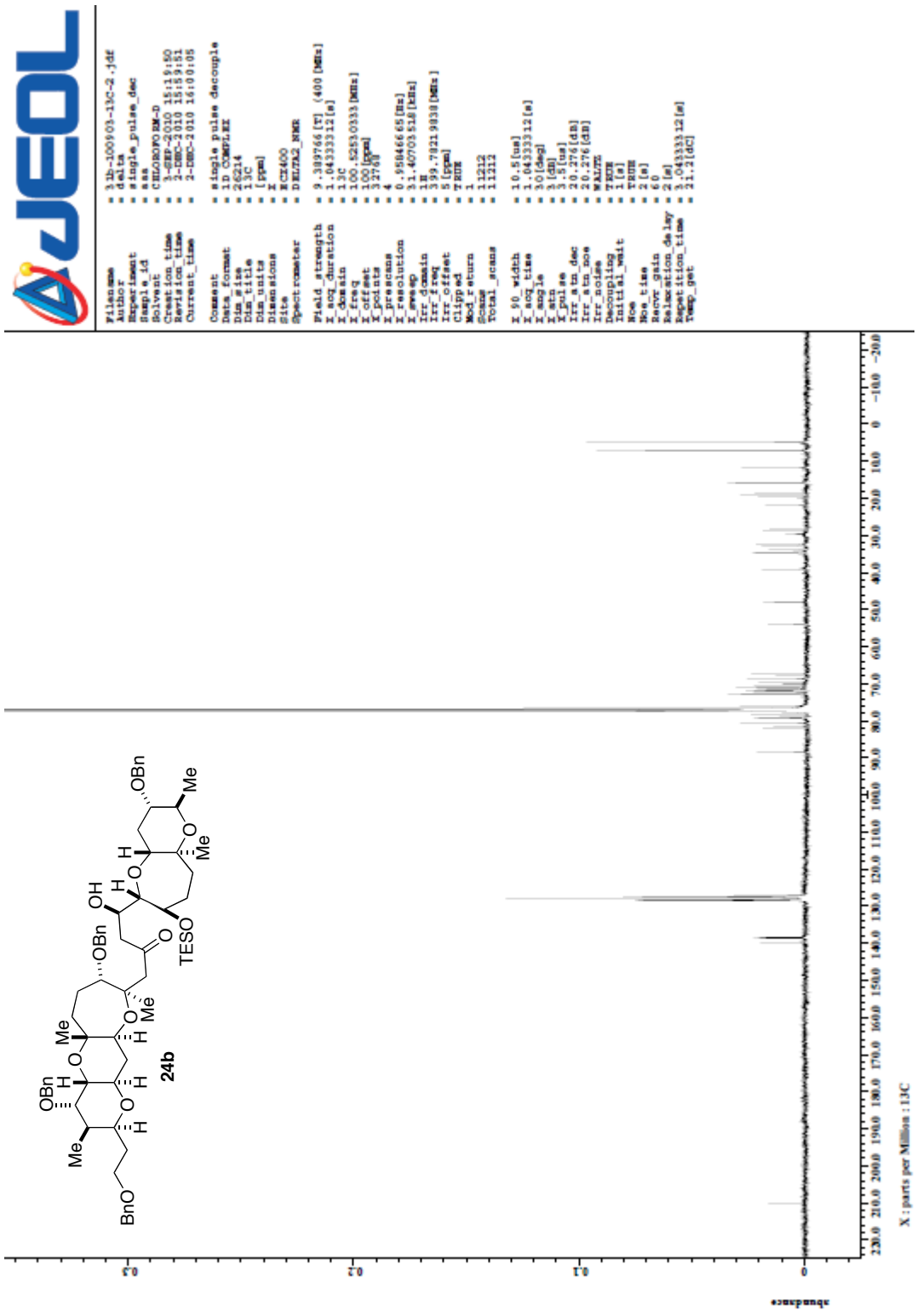
ketone **24a**


Filename = 31a-100902-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = aaa
Solvent = CHLOROFORM-D
Creation_time = 2-SEP-2010 15:16:57
Revision_time = 2-DEC-2010 15:59:27
Current_time = 2-DEC-2010 15:59:43
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32k
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.043333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 3276.8[Hz]
X_points = 4
X_prescans = 4
X_resolution = 0.958466665[Hz]
X_sweep = 31.407035156[kHz]
Irr_domain = 1H
Irr_freq = 399.782199338[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 12099
Total_scans = 12099
X_90_width = 10.5[us]
X_acq_time = 1.043333312[s]
X_angle = 30[deg]
X_atn = 3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.043333312[s]
Temp_get = 21.2[deg]
OBn
Me
O
H
OH
TESO
BnO
24a
abundance
X : parts per Million : 13C

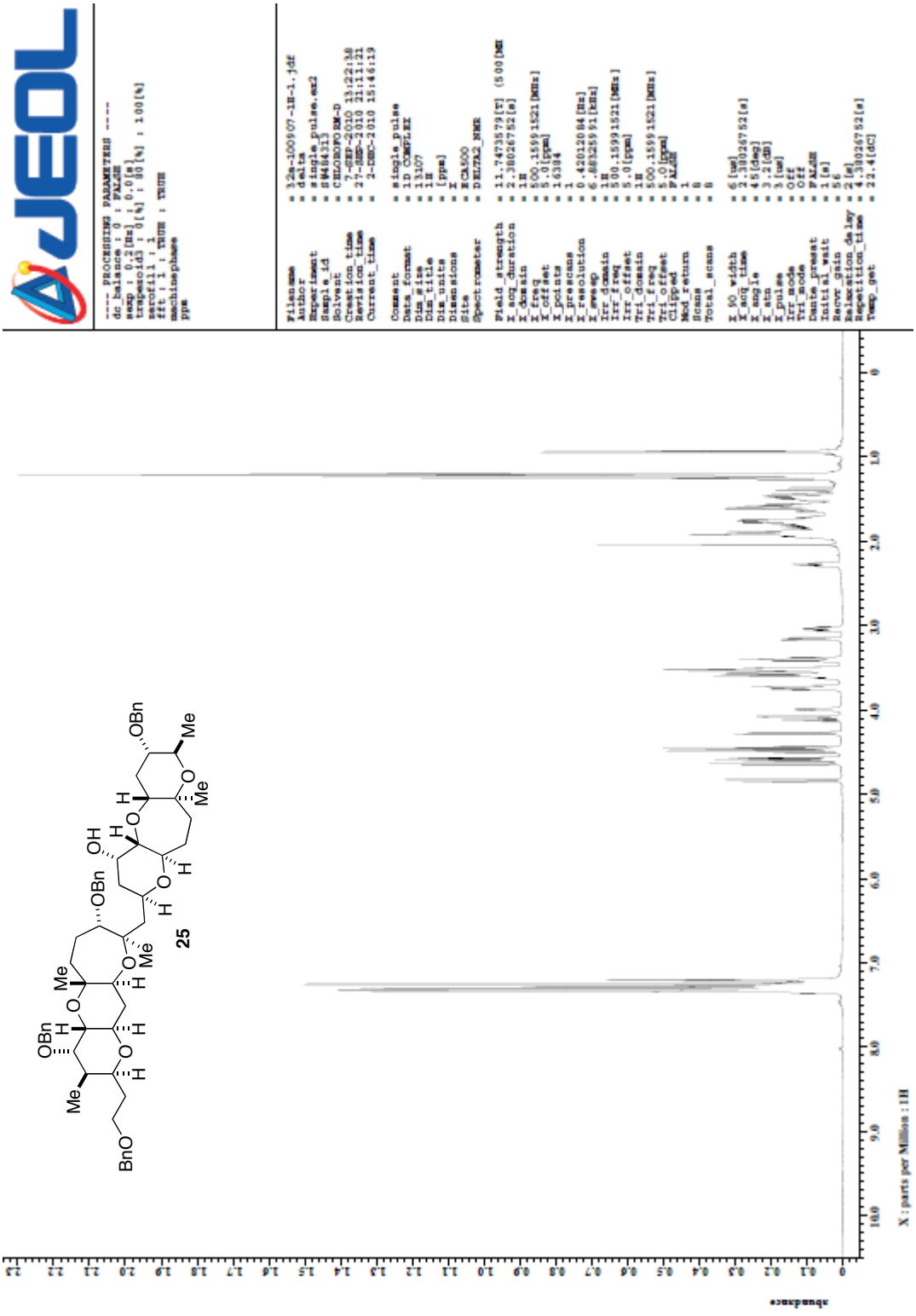
ketone **24b**



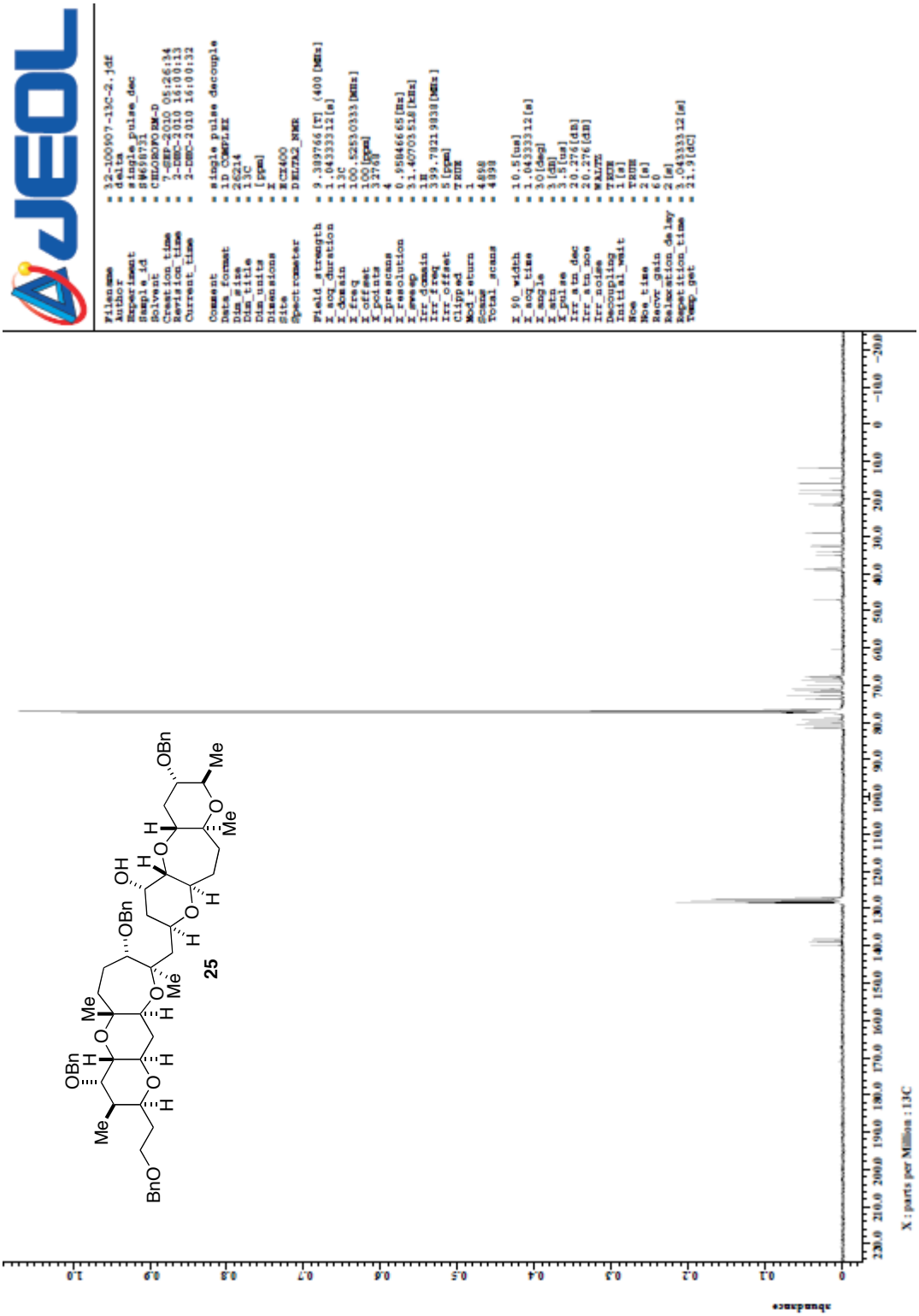
ketone **24b**


Filename = 3b-100903-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = sss
Solvent = CHLOROFORM-D
Creation_time = 3-SEP-2010 15:19:50
Revision_time = 2-DEC-2010 15:59:51
Current_time = 2-DEC-2010 16:09:05
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32k
Dim_title = 13C
Dim_units = [ppm]
Dimensions = 1
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466 65[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.7821 9838[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 11212
Total_scans = 11212
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]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.2[deg]
OBn
Me
O
H
OH
TESO
Me
BnO
24b
abundance
X : parts per Million : 13C

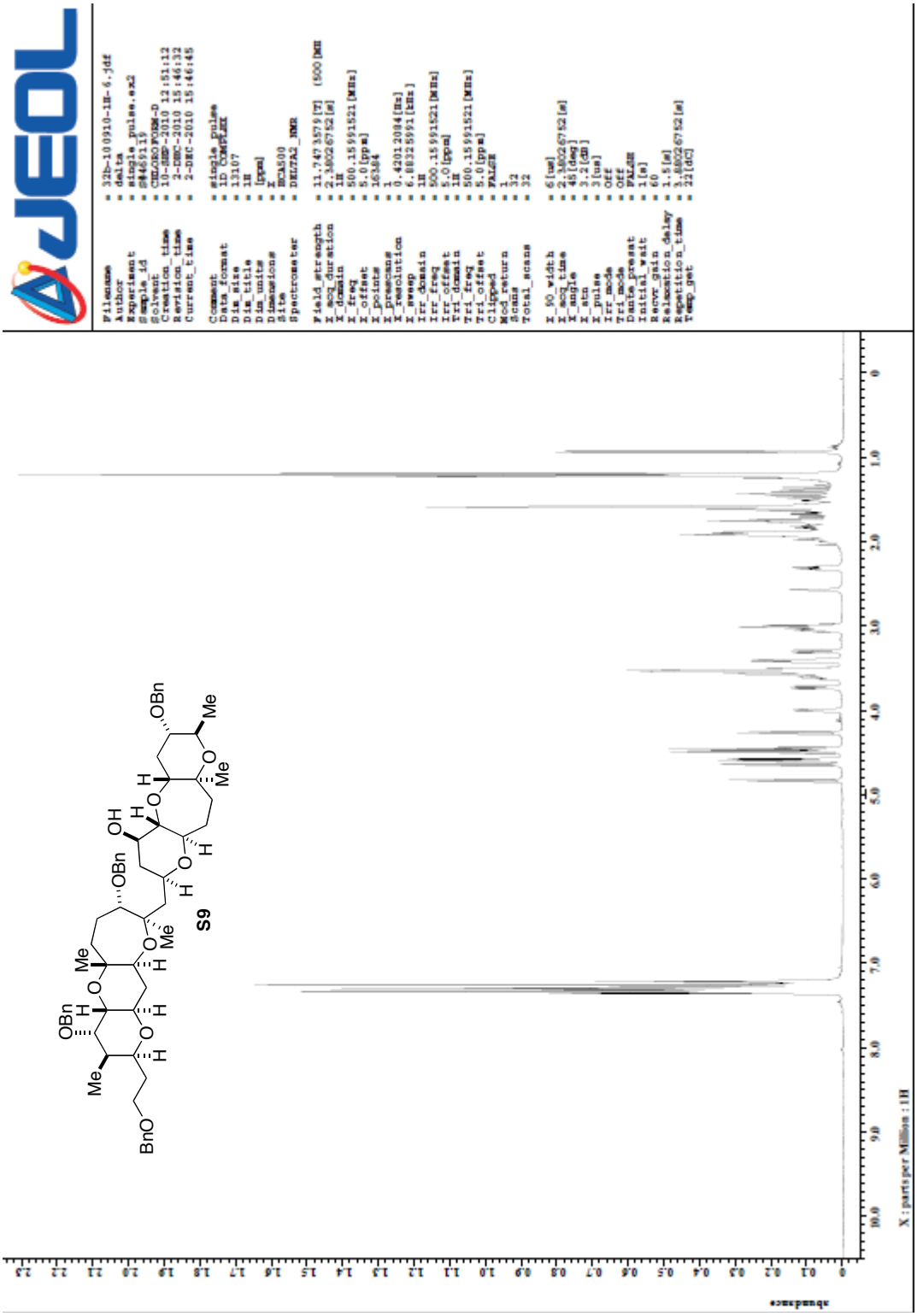
alcohol **25**



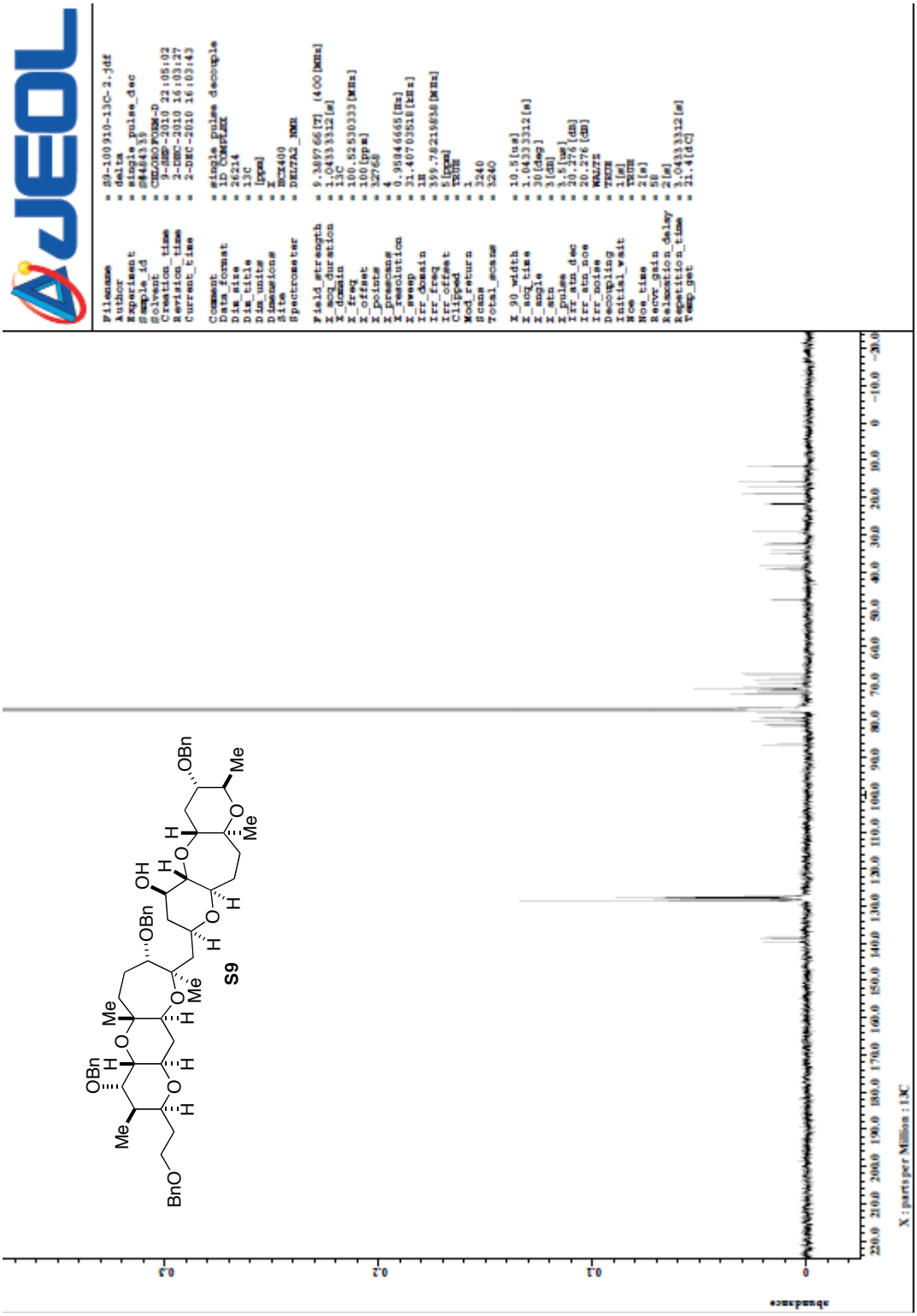
alcohol **25**


Filename = 32-100907-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 8969731
Solvent = CHLOROFORM-D
Creation_time = 7-SEP-2010 05:26:34
Revision_time = 2-DEC-2010 16:09:13
Current_time = 2-DEC-2010 16:09:32
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32K
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = JEC400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.525530333[MHz]
X_offset = 3276.80[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
@case = 4898
Total_scans = 4898
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]
Irr_atn_dec = 20.276[dB]
Irr_atn_noe = 20.276[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recy_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 21.9[deg]
25
Abundance
X : parts per Million : 13C

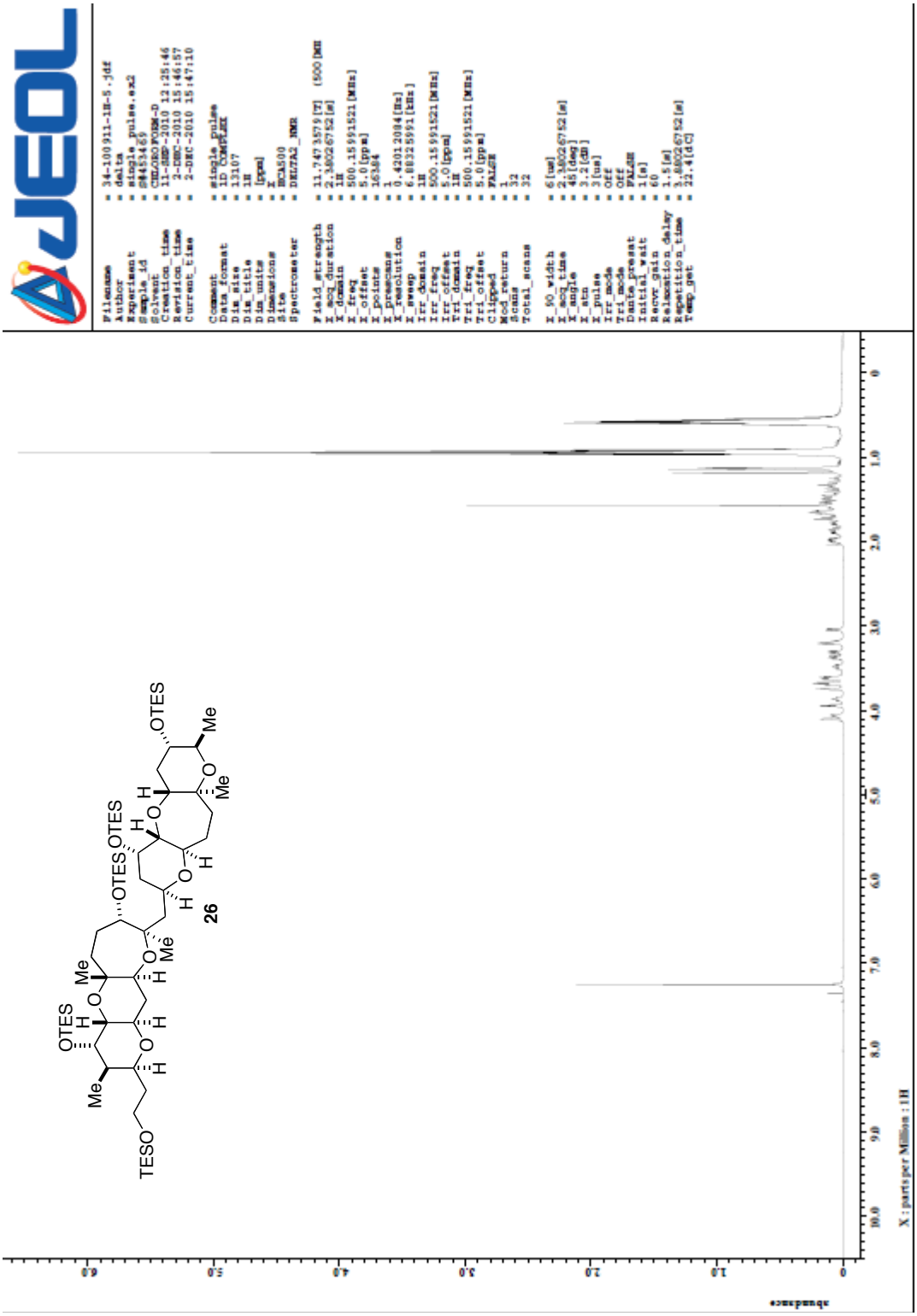
alcohol **S9**



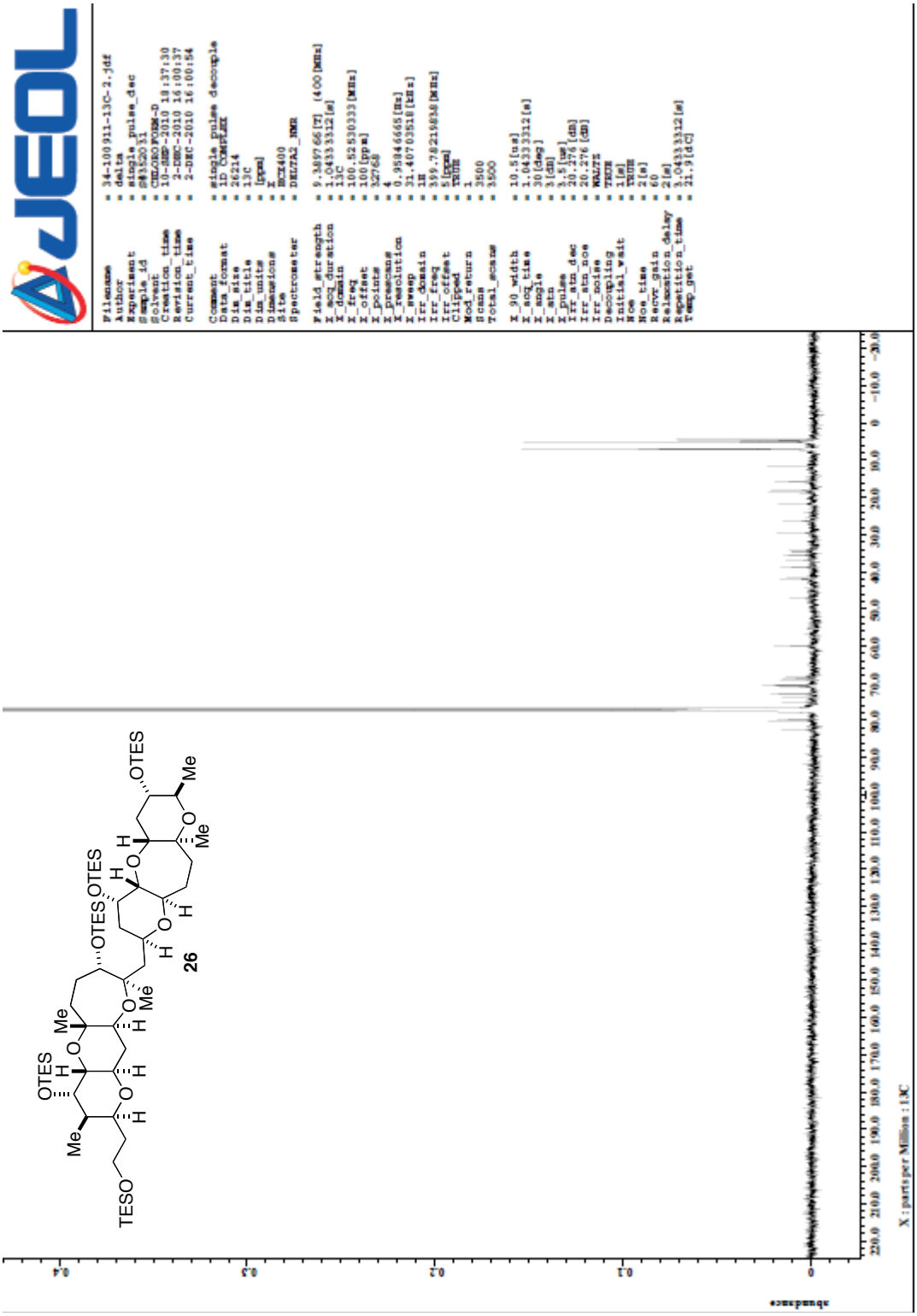
alcohol **S9**



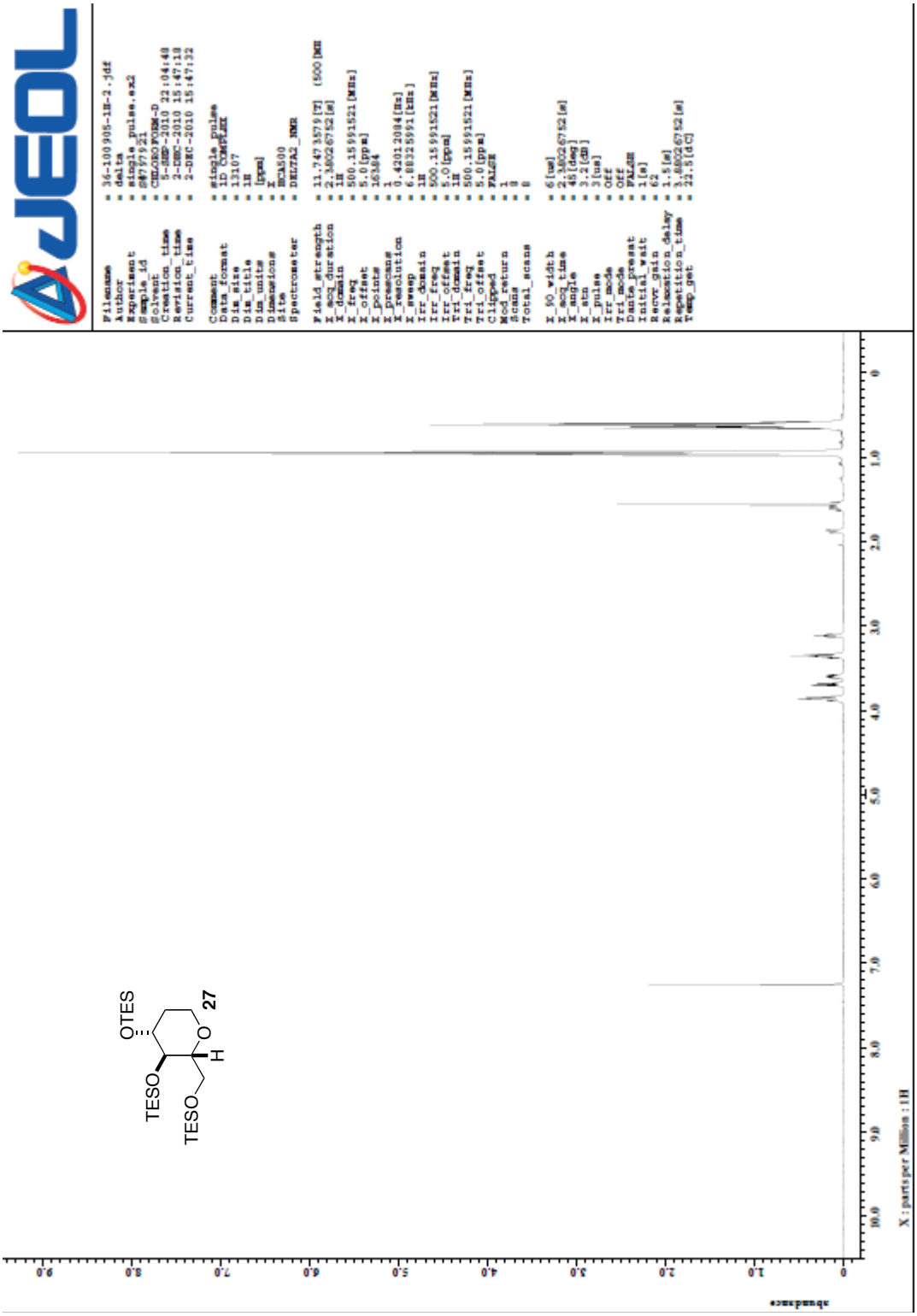
pentakis-TES ether **26**



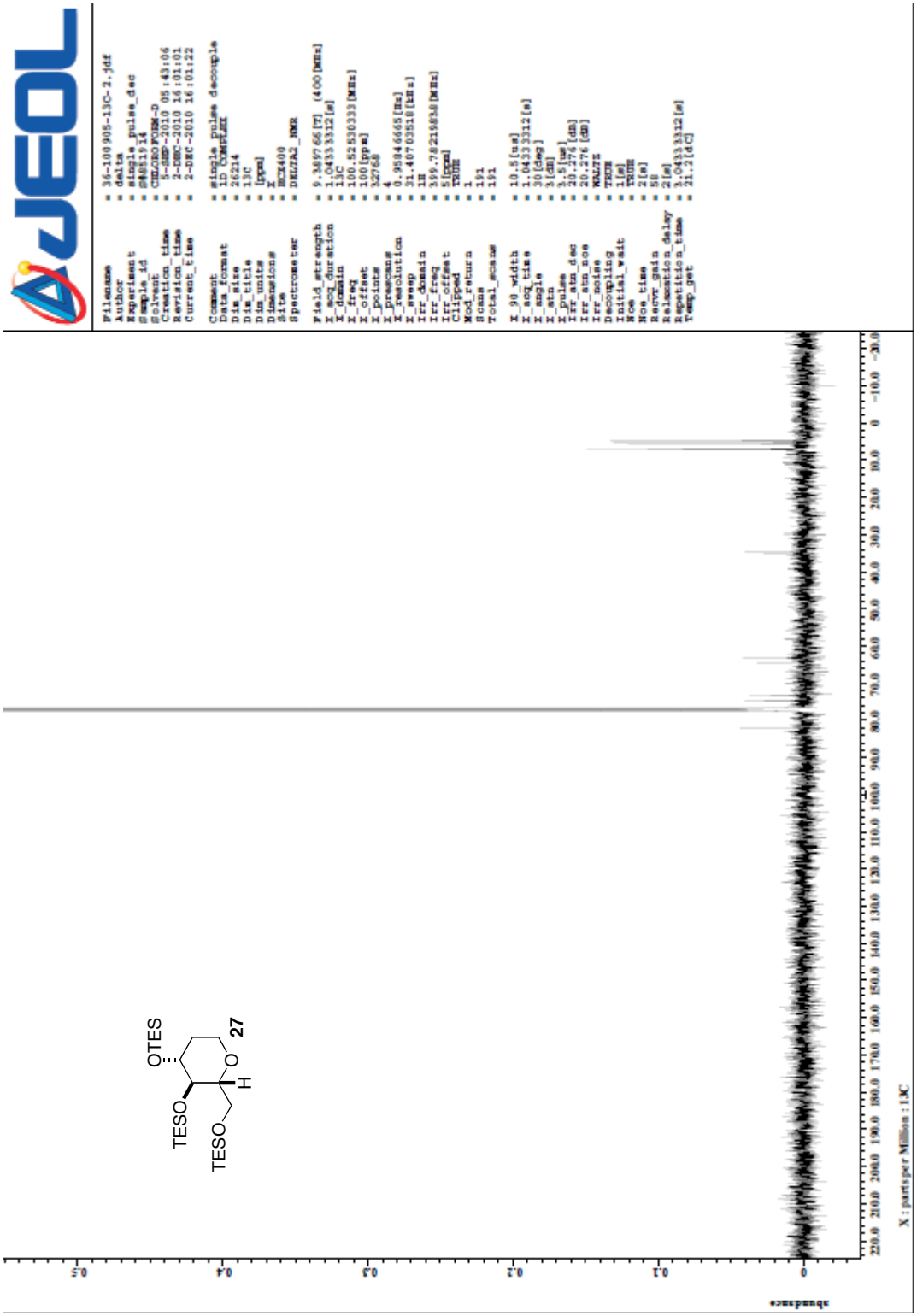
pentakis-TES ether **26**



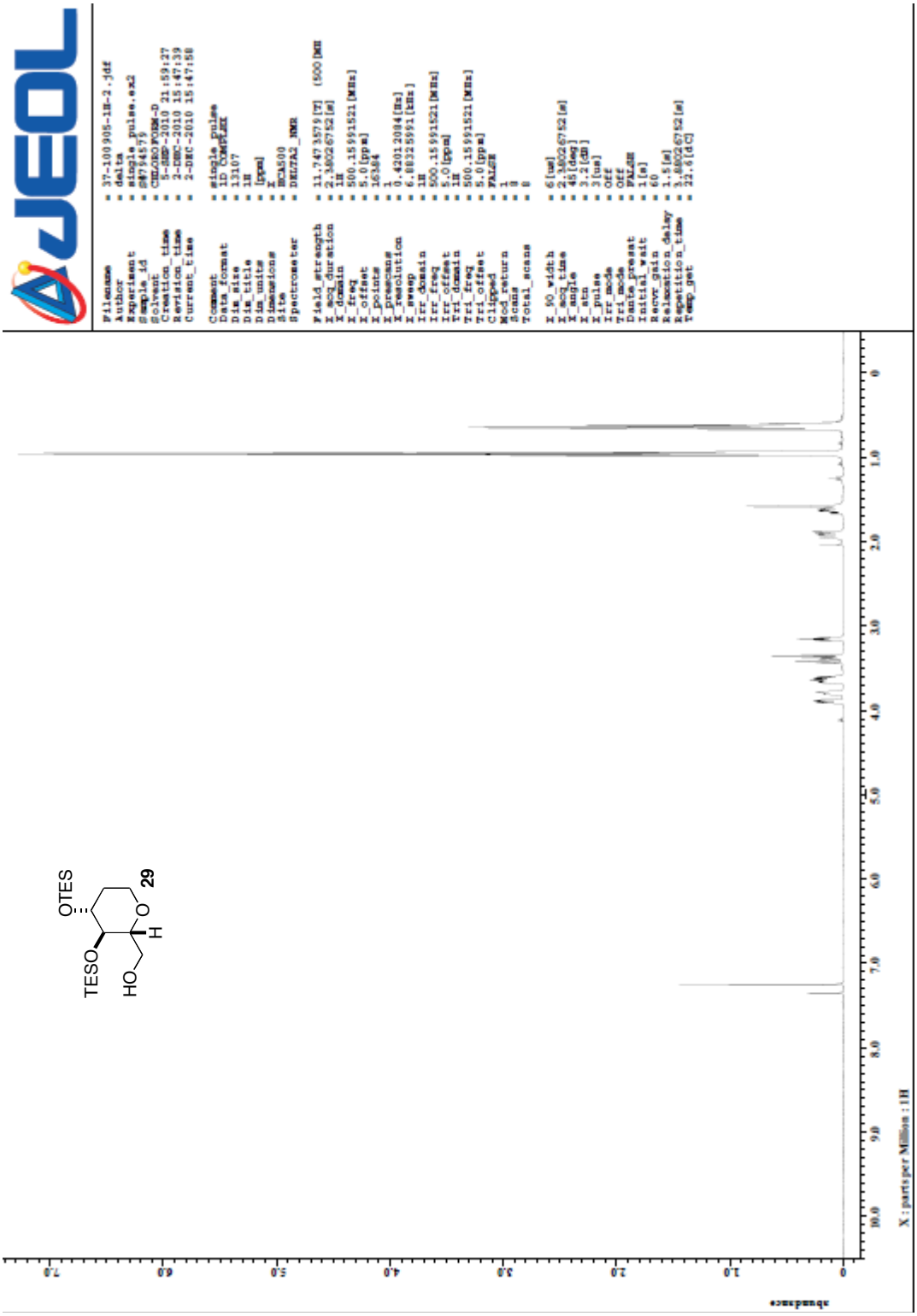
tris-TES ether **27**



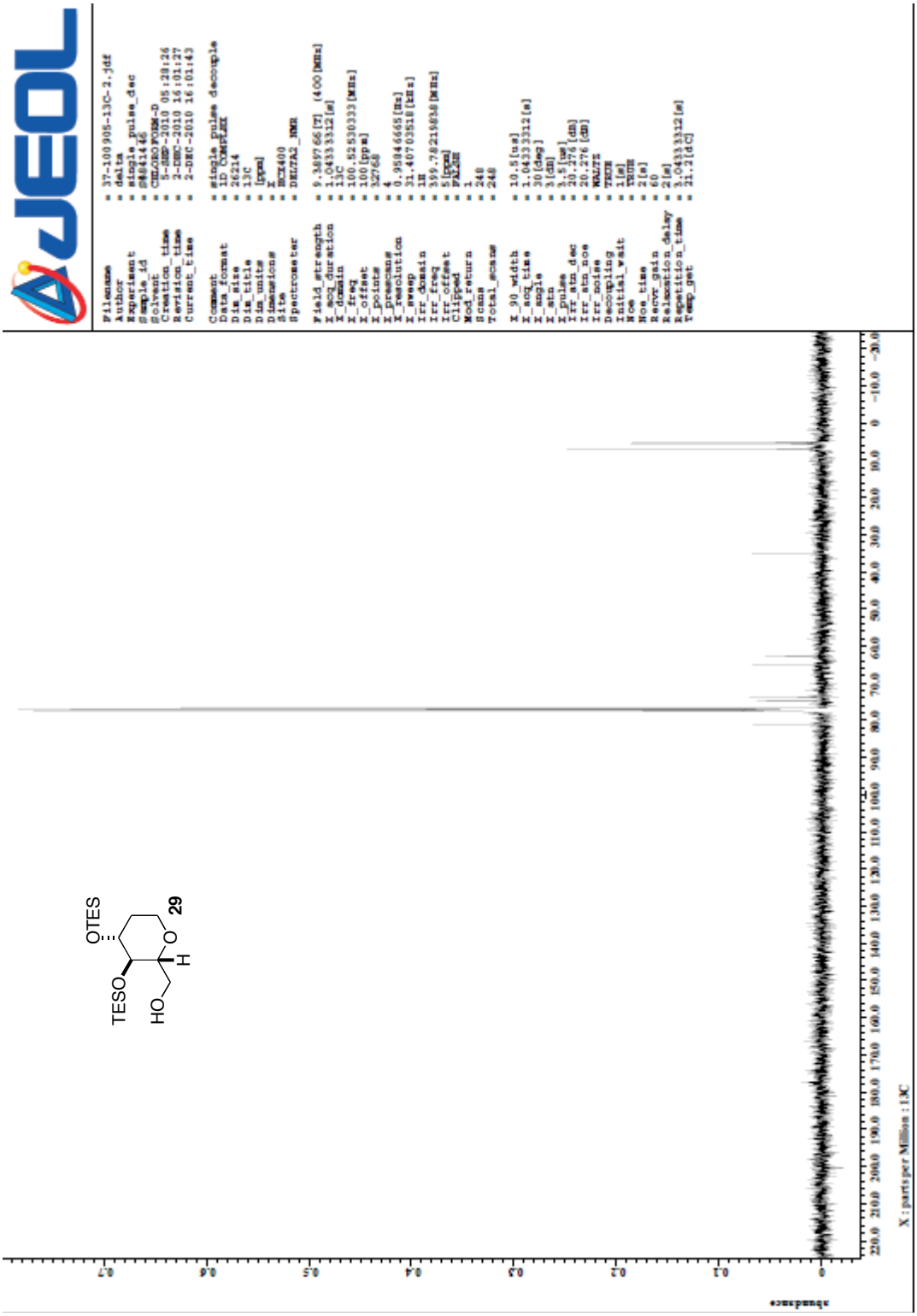
tris-TES ether **27**



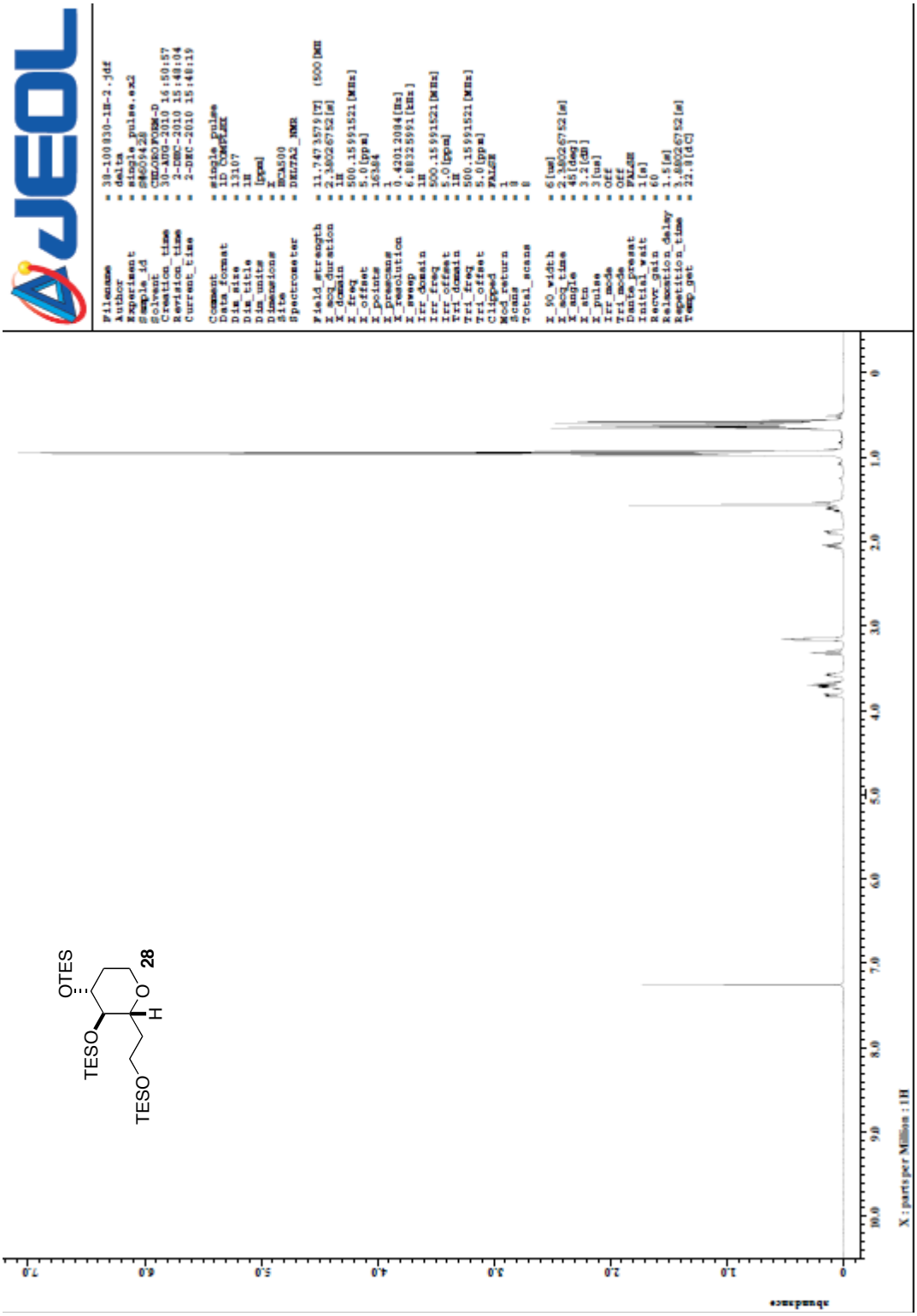
alcohol **29**



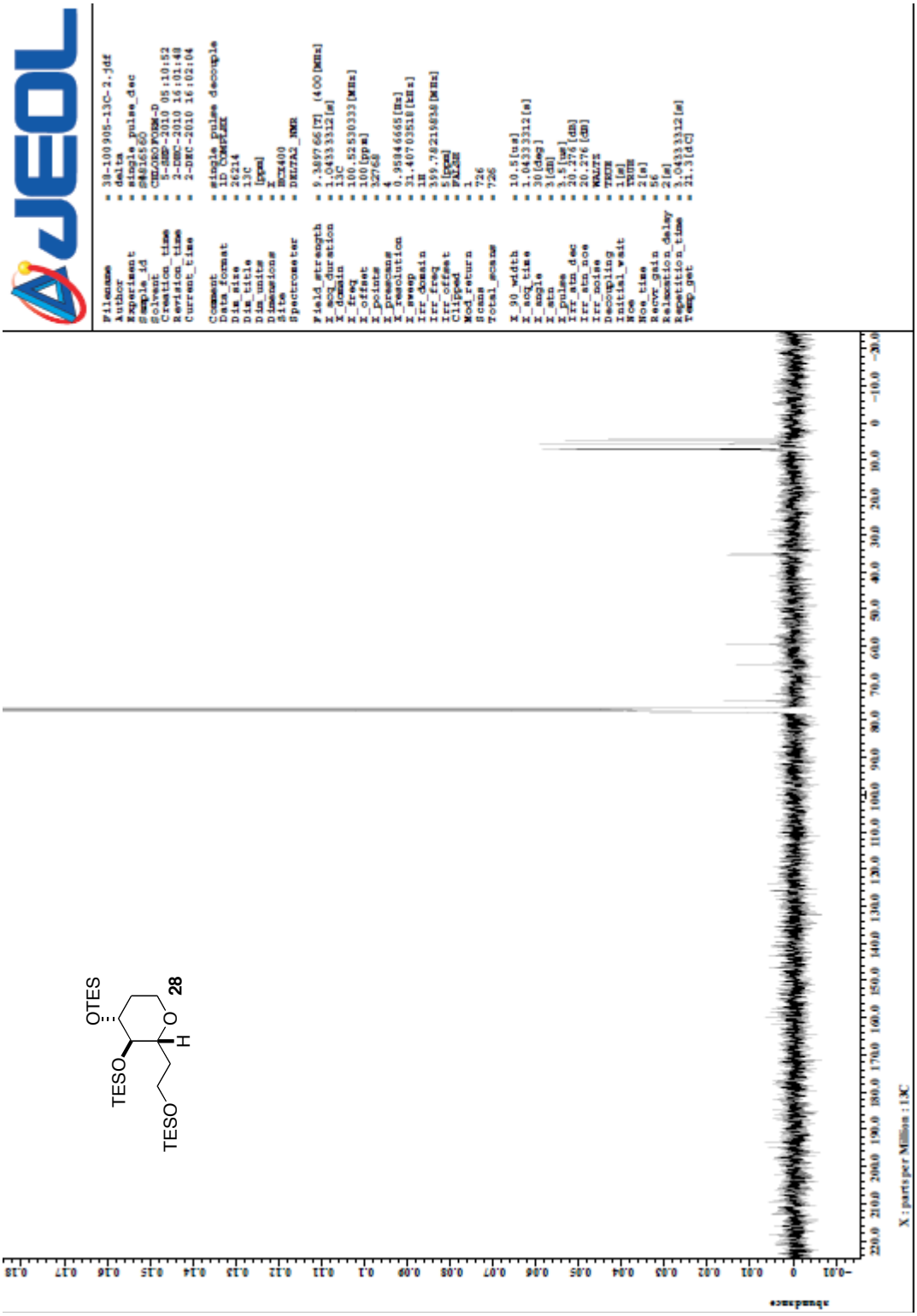
alcohol **29**



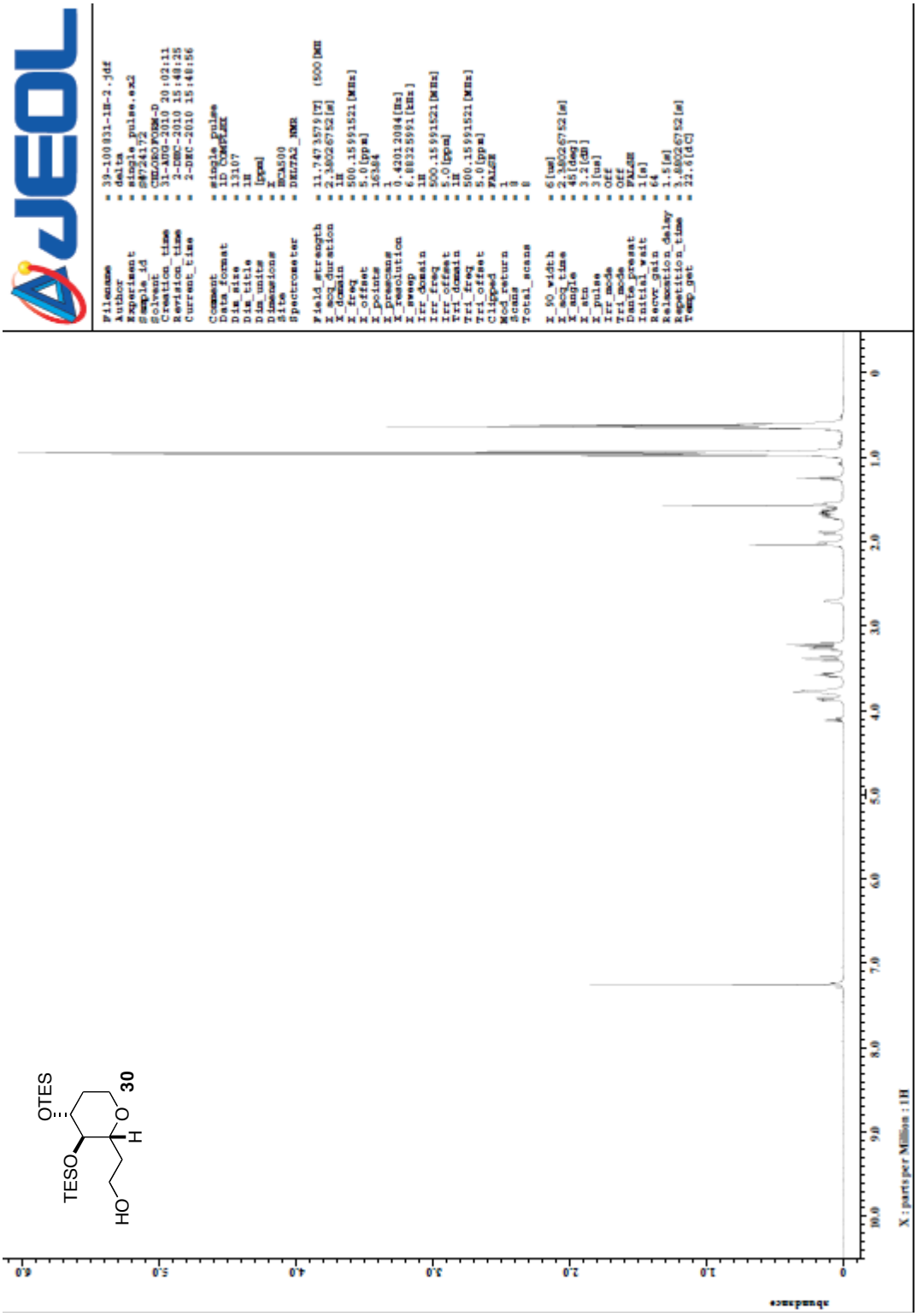
tris-TES ether **28**



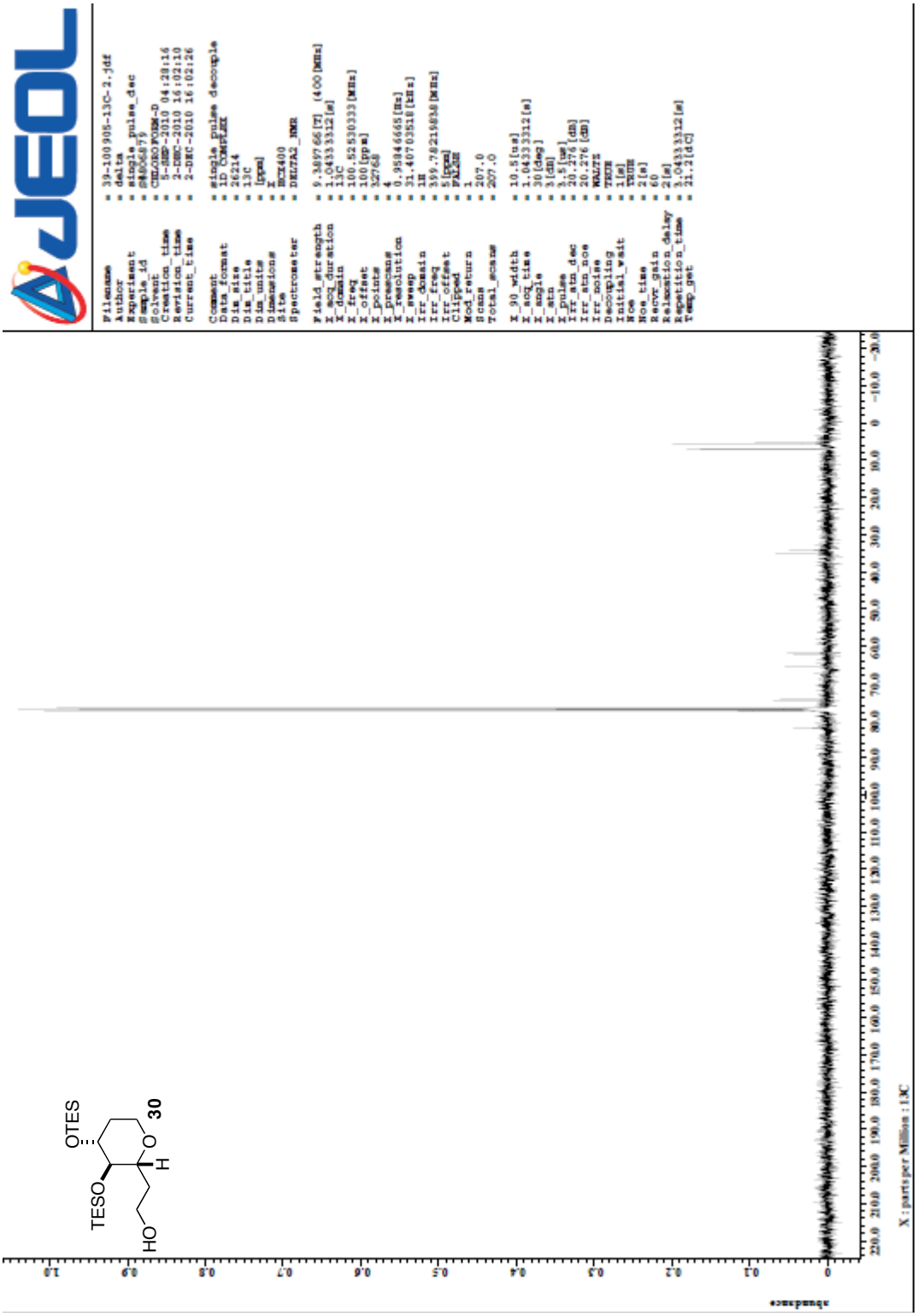
tris-TES ether **28**



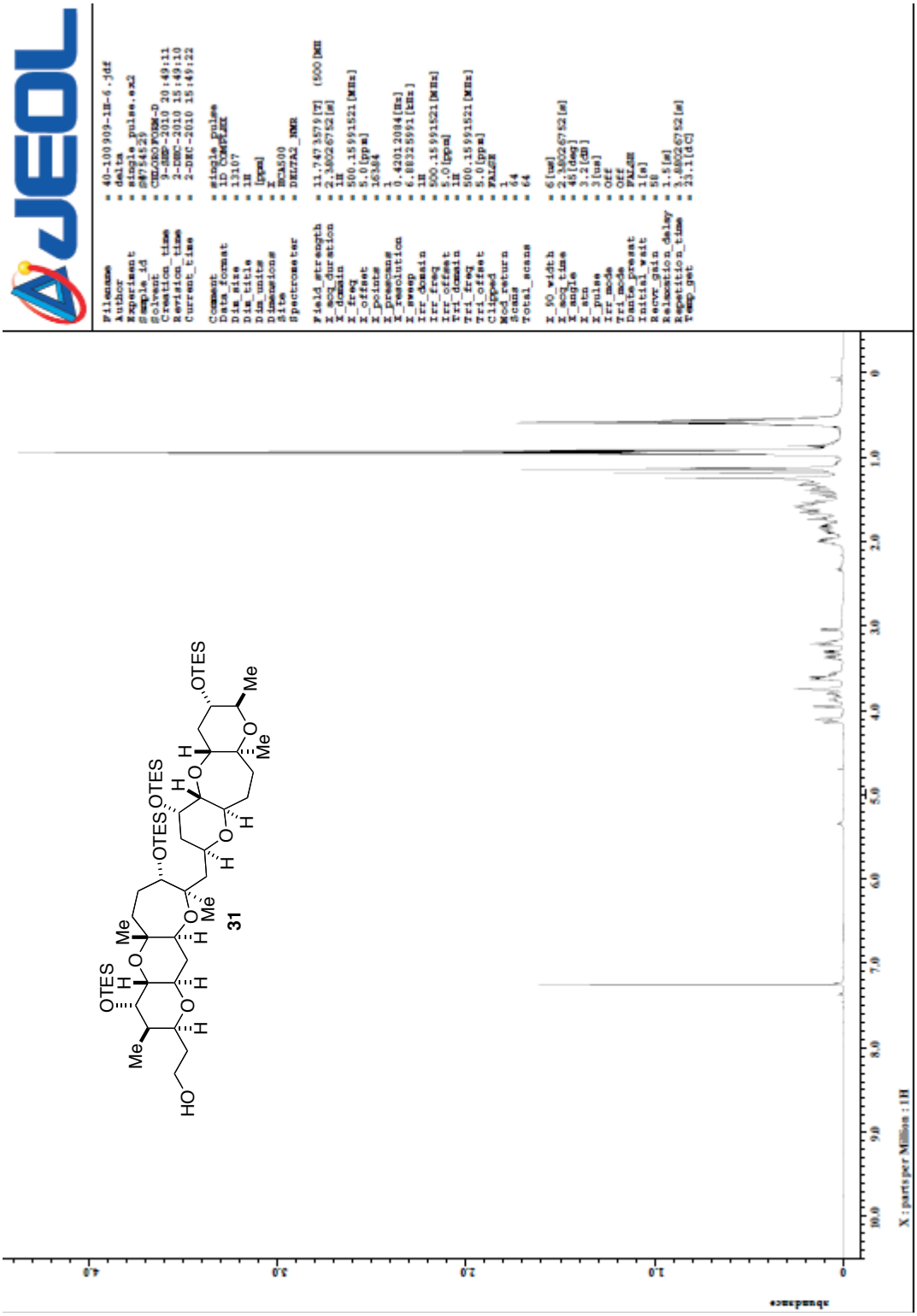
alcohol **30**



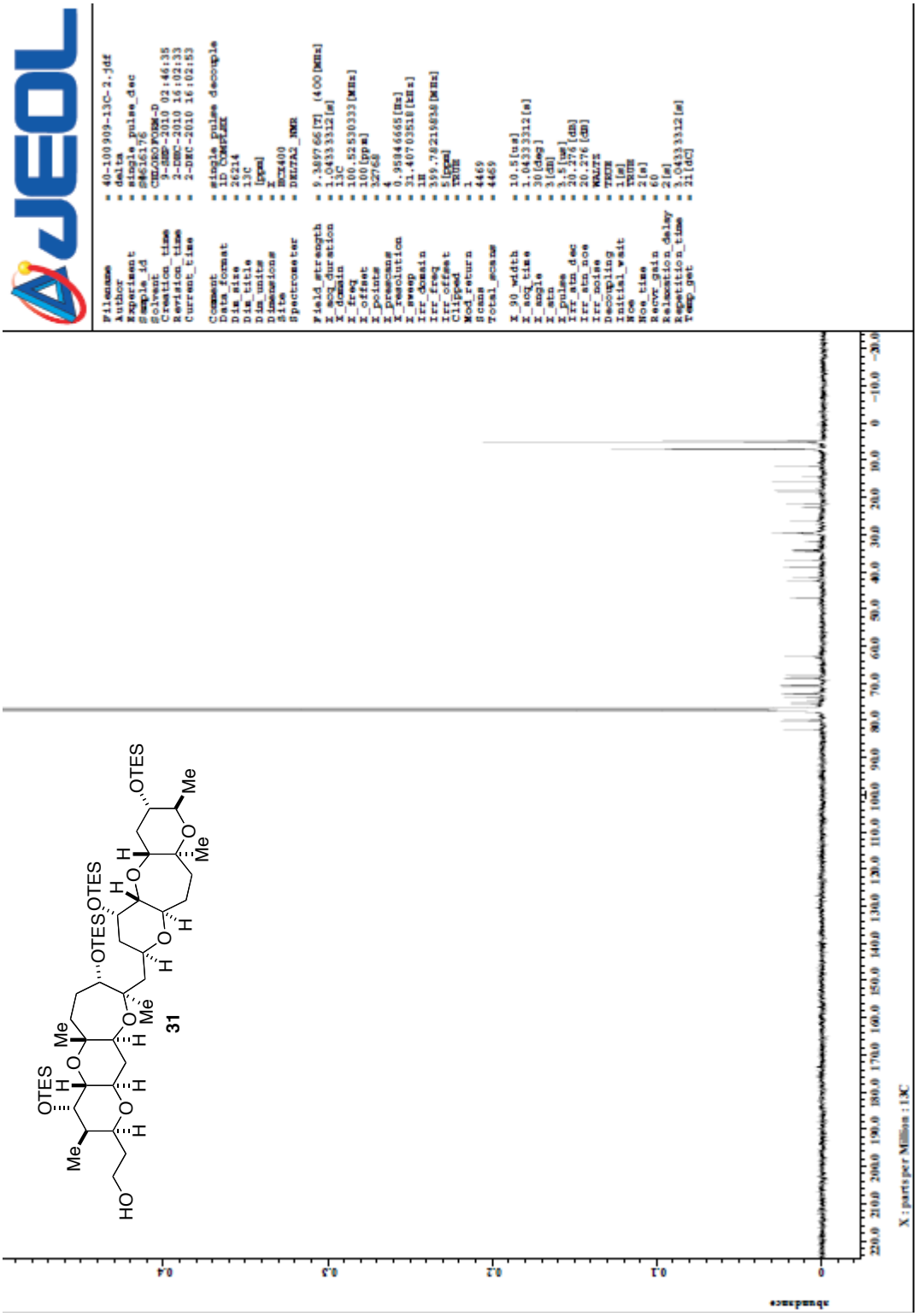
alcohol **30**



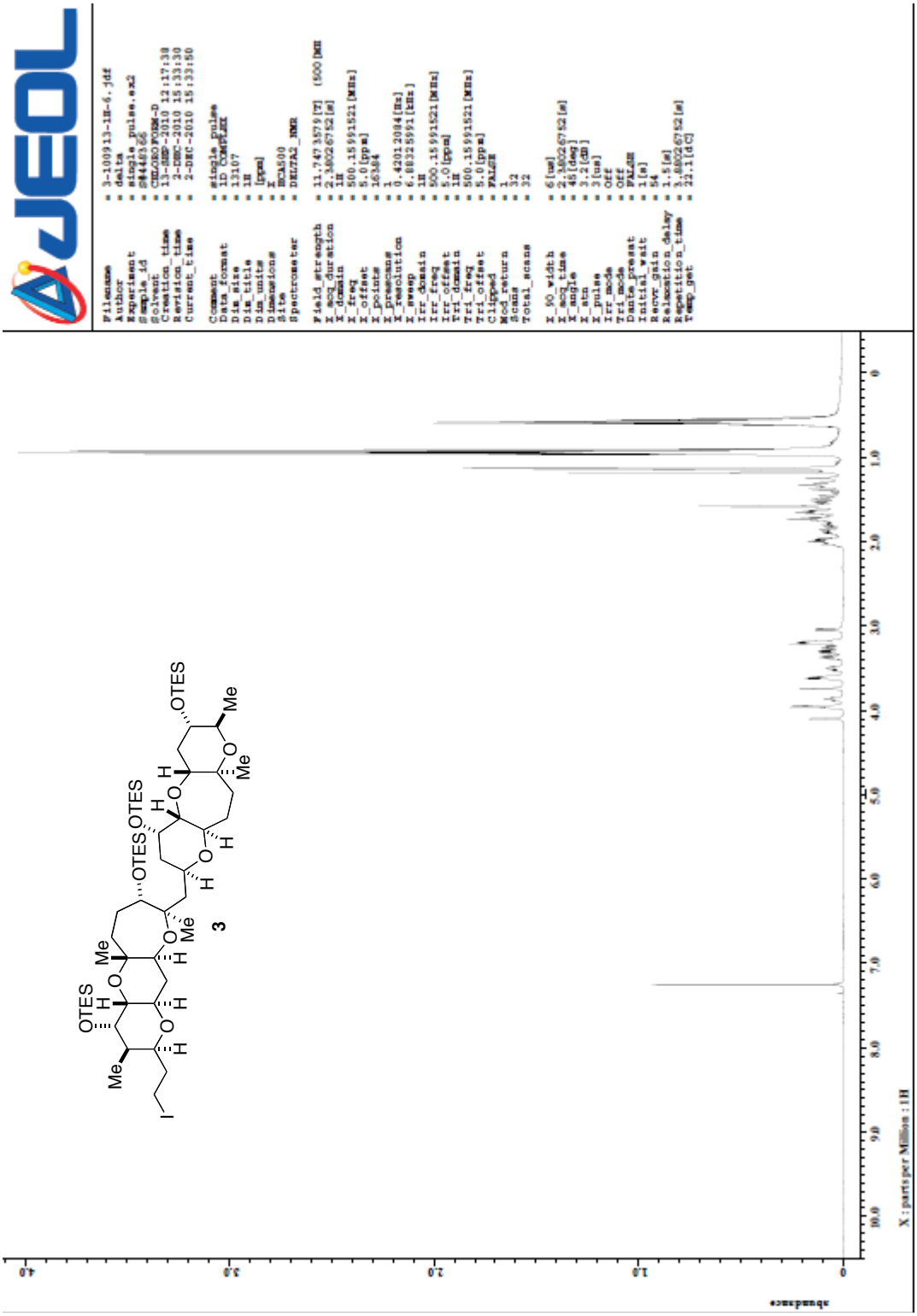
alcohol **31**


JEOL
OTES
OTES
OTES
Me
Me
Me
Me
HO
31
abundance
X : parts per Million : 1H

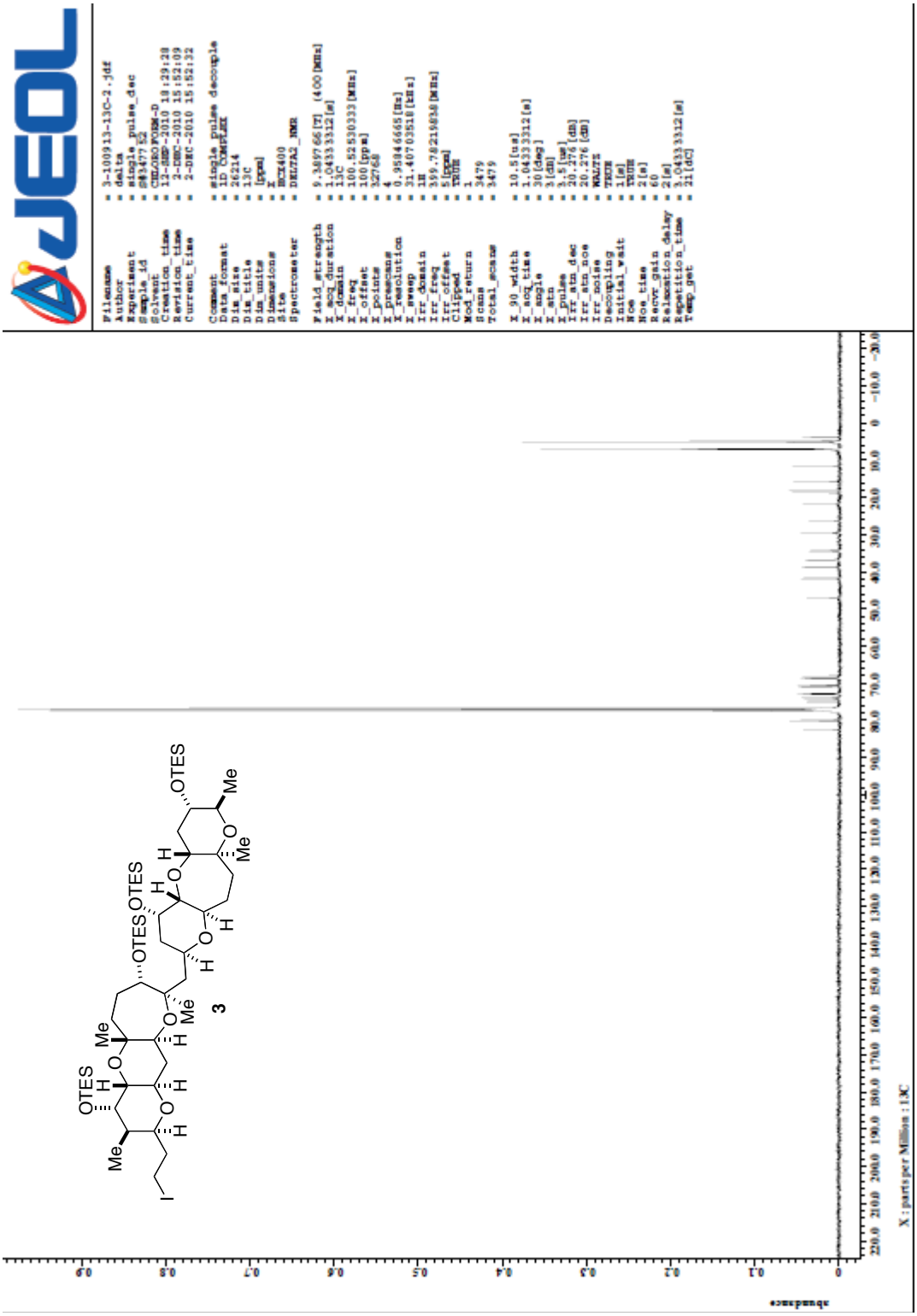
alcohol **31**



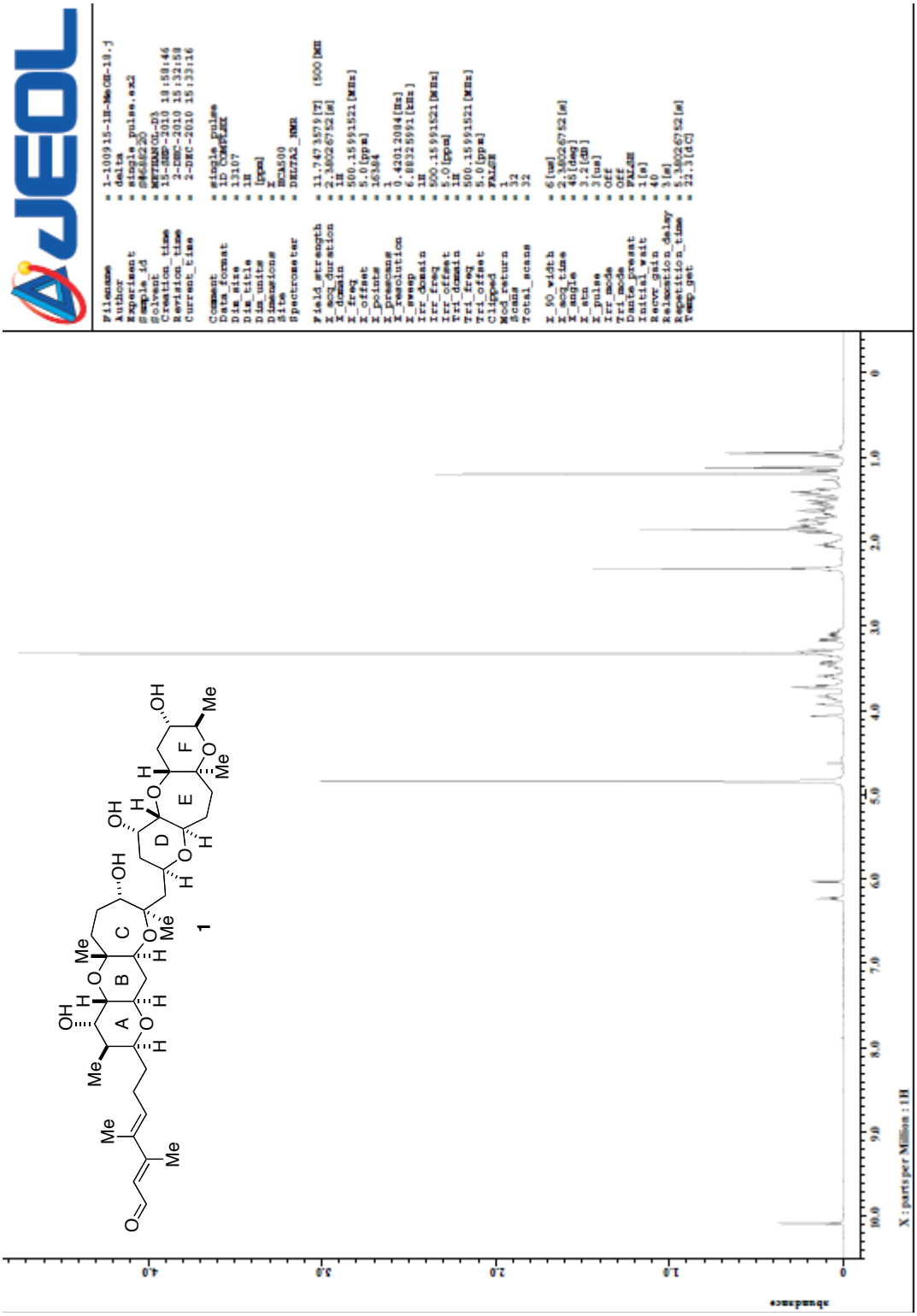
iodide **3**



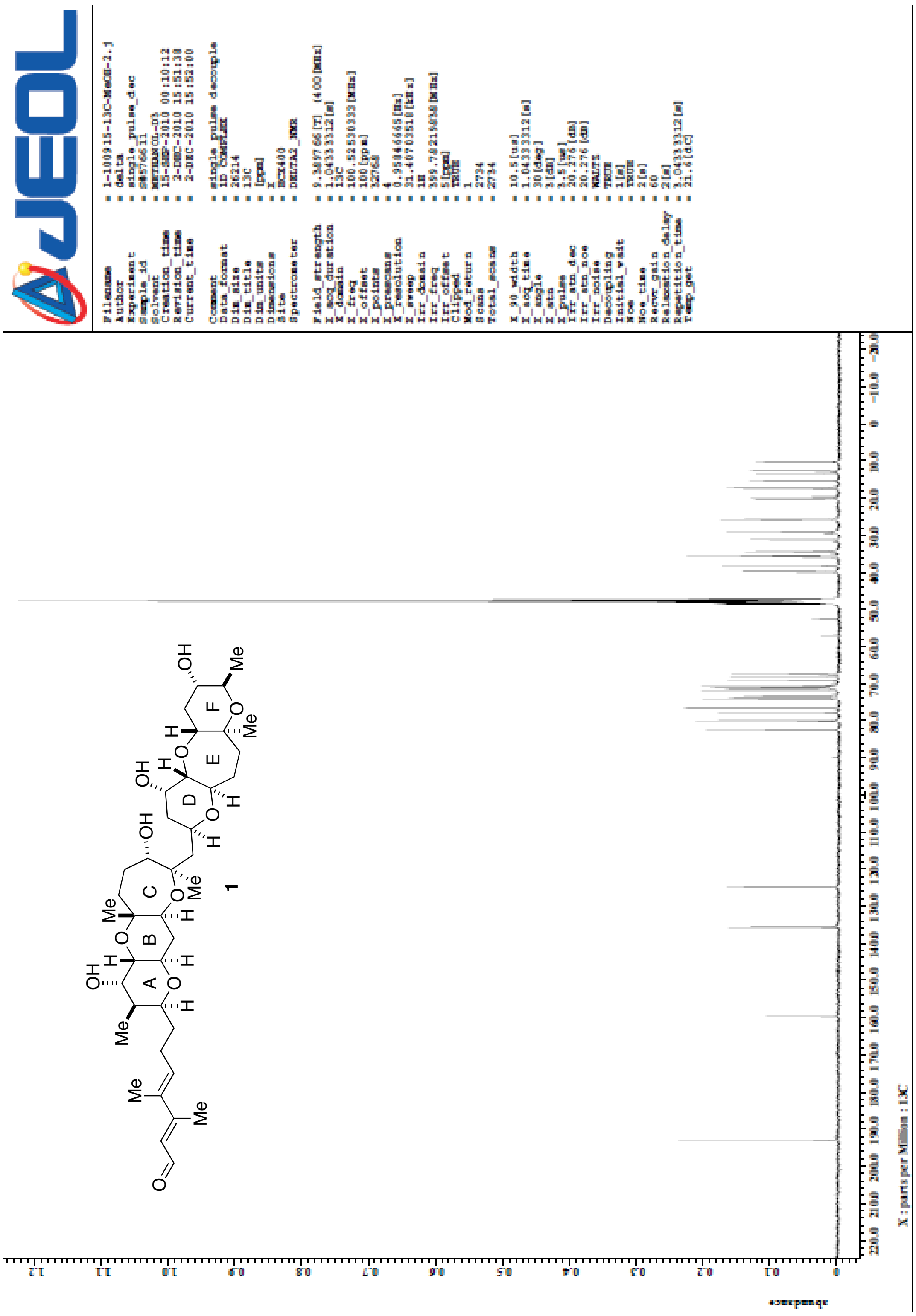
iodide **3**


JEOL
Filename = 3-100913-13C-2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = #83477 S2
Solvent = CHLOROFORM-D
Creation_time = 12-SEP-2010 18:29:28
Revision_time = 2-DEC-2010 15:52:09
Current_time = 2-DEC-2010 15:52:32
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX400
Spectrometer = DELTA2_NMR
Field_strength = 9.389766 [T] (400 [MHz])
X_acq_duration = 1.043333312 [s]
X_domain = 13C
X_freq = 100.525830333 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.958466665 [Hz]
X_sweep = 31.407035181 [kHz]
Irr_domain = 1H
Irr_freq = 399.782159830 [MHz]
Irr_offset = 5 [ppm]
Clipped = TRUE
Mod_return = 1
Scans = 3479
Total_scans = 3479
X_90_width = 10.5 [us]
X_acq_time = 1.043333312 [s]
X_angle = 30 [deg]
X_atn = 3 [dB]
X_pulse = 3.5 [us]
Irr_atn_dec = 20.276 [dB]
Irr_atn_one = 20.276 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Mode = TRUE
Mode_time = 2 [s]
Recvr_gain = 60
Relaxation_delay = 2 [s]
Repetition_time = 3.043333312 [s]
Temp_get = 21 [dC]
OTES
Me
O
H
OTES
OTES
H
O
H
O
Me
Me
O
H
Me
H
O
H
O
H
Me
OTES
Me
I
3
Abundance
X : parts per Million : 13C

brevisin (**1**)



brevisin (**1**)



^{13}C NMR spectrum of natural brevisin